

## Quantum Mechanics: Theory and Applications

*I cannot tell how the truth may be  
I say the tale as it was said to me*  
--- Sir Walter Scott

# **Fundamental Theories of Physics**

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# Quantum Mechanics: Theory and Applications

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We end with the quotation (which we found in a book by G.L. Squires): *I have learnt much from my teachers, but more from my pupils.* To all our pupils, we owe a very special debt.

Ajoy Ghatak  
S. Lokanathan

## Preface

Quantum mechanics has long been recognized as an essential ingredient in the training of a student in Physics, Chemistry and Electrical Engineering. No matter which specialization the student chooses in his later career, it is necessary for him to develop not merely an understanding of the basic principles of quantum mechanics but an ability to apply these principles in his field.

Textbooks on quantum mechanics addressed to students at under-graduate and post-graduate levels generally have few solved problems; moreover, the problems suggested are largely of an academic nature with a greater emphasis on theory than on applications. This book makes an attempt to present the basic concepts in quantum mechanics with emphasis on applications in other areas like nuclear physics, astrophysics, solid state physics, quantum optics, etc. Each chapter is followed by a number of problems. The solutions to most of these problems have been given at the end of the chapter. This will enable the student to refer to the solutions when necessary and at the same time provide him an opportunity, if he so wishes, to solve some or all of these problems by himself before consulting the solutions. The emphasis has not been on rigour but on making results plausible and helping the students to become familiar with methods for solving problems. The book has evolved from lectures given by the authors (to students of physics and engineering) at the Indian Institute of Technology, New Delhi and at University of Rajasthan, Jaipur.

As a prologue to the book we have reprinted an essay, ‘What is Quantum Mechanics?’, by Professor Victor F. Weisskopf. It is so well written that we felt it would motivate the reader to learn more of this fascinating subject. Following the prologue are two short chapters on mathematical preliminaries—one on the Dirac delta function and the other on Fourier transforms. The two topics are so extensively used in quantum mechanics that even if the students are familiar with them, it would be of great advantage to discuss these topics (again) in about two to three lectures right in the beginning of the course.

After the mathematical preliminaries, we have discussed (in Chapter 3) wave-particle duality and the uncertainty principle. In Chapter 4, we have introduced the Schrödinger equation and in Chapter 5, we have discussed the solutions of the Schrödinger equation corresponding to a free particle leading to a study of the time evolution of a wave packet. In Chapter 6 bound state solutions of the Schrödinger equation are discussed.

We have given a somewhat lengthy account of the Dirac notation of bras and kets; since this is used frequently in advanced work, it was felt that the student would benefit greatly if he became familiar with it right at the beginning. Immediately after solving the Schrödinger equation for the linear harmonic oscillator problem (Chapter 7), we usually introduce Dirac's bra and ket algebra (Chapter 11) and then solve again the linear harmonic oscillator problem using the bra-ket algebra (Chapter 12). It is then very straightforward to study the time evolution of the coherent state and its relationship with the classical oscillator; such an analysis brings out many salient aspects of quantum mechanics. After this, we usually discuss the angular momentum problem in detail (Chapters 9, 13 and 15), which allows us to obtain very elegantly the expressions for spherical harmonics. We then obtain solutions of the Schrödinger equation for spherically symmetric potentials—in particular, for the hydrogen atom problem and for the three-dimensional isotropic oscillator problem (Chapter 10). Chapter 14 is on the Stern-Gerlach experiment which is indeed one of the most beautiful experiments in quantum mechanics. The principle of magnetic resonance has also been discussed and, in the process, we have been able to give an exact solution of the Schrödinger equation corresponding to a time dependent Hamiltonian. The chapter also has a short essay on the EPR Paradox.

Chapter 16 discusses the double well problem and also the Kronig-Penney model. In Chapter 17 we have also given a detailed account of the JWKB solutions of the Schrödinger equation; the JWKB methodology represents one of the very powerful approximate methods that is extensively used not only in quantum mechanics but also in many other areas. The first seventeen chapters have been developed into a video course which is now available through FITT (Foundation for Innovation & Technology Transfer) at IIT, New Delhi.

Chapter 18 discusses addition of angular momenta and introduces the Clebsch-Gordan coefficients. Chapters 19, 20, 21 and 22 discuss time independent perturbation theory, effects of magnetic fields, the variational method and the Helium atom. In Chapter 23, we have given a detailed discussion of some select topics which range from the concept of quasi-bound states to the Thomas-Fermi model of the atom.

Chapters 24, 25, 26 and 27 discuss the elementary theory of scattering, time dependent perturbation theory, the semi-classical theory of radiation and the quantum theory of radiation. Finally in Chapter 28, the Dirac equation and some of its solutions are discussed.

In order to have a better appreciation of the theory, most of the figures correspond to actual numerical calculations; these were generated using GNUPLOT and Mathematica.

We do hope the reader enjoys going through the book; we would greatly appreciate receiving suggestions for further improvement.

We have dedicated this book to Professor H.A. Bethe who taught one of us (AG) at Cornell, to Professor R. Serber who taught the other (SL) at Columbia, and to Professor D.S. Kothari and Professor R.C. Majumdar who taught both of us at Delhi University. To them we would like to extend our gratitude and respect for introducing us to the most beautiful subject in science.

Ajoy Ghatak  
S. Lokanathan

## Prologue \*

What is quantum mechanics?

*Victor F. Weisskopf*

There is no doubt that the most outstanding development in modern science was the conception of quantum mechanics. It showed, better than anything else, the human capability to comprehend the fundamental principles that underlie the world in which we live—even when these principles run contrary to our experience in dealing with our everyday environment. The French philosopher–mathematician Henri Poincaré said, *It is hardly necessary to point out how much quantum theory deviates from everything that one has imagined until now; it is, without doubt, the greatest and deepest revolution to which natural philosophy has been subjected since Newton.*

Much happened in physics between the time of Newton and the time of quantum mechanics. The discoveries and insights over the last three centuries share a characteristic feature: seemingly unconnected phenomena turned out to be manifestations of the same fundamental principle. It was a period of unification of disparate fields of experience. Here are some of the most important steps.

Newton showed that the motion of the planets is governed by the same law as the free fall of an object on earth. Thus, he unified terrestrial and celestial mechanics. In contrast to the belief of the ancients, he showed that the world of the earth and of the heavens is governed by the same laws.

Scientists in earlier days believed that heat was some peculiar substance called caloric, which flowed from a hot object to a colder one. Physicists in the nineteenth century recognized that heat is the random motion or random vibration of the constituents of matter. Thus, thermodynamics and mechanics were unified. This feat is connected with the names of J.B. Mayer, B. Rumford, R.E. Clausius, L. Boltzmann, and J.W. Gibbs.

For a long time, the phenomena of electricity, magnetism, and light appeared to be unconnected. In the first half of the nineteenth century, one of the great unifications of physics took place. Faraday and Maxwell, together with many others, were able to show that all three phenomena are manifestations of the electromagnetic field. And so the field concept entered into physics. The simplest example is the electric field of an electric charge that exerts a force on another charge when the latter falls within its range. An electric current produces a magnetic field that

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\* This essay has been reprinted from the book *The Privilege of Being a Physicist* by Victor F. Weisskopf. Copyright ©1989 by Victor F. Weisskopf. Used with kind permission of Professor Weisskopf and W.H. Freeman and Company, New York.

exerts a force on magnetic materials. Such fields may even propagate through space independently of any charges or magnets, in the form of electromagnetic waves, of which visible light is one example. The field concept is less directly connected to our everyday experience than the concept of a particle, but it can easily be realized by our senses. For example, if one feels the attraction of a piece of iron by a magnet, one obtains the immediate impression that there is something surrounding the magnet that acts upon the iron. Finally, Einstein unified space, time, and gravity in his special and general theories of relativity.

Quantum mechanics also united two branches of science: physics and chemistry. But it did much more. In previous great developments in physics, fundamental concepts were not too different from those of our everyday experience, such as particle, position, speed, mass, force, energy, and even field. We often refer to those concepts as *classical*. The world of atoms cannot be described and understood with those concepts. For atoms and molecules, the ideas and concepts formed in dealing with the objects in our immediate environment no longer suffice. Surprising forms of behavior were observed that not only needed a different language but required new concepts to understand the properties of atoms.



Figure 1. Werner Heisenberg, Wolfgang Pauli, and Enrico Fermi at a conference in 1927, reflecting their enthusiasm for and joy of the new quantum mechanics.

A small group of people conceived of and formulated these new ideas in the middle twenties of this century. The most important among them were W. Heisenberg, a German; E. Schrödinger, an Austrian; P.A.M. Dirac, an Englishman; W. Pauli, another Austrian; and M. Born, another German. They worked at different

places, but the centre of activities was in Copenhagen, where they met frequently under the leadership of the great Niels Bohr. Bohr was the ideal leader of such a group. Older than most of the others, who were then in their twenties or early thirties, he contributed enormously to the conception of the new ideas by his constant questioning, by his criticism, and by his enthusiasm. The crowd that assembled around him was a group of devoted forward-looking people who, free of the bonds of convention, attacked the deepest riddles of nature with a spirit of joy that can hardly be described. That joy of insight is a sense of involvement and awe, an elated state of mind akin to what you feel on top of a mountain after a hard climb, at the shore of the blue sea, or when you hear a great work of music. It comes not only after personal achievement, but also after finally understanding an important new insight gained by the work of others. For every real scientist, it is great compensation for the hard work and trouble he must endure (see Fig. 1).

The quantum revolution changed our old concepts of reality in many respects. We are going to describe this drama in five parts—a prologue, plus four acts:

- Prologue Riddles of prequantum physics*
- Act I Discovery of wave-particle duality*
- Act II How wave-particle duality miraculously solves the riddles of prequantum physics*
- Act III Significance of wave-particle duality and the new reality of the quantum state*
- Act IV The quantum ladder: An extension of quantum mechanics to nuclear and subnuclear phenomena and to the history of the universe*

## Prologue:

### RIDDLES OF PREQUANTUM PHYSICS

Before quantum theory was conceived, physicists were unable to explain some of the most ubiquitous phenomena in our environment. Here are a few examples: A piece of iron, when heated, becomes first red, then yellow, then white, but nobody could explain why. The different colors emitted by a piece of matter come from the irregular heat motion of the electrons in the atoms of iron. Fast motion emits higher frequencies of light than slow motion. The frequency determines the color of the light. The laws of thermodynamics tell us that any form of motion should receive the same amount of energy at a given temperature, an amount that increases when the temperature rises. Thus we expect only an increase of intensity of the emitted light, not a change from red to yellow to white. This change represented

an unsolved riddle, somewhat like today's ignorance of the nature of memory. We use memory constantly, but nobody knows precisely what it is.

We can consider more examples of unsolved questions of that period: Why are copper and silver metals and oxygen a gas? Why do metals have properties so different from other solids, such as rocks? Why do these properties persist, even after heating, melting, evaporating, and subsequent cooling to the original temperature? Why do oxygen atoms bind to hydrogen atoms to form water? Why does sodium gas emit yellow light when heated? Why is it that burning 1 kilogram of coal produces approximately 6000 calories? Why is the size of atoms about a hundred millionth of a finger's breadth? No one could provide any answers to these questions at the turn of the century.

More problems were generated by the discovery of the electron by J.J. Thomson in England and H.A. Lorentz in the Netherlands at the end of the last century and, in particular, by further discoveries by E. Rutherford and H.G. Moseley at the beginning of this century. They found that atoms consist of a heavy, positively charged atomic nucleus surrounded by much lighter electrons. Because the electric force between the positively charged nucleus and the negatively charged electrons is of the same form as the attraction between the sun and the planets, they concluded that atoms must be tiny planetary systems, with the nucleus as *sun* and the electrons as *planets*. Moreover, it was found that all elements seem to have this planetary structure and differ only in numbers of electrons. For example, hydrogen has one electron; helium, two; iron, twenty-six; and uranium, ninety-two.

It was difficult to understand how elements that are so different—some are gases, some are metals, some are liquids—differ in their atomic structure by only a few electrons. For example, the element neon, which has ten electrons, is a chemically inactive gas; however, the element sodium, which has eleven electrons, is one of the most chemically active metals. An electron increase of 10 percent completely changes the character of the atom! No one could explain this apparent inconsistency between quantity and quality.

Four observations defied all understanding at the turn of the century.

1. The color of objects at various stages of heating (red, yellow, white).
2. The very different specific properties of elements whose number of electrons is almost the same.
3. The fact that atoms do not change their properties in spite of the many collisions and interactions that they suffer in a gas or in an ordinary piece of matter. They quickly resume their original qualities after the perturbation. Their stability and their ability to regenerate is completely at odds with what we would expect from a planetary system. If our solar system were to collide or pass another star at a close distance its orbits and patterns would be completely changed and it would not return to its original form.

4. The energy content of the atom is *quantized*. An atom can assume a series of definite energies only and never a value in between. This most surprising fact was found at the beginning of this century and is also completely foreign to a planetary system. There is no reason why the energy of planetary motion cannot change by arbitrarily small amounts, for example, when a meteorite hits a planet. An atom, however, can accept or lose only definite amounts of energy, those that would change its energy from one of the values in the series to another.

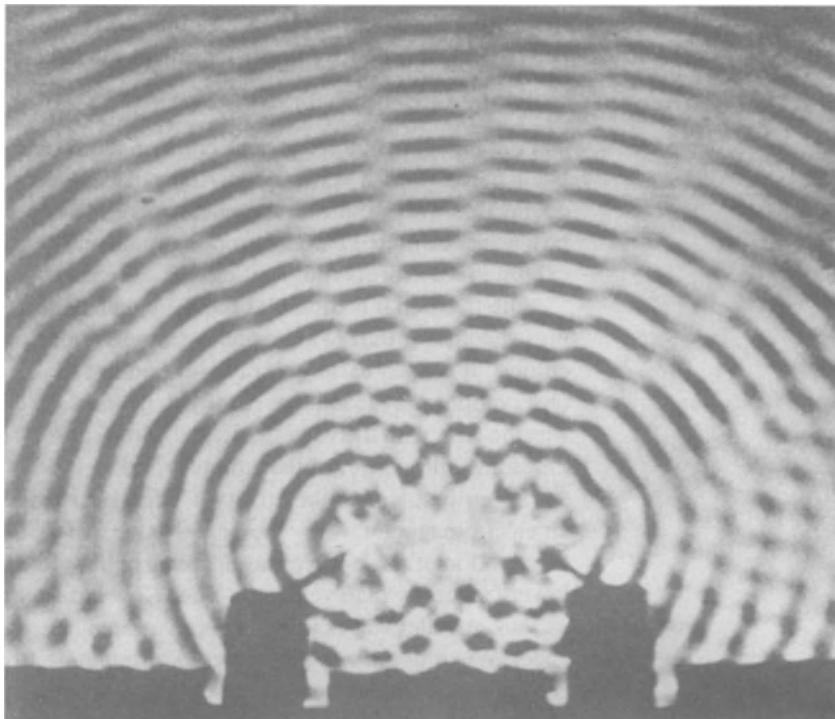
It became clear to prequantum physicists that the analogy between an atom and a planetary system breaks down completely when atomic properties and processes are examined in detail. On the other hand, these observations left no doubt that the atom consisted of a positively charged nucleus surrounded by electrons, which ought to form a planetary system, according to the laws of mechanics known at that time. Everything, including our own bodies, consists of atoms. Obviously, the most urgent problem for physics at that time was to resolve these contradictions and to achieve a better comprehension of the structure and behavior of atoms.

## **Act I: Discovery of wave-particle duality**

Not until the first quarter of this century did physicists find the path to the solution. It all began with a series of startling discoveries that seemingly had no direct connection with atomic structure. These discoveries showed that light, believed to be a wave, exhibited particle properties and that electrons, believed to be particles, exhibited wave properties. Let us call it the wave-particle duality.

Often, when it is difficult to find an explanation for one group of strange findings, another group of unexplained observations helps us to resolve both difficulties. It's often easier to solve two riddles than one. Two different disturbing observations may lead more readily than one such observation to a solution. That was the case with the wave-particle duality, since it showed the way to understand the strange properties of the atomic world.

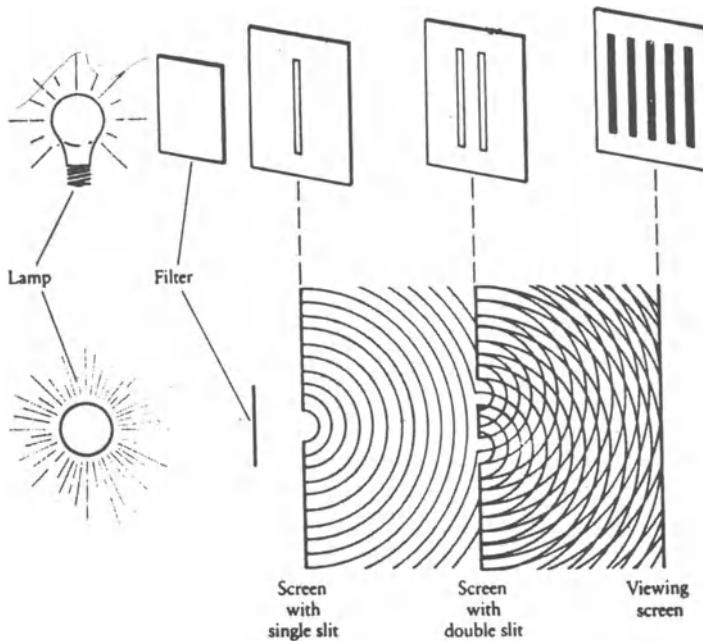
Let us first look at the duality itself. We have all learned in school that light is an electromagnetic wave. We perceive the different wave lengths, or frequencies of vibration of these waves, as different colors. Red has a longer wave length and lower frequency than yellow or blue. How did we know that light is a wave? Let us look at water waves to learn about a characteristic property of waves: interference. When two wave trains merge, originating from two different points, they combine in a typical way. When the crest of one wave coincides with the crest of another, the two together create a stronger motion. When the crest of one wave coincides with the trough of another, the two wave motions cancel each other in a phenomenon called *interference*. Figure 2 shows the interference of two water waves originating



*Figure 2.* Interference patterns produced by two water waves originating from two neighboring points. [Physical Science Study Committee, *Physics*, D.C. Heath, Boston, 1967].

from two different points. We see that they reinforce each other in certain directions and wipe each other out in other directions. The same phenomenon was observed long ago by Thomas Young in light waves, as sketched in Fig. 3 and shown in Fig. 4. The two light waves are produced by illuminating a screen with two slits. Of course, there is a difference between water and light waves: In the former case, the water surface oscillates and in the latter it is the electric and magnetic field strength that oscillates in space.

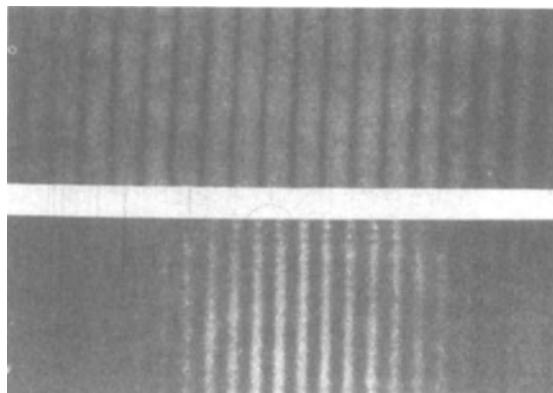
Great was the surprise, therefore, when it turned out that the energy of a light beam cannot be subdivided indefinitely. An ordinary wave can be strong, weak, or still weaker, with no restrictions on its intensity or lack thereof. Not so with light waves! The observed light energy seems to occur in lumps called light quanta, or photons. The energy of a light beam is always a multiple of such lumps, never half a lump or ten-and-a-quarter lumps. This is a strange finding. How could it be that the energy of a wave cannot assume an arbitrary value, but must be a multiple of a definite quantum? The energy of a light wave is indeed quantized; this property was shown beyond any doubt. Figure 5 is an example of how it could be observed. It is a photograph of what we see when a light ray (in this case, an X-ray—light of very



*Figure 3.* Arrangement for demonstrating interference of light. The first slit defines the incoming wave; the second has two openings, thus producing two waves; the third shows the interference stripes seen on the screen at right [After Atkins, *Physics*, Wiley, New York, 1965].

high frequency) penetrates through a *cloud chamber*, that is a container of saturated steam. The vapor is in a state of pressure and temperature at which it is about to form droplets. Just a bit of energy deposited here and there will form a droplet. If the bit of energy is larger, a bigger droplet is formed; if smaller, a tinier one will appear. Now, looking at the picture, we see (as we might well expect) that the light ray gets weaker penetrating the liquid. However, it gets weaker in a special way: The droplets do not become smaller, but their number does. The unchanging size of the droplets indicates that light consists of quanta: the effect of each quantum is the same all along the light beam, but there are fewer droplets farther down the road (to the right of the picture) because part of the energy has already been used up. If the ray were a true wave, its intensity would have become weaker and would have produced smaller droplets. The weakening shows itself not by smaller drops but by fewer ones. Each light quantum maintains the same strength, but there are fewer of them when the beam becomes weaker. These and other similar observations reveal the *graininess* of light.

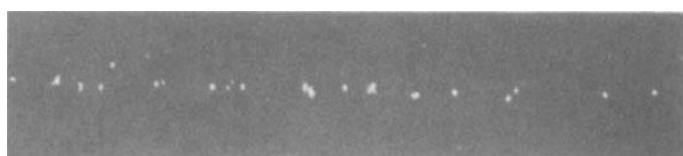
Light *grains* (photons, or light quanta) are very small indeed. That is why they were not discovered earlier. Their energy was found to be proportional to the frequency of light. This relationship is expressed in the simple formula,  $E = hf$ , where  $E$  is the energy of the photon,  $f$  the frequency, and  $h$  is a famous number



*Figure 4.* Patterns seen on the screen at the extreme right of the arrangement of Fig. 3. Upper pattern with red light; lower pattern with violet light. The lower pattern is narrower because of the shorter wave length. [Physical Science Study Committee, *Physics*, D.C. Heath, Boston, 1967].

called Planck's constant. If we measure energies in electron volts and frequencies in ups and downs per second, the numerical value of  $h$  is  $4 \times 10^{-15}$ . Let us keep this formula in mind since it will be a clue to understanding many other riddles. Radio waves have very low frequencies and, therefore, very small quanta, according to this formula. The quanta are so small that it is very difficult to observe them. Visible light has larger quanta, but they are still extremely small. A million millions arriving at the same place and time would be felt as a little prick on a finger. The eye, of course, is very sensitive to them. X-rays are very high frequency radiation, and so their quanta are much larger, but still rather small.

The graininess of light, together with the series of definite energy values of an atom, forces us to a new interpretation of the mechanism of light emission by atoms. The atom may lose or gain energy only by amounts that correspond to the differences between its definite energy values. For example, when an atom happens to be in a state of higher energy, it may get into one of lower energy by emitting a



*Figure 5.* The cloud chamber shows the absorption of photons, one by one, and the weakening of the beam as photons are removed. The photons enter from the left and are absorbed by the argon atoms of the gas. They eject photoelectrons, whose tracks produce little droplets that show white in the photograph. You can see that the beam is weakened if you divide the photograph in half; there are seventeen tracks on the left half and only nine on the right. The *light* is actually an X-ray beam of a wavelength about 0.2 Angstroms. [W. Gentner, N. Maier-Leibnitz, and W. Bothe, *Atlas Typischer Nebelkam-merilder*, Springer Verlag, Berlin, 1940].

photon. The photon would be such as to carry the energy difference. Thus, an atom should emit light with very definite frequencies, namely, those whose quanta are equal in energy to the *differences* between the atomic energy values. This prediction turned out indeed to be the case, and it explains the characteristic frequencies emitted by each atomic species. Quanta of yellow light of a sodium lamp carry an energy equal to the difference between the lowest and the next higher state of the sodium atom. This regularity showed that there is a logical connection between two mysterious facts: the quantized energy of atoms and the graininess of light.

What does this amount to? We come to the startling conclusion that light has particle properties, in spite of the fact that so many indications—interference, for one—have shown that light is a wave!

The mystery deepened considerably as a result of a second surprising discovery: particles—electrons, for example—have wave properties! The French physicist L. de Broglie predicted this duality by ingenious intuitive insight, even before it was discovered by experiment. Under certain conditions, electrons emerging from two nearby points do not add their intensities but give rise to weaker beams in some directions and to stronger beams in others, similar to the interference of two water waves or light beams, as was shown in Figs. 2 and 3. What we call a particle exhibits properties that we ordinarily ascribe only to waves. What is the electron, a particle or a wave? What is a light ray, a wave train or a beam of particles? Eddington found a telling terminology, calling photons and electrons *wavicles*.

The fundamental relation between particle energy and wave frequency,  $E = hf$ , holds also for particles. A similar relation exists between the particle momentum and the wave number  $k$  (the number of wave lengths in one centimeter):  $p = hk$ . These relations are called *de Broglie relations*. They both contain the fundamental number  $h$ , the Planck constant.

Obviously, we run into terrible difficulties and contradictions by assuming that something is a wave and particle at the same time. A school of fish swimming in a lake is completely different from a wave on its surface. Each fish in the school is localized, as is each particle in a particle beam, whereas a wave is necessarily spread out over space. These contradictions will be raised in Act III of our drama. Such everyday concepts as particle and wave are not applicable in the atomic realm without restrictions. This will lead us to a new conception of reality. For the moment, let us assume that entities such as electrons and light are indeed *wavicles*—exhibiting both wave and particle properties—and see what follows from this assumption.

## **Act II: How wave-particle duality miraculously solves the riddles of prequantum physics**

First, we can easily see a solid material becomes first red, then yellow, then blue and white when it is heated to higher temperatures. What are heat and temperature?

In a warm material, atoms and molecules perform irregular vibrations of all kinds. The energy of these random motions, thermal energy, is proportional to the temperature: the hotter the material, the faster the particles vibrate. Atoms and molecules contain electrically charged particles; when they vibrate, they emit light. But light is quantized; it comes in lumps of energy. If the thermal energy is not sufficient to produce a light quantum of a given color, that color *cannot* show up. Thus, a piece of iron at room temperature does not emit visible light because at that temperature the thermal energy is less than the energy of the quanta of visible light. (Iron, at room temperature, does emit infrared light, whose quanta are of lower energy; we cannot see it but we can measure it, and we feel it as a heat radiation). At a higher temperature, thermal energy reaches the energy of a visible quantum. Red light has the lowest frequency and therefore the lowest quantum in the visible range; then comes yellow, then blue. Thus red is the first color to be seen when the iron is heated. As the temperature is increased, iron becomes yellow-red, then white, because the sum of red, yellow, and blue is white.

In 1900, Max Planck was the first to realize that quantum theory would lead to a correct description of the radiation of incandescent matter. His way of explaining it was different from the description given here and somewhat more involved. Nevertheless, his ideas gave impetus to the development of quantum theory.

What is much more impressive, however, is that the wave-particle duality also explains the stability and specificity of atoms and their special quantized states with definite energy values. The wave nature of electrons bestows properties on atoms that are quite different from what we expect of planetary systems.

To understand the difference, we must learn something about confined waves. When a wave is confined to a restricted region in space, it can assume only certain definite wave patterns. A violin string suspended between two end points can set up only those vibrations whose half wave length fits once or twice, or any integral number of times, into the space between the two points of attachment, as shown in Fig. 6.

Not only are the shapes of the vibrations determined, but also the frequencies (the number of ups and downs per second), once the tension of the string is kept fixed. Each of the different vibrations that can be set up has its characteristic frequency; the string can vibrate only a set of selected frequencies. The lowest of these frequencies, the easiest to set up, is the one whose half wavelength just fits the distance between the fixed ends of the string.

The lesson learned from the string is generally true for all kinds of waves. Whenever waves are confined to a finite space, we observe special wave forms and a set of assigned frequencies that are characteristic of the system. Most musical instruments are built on this principle. Stringed instruments make use of the series of discrete frequencies characteristic of the string; a wind instrument is based on natural frequencies of air waves enclosed in the pipe of the instrument, whether it is a trumpet or an organ pipe. Another interesting example of this phenomenon is

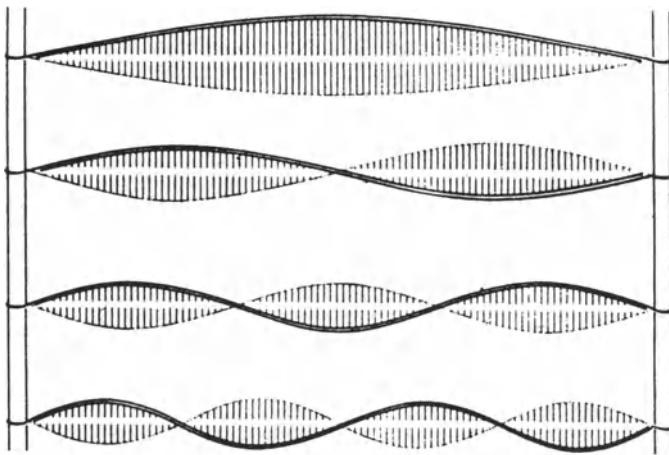


Figure 6. Waveforms of a string fixed at both ends.

a metal plate fixed at its center. If we use a violin bow to set it in vibration, we will find again a definite set of vibrations, with characteristic frequencies and shapes. We make these shapes visible by strewing sand on the plate. The sand accumulates at places where there is no vibration, thus delineating the shapes of the vibrations in *Chladni figures*, as shown in Fig. 7. It is entirely possible to calculate the shape of these patterns and predict at which frequency of vibration they will appear. All we need to know are the shape and elastic properties of the plate.

Can electron waves be confined too? Indeed, they are confined in an atom! The positive charge of the nucleus attracts the electron and prevents it from leaving the immediate neighborhood of the nucleus. Now we come to the most astounding part of the second act of our drama. In 1926, Erwin Schrödinger calculated the shapes and frequencies of the characteristic patterns that develop when electron waves are confined by the electric attraction of the nucleus. It is a straightforward problem of the dynamics of confined waves. What did he get? As expected, he found a series of distinct vibrations, each with its own definite shape and frequency. This is a big step toward solving the riddles of the atom. It not only shows that there are indeed well-defined modes of vibration in the atom but also reveals a connection between the wave nature of the electron and the existence of discrete states in the atom. Here we are touching on the very nerve of nature. When an electron is confined to a limited region around the nucleus, wave properties of the electron permit only certain special, predetermined patterns of vibrations.

The real success of this idea came about when Schrödinger calculated the wave patterns of the hydrogen atom—the simplest of all atoms, with its single electron confined by the nucleus. The result was overwhelming. He found a series of states of vibration that correspond in every respect to the observed quantum states of the hydrogen atom. The extension of waves in space corresponded very well with

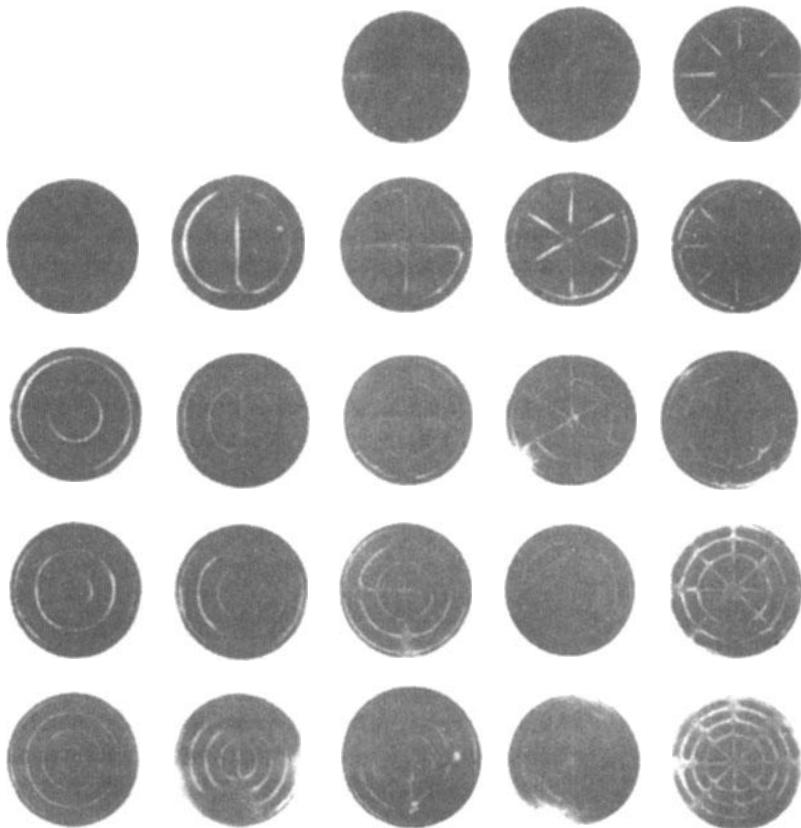


Figure 7. Vibrations of a circular metal plate fixed in the center [Chladni figures].

the observed size of the hydrogen atom. But the most surprising and convincing result of his calculations concerned the energy of quantum states. How do we get at the energies of the different states of vibration? We use the fundamental relation between the frequency  $f$  and the energy  $E$ : energy is frequency multiplied by Planck's constant.

When Schrödinger calculated the frequencies of these vibrations and multiplied them by Planck's constant, he got exactly the observed energies of the quantum states of hydrogen! An incredible success. Everyone who contemplates this fantastic discovery sympathizes with Italian physicist Enrico Fermi, who used to say, when presenting this calculation in his lectures, *It has no business to fit so well!*

Confined electron waves in atoms cannot be observed directly. We can measure their extension, and frequencies (to be exact, we measure the differences between frequencies, which are observed as energy differences), but we cannot see them or photograph them because they would be destroyed by the light we would have to use in order to see them. This will be the topic of the next act in our presentation.

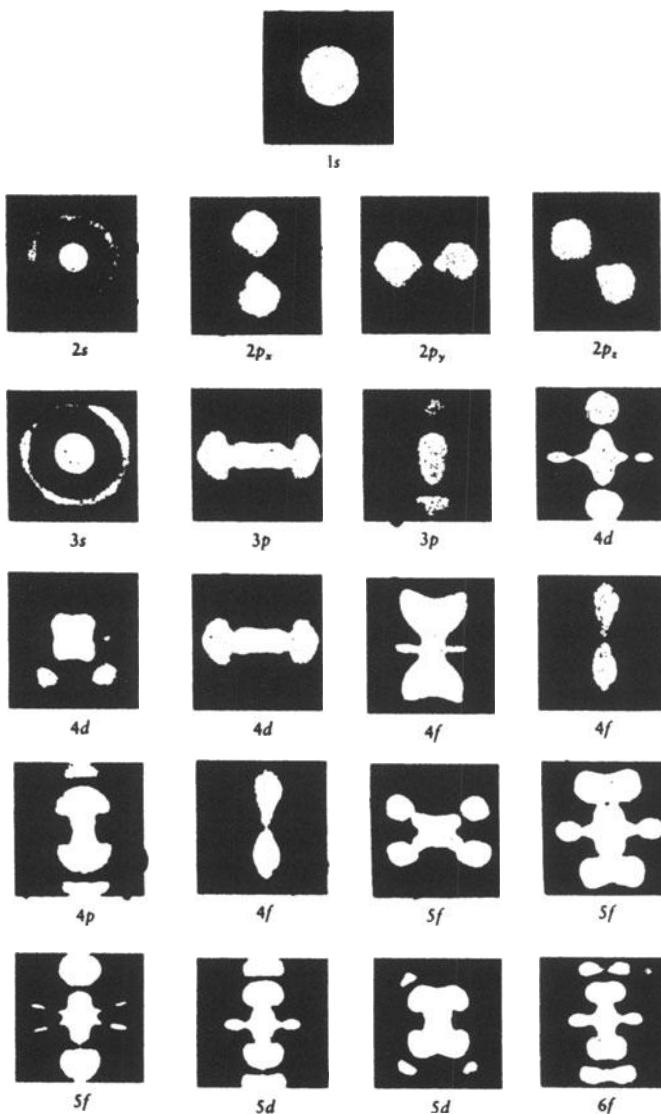


Figure 8. Mathematical models of vibrations of electron waves confined by a central charge. [Adapted from Introduction to Atomic Spectra by H.E. White, McGraw-Hill, 1934.]

One can make models, however, representing the results of Schrödinger's calculations. It is instructive and impressive to look at pictures of these models. Figure 8 shows the electron wave patterns, in order of increasing frequency, or energy, the successive quantum states of an electron confined by a nucleus. The lowest state, the ground state, is the simplest one; it has spherical symmetry. The next states have figure-eight forms; the higher the frequency, the more involved the patterns.

These are the fundamental patterns of matter. They are the shapes, the only shapes, that the electron vibration can assume under conditions prevailing in atoms—that is, under the influence of a central force (the attraction of the nucleus) that keeps the electron confined. We may call them *the primal shapes of nature*. These patterns are the original building blocks from which nature combines and forms everything we find around us.

Let us see how the other properties of atoms are explained in terms of these patterns. We begin with the stability of atoms and the regeneration of their original shapes and properties after being disturbed. Take the hydrogen atom: under ordinary conditions, when temperatures and pressures are not too high, the atom is found in the quantum state of lowest energy: it vibrates in the simplest possible pattern, the uppermost one in Fig. 8. To change from the lowest pattern to the next, the frequency, and therefore the energy, must be increased; for the hydrogen atom, the difference in energy is 10 electron volts (eV). Unless collisions or perturbations are able to deliver that amount of energy or more, a hydrogen atom stays unchanged in the lowest state or pattern. Since, at room temperature, the thermal energy is only  $\frac{1}{40}$  of an electron volt, collisions at room temperature cannot change the hydrogen atom's energy, or frequency. Under these conditions, the atom is stable. It remains in the lowest pattern.

Wave patterns also explain the regeneration ability of atoms. Say a hydrogen atom is deformed during a collision; it must assume the original pattern again when the perturbation is over. There are no other patterns available for the electron except at much higher energies. Let us look at a violin string: the player's finger presses down on the string; that pressure corresponds to a deformation. When the finger is removed, the string assumes its natural vibration.

How do these patterns explain the specificity of atoms and the variety of elements? Here, the *Pauli exclusion principle* enters. It says that no more than two electrons may vibrate in the same pattern and that those two must have opposite spin. Therefore, while the hydrogen atom, with its single electron vibrates in the simplest possible pattern in its lowest state of energy, other atoms exhibit more complex patterns, even in their state of lowest energy. Each second additional electron must assume the next higher pattern of the scale. This accounts for the variety of nature, because otherwise electrons in all atoms would vibrate in the lowest pattern and all elements would have roughly the same properties: the world would not contain as many different materials and forms.

Pauli discovered his principle empirically by analyzing the properties of atoms. But later on he was able to show that it follows from the fundamental laws of quantum mechanics. Unfortunately, his conclusions are too complicated to be explained in the frame of this essay.

The Pauli principle is the reason why neon, with ten electrons, is so different from sodium, with eleven. Since no more than two electrons are allowed to assume the same pattern, the ten electrons in the neon atom vibrate in five different patterns,

the first five shown in Fig. 8. As it happens, these five patterns fit together in such a way that the atom has a rounded shape, without any indentations or elevations. That is why neon is chemically inactive. The sodium atom, however, is irregular because the additional eleventh electron is forced to vibrate in a different pattern, according to the Pauli principle. This *isolated* electron is loosely bound and therefore ready to interact with electrons around other atoms. Sodium, therefore, is chemically active. When an atom's electron patterns fit into a nicely rounded shape, or *closed atomic shell*, the atom is an inactive gas. The atom with the next higher number of electrons can be expected to be a chemically active substance, with very different properties coming from the new occupied pattern. Atoms having one or a few electrons over and above the closed shell are those that form metals, such as sodium. The additional electrons jump easily from atom to atom and therefore give rise to the high electric and thermal conductivity of metals. That is why they feel cold when we touch them. Body heat is quickly carried away by the additional electrons.

Atomic structure provides interesting examples of how quantity determines quality. From the number of electrons in an atom, we can deduce the kind of properties a particular atom will have in its ground state by combining the various patterns of vibration. A telling instance happened when plutonium was produced in nuclear reactions for the first time. (Plutonium does not exist in nature because it is radioactive and decays into other elements in about 40,000 years.) The amounts of plutonium that were created were too small to permit any observation about its properties; however, it was known that the plutonium atom contained ninety-four electrons. Thus, we were able to determine its properties from the patterns of the electrons vibrating around the nucleus. It was found that it must be a metal; it must have specific weight of about 20 grams per cubic centimeter; it must be brown; it must have a certain electric and thermal conductivity and elasticity. All this information could be obtained from the single number ninety-four. It was a great moment when the first cubic millimeter of plutonium was finally produced and these projections were confirmed. This incident illustrates the tremendous predictive power of atomic quantum mechanics.

The connection between quantity (number of electrons) and quality (properties of the atom) points to an essential difference between quantum mechanics and classical physics. In the classical science, there is no well-defined state of lowest energy. If the electrons around the plutonium nucleus followed classical laws, the state of the plutonium atom would depend on the initial positions and velocities of the ninety-four electrons. No two plutonium atoms would be really identical. The same would be true, even for the hydrogen atom, with one electron since there are an infinite number of different ways for the one electron to circle the nucleus with a certain energy. There isn't even a lowest energy. The wave nature of electrons has changed all this. There is only *one* wave of lowest frequency (frequency determines energy), the one at the top of Fig. 8. In plutonium (as in any other atom) there is

only one way to put the electrons in pairs into the wave forms such as those shown in Fig. 8—at the lowest possible energy.

We therefore conclude that atoms with a fixed number of electrons are all alike; they behave identically. Gold, with seventy-nine electrons, has the same properties in the United States as in the Soviet Union because there is only one unique way of putting seventy-nine electrons into patterns of the kind shown in Fig. 8 and obtain the lowest possible energy, the ground state. There are, of course, other ways to distribute the seventy-nine electrons, but then we would obtain higher energies: higher quantum states of gold. They represent a series of energy values—the spectrum of gold—the lowest of which is 2.3 eV above the ground state. These states occur only at very high temperatures, but there will always be the same series of states.

Quantum mechanics introduced a concept that does not exist in classical physics: the concept of exact identity between atomic systems. In the classical picture we can always imagine arbitrary, small differences between atoms. In quantum mechanics, these are either exactly alike or measurably different—an important trait of nature.

The patterns shown in Fig. 8 and their inherent symmetries determine the behaviour of atoms. They also help us to understand how atoms combine to form molecules and how atoms form regular arrays in crystals. The simple beauty of a crystal reflects the fundamental shapes of the atomic patterns on a larger scale. Ultimately, all the regularities of form and structure that we see in nature, ranging from molecular structure to the hexagonal shape of a snowflake or the intricate symmetries of living forms in flowers and animals, are based on the symmetries of these atomic patterns. The world abounds in characteristic forms and shapes, but only quantum mechanics can tell us—at least in principle—where they all come from.

Electron patterns also explain why 6000 calories of heat are produced from burning a kilogram of coal. Energy is gained when carbon dioxide is formed from a carbon atom (in coal) and an oxygen molecule (in air) because the electron patterns of carbon and oxygen fit together better in carbon dioxide and therefore have lower energy than in the oxygen molecule and the carbon crystal. The amount can be calculated, and when multiplied by the number of atoms in a kilogram of coal, the result is 6000 calories. The reason why oxygen combines so easily with hydrogen to give water is that the eight electrons of oxygen are just two electrons short of the closed shell that we found in neon. Thus, they form a round shape when the two holes are filled with the electrons of two hydrogen atoms, so we get  $\text{H}_2\text{O}$ !

Even the phenomena of life are based upon the characteristic electron patterns and their stability. The structure of DNA comes from the specific way in which electron patterns of carbon, hydrogen, oxygen, nitrogen, and other atoms fit together and form the well-known helix. They are resistant to thermal motion at room

temperature; more energy is required to change those patterns and to disentangle them.

Consequently, the DNA helix has its own stability, which explains why the same flowers emerge every spring and children resemble their parents.

Schrödinger's calculations and the subsequent tremendous development of our understanding of the properties of atoms, molecules, gases, liquids, and solids have shown that the structure of matter in our environment is based on the electric force between atomic nuclei and electrons and how the wave-particle duality of the electrons respond to it.

There is an interesting historical relation. Kepler thought that planetary orbits in the solar system had very definite size ratios. He connected them with the size ratios of simple polyhedrons. In fact, it is not so, for the sizes of the planetary orbits are, to a large extent, accidental. But now Kepler's idea reappears in the atomic world, where it is clearly understood as a typical property of electrically confined waves. There is a kind of harmony among the different frequencies of the electron patterns, a *chord* that can be considered a rebirth of the Pythagorean harmony of the spheres. These harmonies may not be particularly pleasing as musical chords to our ears, but they certainly appeal to our intellectual ears when they offer so much insight into the structure of the material world.

### **Act III: Significance of wave-particle duality and the new reality of the quantum state**

Act II demonstrated that the wave-particle duality plays a decisive role in the dynamics of atoms. The wave nature of electrons permitted us to understand the puzzling properties of atoms, such as the stability, specificity, and discrete energy states. But the fundamental question remains: How can the electron be a particle and a wave at the same time? It is not a true particle, because it exhibits wave properties, and it is not a true wave, since its amplitude is fixed in the following sense: if the electron assumes one of the wave patterns of Fig. 8, it vibrates with a certain intensity. It cannot vibrate with half that intensity, since that would correspond to half an electron and there is no such thing. It is neither a wave nor a particle.

Its wave nature is exhibited not only in the patterns of Fig. 8. Beams of free electrons that are not bound to atoms also show wave and particle properties. As mentioned before, electrons emerging from two nearby points exhibit interference under certain conditions, similar to the water waves in Fig. 2. On the other hand, the intensity of the wave representing an electron beam cannot assume any value, as an ordinary wave would, but only those values corresponding to a definite number of particles. Furthermore, when two electron beams cross each other and the electrons of one beam are scattered by the other, scattered electrons have just the momenta and energies we would expect from two *particles* colliding; however,

the directions in which they emerge are distributed according to the scattering laws of waves!

Why can't we find out, by exact observations, whether an electron is a wave or a particle? Couldn't we try to follow the electron motion in the atom, step by step, to see whether it is a localized particle moving along an orbit or a vibrating wave spread over a region? This question goes to the heart of quantum physics. One of the features of classical physics is the *divisibility* of physical processes, the idea that a process can be thought of as a succession of particular partial processes. According to that idea, each process can be followed, step by step, in time and space. The orbit of an electron around the nucleus would be thought of as a succession of small displacements. In contrast, a wave would be thought of as a continuous oscillatory movement spread over a region of space.

Here we meet one of the basic concepts of quantum mechanics. There are fundamental reasons why such tracing cannot be carried out. The idea of divisibility of motion is in serious trouble, and the trouble comes from the graininess of light. In order to see the details of the electron motion in the atom, we must use light waves with a very small wavelength, the size of the atom. Such light, however, has a high frequency and therefore a large energy quantum. In fact, light whose wavelength is as small as an atom has a quantum of energy that would be far more than enough to tear the electron away from the atom. When light hits an electron, it will knock it out of the atom and destroy the very object of our examination. This is so, not only when light is used to observe an object, but quite generally all measurements that could be of use to decide between the wave and the particle nature of the electron have the same result. If we attempt to perform these measurements, the object changes its state completely.

The quantum nature of light or of any other means of observation introduces a coarseness that makes it impossible to decide between wave and particle. It does not allow us to subdivide the atomic orbit into a succession of partial motions, whether they are particle displacements or wave oscillations. If we force a subdivision of the process and try to look more accurately at the wave in order to find out where the electron *really* is, we will have destroyed the subtle individuality of the atom that give rise to all its characteristic properties. The argument that an entity cannot be both a wave and a particle, because a wave is spread over space whereas a particle is concentrated at a definite position, no longer holds within atomic dimensions. The habitual concepts of *location* and *spread* are no longer applicable; any effort to observe them would destroy the object.

Here quantum mechanics enters as a new and revolutionary concept. The great new insight of quantum physics is the recognition that individual states of the atom—we call them quantum states—are each indivisible wholes that exist only as long as they are not attacked by penetrating means of observation. The quantum state is the state the atom assumes when it is left alone to adjust itself to the prevailing conditions. If we try to measure the location of an electron with those

penetrating means, we not only will destroy the quantum state, but will indeed find the electron at some place, but that place is not predictable.

Electrons do not have a predictable position in the atom, because *position* is a classical concept, not directly applicable in the atomic realm. The results of our physical measurements, however, are always classical magnitudes; that is, we measure magnitudes of position, velocity, and energy. Therefore, we should not be surprised if, in some cases, all we can predict are probabilities; furthermore, the quantum state has been thoroughly changed after measurement. What we should be surprised about is that physicists were able to construct a mathematical formalism (quantum mechanics) for dealing with quantum reality that allows us to calculate those probabilities.

The restrictions to the application of classical concepts, such as position, velocity, and momentum, are codified by the famous Heisenberg uncertainty relations. When we ask what is the position or the velocity of an electron in a quantum state, we cannot always expect a definite answer. The Heisenberg uncertainty relations tell us, for example, to what degree, within a quantum state of an atom, the location and the velocity of an electron is left undetermined. They are the warning posts that advise us how far we are allowed to apply habitual classical concepts before we get into trouble with reality. *Up to here and no further may you apply your old-fashioned concepts.*

An important consequence follows. Certain statements about the atom must remain probabilistic because our concepts—for example, *electron position*—are not appropriate in the atomic quantum state. If we force the concept on the atom, we get only a probability for an answer: the electron will be found here with this probability and there with another probability. The phrase, *If you ask a silly question, you get a silly answer*, should be applied in this form: *If you ask an inappropriate question, you get a probabilistic answer*. Outside the confines of the Heisenberg relations, however, for objects much larger than atoms, we can still apply classical concepts without trouble. The orbit of an earth satellite can be calculated and predicted with practically unlimited accuracy.

The quantum state has a more subtle individuality than ordinary macroscopic states of matter. Reality exhibits different, seemingly contradictory properties, when examined in different ways. In the words of David Bohm: *The electron may be regarded as an entity that has potentialities for developing either particle properties or wave properties, depending on the type of instruments with which it interacts.*

Some philosophers like to say that, according to quantum mechanics, the world around us is not real and depends on our minds, because our observations disturb and change the objects. I disagree. True enough, typical quantum properties unfold only if atoms are not subject to methods of observation that penetrate their interior. But they are not exposed to such perturbations under ordinary conditions, and that is why characteristic quantum properties are manifest everywhere: in the color of objects; in the structure of crystals; in the mechanical, electrical, and chemical

properties of different substances; and, in the last instance, in the phenomena of life. In most of our studies of material properties, we try to maintain, not to disturb, the quantum states, since they give rise to the reality of interest to us. Sure enough, if an atomic phenomenon is observed too closely by our clumsy instruments we destroy the very object of interest, its quantum state, with all its seemingly contradictory properties. But just these properties are responsible for the behavior and appearance of matter in our environment. Hence, it is the quantum state that is *real* and exists independently from us. If close observations destroy it, and if we cannot describe it with our everyday concepts, too bad for those observations and concepts! What is real are the objects and their quantum states, since they represent nature. The inapplicability of some of our concepts does not make the objects less real.

Although an unambiguous description of atomic reality is impossible with our ordinary concepts of material processes, we have an unambiguous mathematical scheme that gives the right predictions and probabilities for any observation. A physical description, however, must make use of such seemingly contradictory concepts as the wave picture and the particle picture. Neither can give a complete description, but both are necessary to understand the phenomenon in its entirety. Each of these mutually exclusive perspectives gives only a partial, one-sided view; both are needed for a full understanding. Niels Bohr introduced the term *complementarity* to describe this novel situation. This is why we face a richer reality in the quantum world than the classical picture has ever been able to describe.

## Act IV: The quantum ladder

### An extension of quantum mechanics to nuclear and subnuclear phenomena and to the history of the universe

After its conception, quantum mechanics developed in two distinct directions. The first, broadest development was toward a better understanding of the properties of agglomeration of atoms, such as molecules, liquids, and solids. Quantum mechanics turned out to be the key to many previously unexplained properties of materials—such as their behaviour at high and low temperatures—and of chemical reactions and molecule formations. Knowing the quantum states of atoms made it possible to understand what happens when atoms are joined to molecules, liquids, or solids. Electrical and optical properties of metals, for example, turn out to be consequences of peculiar properties of electronic quantum states in the regular array of atoms in metal. The disappearance of electric resistance in some metals in low temperature (superconductivity) could now be explained. New forms of electric conductors, semiconductors, for example, were found and understood.

These new insights led to the invention of the transistors and the microchip, which revolutionized electronic technology.

The other development of quantum mechanics is less broad but deeper: it goes into the depth of the structure of matter, into the structure of the atomic nucleus, and later into the structure of the constituents of the nucleus. The same quantum mechanics that once explained atomic behavior is now found to operate on a deeper level within atomic nuclei and even within their constituents.

Let us look at the atomic nucleus. It is a very small, massive, positively charged entity, roughly speaking, about 10,000 times smaller in diameter than the atom. It is responsible for the structure of atoms, since its positive electric charge attracts electrons and keeps them confined in the atom. That confinement produces the characteristic quantum states, such as those depicted in Fig. 8.

Rutherford, who in 1911 discovered the internal structure of atoms, observed in 1917 that atomic nuclei also have an internal structure. He found that they contained protons. The proton itself is nothing other than the nucleus of the simplest atom, the hydrogen atom. The additional constituent contained in other nuclei was recognized by Chadwick, who in 1932 discovered the neutron—a particle very similar in mass and character to the proton, except that it carries no electric charge, whereas the proton carries one unit of positive charge. Atomic nuclei were found to be composed of protons and neutrons, with the positive charge of a nucleus provided by its protons.

With this discovery, a new branch of physics began: nuclear physics. First of all, the mere existence of a conglomerate of protons and neutrons suggests the action of a new kind of force. Electric forces could not keep protons and uncharged neutrons together; indeed, protons would be driven out because charged particles of equal sign repel each other. There must be a strongly attractive force acting between neutrons and protons to keep them together in such a small entity as the nucleus. We call it the nuclear force—such a force was indeed observed and measured.

Then, in the 1930s, a repeat performance of quantum mechanics took place. Protons and neutrons are also subject to the wave-particle duality, as are all particles. The nuclear force confines them into a small area of space. Confinement produces characteristic wave patterns, not unlike those shown in Fig. 8. Thus, nuclei, like atoms, are expected to exhibit typical quantum states, with properties such as stability and regeneration, except that the relevant energies and energy differences are much larger.

Here we come to an important principle of quantum mechanics: the energy–size relation. It refers to the energies of quantum states of a confined system of particles. The smaller the size of the system, the greater are those energies and energy differences between quantum states. They also depend on the mass greater of the constituents: the higher the mass, the smaller the energies. We will concentrate on the size dependence here; it is the more important one.

The nucleus is very much smaller than the atom. Therefore, the energies of the quantum states and the energy intervals between them are much greater. We call nuclear physics the next higher rung of the quantum ladder, the lowest rung being atomic and molecular physics. Indeed, it takes millions of electron volts (a unit of one million is a mega-electron-volt or MeV) to lift a nucleus from its lowest quantum state to the next one, whereas in an atom, it takes only a few electron volts (roughly between one and ten). Nuclear reactions imply energy exchanges of millions of electron volts, whereas chemical reactions between atoms deal with exchanges of only a few. This is why nuclear explosives are so much more powerful than ordinary ones.

When a nucleus performs a transition from a higher to a lower quantum state, the energy difference is emitted in the form of a photon, just as it is in an atom, but the *nuclear light* called gamma rays is much more energetic than *atomic light*. In the nuclear regime, another kind of emission appears: sometimes, instead of a photon, a pair of particles is emitted, an electron and a neutrino, in a process known as radioactivity. It could not have occurred in the atomic regime, because it requires energies not available in atomic processes. An electron and a neutrino must be created. According to Einstein's famous equivalence of energy and mass— $E = mc^2$ —the creation of an electron requires the availability of at least  $\frac{1}{2}$  MeV, which is the energy corresponding to the electron mass. A neutrino is massless; it does not require a minimum energy to be created. Such energies as the mass energy of the electron are not available in transitions between atomic quantum states, but they are available in transitions between nuclear quantum states.

Because of the large difference in energy, nuclear processes occur under very different conditions from atomic or molecular ones, processes that require energy exchanges of only a few electron volts. This is approximately the energy of photons coming from the sun. Therefore, the surface of the earth abounds with phenomena based on interactions of atoms and molecules. The atomic nuclei necessarily stay in their lowest quantum state under such conditions and therefore act as unchanging entities. In our terrestrial world, nuclei never get naturally excited; they are never lifted into their higher quantum states; and they appear completely stable. Nuclear physics is dormant on earth. We observe nuclear phenomena only when we construct machines—cyclotrons, synchrotrons, and other particle accelerators or nuclear reactors—that can produce the necessary energies.

The nuclear processes found on earth, apart from man-made ones, are the decays of some naturally radioactive substances, such as radium, thorium, or uranium, responsible for much of the heat produced deep in the interior of the earth. But they are not of terrestrial origin. They were produced when the matter that now constitutes the earth was ejected with tremendous energies by a supernova explosion seven billion years ago. They represent the last embers of the great nuclear fire that created the elements.

The places of nuclear processes in nature are those regions where millions of electron volts are available. That happens in the interior of stars and in the explosions of supernovas. Indeed, nuclear reactions in the center of the sun are the sources of solar heat. They are the nuclear fire in which hydrogen nuclei are burnt to helium nuclei (not unlike the burning of coal to carbon dioxide in a coal fire). It will last four or five billion years before burning out.

There is an even higher rung of the quantum ladder. Certain strange occurrences in cosmic rays, unaccountable on the basis of nuclear physics, had already been observed in the 1930s. The decisive discovery was made in 1950, when E. Fermi and his collaborators found that the proton has an excited quantum state. Soon thereafter, many more quantum states of the proton and neutron were discovered, pointing toward an internal structure of nuclear particles. Like the atom and the nucleus, they seemed to be a composite system made of some constituent particles that are combined by some kind of force and form typical wave patterns that lead to discrete quantum states.

These discoveries opened up a new world of phenomena: the third rung of the quantum ladder, the subnuclear realm. As expected from the energy-size relation, the relevant energies are much larger. They are measured by the giga-electronvolt (GeV), that is, a billion electron volts. The first excited state of the proton is 0.3 GeV above the ground state. This is the reason why subnuclear phenomena are dormant, even in the nuclear realm. New types of accelerators of many GeV are needed to observe them.

It turned out to be a most surprising world, not yet fully exploited and understood. The constituents of the proton and neutron were identified. They received the ugly name *quarks*. A very strong new force was identified that holds quarks together within the proton. So far, the picture turned out to be similar to the one at the lower ranges of the quantum ladder. The different quantum states of the proton and neutron could again be interpreted as confined waves of quarks.

There are a number of unexpected new features that are to some extent still surprising and difficult to explain. For example, it seems to be impossible to extricate a quark from a proton or neutron. They cannot be liberated from confining bonds, but they can be observed to move within the proton and neutron in contrast to the situation on the lower rungs: the atom can be decomposed into nucleons and electrons; the nucleus can be decomposed into protons and neutrons.

Furthermore, a number of new short-lived entities show up: mesons and heavy electrons. Both entities need gigavolt energies to be created. They exist only for a short time. They transform themselves quickly into other known particles, such as ordinary electrons, neutrinos, and photons.

Antimatter comes to play an important role on the third rung: What is it? For every particle there is a corresponding antiparticle with exactly the same mass but opposite charge. There are antiatoms made up of positive antielectrons and negative antinuclei composed of antiprotons and antineutrons. But antimatter cannot exist

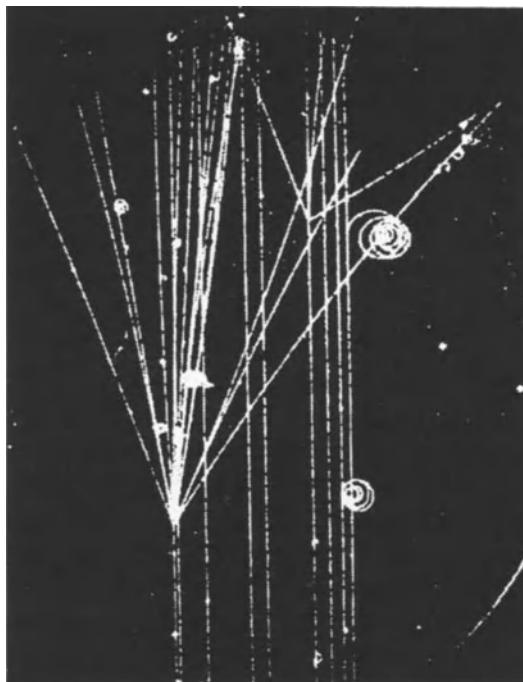
together with ordinary matter, because an antiparticle and a particle annihilate each other on contrast and transform themselves into energy. This is a transformation of one kind of energy into another kind of energy. Inversely, if energy in sufficient concentration is available, it can transform itself into a pair consisting of particle and antiparticle. The energy concentrations necessary for such processes are very high and available to a sufficient degree only at the third rung of the quantum ladder, so as to make antimatter an important ingredient of the subnuclear phenomena.

The existence of antimatter is another triumph of quantum mechanics. In the early 1930s, the British physicist P.A.M. Dirac showed that the equations of quantum mechanics and relativity theory required that there be an antiparticle to every particle. It also followed that particle-antiparticle pairs can be created from other forms of energy and annihilated into energy. Dirac could not believe that result because, at that time, antimatter had not yet been found. He was deeply astonished by these strange consequences of his calculations. These equations seemed to him *more intelligent than their author*. It was an unusual feat of the human mind to predict the existence of antimatter by pure intellectual insight before it was actually observed in nature.

Let us return to the subnuclear world, which is revealed with the help of very high energy beams produced by powerful accelerators. When a particle carrying many gigavolts of energy impinges upon a target, an explosion of newly created particles takes place: protons, antiprotons, electrons, antielectrons, mesons, and other particles emerge all over. Figure 9 gives a telling picture of the variety of such events.

In the past three decades, the quantum ladder has acquired a new significance. There seems to be a connection between the infinitely small, the elementary constituents of matter, and the infinitely large, the origin and history of the universe as a whole. The connecting link is the discovery of the expansion of the universe. There are a number of indications that celestial objects move away. If this is so, we would expect that in the distant past, the concentration of mass ought to have been much greater. Indeed, about fifteen billion years ago, all space should have been filled with almost infinitely concentrated matter. Such concentration would have to be accompanied by extremely high pressure and temperature. Thus, we are led to the tentative conclusion that the universe started with a *primal bang*, where all space was filled with highly concentrated matter of extremely high temperature and energy, which decompressed and diluted itself, first quickly and then more slowly, until it reached its present state.

One of the most uncanny discoveries of the last decade was the observation of a pervading cool radiation coming from all directions in space, with all the properties of an optical reverberation of the radiation emitted during the initial hot period in the life of the universe. It was another indication of the great happening at the beginning of the universe.



*Figure 9.* A bubble-chamber picture of a 25-GeV proton beam impinging on a hydrogen atom and producing new particles. [Courtesy of CERN, Geneva, Switzerland.]

Developments from the primal bang to our present state are intimately connected to the quantum ladder. In the first instants after the bang, energy concentration was indeed so high that the phenomena of the third rung of the quantum ladder was the order of the day, or more appropriately, the order of the microsecond. At that time, space was filled with quarks, antiquarks, gluons, electrons, antielectrons, and neutrinos and with an intense light radiation of extremely energetic photons. Then, as the universe expanded, energy concentration diminished rapidly. Particles and antiparticles annihilated, producing more radiation and short-lived mesons. After a few microseconds, a slight surplus of quarks over antiquarks (not quite understood today) remained, and the quarks assembled into protons and neutrons. Then the temperature dropped further because of the expansion. After about 10 seconds, some protons and neutrons assembled into helium nuclei. We now step down to the second rung of the quantum ladder: the nuclear realm. It probably took several hundred thousand years to cool down sufficiently to allow electrons to be bound by the nuclei to form atoms, arriving at the first rung. It then took billions of years to reach the present situation. Galaxies and stars were formed, and on the surface of some planets, the atomic and molecular world developed the great variety of forms and materials we now see on earth.

This view of the development of the universe is to some extent hypothetical and unproven. It is much less certain than the validity of quantum mechanics and our knowledge of the properties of molecules, atoms, and nuclei.

The quantum ladder symbolized the steady increase in depth of our knowledge about the structure of matter. It started with ordinary chunks of matter composed of atoms and molecules, whose structure was revealed on the first rung. It then proceeded to the structure of atomic nuclei and—finally today—to the quarks as constituents of the proton or neutron. There may exist yet unknown higher rungs of the ladder. The development of the universe happened in the opposite direction, down the quantum ladder, as it were. The very beginnings are shrouded in the unknown, since we know nothing about the higher rungs of the ladder that may come into play in the first, extremely short time intervals. But we have clearer ideas about the evolutionary history of the world from a microsecond after the primal bang to the present universe. It was a series of gradual steps, from the simple to the complicated, from the unordered to the organized, from the hot, formless gas of elementary particles to the cooler, structured atoms and molecules; still further to the more structured liquids and solids, and finally to sophisticated self-reproducing living organisms. Steps in this history that are still hidden in ignorance and guesswork include what happened immediately after the *primal bang*, the mechanisms forming galaxies and clusters of galaxies, and the details of the origin and development of life on our planet.

The drama of the development of quantum mechanics has not ended, but we have arrived at the present limits of our knowledge. This limit lies far beyond what could have been expected at the turn of the century, when quantum mechanics was conceived. Ingenious use of accelerators and instrumentation revealed even deeper structures of matter, still subject to the rules of quantum mechanics in more developed forms. It is certainly an encouraging thought that we were able, in our laboratories, not only to understand the deeper structure of matter, but also to recreate the processes and phenomena that, in all probability, happened in nature only in the first instants of its existence.

# Chronological Development of Quantum Mechanics: A Very Brief Account

The development of quantum mechanics as a unified structure did not take place in the smooth way that is usually presented in a textbook. For a textbook to present this development in chronological fashion is, however, not really a fruitful way of presenting the subject to the student. On the other hand, we feel that every student ought to have some sense of perspective of this development. As mentioned by Ludwig [1] ‘*without taking account of its historical development, an existing theory often appears almost as if it had “fallen from heaven”*’. *However the question of the development of a theory is important not only to satisfy our curiosity but also because much can be learnt from it for the future*’. Keeping this in mind we give a very brief account of the chronological development of quantum mechanics highlighting some of the important facts associated with the development and also giving reference to books (which are usually available in most libraries) where some of the original papers have been reprinted. We hope that this introduction will induce the reader to go back to some of the articles written by the *masters* of the subject so that he is able to get a perspective of the field as it developed.

We should mention that perhaps the most comprehensive account of the chronological development of quantum mechanics is given in the book by Jammer [2] which has also given detailed references of most of the important publications during the development of the field (and where they could be found). There are numerous other books/articles written on the historical development of the subject; particular reference can be made to Born [3], Condon [4], Cropper [5] and ter Haar [6]. We give below a brief account of the chronological development:

**1900:** In a paper entitled ‘*On an improvement of Wien’s equation for the spectrum*’, Planck “guessed” the blackbody radiation formula and found that it is in excellent agreement with the experimental data. In a subsequent paper entitled ‘*On the theory of the energy distribution law of the normal Spectrum*’ he derived this formula by introducing a drastic assumption that the oscillators can only assume discrete energies. Planck wrote “*We consider, however—this is the most essential point of the whole calculation—E to be composed of a very definite number of equal parts and use thereto the constant of nature  $h = 6.65 \times 10^{-27}$  erg sec. This constant multiplied by the common frequency  $v$  of the resonators gives us the energy element  $\epsilon$  in erg, . . .*”. The two papers of Planck are reprinted by ter Haar [6]. It may be of interest to mention that in an unpublished letter to R.W. Wood, Planck wrote (quoted from Ref. 2) that the postulate of energy quanta was ‘an act of desperation’ done because ‘a theoretical explanation *had* to be supplied at all

cost, whatever the price'. Planck was awarded the 1918 Nobel prize in Physics for his *discovery of energy quanta*; his Nobel lecture was on '*The genesis and present state of development of the quantum theory*'.

**1905:** In a paper entitled '*On a heuristic point of view about the creation and conversion of light*' (reprinted in Ref. 6), Einstein introduced the light quanta. In this paper he wrote that for explanation of phenomena like blackbody radiation, production of electrons by ultraviolet light (which is the photoelectric effect) it is necessary to assume that "*when a light ray starting from a point is propagated, the energy is not continuously distributed over an ever increasing volume, but it consists of a finite number of energy quanta, localized in space, which move without being divided and which can be absorbed or emitted only as a whole*". Einstein received the 1921 Nobel prize in Physics for his *discovery of the law of photoelectric effect* and *not* for his theory of relativity. It is interesting to note that Einstein did not have the symbol  $h$  in his paper; he used the quantity  $R\beta_v/N$  for the energy of the light quanta where  $R/N$  and  $\beta$  are actually  $k$  and  $h/k$  respectively.

**1913:** In a paper entitled '*On the constitution of atoms and molecules*' (reprinted in Ref. 6), Bohr gave the first successful interpretation of atomic spectra. (The experimental study of atomic spectra was started around 1860 and in 1885 Balmer gave his famous empirical formula which came to be known as Balmer series). Niels Bohr's logic of argument was somewhat as follows: For an electron rotating in a circular<sup>1</sup> orbit around a proton the potential energy is  $-e^2/a$ , the kinetic energy ( $\frac{1}{2}mv^2$ ) is  $e^2/2a$  and therefore the binding energy is given by

$$E_b = e^2/2a$$

The frequency  $v'$  of the orbiting electron is given by

$$v' = \frac{v}{2\pi a} = \left( \frac{2E_b}{m} \right)^{1/2} \frac{1}{2\pi} \frac{2E_b}{e^2} = \frac{\sqrt{2}E_b^{3/2}}{\pi e^2 m^{1/2}}$$

Bohr then assumed that "*during the binding of the electron, a homogeneous radiation is emitted of a frequency  $v = \frac{1}{2}v'$ ; then from Planck's theory, we might expect that the amount of energy emitted by the process considered is equal to  $\tau h\nu$ , where  $h$  is Planck's constant and  $\tau$  an entire number*". Thus

$$E_b = \tau h\nu = \frac{1}{2}\tau h v' = \frac{1}{2}\tau h \left[ \left( \frac{2}{m} \right)^{1/2} \frac{E_b^{3/2}}{\pi e^2} \right]$$

which gives

$$E_b = \frac{2\pi^2 me^4}{\tau^2 h^2}$$

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<sup>1</sup> Actually Bohr's consideration was for elliptical orbits; here, for the sake of simplicity we are considering circular orbits.

and when an atom makes a transition from one stationary state ( $\tau = \tau_1$ ) to another ( $\tau = \tau_2$ ) a light quantum of frequency

$$\frac{2\pi^2 me^4}{h^2} \left[ \frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right]$$

is emitted. The above formula agreed with the experimental data.

It should be mentioned that the quantization of angular momenta was put forward by Bohr in a subsequent paper in the same year. Bohr was awarded the 1922 Nobel prize in Physics for his *investigation of the structure of atoms, and of the radiation emanating from them*. His Nobel lecture on ‘The structure of the atom’ gives a summary of the important results in atomic theory.

**1914:** In a paper entitled ‘*On the excitation of 2536 Å mercury resonance line by electron collisions*’ (reprinted in Ref. 6), Franck and Hertz showed that by varying the kinetic energies of the electrons hitting an atom it is possible to produce controlled excitation of atoms and molecules; the experiment proved the discrete energy states of atoms, a hypothesis put forward by Bohr in 1913. Franck and Hertz received the 1925 Nobel prize in Physics for *their discovery of the laws governing the impact of an electron upon an atom*.

**1917:** In a paper entitled ‘*On the quantum theory of radiation*’; (reprinted in References 6 and 7), Einstein put forward the existence of stimulated emission and introduced the famous  $A$  and  $B$  coefficients which are now known as the *Einstein coefficients*.

**1922:** Stern and Gerlach performed their famous experiment which demonstrated that in the presence of a strong inhomogeneous magnetic field, a beam of silver atoms split into two beamlets. This provided a confirmation of space quantization.

**1923:** Compton reported his studies on the scattering of X-rays by solid materials (mainly graphite) and showed that the shift of the wavelength of the scattered photon could be explained by assuming the photon having momentum equal to  $h/\lambda$ . Compton shared the 1927 Nobel prize in Physics ‘*for his discovery of the effect named after him*’. The original papers of Compton have been reprinted in a book by Shankland [8].

**1924:** In a paper entitled *Investigations on quantum theory* [reprinted in Ref. 1], de Broglie suggested the idea of waves associated with electrons. He recognized that the condition for the  $k$ th orbit

$$mv_k r_k = n \hbar$$

implies

$$2\pi r_k = n \frac{\hbar}{mv_k} = n \lambda$$

i.e. the circumference of the allowed orbit contains an integral number of wavelengths. He wrote ‘*in order to have a stable state the length of the channel must be in resonance with the wave*’. De Broglie was awarded the 1929 Nobel prize in Physics for his ‘*discovery of the wave nature of electrons*’.

**1925:** Pauli in his paper entitled ‘*On the connection between the completion of electron groups in an atom with the complex structure of spectra*’ (reprinted in Ref. 6) put forward the “fourth quantum number of the electron” and the exclusion principle. He was awarded the 1945 Nobel prize in Physics for the *discovery of the exclusion principle*.

**1925:** After studying Pauli’s paper, Uhlenbeck and Goudsmit put forward the idea of the spinning electron.

**1925 to 1928:** In 1925 Heisenberg put forward the ‘*quantum-theoretical mechanics based exclusively on relationships between quantities observable in principle*’, which was further developed by Born and Jordan in the same year. The commutation relation was first introduced by Born and Jordan. Born later wrote ‘*I shall never forget the thrill I experienced when I succeeded in condensing Heisenberg’s ideas on quantum conditions in the mysterious equation  $pq - qp = h/2\pi i$* ’. Schrödinger’s papers came in 1926. His three famous papers under the same title ‘*Quantization as an eigenvalue problem*’ appeared in quick succession in 1926. In between he had also published a paper with the self-explanatory title ‘*On the relationship of the Heisenberg-Born-Jordan Quantum Mechanics to mine*’. The original papers of Schrödinger, Heisenberg, Born and Jordan are reprinted in Ref. 1. In 1926 Born suggested that the square of the wave function should be interpreted as the probability density of particles. In 1927 Heisenberg formulated his famous uncertainty principle<sup>2</sup> and in the same year Born developed the quantum mechanical theory of scattering of electrons by atoms and Dirac succeeded in developing the quantum theory of radiation which could explain satisfactorily the phenomena of interference as well as the emission and absorption of light by matter<sup>3</sup>. In 1928 Dirac gave his relativistic equation which led to the prediction of the ‘*positive electron*’ which was later called the *positron*. In 1932, Anderson observed such a particle in cosmic radiation where they could be distinguished from electrons by the opposite curvature of their tracks in the presence of a magnetic field.

The 1932 Nobel prize in Physics went to Heisenberg for the creation of quantum mechanics. The 1933 Nobel prize in Physics was shared by Schrödinger and

<sup>2</sup> Heisenberg’s book *The Physical Principles of Quantum Mechanics* is a very entertaining book to read on the uncertainty principle.

<sup>3</sup> A very nice account of Dirac’s quantum theory of radiation has been given in a review paper by Fermi [9]; of course, the classic treatise by Dirac [10] should be a must for all persons trying to understand quantum mechanics.

Dirac for the discovery of new productive forms of atomic theory and the 1954 Nobel prize in Physics went to Max Born for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wave function.

**1927:** Davisson and Germer and independently G.P. Thomson observed electron diffraction patterns produced by metal foils which established the existence of de Broglie waves. The 1937 Nobel prize in Physics was shared by Davisson and Thomson for their experimental discovery of the diffraction of electrons by crystals.

**1928:** Gamow in Germany and Gurney and Condon in USA reported the first major application of quantum mechanics, namely, the barrier leakage interpretation of the natural radioactive decay of some elements emitting alpha particles. The theory could satisfactorily explain the fact that an alpha particle can remain inside a nucleus for about  $10^9$  years before it comes out. Condon in 1952 wrote: “*I think it is fair to say that the barrier-leakage idea was the opening of the modern period of the application of quantum mechanics to nuclear physics*”.

**1931:** In order to explain the continuous beta ray spectrum, Pauli in 1931 suggested the existence of the neutrino.

**1934:** Fermi developed the famous theory of beta decay.

Although the development of quantum mechanics continues even today, we felt that Fermi’s beta decay theory should be an appropriate point to ‘sign off’ (keeping in view the scope of the present book). We conclude by mentioning the following incident (quoted from May 1982 issue of *Physics Today*):

After attending a seminar given by one of Oppenheimer’s pupils on Fermi’s beta ray theory, Fermi remarked to Emilio Segre, ‘Emilio, I am getting rusty and old. I cannot follow the highbrow theory developed by Oppenheimer’s pupils any more. I went to their seminar and was depressed by my inability to understand them; only the last sentence cheered me up. It was: “*And this is Fermi’s theory of beta decay*”.’

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7. F.S. Barnes, *Laser Theory*, IEEE Press, New York (1972).
8. R.S. Shankland (Ed.), *Scientific Papers of A.H. Compton*, University of Chicago Press, Chicago (1973).
9. E. Fermi, *Quantum Theory of Radiation*, Reviews of Modern Physics, **4**, 87 (1932).
10. P.A.M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press, Oxford (1958).

# Physical Constants

C = coulomb; esu = electrostatic units;  
eV = electron volt; F = farad; G = gauss;  
H = henry; Hz = hertz = cycles/s; J = joule;  
K = kelvin (degree Kelvin); m = metre; N = newton;  
s = second; T = tesla

Digits in parentheses following each quoted value represent the standard deviation error in the final digits of the quoted value; e.g., 1.60217733(49) implies  $1.60217733 \pm 0.00000049$ , etc. Most of the quoted values are taken from ‘The Fundamental Physical Constants’ by E. Richard Cohen and Barry N. Taylor, *Physics Today*, August 1995.

## Conversion factors

$$1\text{N} = 10^5 \text{ dynes}$$

$$1\text{J} = 10^7 \text{ ergs}$$

$$1\text{eV} = 1.60217733(49) \times 10^{-19} \text{ J}$$

$$1\text{C} = 1\text{amp} \cdot \text{s} = 2.997924580(12) \times 10^9 \text{ esu}$$

$$1\text{T} = 1\text{weber} \cdot \text{m}^{-2} = 10^4 \text{ G}$$

$$1\text{F} = 1\text{C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$$

$$1\text{H} = 1\text{weber} \cdot \text{amp}^{-1} = 1\text{N} \cdot \text{m} \cdot \text{s}^2 \cdot \text{C}^{-2}$$

$$1\text{ Electron mass } (= m_0 c^2) = 0.51099906(15) \text{ MeV}$$

$$1\text{ Proton mass } (= m_p c^2) = 938.27231(28) \text{ MeV}$$

$$1\text{ Neutron mass } (= m_n c^2) = 939.56563(28) \text{ MeV}$$

$$1\text{ atomic mass unit} = 1.6605402(10) \times 10^{-27} \text{ kg}$$

(atomic mass unit in the unified atomic mass scale  $^{12}\text{C} = 12$ )

Quantity	Symbol	Value	Uncertainty (parts per million)
Speed of light in vacuum	$c$	299792458 m.s <sup>-1</sup>	Exact
Planck's constant	$\hbar = h/2\pi$	$1.05457266(63) \times 10^{-34}$ J.s	0.60
Electronic charge	$q$ (mks)	$1.60217733(49) \times 10^{-19}$ C	0.30
Electron rest mass	$m_e$	$9.1093897(54) \times 10^{-31}$ kg	0.59
Proton rest mass	$m_p$	$1.6726231(10) \times 10^{-27}$ kg	0.59
Ratio of proton mass to electron mass	$m_p/m_e$	1836.152701(37)	0.02
Neutron rest mass	$m_n$	$1.6749286(10) \times 10^{-27}$ kg	0.59
Deuteron mass	$m_d$	$3.3435860(20) \times 10^{-27}$ kg	0.59
Permeability of vacuum	$\mu_0$	$4\pi (= 12.566370614\dots) \times 10^{-7}$ H.m <sup>-1</sup>	Exact
Permittivity of vacuum	$\epsilon_0 = 1/\mu_0 c^2$	$8.854187817\dots \times 10^{-12}$ F.m <sup>-1</sup>	Exact
Fine structure constant	$\alpha = \frac{q^2}{4\pi\epsilon_0\hbar c}$ (mks) $= e^2/\hbar c$ (cgs)	$7.29735308(33) \times 10^{-3}$ $1/\alpha = 137.0359895(61)$	0.045 0.045
Rydberg constant	$R_\infty = \left(\frac{q^2}{4\pi\epsilon_0}\right)^2$ $= m_e/4\pi\hbar^3 c$ (mks) $= m_e e^4/4\pi\hbar^3 c$ (cgs)	$10973731.534(13)$ m <sup>-1</sup> $109737.31534(13)$ cm <sup>-1</sup>	0.0012 0.0012
Non-relativistic ionization potential of hydrogen atom with infinite proton mass	$R_\infty\hbar c$	$2.1798741(13) \times 10^{-18}$ J $13.6056981(40)$ eV	0.60 0.30
Bohr radius	$a_0 = \left(\frac{4\pi\epsilon_0\hbar^2}{m_e q^2}\right)$ (mks) $= \hbar^2/m_e e^2$ (cgs)	$0.529177249(24) \times 10^{-10}$ m $0.529177249(24) \times 10^{-8}$ cm	0.045 0.045
Bohr magneton	$\mu_B = q\hbar/2m_e$ (mks) $= e\hbar/2m_ec$ (cgs)	$9.2740154(31) \times 10^{-24}$ J.T <sup>-1</sup> $9.2740154(31) \times 10^{-21}$ erg.G <sup>-1</sup>	0.34 0.34
Electron magnetic moment	$\mu_e [= (g_e/2)\mu_B]$	$9.2847701(31) \times 10^{-24}$ J.T <sup>-1</sup>	0.34
Free-electron <i>g</i> -factor	$g_e = 2\mu_e/\mu_B$	2.002319304386(20)	$1 \times 10^{-5}$
Proton magnetic moment	$\mu_p$	$1.41060761(47) \times 10^{-26}$ J.T <sup>-1</sup>	0.34
Neutron magnetic moment	$ \mu_n $	$0.96623707(40) \times 10^{-26}$ J.T <sup>-1</sup>	0.41
Nuclear magneton	$\mu_N = \frac{q\hbar}{2m_p}$	$5.0507866(17) \times 10^{-27}$ J.T <sup>-1</sup>	0.34
Boltzmann constant	$k$	$1.380658(12) \times 10^{-23}$ J.K <sup>-1</sup> $8.617385(73) \times 10^{-5}$ eV.K <sup>-1</sup>	8.5 8.4

**Part I**

**Mathematical Preliminaries**

# Chapter 1

## The Dirac Delta Function

... Strictly, of course,  $\delta(x)$  is not a proper function of  $x$ , but can be regarded only as a limit of a certain sequence of functions. All the same one can use  $\delta(x)$  as though it were a proper function for practically all the purposes of quantum mechanics without getting incorrect results. One can also use the differential coefficients of  $\delta(x)$ , namely,  $\delta'(x), \delta''(x), \dots$ , which are even more discontinuous and less ‘proper’ than  $\delta(x)$  itself.

— P.A.M. DIRAC in *The Physical Interpretation of Quantum Dynamics*,  
Proceedings of the Royal Society of London (A) **113**, 621-641  
(1926).

### 1.1. Introduction

The Dirac delta function is used so extensively in quantum mechanics that we felt we should discuss it right in the beginning of the book, rather than relegating it to an appendix!

The Dirac delta function is defined through the equations

$$\delta(x - a) = 0 \quad x \neq a \quad (1)$$

$$\int_{a-\alpha}^{a+\beta} \delta(x - a) \, dx = 1 \quad (2)$$

where  $\alpha, \beta > 0$ . Thus the delta function has an infinite value at  $x = a$  such that the area under the curve is unity. For an arbitrary function that is continuous at  $x = a$ , we have

$$\begin{aligned} \int_{a-\alpha}^{a+\beta} f(x) \delta(x - a) \, dx &= f(a) \int_{a-\alpha}^{a+\beta} \delta(x - a) \, dx \\ &\quad [\text{because of Eq. (1)}] \\ &= f(a) \end{aligned} \quad (3)$$

It is readily seen that if  $x$  has the dimension of length,  $\delta(x - a)$  would have the dimension of inverse length. Similarly, if  $x$  has the dimension of energy then  $\delta(x - a)$  would have the dimension of (energy) $^{-1}$ .

## 1.2. Representations of the Dirac delta function

There are many representations of the Dirac delta function. Perhaps the simplest representation is the limiting form of the rectangle function  $R_\sigma(x)$  defined through the following equation

$$\begin{aligned} R_\sigma(x) &= \frac{1}{2\sigma} && \text{for } -\sigma < x - a < \sigma \\ &= 0 && \text{for } |x - a| > \sigma \end{aligned} \quad (4)$$

The function  $R_\sigma(x)$  is plotted in Fig. 1.1 for various values of  $\sigma$ . Now

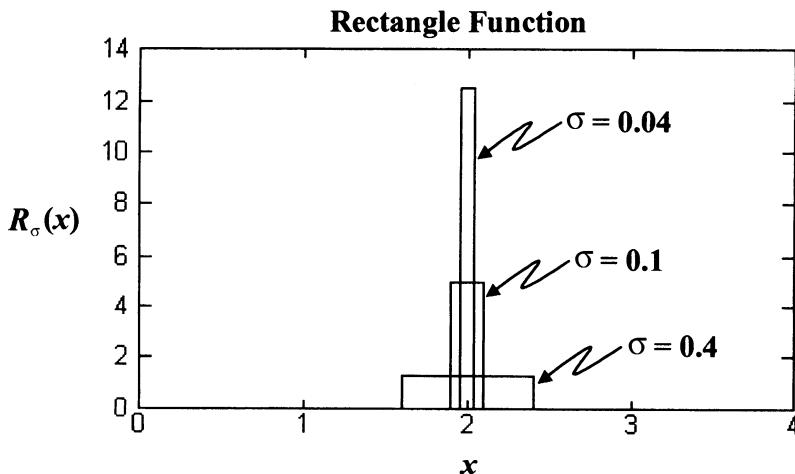


Figure 1.1. Plots of  $R_\sigma(x)$  for  $a = 2$  and  $\sigma = 0.04, 0.1$  and  $0.4$ . In each case the area under the curve is unity. For  $\sigma \rightarrow 0$ , the function  $R_\sigma(x)$  has all the properties of the Dirac delta function.

$$\int_{-\infty}^{+\infty} R_\sigma(x) dx = \frac{1}{2\sigma} \int_{a-\sigma}^{a+\sigma} dx = 1 \quad (\text{irrespective of the value of } \sigma)$$

For  $\sigma \rightarrow 0$ , the function  $R_\sigma(x)$  becomes more and more sharply peaked but the area under the curve remains unity. In the limit of  $\sigma \rightarrow 0$ , the function  $R_\sigma(x)$  has all the properties of the delta function and we may write

$$\delta(x - a) = \lim_{\sigma \rightarrow 0} R_\sigma(x) \quad (5)$$

Now,

$$\int_{-\infty}^{+\infty} f(x) R_\sigma(x) dx = \frac{1}{2\sigma} \int_{a-\sigma}^{a+\sigma} f(x) dx$$

We assume the function  $f(x)$  to be continuous at  $x = a$ . Thus when  $\sigma \rightarrow 0$ , in the infinitesimal interval  $-\sigma < x - a < \sigma$ ,  $f(x)$  may be assumed to be a constant  $[= f(a)]$  and taken out of the integral. Thus

$$\begin{aligned} \int_{-\infty}^{+\infty} f(x) \delta(x - a) dx &= \lim_{\sigma \rightarrow 0} \int_{-\infty}^{+\infty} f(x) R_\sigma(x) dx \\ &= \lim_{\sigma \rightarrow 0} \frac{1}{2\sigma} f(a) \int_{a-\sigma}^{a+\sigma} dx \\ &= f(a) \end{aligned}$$

Another very useful representation of the delta function is the limiting form of the Gaussian function (see Fig. 1.2)

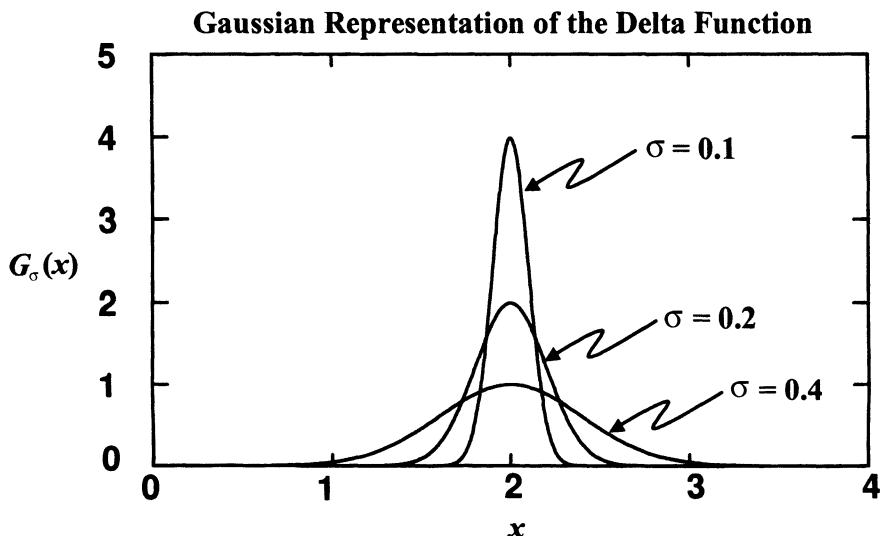


Figure 1.2. Plots of  $G_\sigma(x)$  for  $a = 2$  and  $\sigma = 0.04, 0.2$  and  $0.4$ . In each case the area under the curve is unity. For  $\sigma \rightarrow 0$ , the function  $G_\sigma(x)$  has all the properties of the Dirac delta function.

$$G_\sigma(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-a)^2}{2\sigma^2}\right], \quad \sigma > 0 \quad (6)$$

Since

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2 + \beta x} dx = \sqrt{\frac{\pi}{\alpha}} \exp\left[\frac{\beta^2}{4\alpha}\right]$$

[see Appendix A], we readily get

$$\int_{-\infty}^{+\infty} G_\sigma(x) dx = 1 \quad (7)$$

irrespective of the value of  $\sigma$  which is assumed to be positive. Further, the function has a width  $\sim \sigma$  and at  $x = a$ , it has a value  $1/(\sigma\sqrt{2\pi})$ . Thus, in the limit of  $\sigma \rightarrow 0$ ,  $G_\sigma(x)$  has all the properties of the delta function (see Fig. 1.2) and we therefore have the following representation of the delta function

$$\delta(x - a) = \lim_{\sigma \rightarrow 0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-a)^2}{2\sigma^2}\right], \quad \sigma > 0 \quad (8)$$

Another important representation of the Dirac delta function is through the following integral

$$\delta(x - a) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{\pm i k(x-a)} dk \quad (9)$$

In order to prove Eq. (9) we first note that

$$\frac{1}{2\pi} \int_{-g}^{+g} e^{\pm i k(x-a)} dk = \frac{\sin g(x-a)}{\pi(x-a)} \quad (10)$$

Using Laplace transform or complex variable techniques one can show that

$$\frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\sin g(x-a)}{(x-a)} dx = 1, \quad g > 0 \quad (11)$$

irrespective of the value of  $g$  which is assumed to be greater than zero. Now

$$\lim_{x \rightarrow 0} \frac{\sin gx}{x} = g$$

Thus for a large value of  $g$ , the function

$$\frac{\sin g(x-a)}{\pi(x-a)}$$

is sharply peaked around  $x = a$  (see Fig. 1.3) and has a unit area under the curve irrespective of the value of  $g$ ; thus in the limit of  $g \rightarrow \infty$ , it has all the properties of the delta function and we may write

$$\delta(x-a) = \lim_{g \rightarrow \infty} \frac{\sin g(x-a)}{\pi(x-a)} \quad (12)$$

Equation (9) readily follows from Eqs (10) and (12).

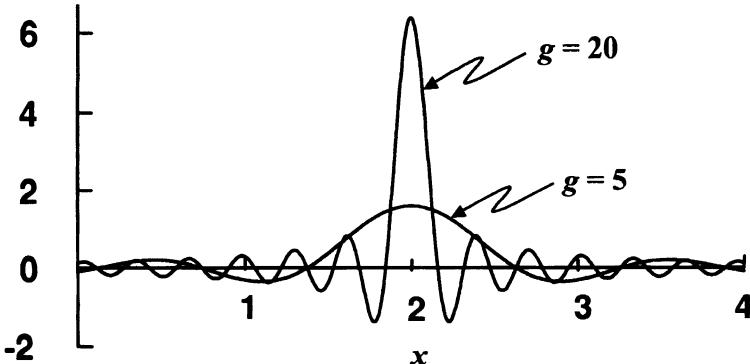


Figure 1.3. Plots of the function  $\sin[g(x-a)/\pi(x-a)]$  for  $a = 2$  and  $g = 5, 20$ . In each case the area under the curve is unity. For  $g \rightarrow \infty$ , the function is very sharply peaked at  $x = a$  and has all the properties of Dirac delta function.

### 1.3. Derivative at a discontinuity

We next consider a ramp function defined by the following equation (see Fig. 1.4);

$$F_\sigma(x) = \begin{cases} 0 & \text{for } x < a - \sigma \\ \frac{1}{2\sigma}(x - a + \sigma) & \text{for } |x - a| < \sigma \\ 1 & \text{for } x > a + \sigma \end{cases} \quad (13)$$

It can be readily seen that

$$\frac{dF_\sigma}{dx} = R_\sigma(x) \quad (14)$$

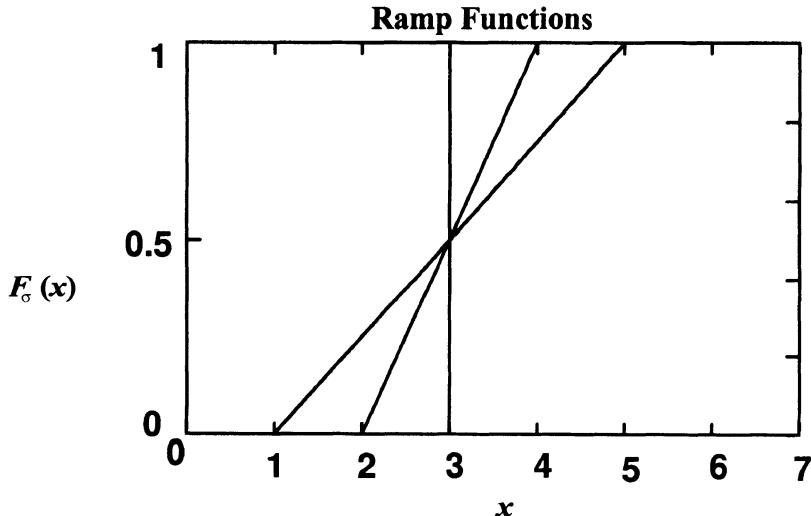


Figure 1.4. The ramp function defined by Eq. (13) for  $a = 3$  and  $\sigma = 0, 1$  and  $2$ .

where  $R_\sigma(x)$  is the rectangle function defined by Eq. (4). Now

$$\lim_{\sigma \rightarrow 0} F_\sigma(x) = H(x - a) \quad (15)$$

where  $H(x - a)$  is known as the Heaviside unit step function defined by the following equation (see Fig. 1.5)

$$\begin{aligned} H(x - a) &= 0 & x < a \\ &= 1 & x > a \end{aligned} \quad (16)$$

Thus

$$\frac{d}{dx} H(x - a) = \delta(x - a) \quad (17)$$

implying that the derivative of the unit step function is the Dirac delta function which is shown in Fig. 1.5; usually  $c\delta(x - a)$  is shown as a vertical arrow of height  $c$  at  $x = a$ . Equation (17) also follows from the fact that for a continuous function  $f(x)$  (with  $\alpha, \beta > 0$ )

$$\begin{aligned} \int_{a-\alpha}^{a+\beta} f(x) \frac{d}{dx} H(x - a) dx &= f(x) H(x - a) \Big|_{a-\alpha}^{a+\beta} - \int_{a-\alpha}^{a+\beta} f'(x) H(x - a) dx \\ &= f(a + \beta) - \int_a^{a+\beta} f'(x) dx \\ &= f(a + \beta) - [f(a + \beta) - f(a)] \\ &= f(a) \end{aligned}$$

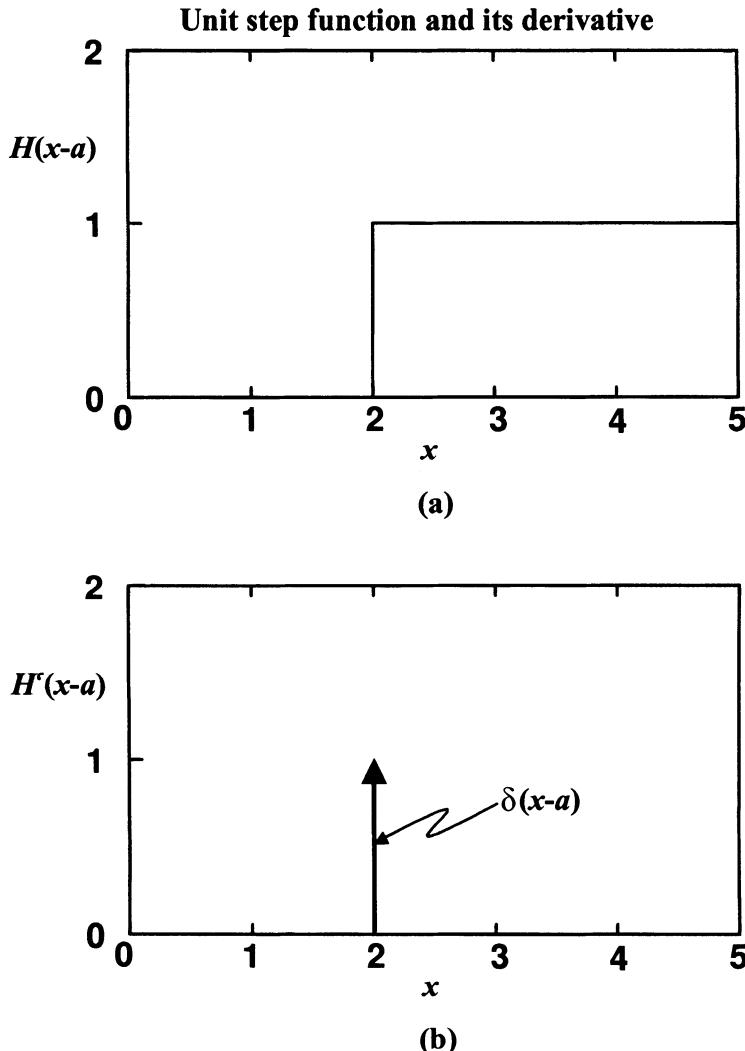


Figure 1.5. (a) The Heaviside unit step function. (b) Its derivative is the Dirac delta function which is usually represented by a vertical arrow of unit height.

We therefore get

$$\int_{a-\alpha}^{a+\beta} f(x) \frac{d}{dx} H(x-a) dx = f(a) ; \quad \alpha, \beta > 0 \quad (18)$$

Comparing the above equation with Eq. (3) we readily get Eq. (17). Obviously

$$\frac{d}{dx} [\alpha H(x - a)] = \alpha \delta(x - a) \quad (19)$$

Thus we get the following important result:

If a function has a discontinuity of  $\alpha$  at  $x = a$  then its derivative (at  $x = a$ ) is  $\alpha \delta(x - a)$ .

---

**Example 1.1** We consider the symmetric function

$$\psi(x) = A e^{-K|x|} \quad (20)$$

Thus

$$\begin{aligned} \psi(x) &= \begin{cases} A e^{Kx} & x < 0 \\ A e^{-Kx} & x > 0 \end{cases} \end{aligned} \quad (21)$$

and

$$\begin{aligned} \psi'(x) &= \begin{cases} KA e^{Kx} & x < 0 \\ -KA e^{-Kx} & x > 0 \end{cases} \end{aligned} \quad (22)$$

which are plotted in Fig. 1.6 for  $K = 1, A = 1$ . Since  $\psi'(x)$  has a discontinuity of  $-2KA$  at  $x = 0$ , we get

$$\psi''(x) = K^2 \psi(x) - 2A K \delta(x) \quad (23)$$

which is also plotted in Fig. 1.6.

---

## 1.4. Important properties of the Dirac delta function

$$\delta(x - a) = \delta(a - x) \quad (24)$$

$$f(x) \delta(x - a) = f(a) \delta(x - a) \quad (25)$$

$$\int_{-\infty}^{+\infty} f(x) \delta'(x - a) dx = -f'(a) \quad (26)$$

$$\delta[c(x - a)] = \frac{1}{|c|} \delta(x - a) \quad (27)$$

where  $c$  is real and not equal to zero. In Eqs (25) and (26),  $f(x)$  is assumed to be a “well-behaved” function and continuous at  $x = a$ . The proof of Eq. (26) is simple:

$$\begin{aligned} \int_{-\infty}^{+\infty} f(x) \delta'(x - a) dx &= f(x) \delta(x - a) \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} f'(x) \delta(x - a) dx \\ &= -f'(a) \end{aligned}$$

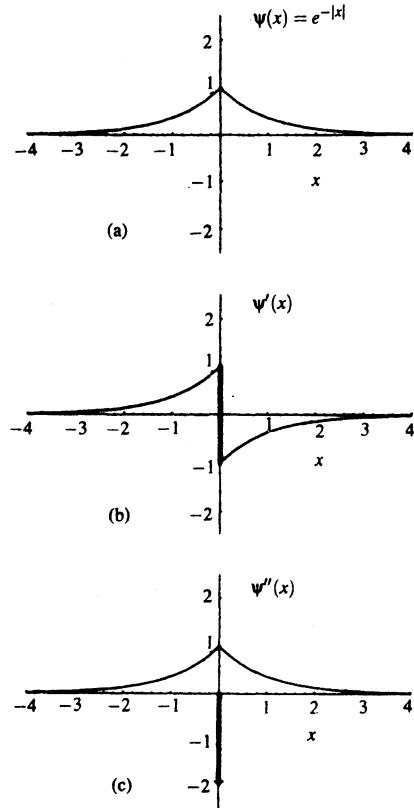


Figure 1.6. (a) A plot of the symmetric function as given by Eq. (20) for  $K = 1$ ,  $A = 1$ . Its first and second derivatives are plotted in (b) and (c). Since  $\psi'(x)$  has a discontinuity of  $-2KA$  at  $x = 0$ ,  $\psi''(x)$  is  $-2KA\delta(x)$  at  $x = 0$ .

Further

$$\begin{aligned}\delta(x^2 - a^2) &= \delta[(x - a)(x + a)] \\ &= \frac{1}{2a} [\delta(x - a) + \delta(x + a)], \quad a > 0\end{aligned}\quad (28)$$

We also have

$$\int_{-\infty}^{+\infty} \delta(x - x') \delta(x - x'') dx = \delta(x' - x'') \quad (29)$$

In order to prove Eq. (29) we write

$$F(x', x'') = \int_{-\infty}^{+\infty} \delta(x - x') \delta(x - x'') dx \quad (30)$$

Now

$$\begin{aligned} \int_{-\infty}^{+\infty} f(x') F(x', x'') dx' &= \int_{-\infty}^{+\infty} dx \delta(x - x'') \int_{-\infty}^{+\infty} dx' f(x') \delta(x - x') \\ &= \int_{-\infty}^{+\infty} dx \delta(x - x'') f(x) \\ &= f(x'') \end{aligned}$$

If we compare the above equation with Eq. (3) we get Eq. (29).

### 1.5. The completeness condition in terms of the Dirac delta function

Let  $\psi_n(x)$  form a complete set of orthonormal functions in the domain  $-\infty < x < \infty$ . The orthonormality condition would require

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx = \delta_{mn} \quad (31)$$

where  $\delta_{mn}$  is the Kronecker delta function defined through the following equation

$$\delta_{mn} = \begin{cases} 0 & \text{for } m \neq n \\ 1 & \text{for } m = n \end{cases} \quad (32)$$

Since  $\psi_n(x)$  form a complete set of functions, we can expand an arbitrary “well-behaved” function  $\phi(x)$  in terms of  $\psi_n(x)$ :

$$\phi(x) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) \quad (33)$$

In order to determine  $c_n$ , we multiply the above equation by  $\psi_m^*(x)$  and integrate to obtain

$$\begin{aligned} \int_{-\infty}^{+\infty} \psi_m^*(x) \phi(x) dx &= \sum_{n=0,1,\dots}^{\infty} c_n \int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx \\ &= \sum_{n=0,1,2,\dots}^{\infty} c_n \delta_{mn} \\ &= c_m \end{aligned}$$

Thus

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x) \phi(x) dx \quad (34)$$

Substituting in Eq. (33) we get

$$\phi(x) = \sum_{n=0,1,2,\dots}^{\infty} \left[ \int_{-\infty}^{+\infty} \psi_n^*(x') \phi(x') dx' \right] \psi_n(x)$$

where we have put a prime on the integration variable so that it does not get confused with the variable of  $\psi_n(x)$ . Carrying out the summation first we get

$$\phi(x) = \int_{-\infty}^{+\infty} dx' \phi(x') \sum_{n=0,1,2,\dots}^{\infty} \psi_n^*(x') \psi_n(x)$$

Comparing with Eq. (3) we may write

$$\sum_{n=0,1,2,\dots}^{\infty} \psi_n^*(x') \psi_n(x) = \delta(x - x') \quad (35)$$

which represents the completeness condition.

As an example, the Hermite Gauss functions

$$\psi_n(x) = N_n H_n(x) e^{-\frac{1}{2}x^2} ; \quad n = 0, 1, 2, \dots \quad (36)$$

with

$$N_n = \frac{1}{\sqrt{\pi^{\frac{1}{2}} 2^n n!}} \quad (37)$$

form a complete set of orthonormal functions (in the domain  $-\infty < x < \infty$ ) satisfying Eqs (31) and (35); in Eq. (36)  $H_n(x)$  are the Hermite polynomials (see Sec. 7.3). Thus

$$\frac{1}{\sqrt{\pi}} \sum_{n=0,1,2,\dots}^{\infty} \frac{1}{2^n n!} H_n(x) H_n(x') \exp \left[ -\frac{1}{2} (x^2 - x'^2) \right] = \delta(x - x') \quad (38)$$

Similarly the functions

$$\psi_n(x) = \left( \frac{2n+1}{2} \right)^{\frac{1}{2}} P_n(x) ; \quad n = 0, 1, \dots \quad (39)$$

form a complete set of orthonormal functions in the domain  $-1 \leq x \leq +1$ . In Fig. 1.7 we have plotted the function

$$\sum_{n=0,1,2,\dots}^N \left( \frac{2n+1}{2} \right) P_n(x) P_n(x')$$

for  $x' = 0.6$  with  $N = 12$  and  $20$ . As  $N \rightarrow \infty$ , the sum will sharply peak at  $x = 0.6$  and approach  $\delta(x - 0.6)$ .

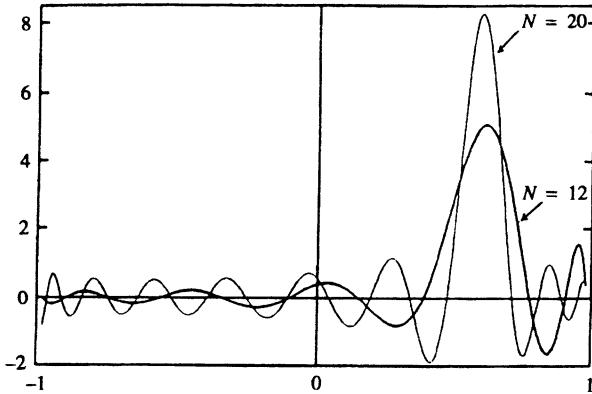


Figure 1.7. The sum  $\sum_{n=0,1,\dots}^N \left( \frac{2n+1}{2} \right) P_n(x) P_n(0.6)$  for  $N = 12$  and  $N = 20$ . As  $N$  becomes large, the sum will sharply peak at  $x = 0.6$  approaching  $\delta(x - 0.6)$ .

## 1.6. Delta function as a distribution

We should point out that the delta function is actually a distribution. In order to understand this let us consider the Maxwellian distribution

$$N(v) = 4\pi N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 \exp \left[ -\frac{mv^2}{2kT} \right] \quad (40)$$

where  $k$  represents the Boltzmann's constant,  $T$  the absolute temperature and  $m$  the mass of each molecule. In Eq. (40),  $N(v) dv$  represents the number of molecules whose speeds lie between  $v$  and  $v + dv$ . The total number of molecules is given by  $N_0$ :

$$\begin{aligned} \int_0^\infty N(v) dv &= 4\pi N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^\infty v^2 \exp \left[ -\frac{mv^2}{2kT} \right] dv \\ &= 4\pi N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \left( \frac{2kT}{m} \right)^{\frac{3}{2}} \frac{1}{2} \int_0^\infty x^{\frac{1}{2}} e^{-x} dx \end{aligned}$$

where  $x \equiv mv^2 / (2kT)$ . The integral is  $\Gamma(\frac{3}{2}) = \frac{1}{2}\sqrt{\pi}$ . Thus

$$\int_0^\infty N(v) dv = N_0 \quad (41)$$

It may be noted that whereas  $N_0$  is just a number, the quantity  $N(v)$  has the dimensions of  $(\text{velocity})^{-1}$ . Obviously, if we ask ourselves how many molecules have the precise speed  $v_0$ , the answer would be zero. This is the characteristic of a distribution. On the other hand, in addition to the distribution given by Eq. (40), if we do have  $N_1$  molecules all of them having the same speed  $v_1$ , the corresponding distribution function would be given by

$$N(v) = 4\pi N_0 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 \exp \left[ -\frac{mv^2}{2kT} \right] + N_1 \delta(v - v_1) \quad (42)$$

where  $\delta(v - v_1)$  represents the Dirac delta function and has the dimensions of inverse velocity.

## 1.7. The three-dimensional Dirac delta function

The three-dimensional Dirac delta function  $\delta(\mathbf{r} - \mathbf{r}')$  is defined by the following equation

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(x - x') \delta(y - y') \delta(z - z') \quad (43)$$

Thus

$$\iiint f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') d\tau = f(\mathbf{r}') \quad (44)$$

where the domain of integration over the variable  $\mathbf{r}$  should include the point  $\mathbf{r}'$ ;  $d\tau = dx dy dz$ . It is obvious that we can have many representations of the three-dimensional Dirac delta function. For example, we may write [cf. Eqs (6) and (9)]

$$\delta(\mathbf{r} - \mathbf{r}') = \lim_{\sigma \rightarrow 0} \frac{1}{(2\pi)^{\frac{3}{2}} \sigma^3} \exp \left[ -\frac{(x - x')^2 + (y - y')^2 + (z - z')^2}{2\sigma^2} \right] \quad (45)$$

and also

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{i \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} dk_x dk_y dk_z \quad (46)$$

where  $\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')$  is a compact form of writing

$$k_x(x - x') + k_y(y - y') + k_z(z - z')$$

Further, if  $(r, \theta, \phi)$  represent the spherical polar coordinates then

$$\begin{aligned}\delta(\mathbf{r} - \mathbf{r}') &= \frac{\delta(r - r')\delta(\theta - \theta')\delta(\phi - \phi')}{r^2 \sin \theta} \\ &= \frac{\delta(r - r')}{r^2} \delta(\Omega - \Omega')\end{aligned}$$

where  $\Omega$  represents the solid angle and

$$\begin{aligned}\delta(\Omega - \Omega') &= \frac{\delta(\theta - \theta')\delta(\phi - \phi')}{\sin \theta} \\ &= \sum_{l=0,1,\dots} \sum_{m=-l}^{+l} Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi)\end{aligned}$$

Further

$$\delta(\mathbf{r}) = \delta(x) \delta(y) \delta(z) = \frac{\delta(r)}{4\pi r^2}$$

with

$$\int_0^\infty \delta(r - r') dr' = 1$$

We also have

---


$$(\nabla^2 + k^2) \frac{e^{ikr}}{r} = -4\pi \delta(\mathbf{r})$$

## 1.8. Problems

**Problem 1.1** For  $f(x) = |x|$ , show that

$$f''(x) = 2\delta(x)$$

**Problem 1.2** Consider the following

$$f_\sigma(x) = \begin{cases} 0 & x < a \\ \sigma e^{-\sigma(x-a)} & x \geq a \end{cases}$$

where  $\sigma > 0$ . Plot the above function for  $\sigma = 1$  and  $10$  and show that we may write

$$\delta(x - a) = \lim_{\sigma \rightarrow \infty} f_\sigma(x)$$

**Problem 1.3** Consider the function

$$\psi(x) = \begin{cases} -x(1-a) & 0 < x < a \\ -(1-x)a & a < x < 1 \end{cases}$$

Show that

$$\frac{d^2\psi}{dx^2} = \delta(x - a)$$

**Problem 1.4** Prove that

$$x\delta'(x) = -\delta(x)$$

**Problem 1.5** The functions

$$\psi_n(x) = \sqrt{2} \sin(n\pi x)$$

form a complete set of functions in the interval  $0 \leq x \leq 1$  satisfying the boundary conditions

$$\psi(0) = 0 = \psi(1)$$

Plot

$$2 \sum_{n=0,1,2,\dots}^N \sin(n\pi x) \sin(n\pi x')$$

with  $x' = 0.6$  (in the domain  $-1 < x < 1$ ) for  $N = 10$  and  $20$ . As  $N \rightarrow \infty$  the sum will approach  $\delta(x - 0.6)$ .

---

## 1.9. Sample questions

Q. 1

$$\begin{aligned}\psi(x) &= 0 \quad \text{for } x < 0 \\ &= 4x \quad \text{for } x > 0\end{aligned}$$

Evaluate  $\psi''(x)$ .

Q. 2 Consider a function

$$\begin{aligned}f(x) &= 20 & x < 0 \\ &= (50/\sigma)x & 0 < x < \sigma \\ &= 50 & x > \sigma\end{aligned}$$

Plot  $f(x)$  and  $df/dx$  as a function of  $x$ .

Q. 3 Evaluate

$$\begin{aligned}(a) \quad &\text{Lt}_{\sigma \rightarrow 0} \frac{1}{\sigma} \exp\left(-\frac{(x-a)^2}{2\sigma^2}\right) \\ (b) \quad &\text{Lt}_{g \rightarrow \infty} \frac{\sin g(x-a)}{(x-a)}\end{aligned}$$

[**Answer: (b)**  $\pi\delta(x - a)$ ]

Q. 4 Consider the function

$$\begin{aligned} f(x) &= \alpha x & 0 < x < a \\ &= \alpha a \frac{L-x}{L-a} & a < x < L \end{aligned}$$

Evaluate and plot  $f(x)$ ,  $f'(x)$  and  $f''(x)$  in the domain  $0 < x < L$ .

Q. 5 Consider the function  $\psi(x) = A \exp[-\kappa|x|]$ . Evaluate and plot  $\psi(x)$ ,  $\psi'(x)$  and  $\psi''(x)$ . Determine the second order differential equation satisfied by  $\psi(x)$ .

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### 1.10. References and suggested reading

1. P.A.M. Dirac, *The Principles of Quantum Mechanics* (Fourth Edition), Clarendon Press, Oxford (1958).
2. J. Lighthill, *Introduction to Fourier Analysis and Generalised Functions*, Cambridge University Press (1958).
3. A.K. Ghatak, I.C. Goyal and S.J. Chua, *Mathematical Physics*, Macmillan India Limited, New Delhi (1995).

# Chapter 2

## Fourier Transforms

*The greatest mathematics has the simplicity and inevitableness of supreme poetry and music, standing on the borderland of all that is wonderful in Science, and all that is beautiful in Art. Mathematics transfigures the fortuitous concourse of atoms into the tracery of the finger of God.*

— H.W. TURNBULL  
in *The Great Mathematicians*

### 2.1. Introduction

Fourier transforms play an important role in quantum mechanics and as such, we devote a (short) chapter giving a brief account of Fourier transforms.

### 2.2. Fourier integral theorem

In the previous chapter we had shown the following integral representation of the Dirac delta function

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{\pm i k(x-x')} dk \quad (1)$$

Since

$$f(x) = \int_{-\infty}^{+\infty} \delta(x - x') f(x') dx' \quad (2)$$

we may write

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{\pm i k(x-x')} f(x') dx' dk \quad (3)$$

Thus if we define

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} dx \quad (4)$$

then

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{+ikx} dx \quad (5)$$

The function  $F(k)$  is known as the Fourier transform of the function  $f(x)$  and Eq. (5) enables us to calculate the original function from the Fourier transform. Equations (4) and (5) constitute what is known as the *Fourier Integral Theorem* which is valid when the following conditions are satisfied (see, e.g. Ref. 1 and 2):

- (i) The function  $f(x)$  must be a single valued function of the real variable  $x$  throughout the range  $-\infty < x < \infty$ . It may however have a finite number of finite discontinuities.
- (ii) The integral  $\int_{-\infty}^{+\infty} |f(x)| dx$  must exist.

From Eq. (3) it is obvious that in Eqs (4) and (5) there is no reason why the factors  $e^{ikx}$  and  $e^{-ikx}$  cannot be interchanged, i.e. we could have defined

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{ikx} dx \quad (6)$$

Then

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{-ikx} dx \quad (7)$$

However, in all of what follows we will use the definitions given by Equations (4) and (5).

**Example 2.1** As an example we consider a Gaussian function given by

$$f(x) = A e^{-x^2/2\sigma^2} \quad (8)$$

Its Fourier transform is given by

$$F(k) = \frac{A}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-x^2/2\sigma^2} e^{-ikx} dx$$

or

$$F(k) = A\sigma \exp\left[-\frac{1}{2}k^2\sigma^2\right] \quad (9)$$

where we have made use of the following integral (see Appendix A):

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2 + \beta x} dx = \sqrt{\frac{\pi}{\alpha}} \exp\left[\frac{\beta^2}{4\alpha}\right]; \text{ Re } \alpha > 0 \quad (10)$$

As can be seen from Eq. (9), the function  $F(k)$  is also a Gaussian; thus the Fourier transform of a Gaussian is a Gaussian. We may note that the Gaussian function given by Eq. (8) has a spatial width given by [see Fig. 2.1(a)]

$$\Delta x \sim \sigma \quad (11)$$

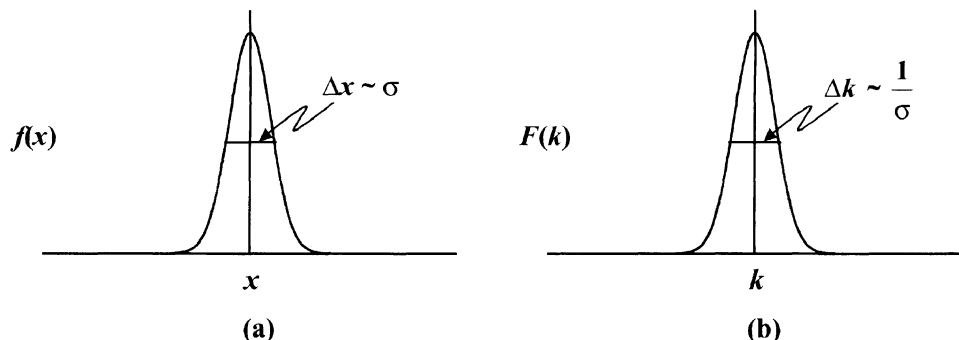


Figure 2.1. (a) The Gaussian function  $f(x)$  as given by Eq. (8). (b) The Fourier transform of the Gaussian function is also a Gaussian in the  $k$ -space.

Its Fourier transform,  $F(k)$ , has a width given by [see Fig. 2.1(b)]

$$\Delta k \sim \frac{1}{\sigma} \quad (12)$$

Thus

$$\Delta x \Delta k \sim 1 \quad (13)$$

which is a general characteristic of the Fourier transform pair.

**Example 2.2** As another example, we calculate the Fourier transform of the rectangle function

$$f(x) = \text{rect}\left(\frac{x}{a}\right) = \begin{cases} 1 & , |x| < \frac{1}{2}a \\ 0 & , |x| > \frac{1}{2}a \end{cases} \quad (14)$$

Its Fourier transform will be given by (see Fig. 2.2):

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-a/2}^{+a/2} e^{-ikx} dx$$

or

$$F(k) = \sqrt{\frac{2}{\pi}} \frac{\sin(ka/2)}{k} \quad (15)$$

Once again, the rectangle function has a width  $a$  and its Fourier transform has a width

$$\Delta k \sim \frac{\pi}{a}$$

In quantum mechanics, one uses the variable

$$p = \hbar k \quad (16)$$

where

$$\hbar = \frac{h}{2\pi} \quad (17)$$

$h$  ( $\simeq 6.626 \times 10^{-34}$  J-s) represents the Planck's constant. In terms of the variable  $p$ , Eq. (3) can be written in the form

$$\psi(x) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{\pm i p(x-x')/\hbar} \psi(x') dx' dp \quad (18)$$

Thus, if we define

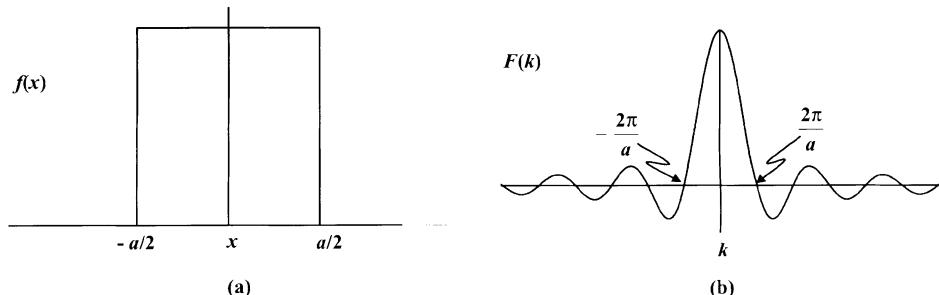


Figure 2.2. The rectangle function is shown in (a). Its Fourier transform is shown in (b).

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \psi(x) \exp\left[-\frac{i}{\hbar} px\right] dx \quad (19)$$

then

$$\psi(x) = \frac{1}{\sqrt{2\pi}\hbar} \int_{-\infty}^{+\infty} a(p) \exp\left[\frac{i}{\hbar} px\right] dp \quad (20)$$

We will use the above equation in Chapter 5.

---

### 2.3. Parseval's theorem

The equality expressed by the following equation

$$\int_{-\infty}^{+\infty} |f(x)|^2 dx = \int_{-\infty}^{+\infty} |F(k)|^2 dk \quad (21)$$

is known as Parseval's theorem. The proof is simple:

**Proof**

$$\begin{aligned} \int_{-\infty}^{+\infty} |f(x)|^2 dx &= \int_{-\infty}^{+\infty} f^*(x) f(x) dx \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dx \left[ \int_{-\infty}^{+\infty} F^*(k) e^{ikx} dk \right] \left[ \int_{-\infty}^{+\infty} F(k') e^{-ik'x} dk' \right] \end{aligned}$$

where we have used Eq. (5) and its complex conjugate. Thus

$$\begin{aligned} \int_{-\infty}^{+\infty} |f(x)|^2 dx &= \int_{-\infty}^{+\infty} dk \int_{-\infty}^{+\infty} dk' F^*(k) F(k') \left[ \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i(k-k')x} dx \right] \\ &= \int_{-\infty}^{+\infty} dk \int_{-\infty}^{+\infty} dk' F^*(k) F(k') \delta(k - k') \\ &= \int_{-\infty}^{+\infty} dk |F(k)|^2 \end{aligned}$$

Similarly, we can easily show from Eqs (19) and (20) that

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = \int_{-\infty}^{+\infty} |a(p)|^2 dp \quad (22)$$

The implication of the above equation will be discussed in Chapter 5.

## 2.4. Fourier transform of a time-dependent function

In order to get a better physical insight to the Fourier transform, we consider a time dependent function  $f(t)$ . For such a function we write the Fourier transform in the following form

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(t) e^{i\omega t} dt \quad (23)$$

Thus

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(\omega) e^{-i\omega t} d\omega \quad (24)$$

The above equations are nothing but Eqs. (6) and (7) with  $x$  and  $k$  replaced by  $t$  and  $\omega$  respectively. As a simple example, we consider an optical pulse having a Gaussian envelope:

$$f(t) = A e^{-t^2/2\tau^2} e^{-i\omega_0 t} \quad (25)$$

whose real part represents the actual electric field which is plotted in Fig. 2.3(a) for  $\omega_0\tau = 15$ . The Fourier transform can be readily evaluated and is given by

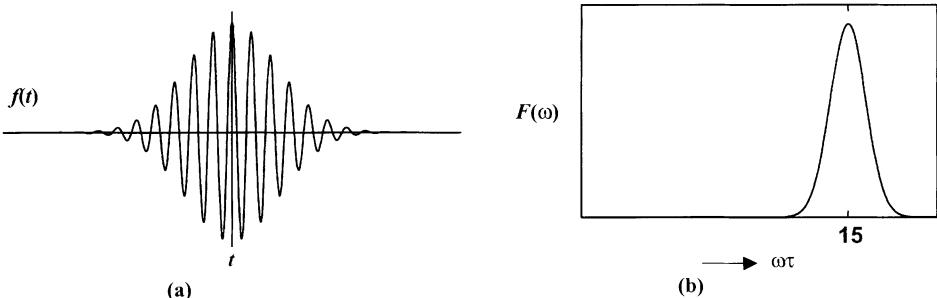


Figure 2.3. (a) The real part of the function as given by Eq. (25) for  $\omega_0\tau = 15$ . (b) The corresponding Fourier transform.

$$F(\omega) = A \sigma \exp \left[ -\frac{(\omega - \omega_0)^2 \tau^2}{2} \right] \quad (26)$$

where we have used Eq. (10). The function  $F(\omega)$  is known as the frequency spectrum and is plotted in Fig. 2.3(b). One can see that the duration of the pulse is  $\sim \tau$

and the corresponding spectral width is given by

$$\Delta\omega \sim \frac{1}{\tau} \quad (27)$$

implying

$$\tau \Delta\omega \sim 1 \quad (28)$$

Thus a pulse of duration  $\tau$  has necessarily a spectral width  $\sim 1/\tau$ ; this is indeed the result obtained in coherence theory (see, e.g. Chapter 14 of Ref. 3).

---

## 2.5. Problems

**Problem 2.1 (a)** Show that the Fourier transform of the function

$$f(x) = A e^{-\alpha|x|}; \alpha > 0 \quad (29)$$

is given by

$$F(k) = \frac{A}{\sqrt{2\pi}} \frac{2\alpha}{\alpha^2 + k^2} \quad (30)$$

which is known as the Lorentzian distribution.

**(b)** Hence show that

$$\int_{-\infty}^{+\infty} \frac{e^{ikx}}{\alpha^2 + k^2} dk = \frac{\pi}{\alpha} e^{-\alpha|x|} \quad (31)$$

**(c)** Use Parseval's theorem to prove

$$\int_{-\infty}^{+\infty} \frac{1}{(\alpha^2 + k^2)^2} dk = \frac{\pi}{2\alpha^3} \quad (32)$$

**Problem 2.2** Using Eqs (8) and (9) show that

$$\int_{-\infty}^{+\infty} |f(x)|^2 dx = \int_{-\infty}^{+\infty} |F(k)|^2 dk$$

which is the Parseval's theorem.

**Problem 2.3** Assume

$$\begin{aligned} \psi(x) &= \frac{1}{\sqrt{2L}} \exp \left[ \frac{i}{\hbar} p_0 x \right] & |x| < L \\ &= 0 & |x| > L \end{aligned} \quad (33)$$

Use Eqs (19) and (20) to calculate  $a(p)$  and interpret the result physically. Use Parseval's theorem to prove

$$\int_{-\infty}^{+\infty} \frac{\sin^2 \xi}{\xi^2} d\xi = \pi \quad (34)$$

**Problem 2.4** Assume

$$f(t) = A e^{-i\omega_0 t} \quad (35)$$

Calculate  $F(\omega)$  and interpret the result physically.

---

## 2.6. Sample questions

Q. 1 Consider the function

$$f(t) = A e^{-t^2/2\tau^2} e^{i\omega_0 t}$$

Calculate its Fourier spectrum

$$g(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt$$

and evaluate approximately  $\Delta\omega\Delta t$ . Evaluate  $f(t)$  using the expression for  $g(\omega)$ .

Q. 2 Consider the function

$$f(x) = a e^{-x^2/2\sigma^2} e^{ik_0 x}$$

Calculate its Fourier spectrum

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} dx$$

and evaluate approximately  $\Delta x\Delta k$ . Evaluate  $f(x)$  using the expression for  $g(k)$ .

Q. 3 Calculate the Fourier transform of the following functions

a)

$$\begin{aligned}f(x) &= A e^{ik_0 x} \quad |x| < L/2 \\&= 0 \quad \quad \quad |x| > L/2\end{aligned}$$

b)  $f(x) = A e^{-|x|/L}$

c)  $f(x) = A \quad -\infty < x < \infty$

In each case make an estimate of  $\Delta x$  and  $\Delta k$  and interpret physically.

---

## 2.7. References and suggested reading

1. R.N. Bracewell, *The Fourier Transform and its Applications*, McGraw-Hill, New York (1986).
2. E.C. Titchmarsh, *Introduction to the Theory of Fourier Integrals*, Clarendon Press, Oxford (1948).
3. A. Ghatak, *Optics*, (Second Edition), Tata McGraw-Hill, New Delhi (1992).

**Part II**

**Basic Quantum Mechanics**

# Chapter 3

## Particles and Waves and the Uncertainty Principle

*For the rest of my life, I will reflect on what light is.*

— ALBERT EINSTEIN, CA. 1917.

*All the fifty years of conscious brooding have brought me no closer to the answer to the question, ‘What are light quanta?’ Of course today every rascal thinks he knows the answer, but he is deluding himself.*

— ALBERT EINSTEIN, 1951.

### 3.1. Introduction

As we know, the values of the mass and charge of electrons, protons, neutrons, alpha-particles, etc., are known with tremendous accuracy—approximately one part in a billion. Their velocities can also be changed by application of electric and magnetic fields. Thus, we usually tend to visualize them as tiny particles. However, they also exhibit diffraction and other effects which can only be explained if we assume them to be *waves*. Similarly, using light beams, there are experiments on interference, diffraction, etc., which can only be explained if we assume a wave model for light. There are also phenomena, like photoelectric effect, which can only be explained if we assume a particle model of light. Thus, answers to questions like *what is an electron or what is light* are very difficult. Indeed electrons, protons, neutrons, photons, alpha-particles, etc. are *neither particles nor waves*. The modern quantum theory describes them in a very abstract way which cannot be connected with everyday experience. To quote Feynman [Ref.1]:

*Newton thought that light was made up of particles, but then it was discovered that it behaves like a wave. Later, however (in the beginning of the twentieth century), it was found that light did indeed sometimes behave like a particle. Historically, the electron, for example, was thought to behave like a particle, and then it was found that in many respects it behaved like a wave. So it really behaves like neither. Now we have given up. We say: ‘It is like neither’.*

*There is one lucky break, however—electrons behave just like light. The quantum behaviour of atomic objects (electrons, protons, neutrons, photons, and so on) is the same for all, they are all ‘particle-waves’, or whatever you want to call them.*

In this chapter, we will qualitatively discuss the wave-particle duality and how it can be explained on the basis of the uncertainty principle and the probabilistic interpretation of matter waves.

### 3.2. The corpuscular and wave models of light

The corpuscular model is perhaps the simplest model of light. According to this model, a luminous body emits a stream of particles in all directions. The particles are assumed to be very tiny so that when two light beams overlap, a collision between two particles rarely occurs. Using the corpuscular model, one can explain the laws of reflection and refraction. Contrary to popular belief, the corpuscular model of light is due to Descartes rather than to Newton. The law of refraction was discovered experimentally in 1621 by Snell. Descartes' derivation of Snell's law was published in 1637; this derivation is equivalent to the corpuscular derivation, which is usually attributed to Newton. Newton was only about eight years old when Descartes died and the first edition of Newton's *Optiks* (in which he had discussed the corpuscular model) was published in 1704. It was probably because of the popularity of Newton's Optiks that the corpuscular theory is usually attributed to Newton.

Although the corpuscular model explains the propagation of light through free space and can be made to predict the correct forms of the laws of reflection and refraction, there came up a large number of experimental observations (like interference, diffraction, polarization etc.), which could not be explained on the basis of the corpuscular model of light. Indeed, in 1804, Thomas Young performed the famous two slit interference experiment which could only be explained on assuming a wave model of light. Young showed that the wavelength of the light waves was around  $6 \times 10^{-5}$  cm. Because of the smallness of the wavelength, the diffraction effects are small and therefore light approximately travels in straight lines. Around 1816, Fresnel gave a satisfactory explanation of the diffraction phenomenon by means of a wave theory and calculated the diffraction patterns produced by various types of apertures and edges. In 1816, Fresnel along with Arago performed the famous experiment on the superposition of linearly polarized light waves, which was explained by Young, by assuming that light waves were transverse in character.

Around the second quarter of the nineteenth century, the wave theory seemed to be well established and since it was thought that a wave requires a medium for its propagation, the elastic ether theory was developed. Indeed, in 1832 Fresnel derived the expressions for the reflection and transmission coefficients by using

models for ether vibrations. However, there were considerable difficulties in the understanding of the ether theory and since we now know that the ether does not exist, we will not go into the details of the various theories.

The nineteenth century also saw the development of electricity and magnetism. Around 1857 Maxwell generalized Ampere's law by stating that a changing electric field can also set up a changing magnetic field. He summed up all the laws of electricity and magnetism in the form of equations which are now referred to as Maxwell's equations. From these equations, he derived a wave equation and predicted the existence of electromagnetic waves (see, e.g., Chapter 19 of Ref. 2). From the wave equation so derived, he showed that the velocity of the electromagnetic waves can be calculated from experiments in which a certain quantity of electric charge is measured by two different methods. These measurements were carried out in 1856 by Kohlrausch and Weber, and from their data, Maxwell found that the speed of the electromagnetic waves in air should be about  $3.107 \times 10^8$  m/s. He found that this value was very close to the measured value of the speed of light which according to the measurement of Fizeau in 1849 was known to be  $3.14858 \times 10^8$  m/s. Maxwell argued that these two numbers cannot be accidentally equal and with *faith in rationality of nature*, he propounded his famous electromagnetic theory of light according to which, light waves are electromagnetic in nature. Associated with a light wave, there would be changing electric and magnetic fields, the changing magnetic field produces a time and space varying electric field and the changing electric field produces a time and space varying magnetic field, this results in the propagation of the electromagnetic wave even in free space. In 1888, Heinrich Hertz carried out experiments which could produce and detect electromagnetic waves produced by discharging electrically charged plates through a spark gap. The frequency of the emitted electromagnetic waves depended on the values of the inductance and capacitance of the circuit. Hertz's experimental results provided dramatic confirmation of Maxwell's electromagnetic theory. In addition, there were so many other experimental results which were quantitatively explained by using Maxwell's theory that around the end of the nineteenth century physicists thought that one finally understood what light really was.

### 3.3. Particle nature of radiation: the photoelectric effect

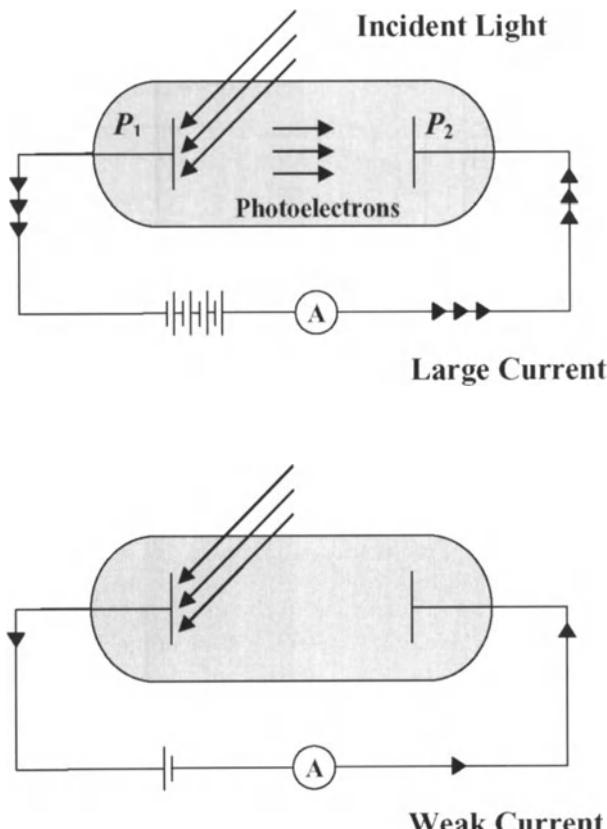
In 1887, Hertz discovered that a metal irradiated by a light beam would emit electrons. These electrons are known as photoelectrons and can be collected by a metal plate  $P_2$  as shown in Fig. 3.1. The photoelectrons constitute a current between the plates  $P_1$  and  $P_2$  which can be detected by means of an ammeter  $A$ . When the voltage across the plates is varied, the current also varies; typical variations of the current with voltage are shown in Fig. 3.2. The figure corresponds to monochromatic light of a particular wavelength and different curves correspond

to different intensities of the beam. From the figure one can draw the following conclusions:

- (i) At zero voltage there is a finite value of the current implying that some of the emitted photoelectrons reach the metal surface  $P_2$ .
- (ii) As the voltage is increased, the current increases till it reaches a saturation value; this will happen when the plate  $P_2$  collects all the emitted photoelectrons.
- (iii) If the plate  $P_2$  is kept at a slightly negative potential, there is a weak current implying that some of the photoelectrons do manage to reach the plate  $P_2$ . However, beyond a certain voltage (which is shown as  $-V_c$  in the figure) the current is zero;  $V_c$  is known as the cutoff voltage and the quantity  $|q|V_c$  will represent the maximum kinetic energy of the photoelectrons ( $q$  represents the charge of the electron). For example, for sodium  $V_c \approx 2.3$  Volts and for copper  $V_c \approx 4.7$  Volts.
- (iv) If we do not change the wavelength of the incident radiation but make it more intense, the magnitude of the current will become larger as shown in Fig. 3.2 implying a greater emission of photoelectrons. Notice that the value of the cutoff potential remains the same; this important result implies that the maximum kinetic energy of the emitted photoelectrons does not depend on the intensity of the incident radiation.
- (v) If the frequency of the incident radiation is increased then the cutoff potential and hence the maximum kinetic energy of the electron ( $= |q|V_c$ ) varies linearly with the frequency as shown in Fig. 3.3. Further, for frequencies less than a critical value (shown as  $v_c$  in Fig. 3.3), there is no emission of photoelectrons no matter what the intensity of the incident radiation may be.

At first sight it appears that since electromagnetic waves carry energy, the wave model for light should be able to explain the emission of photoelectrons from a metal surface. However, there are certain peculiarities associated with photoelectric effect, which cannot be satisfactorily explained by means of a wave model:

1. The first peculiarity is the fact that the maximum kinetic energy of the electrons does not depend on the intensity of the incident radiation, it only depends on its frequency; further, a greater intensity leads to a larger number of electrons constituting a larger current. Thus, a faint violet light would eject electrons of greater kinetic energy than an intense yellow light although the latter would produce a large number of electrons. A wave model would, however, predict that a large intensity of the incident radiation would result in a greater kinetic energy of the emitted electrons.



*Figure 3.1.* If light (of certain frequency) is allowed to fall on a metal like sodium, electrons are emitted which can be collected by the plate B. (a) and (b) correspond to positive and negative voltage applied to the plate B. Even when the plate is kept at a low negative voltage, one can detect a small current.

2. The second peculiarity is the fact that there is almost no time lag between the times of incidence of the radiation and the ejection of the photoelectron. For weak intensities of the incident beam the wave theory predicts a considerable time lag for the electrons to absorb enough energy to leave the metal surface. This can be illustrated by considering a specific example. One can observe a detectable photocurrent if the surface of sodium metal is illuminated by violet light of intensity as low as  $10^{-10} \text{ W/cm}^2$ . Now, ten layers of sodium will contain

$$\frac{6 \times 10^{23} \times 10 \times 10^{-8}}{23} \approx 2 \times 10^{15} \text{ atoms/cm}^2$$

where we have assumed the density of sodium to be  $\approx 1 \text{ g/cm}^3$ .

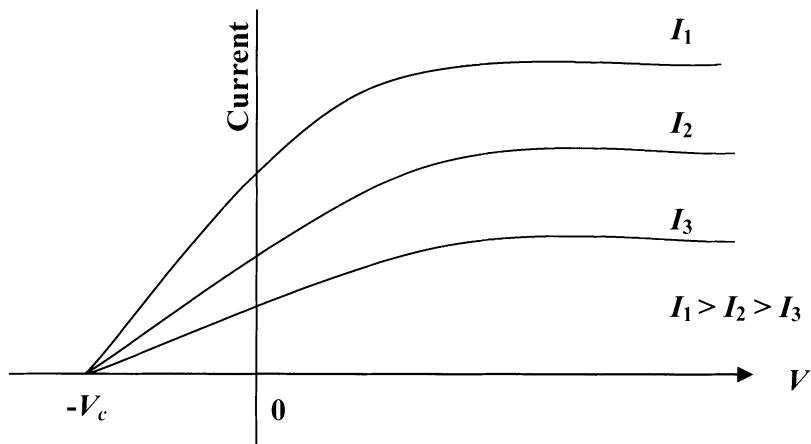


Figure 3.2. Typical variation of the photocurrent with voltage. The curves correspond to light (of the same frequency) having different intensities.

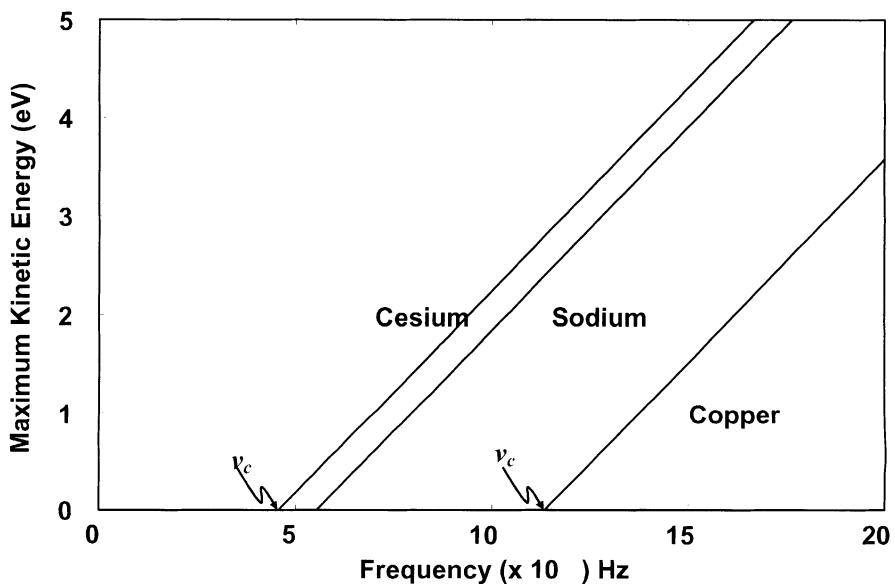


Figure 3.3. The variation of the maximum kinetic energy of the electrons as a function of frequency of the incident light for cesium, sodium and copper. The intercepts on the horizontal axis represent the cutoff frequencies of different metals.

Assuming that the energy is uniformly absorbed by the upper ten layers of sodium, each atom would receive energy at the rate of

$$\frac{10^{-10}}{2 \times 10^{15}} \approx 5 \times 10^{26} \text{ J/s} \approx 3 \times 10^{-7} \text{ eV/s}$$

Assuming that an electron should acquire an energy  $\sim 1$  eV to escape from the metal, we should expect a time lag of order  $10^7$  sec ( $\sim$  few months). However, the experiments show that there is no detectable time lag between the incidence of the radiation and the emission of the photoelectrons.<sup>1</sup>

In 1905, Einstein provided a simple explanation of the above mentioned peculiarities. He argued that light consisted of quanta of energy  $h\nu$  (where  $\nu$  is the frequency) and that the emission of a photoelectron was the result of the interaction of a single quantum (i.e., of the photon<sup>2</sup>) with an electron. In his 1905 paper,<sup>3</sup> Einstein wrote

*Monocromatic radiation behaves as if it consists of mutually independent energy quanta of magnitude [hν].*

Einstein's photon theory gives a very satisfactory explanation of the photoelectric effect. According to this theory a light beam (of frequency  $\nu$ ) essentially consists of individual corpuscles called photons. Each photon carries an energy equal to  $h\nu$ . This corpuscular model can explain all the observations discussed above. Thus, for all frequencies below the cutoff  $\nu_c$ , each photon will carry energy less than  $h\nu_c$  which will not be sufficient to eject the electron from the metal. For  $\nu > \nu_c$ , a major fraction of the excess energy [=  $h(\nu - \nu_c)$ ] appears as kinetic energy of the emitted electron. Further, the non-measurable time lag between the incidence of the radiation and the ejection of the electron follows immediately from the corpuscular nature of the radiation.

Indeed, the observed maximum kinetic energy of the photoelectrons is linearly related to the frequency of the incident radiation and one may write (see Fig. 2.3)

$$T_{\max} = -B + h\nu = h(\nu - \nu_c), \quad (1)$$

where  $B (= h\nu_c)$  is a constant and  $h$  is the Planck's constant ( $= 6.627 \times 10^{-27}$  erg-sec). The frequency  $\nu_c$  represents the cutoff frequency and is a characteristic of the metal. For example,

$$\text{for cesium } B \approx 1.9 \text{ eV} \Rightarrow \nu_c \approx 4.6 \times 10^{14} \text{ Hz}$$

$$\text{for sodium } B \approx 2.3 \text{ eV} \Rightarrow \nu_c \approx 5.6 \times 10^{14} \text{ Hz}$$

$$\text{for copper } B \approx 4.7 \text{ eV} \Rightarrow \nu_c \approx 11.4 \times 10^{14} \text{ Hz}$$

<sup>1</sup> Indeed, in 1928, Lawrence and Beams had devised an experiment to find out whether the time lag was  $\leq 3 \times 10^{-9}$  sec; the experiment gave a negative result.

<sup>2</sup> The term *photon* was introduced by G.N. Lewis in 1926.

<sup>3</sup> Annalen der Physik, **17**, 132 (1905).

In Fig. 3.3,  $v_c$  is the intercept on the horizontal axis. In 1909, Einstein wrote [quoted from Ref. 3]

*It is undeniable that there is an extensive group of data concerning radiation which shows that light has certain fundamental properties that can be understood much more readily from the standpoint of the Newton emission (particle) theory than from the standpoint of the wave theory. It is my opinion, therefore, that the next phase of the development of theoretical physics will bring us a theory of light that can be interpreted as a kind of fusion of the wave and emission theories.*

We may note the prediction of Einstein. Einstein received the 1921 Nobel prize in Physics for his *discovery of the law of photoelectric effect* and *not* for his theory of relativity. To quote Max Jammer (Ref. 4).

*Owing to Einstein's paper of 1905, it was primarily the photoelectric effect to which physicists referred as an irrefutable demonstration of the existence of photons and which thus played an important part in the conceptual development of quantum mechanics.*

The validity of Eq.(1) was established in a series of beautiful experiments by Millikan who also made the first direct determination of Planck's constant  $h$ . In his Nobel lecture, Millikan said (see Ref. 5)

*After ten years of testing and changing and learning and sometimes blundering, all efforts being directed from the first toward the accurate experimental measurement of the energies of emission of photoelectrons, now as a function of temperature, now of wavelength, now of material (contact e.m.f. relation), this work resulted, contrary to my own expectation, in the first direct experimental proof in 1914 of the exact validity, within narrow limits of experimental error, of the Einstein equation [Eq.(1)], and the first direct photoelectric determination of Planck's constant  $h$ .*

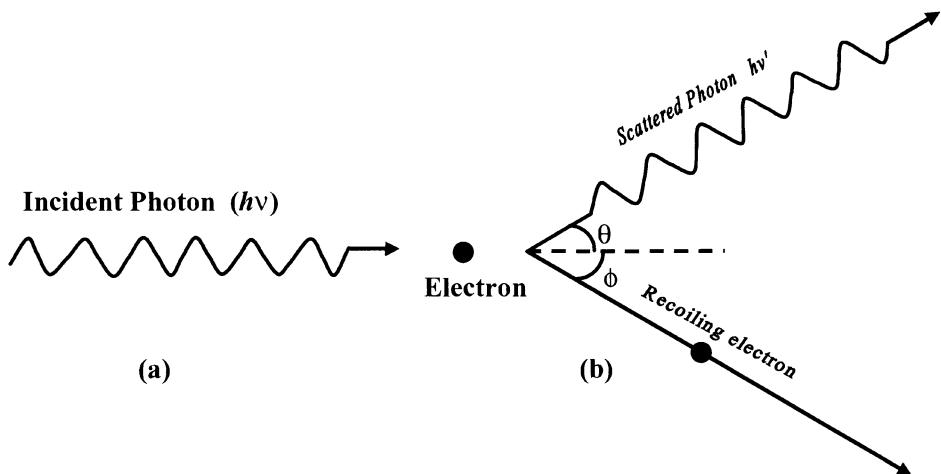
Millikan further wrote: *Einstein's equation is one of exact validity (always within the present small limits of experimental error) and of very general applicability, is perhaps the most conspicuous achievement of Experimental Physics during the past decade.*

We may mention here that after a year or two after the foregoing photoelectric work was completed, Duane and his associates found unambiguous proof of a relation, which is just the inverse of Einstein's. They bombarded a metal target with electrons of known and constant energy and found that the maximum frequency of the emitted X-rays was given, with much precision, by the following equation

$$\frac{1}{2}mv^2 = h\nu \quad (2)$$

In making this transition from Planck's *quantised oscillators* to *quanta of radiation*, Einstein had made a very important conceptual transition, namely, he introduced

the idea of corpuscular behaviour of radiation. Although Newton had described light as a stream of particles, this view had been completely superseded by the wave picture of light, a picture that culminated in the electromagnetic theory of Maxwell. The revival of the particle picture now posed a severe conceptual problem, one of reconciling wave and particle like behaviour of radiation. It also soon became apparent that matter also exhibited both types of behaviour. For example, an electron with an accurately measured value of mass and charge could undergo diffraction in a manner similar to that of light waves. We will now give a brief account of some of the other important experimental evidence showing wave-particle duality which led to the development of the quantum theory.



*Figure 3.4.* The Compton scattering of a photon: (a) shows the incidence of a photon (of frequency  $\nu$ ) on an electron at rest, (b) shows the scattered photon (having a reduced frequency  $\nu'$ ) propagating along the direction which makes an angle  $\phi$  with the original direction; the electron also acquires a momentum.

### 3.4. The Compton effect

We have seen that Einstein's explanation for the photoelectric effect implies that quanta of light (photons) carry a definite amount of energy. The Compton effect provided an unambiguous example of a process in which a quantum of radiation carrying energy as well as momentum scatters off an electron [see Fig. 3.4]. Now, if  $u$  represents the energy per unit volume associated with a plane electromagnetic wave, Maxwell's equations predict that the momentum per unit volume associated with the electromagnetic wave would be  $u/c$ , where  $c$  represents the speed of light in free space. Since each photon carries an energy equal to  $h\nu$ , it should have a

momentum given by the following equation:

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \quad (3)$$

In 1923 Compton investigated the scattering of X-rays by a block of paraffin and found that the wavelength of the radiation scattered at an angle of  $90^\circ$  is greater than the wavelength of the incident radiation. In other words, the frequency  $\nu'$  of the scattered wave is smaller than the frequency of the incident wave. Compton was able to explain the result<sup>4</sup> quantitatively as that of an elastic collision between a photon of energy  $E = h\nu$  and the momentum given by Eq.(3). Compton was awarded the 1927 Nobel Prize in Physics "for his discovery of the effect named after him".

The light quantum imparts some of its energy to the electron and emerges with less energy. Thus the scattered radiation has a lower frequency. The kinematics of this collision process can be worked out on elementary application of the laws of conservation of energy and momentum [see Sec. 3.4.1]. These calculations give the following expression for the shift in the wavelength

$$\Delta\lambda = \frac{2h}{m_0 c} \sin^2 \frac{\theta}{2} \quad (4)$$

where  $\lambda$  is the angle of scattering of the light quantum [see Fig. 3.4] and  $m_0$  represents the rest mass of the electron. If we substitute the values of  $h$ ,  $m_0$  and  $c$ , we obtain

$$\Delta\lambda = \lambda' - \lambda = 0.0485 \sin^2 \frac{\theta}{2} \quad (5)$$

where  $\lambda$  is measured in Angstroms. The above equation shows that the maximum change in the wavelength is about  $0.05 \text{ \AA}$ , and as such for a measurable shift one must use radiation of smaller wavelength. In Fig. 3.5 we have given the schematic of the experimental arrangement for the measurement of the Compton shift. A monochromatic beam of X-rays (or  $\gamma$ -rays) is allowed to fall on a sample scatterer and the scattered photons were detected by means of a crystal spectrometer. The crystal spectrometer allows one to find the intensity distribution (as a function of  $\lambda$ ) for a given value of  $\gamma$ . In Fig. 3.6 we have shown the wavelength of the scattered photon at different angles with respect to the primary beam as obtained by Compton in his original experiment<sup>5</sup> in 1923. The solid curve corresponds

<sup>4</sup> According to the classical explanation of Compton scattering, the electron undergoes oscillatory motion because of the electric field associated with the incident electromagnetic radiation. The accelerated electron emits electromagnetic waves and because of Doppler shifts due to the motion of the electron, the emitted wavelength differs from the wavelength of the incident radiation; however, the classical theory predicts that for a given angle of scattering a continuous range in the value of the scattered wavelength should be formed, which is contrary to experimental findings. The details of this analysis are given in Section 2.9 of Ref. 6.

<sup>5</sup> The original papers of Compton have been published in a book on *Scientific Papers of L.H. Compton: X-ray and Other Studies*, edited by R.S. Shankland, University of Chicago Press, 1975.

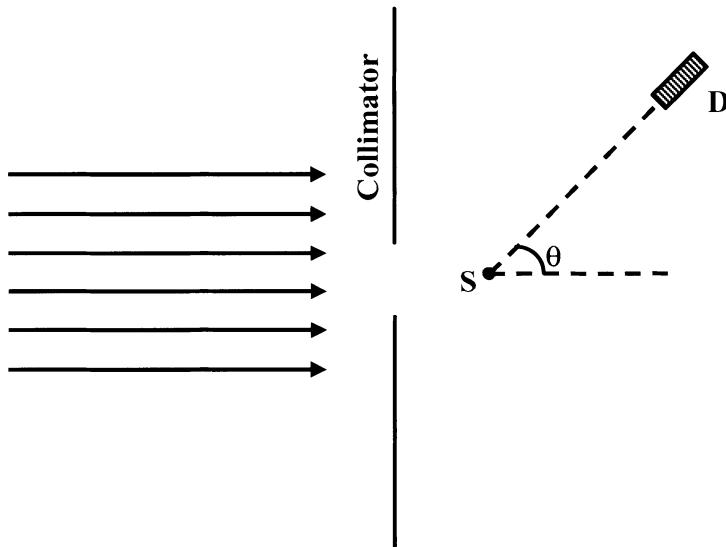


Figure 3.5. Outline of the experimental arrangement for the measurement of the Compton shift. A collimated beam of monochromatic X-rays is scattered by the scatterer  $S$ ; the wavelength of the scattered photon is measured by the detector  $D$ .

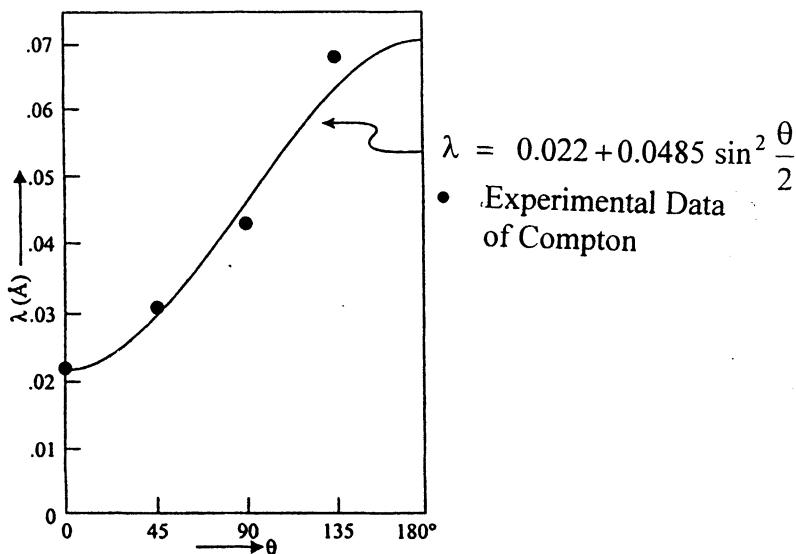


Figure 3.6. The variation of wavelength of the scattered photon with the angle of scattering. The solid curve corresponds to Eq.(5) with  $\lambda = 0.022 \text{ \AA}$ . The dots represent the experimental points obtained by Compton. The figure has been adapted from the original paper of A.H. Compton on *A Quantum theory on the scattering of X-rays by Light Elements*, Physical Review, 1923, Vol. 21, 382.

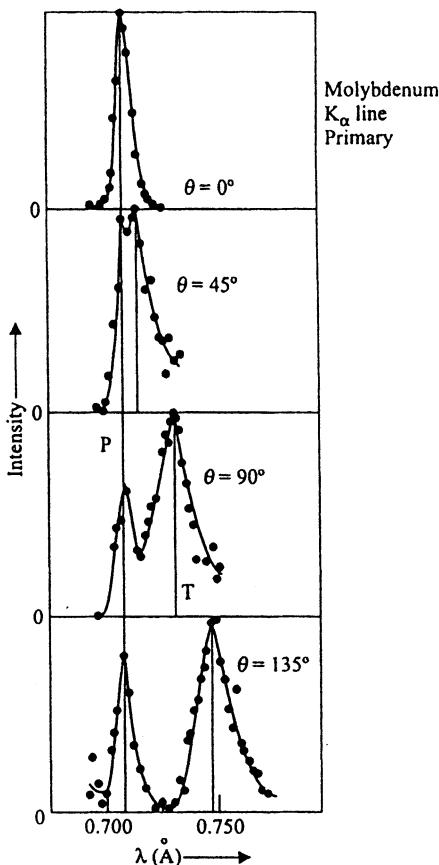


Figure 3.7. The intensity variation as a function of the wavelength of the scattered photon. The vertical line (marked P) corresponds to the unmodified wavelength  $\lambda = 0.711 \text{ \AA}$ . The second vertical line (marked T) corresponds to the wavelength as predicted by Eq.(4). The figure has been adapted from A.H. Compton's original paper on "The spectrum of Scattered X-rays". Physical Review, 1923, 22, 409.

to Eq.(5) with  $\lambda = 0.022 \text{ \AA}$ . (Notice that the corresponding photon energy is  $\sim 6.6 \times 10^{-27} \times 3 \times 10^{10} / 2.2 \times 10^{-10} \text{ ergs} > 0.5 \text{ MeV}$ , which corresponds to a  $\gamma$ -ray). The good agreement between theory and experiment proves that radiation behaves as if it consists of corpuscles of energy  $h\nu$  having a momentum  $h\nu/c$ .

The experimental findings of Compton are shown in Fig. 3.7; the experiment corresponds to the Molybdenum  $K\alpha$  line ( $\lambda = 0.711 \text{ \AA}$ ). The sample used was graphite. Notice that at each value of  $\theta$ , there are two peaks; the first peak appears at almost the same wavelength as the primary beam. This peak is because of the fact that the photon may be scattered by the whole atom; consequently, the quantity  $m_0$  appearing in Eq.(4) is not the electron mass but the mass of the carbon atom (which is about 22,000 times that of the mass of the electron). Thus the wavelength shift

is negligible. The second peak corresponds to the Compton shift. In each figure, the two vertical lines correspond to the unmodified wavelength and the modified wavelength as given by Eq.(5) and one can see a good agreement between the predicted and observed values.

Further evidence of the validity of the above theory was provided by the experiments carried out by Compton and Simon who studied the scattering of X-rays through supersaturated water-vapor. In the scattering process, the recoil electrons formed tracks of condensed droplets; however, the light quantum did not leave any track. Now, if the light quantum undergoes another Compton scattering then from the track of the second recoil electron one can determine the path of the light quantum by simply joining the line of the starting points of the two recoil electrons. Although there was considerable uncertainty in the analysis of the experimental data (because of the presence of many tracks) Compton and Simon could establish agreement between theoretical results and experimental data.

### 3.4.1. KINEMATICS OF COMPTON SCATTERING

We next consider the scattering of a photon by an electron as shown in Fig. 3.4. The scattered photon is assumed to have a frequency  $\nu'$ . Conservation of energy leads to

$$h\nu = h\nu' + E_k \quad (6)$$

where  $E_k$  represents the kinetic energy imparted to the electron. Conserving the  $x$  and  $y$  components of the momentum, we have

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos \theta + p \cos \phi \quad (7)$$

and

$$0 = \frac{h\nu'}{c} \sin \theta - p \sin \phi \quad (8)$$

where  $p$  represents the momentum of the electron after collision,  $\theta$  and  $\phi$  represent the angles made by the scattered photon and the electron with the original direction of the photon (see Fig. 3.4). It will be shown that for a measurable Compton's effect, the frequency  $\nu$  should be in the X-ray or in the  $\gamma$ -ray region (for X-rays  $\lambda \leq 1 \text{ \AA}$  and  $h\nu \geq 10^4 \text{ eV}$ ). For such high energy photons, the velocity imparted to the electron is comparable to the speed of light and one must use proper relativistic expressions for  $E_k$  and  $p$ .

According to the theory of relativity, the kinetic energy  $E_k$  of the scattered electron would be given by

$$E_k = E - m_0 c^2 = mc^2 - m_0 c^2 = \frac{m_0 c^2}{\sqrt{1 - \beta^2}} - m_0 c^2 \quad (9)$$

where  $\beta = v/c$ ,  $m_0$  represents the rest mass of the electron,  $v$  the speed of the electron and  $c$  the speed of light in free-space; the quantities  $E$  and  $m_0c^2$  are known as the total energy and the rest mass energy of the electron. Further, the relativistic momentum of the electron is given by

$$p = mv = \frac{m_0v}{\sqrt{1 - \beta^2}} \quad (10)$$

Now,

$$\begin{aligned} p^2c^2 + m_0^2c^4 &= \frac{m_0^2v^2c^2}{1 - v^2/c^2} + m_0^2c^4 \\ &= \frac{m_0^2c^4}{1 - v^2/c^2} = m^2c^4 \end{aligned}$$

or

$$p^2c^2 + m_0^2c^4 = E^2 = (E_k + m_0c^2)^2 = E_k^2 + m_0^2c^4 + 2E_km_0c^2$$

Thus,

$$E_k^2 + 2E_km_0c^2 = p^2c^2$$

Substituting for  $E_k$  from Eq.(3), we get

$$h^2(v - v')^2 + 2h(v - v')m_0c^2 = p^2c^2 \quad (11)$$

Further, Eqs.(7) and (8) can be rewritten in the form

$$p \cos \phi = \frac{h\nu}{c} - \frac{h\nu'}{c} \cos \theta \quad (12)$$

and

$$p \sin \phi = \frac{h\nu}{c} \sin \theta \quad (13)$$

In order to eliminate  $\phi$ , we square and add to obtain

$$p^2 = \left(\frac{h\nu}{c}\right)^2 + \left(\frac{h\nu'}{c}\right)^2 - \frac{2h^2\nu\nu'}{c^2} \cos \theta \quad (14)$$

Substituting in Eq.(11), we obtain

$$\begin{aligned} h^2(v^2 - 2vv' + v'^2) + 2h(v - v')m_0c^2 \\ = h^2v^2 + h^2v'^2 - 2h^2\nu\nu' \cos \theta \end{aligned}$$

or

$$\frac{2h(v - v')m_0c^2}{2vv'} = h^2(1 - \cos \theta)$$

or

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0 c} (1 - \cos \theta)$$

or

$$\Delta\lambda = \frac{2h}{m_0 c} \sin^2 \frac{\theta}{2} \quad (15)$$

which gives us the Compton shift.<sup>6</sup>

### 3.5. The photon mass

Because of the fact that the photon has energy ( $= h\nu/c$ ) we may assume it to have an inertial mass given by

$$m = \frac{h\nu}{c^2} \quad (16)$$

Thus when a light beam passes near a heavy star, its trajectory ought to get deflected. Indeed, the light coming from a distant star does get slightly deflected when passing near the sun, which has been experimentally observed.

Also, we may expect that when a photon leaves a star, its energy should decrease because of the gravitation field. This indeed happens and manifests itself in decrease in frequency which is usually referred as the *gravitational red shift*. One can approximately calculate the red shift by noting that the potential energy on the surface of the star would be

$$V \approx -\frac{GMm}{R} = -\frac{GM}{R} \cdot \frac{h\nu}{c^2} \quad (17)$$

where  $M$  is the mass of the star,  $R$  its radius and  $G$  the gravitational constant. Thus when the light beam reaches earth its frequency would become

$$h\nu' = h\nu - \frac{GM}{R} \frac{h\nu}{c^2}$$

or

$$\frac{\Delta\nu}{\nu} = \frac{\nu - \nu'}{\nu} = \frac{GM}{Rc^2} \quad (18)$$

(we have neglected the effect of the earth's gravitational field). From the above equation, we see that if the mass of the star is so large so that the RHS exceeds unity then the light beam will not be able to escape from the star—that is a black hole. We should mention that in discussing black holes, we must use general theory

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<sup>6</sup> In the derivation of the Compton shift we have assumed that the electron is free although we know that the electrons are bound to the atoms. The assumption of a free electron is justified because the binding energy ( $\approx$  few eV) is usually very much smaller in comparison to the photon energy ( $< 1000$  eV).

of relativity using which one obtains the following value for the limiting radius of the star:

$$R_s = \frac{2GM}{c^2} \quad (19)$$

which is known as the Schwarzschild radius. If the mass of the star is contained inside a sphere of radius

$$R < R_s$$

then a light beam will never leave the star and the star will be known as a black hole. Thus if

$$M \approx 10M_s \approx 2 \times 10^{34} \text{ g}$$

(where  $M_s$  is the mass of the sun—see Table 6.1)

$$\begin{aligned} R_s &\approx \frac{2 \times 6.67 \times 10^{-8} \times 2 \times 10^{34}}{(3 \times 10^{10})^2} \text{ cm} \\ &\approx 30 \text{ km} \end{aligned}$$

Indeed black holes with radius  $\sim 10$  km have been detected!

### 3.6. Wave nature of matter

Experiments by Wilson with his cloud chamber had clearly shown the particle like behaviour of alpha and beta particles. These are emitted by radioactive elements and when they pass through supersaturated vapor, they form tracks of condensed droplets. For alpha particles, these tracks are nearly straight lines; however, for electrons, the tracks are irregularly curved. The existence of continuous tracks suggest that the emissions from the radioactive substance can be regarded as minute particles moving with high speed. Further, the fact that electrons could be deflected by electric and magnetic fields and also the fact that one could accurately determine the ratio of their charge to mass suggest very strongly that electrons are particles. This view remained unchallenged for a number of years. [C.T.R. Wilson was awarded the 1927 Nobel Prize in Physics “*for his method of making the paths of electrically charged particles visible by condensation of vapor*”].

At this stage one could ask if matter may not show wave-like behaviour also just as light exhibited corpuscular and wave-like behaviour. In 1925, de Broglie proposed just such a hypothesis and argued that the relation given by Eq.(3), between wavelength and momentum applied for electrons as well. In his 1925 paper, he wrote: *The basic idea of quantum theory is, of course, the impossibility of considering an isolated fragment of energy without assigning a certain frequency to it;* de Broglie was awarded the 1929 Nobel Prize in Physics “*for his discovery of the wave nature of electrons*”. Later, de Broglie wrote [quoted from p. 58 of Ref. 3]

*I was convinced that the wave-particle duality discovered by Einstein in his theory of light quanta was absolutely general and extended to all of the physical world, and it seemed certain to me, therefore, that the propagation of a wave is associated with the motion of a particle of any sort—photon, electron, proton or any other.*

In 1927, Davisson and Germer studied the diffraction of electrons from single crystals of nickel and showed that the diffraction patterns could be explained if the electrons were assumed to have a wavelength given by the de Broglie relation

$$\lambda = \frac{h}{p} \quad (20)$$

where  $p$  is the momentum of the electron. Shortly afterwards, in 1928, G.P. Thomson carried out electron diffraction experiments by passing electrons through thin polycrystalline metal targets. The diffraction pattern consisted of concentric rings similar to the Debye-Scherrer rings obtained in the X-ray diffraction pattern. By measuring the diameters of the rings and from the known structure of the crystals, Thomson calculated the wavelength associated with the electron beam which was in agreement with the de-Broglie relation. In 1937, Davisson and Thomson shared the Nobel prize for *their experimental discovery of the diffraction of electrons by crystals*. Max Jammer [Ref. 4] has written: *Thomson, the father, was awarded the Nobel prize for having shown that the electron is a particle, and Thomson, the son, for having shown that the electron is a wave.*

### 3.6.1. DIFFRACTION OF X-RAYS BY CRYSTALS

Before we discuss the Davisson-Germer experiment, we thought it would be more appropriate to discuss briefly the diffraction of X-rays by crystals. We consider a monochromatic beam of X-rays to be incident on a crystal. In Fig. 3.8 the horizontal dotted lines represent a set of parallel crystal planes with Miller indices  $(hkl)$ .  $W_1 W_2$  and  $W_3 W_4$  represent the incident and reflected wavefronts respectively. Obviously, the secondary wavelets emanating from the points  $A$ ,  $B$  and  $C$  are in phase on  $W_3 W_4$  and the waves emanating from the points  $A_1$ ,  $B_1$  and  $C_1$  will also be in phase on  $W_3 W_4$  if

$$XB_1 + B_1 Y = m\lambda, \quad m = 1, 2, 3, \dots \quad (21)$$

or when

$$2d_{hkl} \sin \theta = m\lambda \quad (22)$$

where  $d_{hkl}$  is the interplanar spacing between crystal planes of indices  $(hkl)$ ,  $m = 1, 2, 3, \dots$  is called the order of diffraction and  $\theta$  is known as the Bragg angle.<sup>7</sup>

<sup>7</sup> W.H. Bragg (the father) and W.L. Bragg (the son) were awarded the 1915 Nobel Prize in Physics “for their services in the analysis of crystal structure by means of Röntgen rays”.

Equation (22) is known as Bragg's law and gives the angular positions of the reinforced diffracted beams in terms of the wavelength  $\lambda$  of the incoming X-rays and of the interplanar spacings  $d_{hkl}$  of the crystal planes. When the condition expressed by Eq.(22) is not satisfied, destructive interference occurs and no reinforced beam will be produced. Constructive interference occurs when the condition given by Eq.(22) is satisfied leading to peaks in the intensity distribution. For solids which crystallize in cubic structures (which are discussed later), the interplanar spacing  $d_{hkl}$  between two closest parallel planes with Miller indices  $(hkl)$  is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (23)$$

where  $a$  represents the lattice constant. In order to calculate the angles of diffraction we substitute Eq.(23) in the Bragg's law [Eq.(22)] to obtain

$$\frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin \theta = m\lambda \quad (24)$$

We restrict ourselves only to first order reflections ( $m = 1$ ); higher order reflections are usually rather weak. Thus, Eq.(24) can be written in the form:

$$\sin \theta = \frac{\lambda}{2a} \sqrt{N} \quad (25)$$

where

$$N \equiv h^2 + k^2 + l^2 \quad (26)$$

Now, for a simple cubic lattice, all values of  $(hkl)$  are possible implying the following possible values of  $N$ :

$$N = 1, 2, 3, 4, 5, 6, 7, \dots \quad (\text{SC}) \quad (27)$$

Similarly, for a BCC lattice  $h + k + l$  must be even implying

$$N = h^2 + k^2 + l^2 = 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, \dots \quad (\text{BCC}) \quad (28)$$

Finally, for an FCC lattice, Miller indices are either all even or all odd implying

$$N = h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, \dots \quad (\text{FCC}) \quad (29)$$

For a given structure and for given values of  $\lambda$  and  $a$ , one can now easily calculate the different values of  $\theta$ . For example, if we consider  $\lambda = 1.540 \text{ \AA}$  and  $1.544 \text{ \AA}$  (corresponding to the  $\text{CuK}_{\alpha^1}$  and  $\text{CuK}_{\alpha^2}$  lines) then for sodium (which is a BCC structure with  $a = 4.2906 \text{ \AA}$ ), the various values of  $\theta$  are

$$\begin{aligned} & (14.70^\circ, 14.74^\circ) (21.03^\circ, 21.09^\circ) (26.08^\circ, 26.15^\circ) (30.50^\circ, 30.59^\circ) \\ & (34.58^\circ, 34.68^\circ) (38.44^\circ, 38.56^\circ) (42.18^\circ, 42.32^\circ) (45.88^\circ, 46.03^\circ) \\ & (49.59^\circ, 49.76^\circ) (53.38^\circ, 53.58^\circ) (57.33^\circ, 57.56^\circ) (61.54^\circ, 61.82^\circ) \\ & (66.22^\circ, 66.56^\circ) (79.41^\circ, 80.23^\circ) \dots \end{aligned}$$

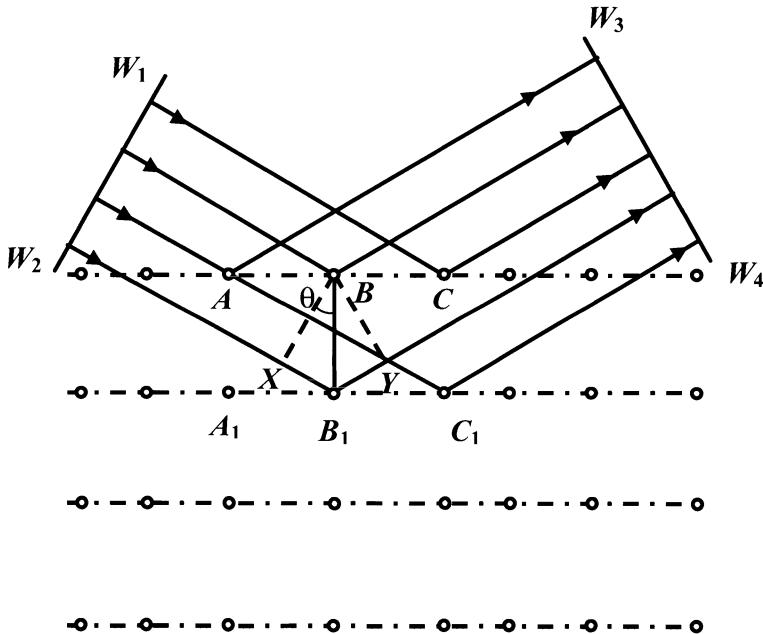


Figure 3.8. Reflection of a plane wave by a set of parallel crystal planes characterized by the Miller indices  $(hkl)$ . When the Bragg condition  $2d \sin \theta = m\lambda$  is satisfied, the waves scattered from different rows will be in phase.

The two values inside the parentheses correspond to the two wavelengths  $1.540 \text{ \AA}$  and  $1.544 \text{ \AA}$  respectively. Because of the presence of two wavelengths one obtains double lines for each family of planes which become resolvable only at higher scattering angles.

We do not wish to go into the details of X-ray crystallography, we would only like to mention that for given X-ray wavelengths, one measures different values of  $\theta$ —an analysis of which gives the crystal structure; interested readers may look up any book on solid state physics [see, e.g., Ref. 7].

We may point out that when one uses monochromatic X-rays, Bragg's formula cannot be satisfied for an arbitrary value of  $\theta$ . Hence one rotates the single crystal so that reflection can occur for a discrete set of  $\theta$  values. This method can only be employed if single crystals of reasonable size are available. If this is not the case, one can still use monochromatic X-rays provided the sample is in the powder form so that there are always enough crystallites of the right orientation available to satisfy the Bragg relation. A powder will consist of a large number of randomly oriented micro-crystals; each micro-crystal is essentially a single crystal. As the X-ray beam passes through such a polycrystalline material, the orientation of any given set of planes, with reference to the X-ray beam, changes from one micro-crystal to the other. Thus, corresponding to any given set of planes there will be a

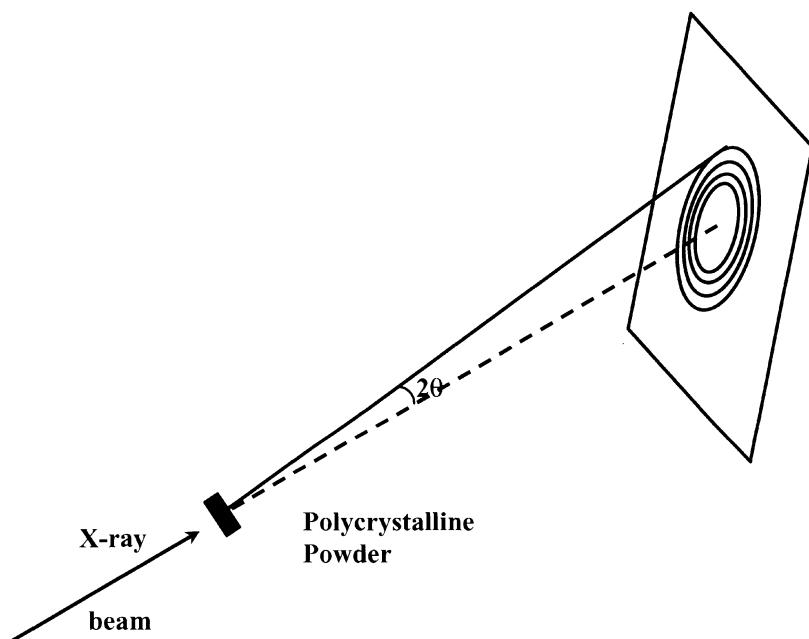


Figure 3.9. When a monochromatic X-ray beam falls on a polycrystalline sample one obtains the Debye-Scherrer rings.

large number of crystals for which Bragg's condition will be satisfied, and on the photographic plate one will obtain concentric rings [see Fig. 3.9]; each ring will correspond to a particular value of  $d_{hkl}$  and a particular value of  $m$ .

### 3.6.2. THE DAVISSON-GERMER EXPERIMENT

Figure 3.10 gives a schematic of the original experimental set up of Davisson and Germer (some details are given in the Nobel lecture of Davisson—see Ref. 8). In the experiment, an electron beam [accelerated by a (variable) potential] was incident normally on a single crystal of nickel. A collector was designed to accept only elastically scattered electrons. Corresponding to a particular set up, Fig. 3.11 shows the intensity variation as a function of  $\phi$  for different accelerating potentials;  $\phi$  represents the angle between the incident and the scattered beams (see Fig. 3.10). It may be seen that for 54 eV electrons, the scattered intensity is maximum which occurs at  $\phi \approx 50^\circ$ . Now

$$2\theta = \pi - \phi$$

Thus the Bragg angle is given by  $\theta \approx 65^\circ$ . Further, for 54 eV electrons use of non-relativistic formulae will give accurate results and therefore the corresponding

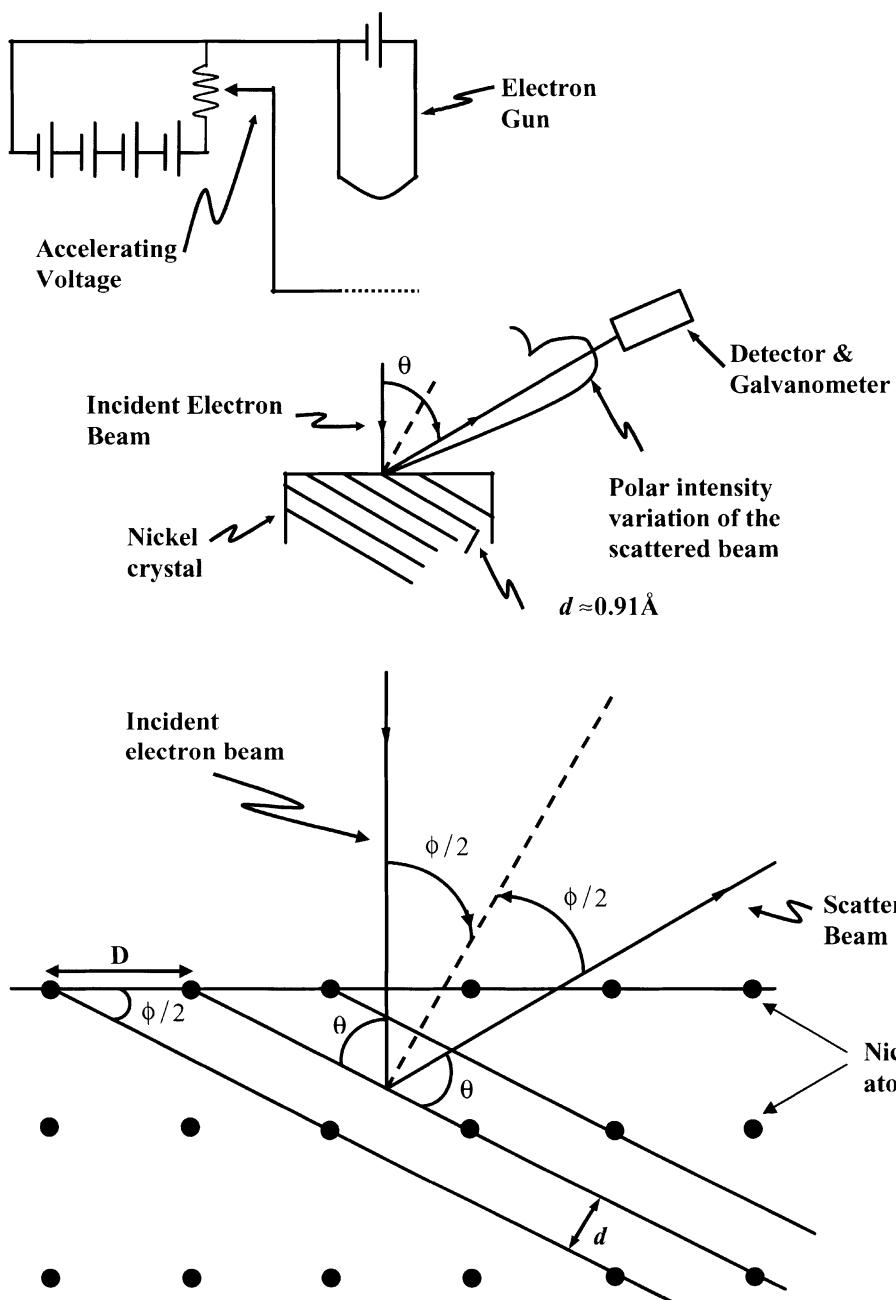


Figure 3.10. Schematic of the original setup of Davisson and Germer, (b) Bragg reflection from atomic planes of nickel.

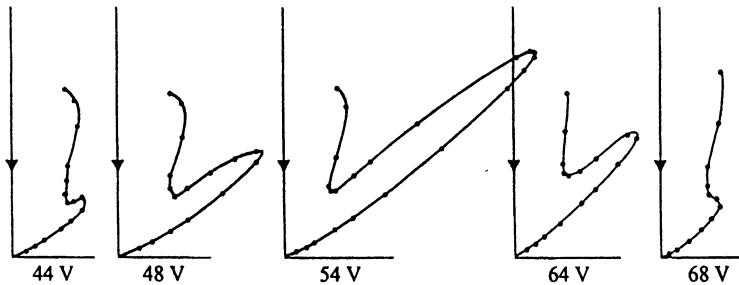


Figure 3.11. Polar diagram showing intensity variation as a function of  $\phi$  for different accelerating potentials (adopted from Ref. 8).

de-Broglie wavelength is given by

$$\begin{aligned} \lambda &= \frac{h}{p} = \frac{h}{\sqrt{2mE}} \\ &= \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.109 \times 10^{-34} \times (54 \times 1.602 \times 10^{-19})}} \approx 1.67 \times 10^{-10} \text{ m} \\ &\approx 1.67 \text{ \AA} \end{aligned} \quad (30)$$

Now, for nickel

$$D \approx 2.15 \text{ \AA} \quad (31)$$

And the inter-planar spacing will be given by

$$\begin{aligned} d &= D \sin \frac{\phi}{2} \\ &= 2.15 \sin 25^\circ \approx 0.909 \text{ \AA} \end{aligned} \quad (32)$$

The Bragg angle  $\theta = 65^\circ$ , thus Eq.(22) [with  $m = 1$ ] will give

$$\lambda = 2d \sin \theta \approx 1.65 \text{ \AA} \quad (33)$$

which compares well with Eq.(30). In Fig. 3.12(a) we have shown the Debye-Scherrer rings produced by scattering of X-rays by zirconium oxide crystals and Fig. 3.12(b) shows the rings produced by scattering of electrons by gold crystals. The two figures clearly show the similarity in the wave-like properties of X-rays and electrons.

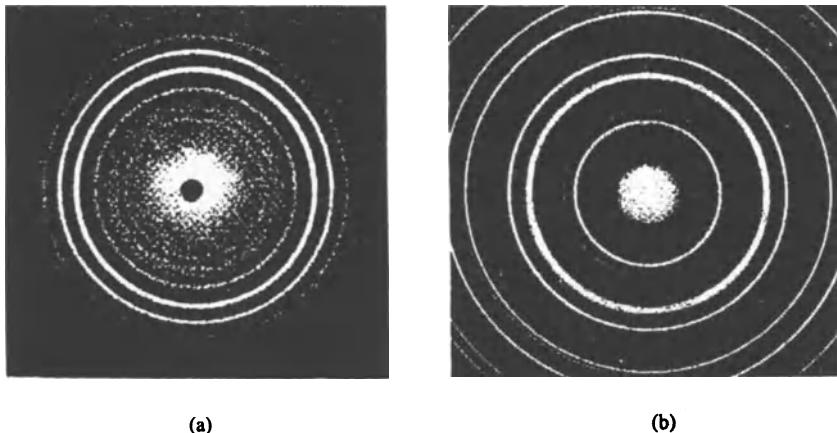


Figure 3.12. (a) Debye-Scherrer rings produced by scattering of X-rays by zirconium crystals. (b) Debye-Scherrer rings produced by scattering of electrons by gold crystals [after Ref. 9].

### 3.7. Uncertainty principle

The reconciliation of the corpuscular nature with the wave character of light (and also of the electron) has been brought about through the modern quantum theory; and perhaps the best known consequence of wave-particle duality is the uncertainty principle of Heisenberg which can be stated as follows:

If the x-coordinate of the position of a particle is known to an accuracy  $\Delta x$ , then the  $x$ -component of the momentum cannot be determined to an accuracy better than  $\Delta p_x \approx h/\Delta x$ , where  $h$  is the Planck's constant.

Alternatively, one can say that if  $\Delta x$  and  $\Delta p_x$  represent the accuracies with which the  $x$ -coordinate of the position and the  $x$ -component of the momentum can be determined, then the following inequality must be satisfied

$$\Delta x \Delta p_x \geq h \quad (34)$$

We do not feel the effect of this inequality in our everyday experience because of the smallness of the value of Planck's constant ( $\approx 6.6 \times 10^{-27}$  erg sec). For example, for a tiny particle of mass  $10^{-6}$  gm, if the position is determined within an accuracy of about  $10^{-6}$  cm, then according to the uncertainty principle, its velocity cannot be determined within an accuracy better than  $\Delta v \approx 6 \times 10^{-16}$  cm/sec. This value is much smaller than the accuracies with which one can determine the velocity of the particle. For a particle of a greater mass,  $\Delta v$  will be even smaller. Indeed, had the value of Planck's constant been much larger, the world would have been totally different. In a beautifully written book, Gamow (Ref. 10) has discussed what our world would be like if the effect of the uncertainty principle were perceivable by our senses.

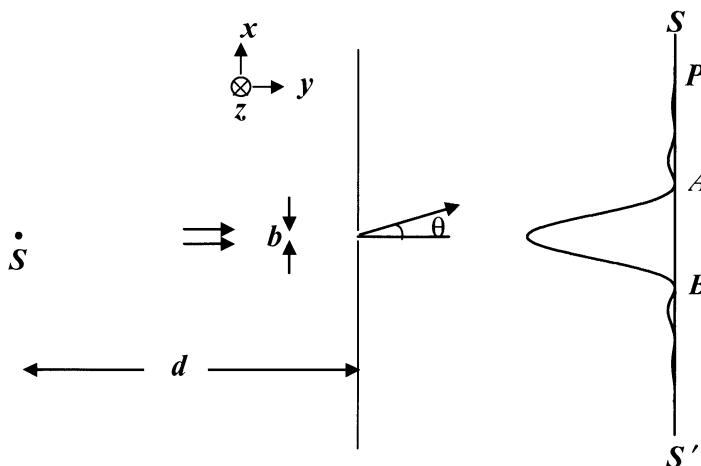


Figure 3.13. Diffraction of a photon (or an electron) beam by a long narrow slit of width  $b$ .

### 3.7.1. THE SINGLE SLIT DIFFRACTION EXPERIMENT

We will now show how the diffraction of a light beam (or an electron beam) can be explained on the basis of the corpuscular nature of radiation and the uncertainty principle. Consider a long narrow slit of width  $b$  as shown in Fig. 3.13. Now, one can always choose the distance between the source and the slit large enough so that  $p_x$  can be assumed to have an arbitrarily small value. For example, for the source at a distance  $d$ , the maximum value of  $p_x$  of the photons approaching the slit will be

$$p \frac{b}{d} = \frac{h\nu}{c} \cdot \frac{b}{d}$$

which can be made arbitrarily small by choosing a large enough value of  $d$ . Thus we may assume the light source to be sufficiently far away from the slit so that the photons approaching the slit can be assumed to have momentum only in the  $y$ -direction. Now, according to the particle model of radiation, the number of particles reaching the point  $P$  (which lies in the geometrical shadow) will be extremely small; further, if we decrease the width of the slit, the intensity should decrease, which is quite contrary to the experimental results because we know that the beam undergoes diffraction and the intensity at a point like  $P$  would normally increase if the width of the slit is made smaller. Thus, the classical corpuscular model is quite incapable of explaining the phenomenon of diffraction. However, if we use the uncertainty principle in conjunction with the corpuscular model, the diffraction phenomenon can be explained in the following manner: When a photon (or an electron) passes through the slit, one can say that

$$\Delta x \approx b$$

which implies that we can specify the position of the photon to an accuracy  $b$ . If we now use the uncertainty principle, we would have

$$\Delta p_x \approx \frac{h}{b} \quad (35)$$

i.e., just by making the photon pass through a slit of width  $b$ , the slit imparts a momentum in the  $x$ -direction which is  $\approx h/b$ . It may be pointed out that *before* the photon entered the slit,  $p_x$  (and hence  $\Delta p_x$ ) can be made arbitrarily small by putting the source sufficiently far away. Thus we may write  $\Delta p_x \approx 0$ . It would however be wrong to say that by making the photon pass through the slit,  $\Delta p_x \Delta x$  is zero; this is because of the fact that  $\Delta p_x \approx 0$  *before* the photon entered the slit. After the photon has entered the slit, it is confined within a distance  $b$  in the  $x$  direction and hence  $\Delta p_x \approx h/b$ . Further, since before the photon entered the slit  $p_x \approx 0$ , we will therefore have

$$|p_x| \approx \Delta p_x \approx \frac{h}{b}$$

But  $p_x = p \sin \theta$ , where  $\theta$  is the angle that the photon coming out of the slit makes with the  $y$ -axis (see Fig. 3.13). Thus

$$p \sin \theta \approx \frac{h}{b}$$

or

$$\sin \theta \approx \frac{h}{pb} \quad (36)$$

The above equation predicts that the possibility of a photon travelling at an angle  $\theta$  with the  $y$ -direction is inversely proportional to the width of the slit; i.e., smaller the value of  $b$ , greater is the value of  $\theta$  and greater is the possibility of the photon to reach deep inside the geometrical shadow. This is indeed the diffraction phenomenon. Now, the momentum of a photon is given by

$$p = \frac{h}{\lambda} \quad (37)$$

Thus Eq.(36) becomes

$$\sin \theta \approx \frac{\lambda}{b} \quad (38)$$

which is the familiar diffraction theory result. We can therefore say that the wave-particle duality is a consequence of the uncertainty principle and the uncertainty principle is a consequence of the wave-particle duality. To quote Max Born [Ref. 11]

*Physicists of today have learnt that not every question about the motion of an electron or a photon can be answered, but only those questions which are compatible with the uncertainty principle.*

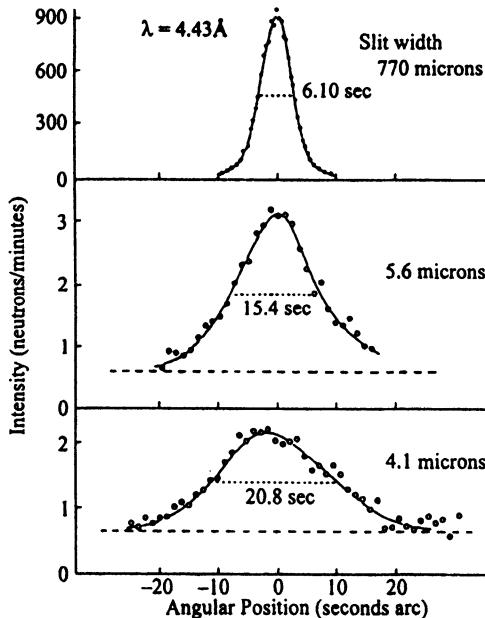


Figure 3.14. Angular broadening of a neutron beam by small slits [after Ref. 12].

Returning to Eq.(37), we may mention that de Broglie had suggested that the equation  $\lambda = h/p$  is not only valid for photons but is also valid for all particles like electrons, protons, neutrons, etc. Indeed, the de Broglie relation has been verified by studying the diffraction patterns produced when electrons, neutrons, etc. pass through a single crystal; the patterns can be analysed in a manner similar to the X-ray diffractions. In Fig. 3.14, we show the experimental data of Shull (Ref. 12) who studied the Fraunhofer diffraction of neutrons by a single slit and his experimental results agree with the intensity distribution as predicted by the wave theory with  $\lambda$  given by Eq.(37).

### 3.8. Probabilistic interpretation of matter waves

In the previous section we have seen that if a photon passes through a slit of width  $b$ , then the momentum imparted in the  $x$ -direction (which is along the width of the slit) is  $\approx h/b$ . The question arises whether we can predict the trajectory of an individual photon. The answer is no. We cannot say where an individual photon will land up on the screen; we can only predict the probabilities of arrival of the photon in a certain region of the screen. We may, for example say that the probability for the arrival of the photon in the region lying between the points  $A$  and  $B$  (see Fig. 3.13) is 0.85. This would imply that if the experiment was carried out with a large

number of photons, about 85% of them would land up in the region  $AB$ ; but the fate of an individual photon can never be predicted. This is in sharp contrast to Newtonian mechanics where the trajectories are always predetermined. It should be mentioned that if we place a light detector on the screen, then it will always record one photon or none and never half of a photon. This essentially implies the corpuscular nature of the radiation. However, the probability distribution is the same as predicted by the wave theory and therefore if one performs an experiment with a large number of photons (as is indeed the case in most experiments) the intensity distribution recorded on the screen is the same as predicted by the wave theory.

In order to explicitly show that diffraction is not a many photon phenomenon, Taylor in 1909 carried out a beautiful experiment which consisted of a box with a small lamp which casts the shadow of a needle on a photographic plate. The intensity of the light was so weak that between the slit and the photographic plate, it was almost impossible to find two photons. In fact to get a good fringe pattern Taylor made an exposure lasting for several months. The diffraction pattern obtained on the photographic plate, was the same as predicted by the wave theory.

The corpuscular nature of radiation and the fact that one cannot predict the trajectory of an individual photon can be seen from Fig. 3.15 which consists of series of photographs showing the quality of pictures obtainable from various number of photons. The photograph clearly shows that the picture is built up by the arrival of concentrated packets of energy and the point at which a particular photon will arrive is entirely a matter of chance. The figure also shows that the photograph is featureless when a small number of photons are involved and as the number of photons reaching the photographic plate increases, the intensity distribution becomes the same as would be predicted by the wave theory. To quote Feynman

*... it would be impossible to predict what would happen. We can only predict the odds! This would mean, if it were true, that physics has given up on the problem of trying to predict exactly what will happen in a definite circumstance. Yes! physics has given up. We do not know how to predict what would happen in a given circumstance, and we believe now that it is impossible—that the only thing that can be predicted is the probability of different events. It must be recognized that this is a retrenchment in our earlier idea of understanding nature. It may be a backward step, but no one has seen a way to avoid it.*

A somewhat similar situation arises in radioactivity. Consider a radioactive nucleus having a half-life of say 1 hour. If we start with 1000 such nuclei, then on an average 500 of them would undergo radioactive decay in 1 hour and about 250 of them in the next 1 hour and so on. Thus, although to start with, all nuclei are identical, some nuclei would decay in the very first minute and some nuclei can survive for hours without undergoing radioactive decay. Thus, one can never predict as to which nucleus will undergo decay in a specified period; one can only

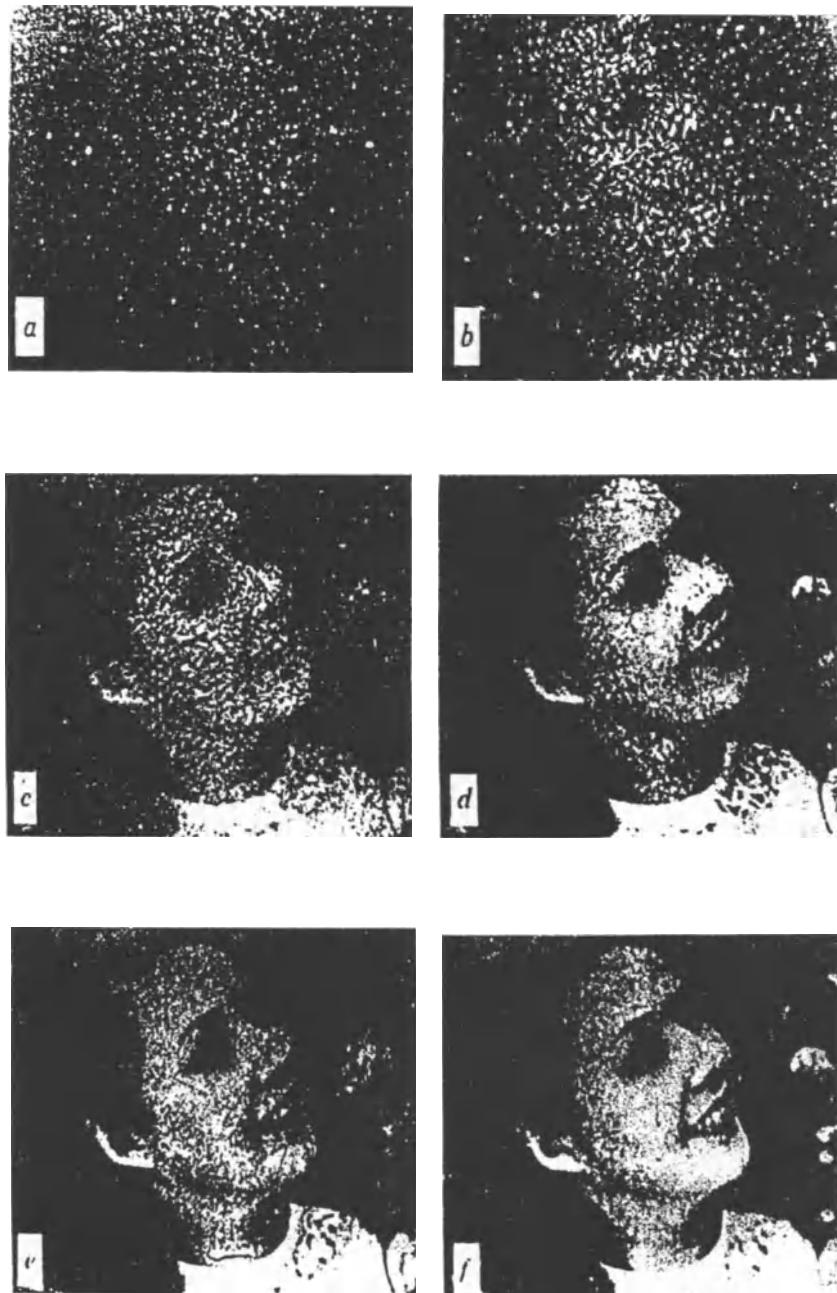


Figure 3.15. Photographs showing the quality of a picture obtainable from various numbers of photons: (a), (b), (c), (d), (e) and (f) correspond to  $3 \times 10^3$  photons,  $1.2 \times 10^4$  photons,  $9.3 \times 10^4$  photons,  $7.6 \times 10^5$  photons,  $3.6 \times 10^6$  photons and  $2.8 \times 10^7$  photons respectively. (From A. Rose, *Quantum Effects in Human Vision*, Advances in Biological and Medical Physics, Vol. V, Academic Press, 1957).

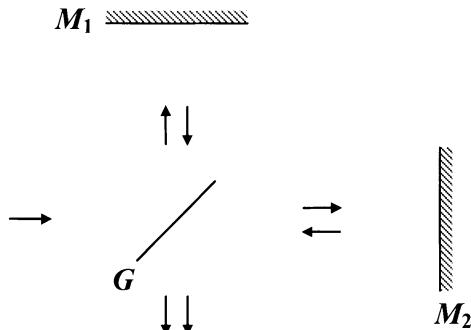


Figure 3.16. Schematic of the setup of the Michelson interferometer.  $G$  represents a beam splitter,  $M_1$  and  $M_2$  represent plane mirrors.

predict the probability of its undergoing decay in a certain interval of time. This is indeed a beautiful manifestation of quantum mechanics. To quote Feynman again

*A philosopher once said it is necessary for the very existence of science that the same conditions always produced the same results. Well they don't!*

### 3.9. An understanding of interference experiments

Let us consider the interference experiment involving the Michelson interferometer in which a light beam is partially reflected by a beam splitter and the resulting beams are made to interfere (see Fig. 3.16). According to Dirac [Ref. 13]

*... we describe the photon as going partly into each of the two components into which the incident beam is split. The photon is then, as we may say, in a translational state given by the superposition of the two translational states associated with the two components . . . For a photon to be in a definite translational state it need not be associated with one single beam of light, but may be associated with two or more beams of light, which are the components into which one original beam has been split. In the accurate mathematical theory each translational state is associated with one of the wave functions of ordinary wave optics, which may describe either a single beam or two or more beams into which one original beam has been split.*

These translational states can be superposed in a manner similar to the one employed while considering the interference of two beams. Thus, each photon goes partly into each of the two components and interferes only with itself. If we try to determine the fate of a single photon by measuring the energy in one of the components then Dirac argues:

*The result of such a determination must be either a whole photon or nothing at all. Thus the photon must change suddenly from being partly in one beam*

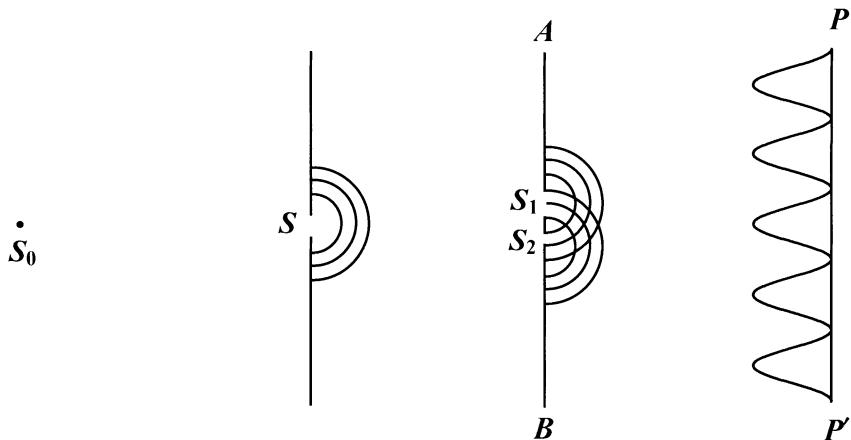


Figure 3.17. Young's double hole experimental arrangement for obtaining the interference pattern.

*and partly in the other to be entirely in one of the beams. This sudden change is due to the disturbance in the translational state of the photon which the observation necessarily makes. It is impossible to predict in which of the two beams the photon will be found. Only the probability of either result can be calculated. Our description of the photon allows us to infer that, after such an energy measurement, it would not be possible to bring about any interference effects between the two components. So long as the photon is partly in one beam and partly in the other, interference can occur when the two beams are superposed, but this probability disappears when the photon is forced entirely into one of the beams by an observation.*

In a similar manner, we may consider the two-hole interference experiment similar to that performed by Young. The experimental arrangement is shown in Fig. 3.17 where a weak light source  $S_0$  illuminates the hole  $S$  and the light emerging from the holes  $S_1$  and  $S_2$  produce the interference pattern on the screen  $PP'$ . The intensity is assumed to be so weak that in the region between the planes  $AB$  and  $PP'$  there is almost never more than one photon. Individual photons are also counted by a detector on the screen  $PP'$  and one finds that the intensity distribution has a  $\cos^2$  pattern similar to that shown in Fig. 3.17. The corpuscular nature of the radiation is evident from its detection in the form of single photons and never a fraction of a photon. The appearance of the interference pattern is because of the fact that a photon interferes with itself. The quantum theory tells us that a photon partially passes through the hole  $S_1$  and partially through  $S_2$ . This is not the splitting of the photon into two halves but only implies that if we wish to find out through which hole the photon passed, then half the time it will be found to have passed through the hole  $S_1$  and half the time through  $S_2$ . As in the case of the Michelson interferometer, the photon is in a state which is a superposition of

two states, one corresponding to the wave emanating from hole  $S_1$  and the other to the one emanating from hole  $S_2$ . The superposed state will give rise to an intensity distribution similar to that obtained by considering the superposition of two waves. It may be noted that if we had employed a device (like a microscope) which would have determined which hole the photon had passed through, then the interference pattern on the screen would have been washed out. This is a consequence of the fact that a measurement always disturbs the system. This is beautifully discussed in Ref. 1. Thus we may say that the photons would arrive as packets of energy but the probability distribution (on the screen) will be proportional to the intensity distribution predicted by using a wave model.

In a recent paper, Tonomura and his co-workers (Ref. 14) have demonstrated the single electron build up of an interference pattern. Their results are shown in Fig. 3.18. It may be seen that when there are very few electrons they arrive randomly; however, when a large number of electrons are involved, one obtains an intensity distribution similar to the one predicted by wave theory.

**Example 3.1** In this example we will use the uncertainty principle to determine the size of the hydrogen atom. The example demonstrates the far-reaching consequences of the uncertainty principle.

We consider the hydrogen atom which consists of a proton and an electron. Since the proton is very much heavier than the electron, we consider only the motion of the electron. Let the electron be confined to a region of linear dimension  $\approx a$ . Thus according to the uncertainty principle

$$p \approx \Delta p \approx \hbar/a \quad (39)$$

where  $\hbar = h/2\pi$ ; the reason for using  $\hbar$  rather than  $h$  will be mentioned later. The kinetic energy of the electron will be given by

$$\text{K.E.} = \frac{p^2}{2m} \approx \frac{\hbar^2}{2ma^2} \quad (40)$$

Now, there exists an electrostatic attraction between the two particles; the corresponding potential energy being given by

$$\text{P.E.} = -\frac{q^2}{4\pi\epsilon_0 a} \quad (41)$$

where  $q$  ( $\approx 1.6 \times 10^{-19}$  C) represents the magnitude of the charge of the electron and  $\epsilon_0$  ( $\approx 8.854 \times 10^{-12}$  CN $^{-2}$ m $^{-2}$ ) represents the permittivity of free space. Thus the total energy is given by

$$\begin{aligned} E &= \text{K.E.} + \text{P.E.} \\ &= \frac{\hbar^2}{2ma^2} - \frac{q^2}{4\pi\epsilon_0 a} \end{aligned} \quad (42)$$

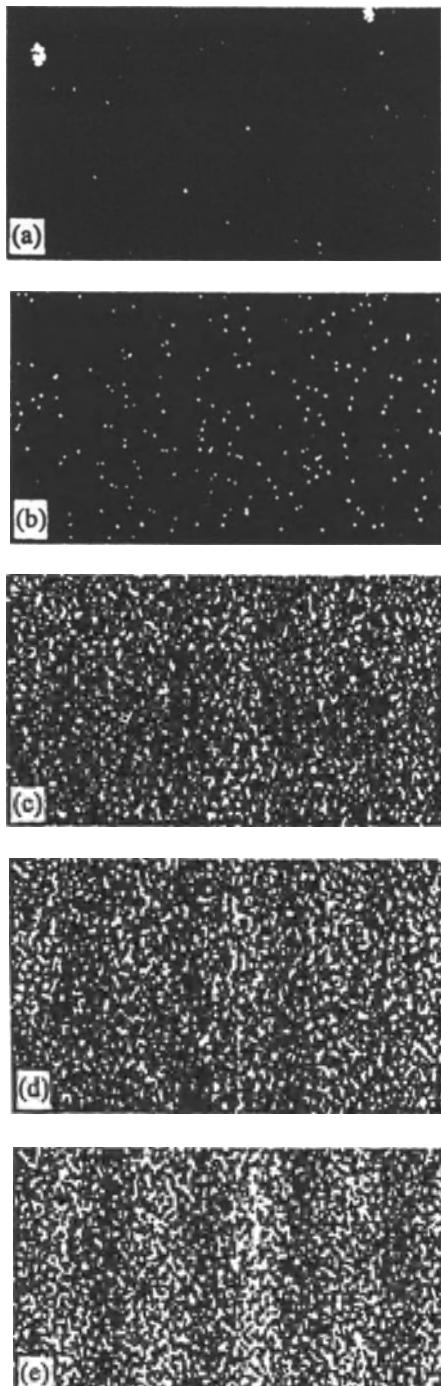


Figure 3.18. Buildup of the electron interference pattern. Number of electrons in (a), (b), (c), (d) and (e) are 10, 100, 3000, 20000 and 70000 respectively. [Adapted from Ref. 14].

The system would settle to a state of lowest energy; thus we must set  $dE/da$  equal to zero:

$$0 = \frac{dE}{da} = -\frac{\hbar^2}{ma^3} + \frac{q^2}{4\pi\varepsilon_0 a^2}$$

implying

$$a = a_0 = \frac{\hbar^2}{m \left( \frac{q^2}{4\pi\varepsilon_0} \right)} \quad (43)$$

If we substitute the values of  $\hbar$  ( $\approx 1.055 \times 10^{-34}$  Js),  $m$  ( $\approx 9.11 \times 10^{-31}$  kg),  $\varepsilon_0$  and  $q$  we would obtain

$$a = a_0 \approx 0.53 \times 10^{-10} \text{ m} = 0.53 \text{ \AA} \quad (44)$$

Thus we get the remarkable result that the size of the hydrogen atom is a direct consequence of the uncertainty principle. To quote Feynman:

*So we now understand why we do not fall through the floor .... In order to squash the atoms close together, the electrons would be confined to smaller space and by the uncertainty principle, their momenta would have to be higher on the average, and that means high energy; the resistance to atomic compression is a quantum mechanical effect ...*

We next substitute the value of  $a$  from Eq.(43) in Eq.(42) to obtain

$$\begin{aligned} E &= \frac{\eta^2}{2m} \left( \frac{m}{\hbar^2} \frac{q^2}{4\pi\varepsilon_0} \right)^2 - \frac{q^2}{4\pi\varepsilon_0} \left( \frac{m}{\hbar^2} \frac{q^2}{4\pi\varepsilon_0} \right) \\ &= -\frac{m}{2\hbar^2} \left( \frac{q^2}{4\pi\varepsilon_0} \right)^2 \end{aligned} \quad (45)$$

Substituting the values of  $\nabla$ ,  $m$ ,  $q$  and  $\varepsilon_0$ , we get

$$\begin{aligned} E &\approx -2.17 \times 10^{-19} \text{ J} \\ &\approx -13.6 \text{ eV} \end{aligned} \quad (46)$$

which is nothing but the ground state energy of the hydrogen atom. Thus, that the ionization potential of hydrogen atom is  $\approx 13.6$  eV follows from the uncertainty principle. We may point out that the uncertainty principle can be used to give only an order of magnitude of the size of the hydrogen atom or its ionization potential; we had intentionally chosen the constants in such a way that the ground state energy comes out to be correct. It is for this reason that we had chosen  $\hbar$  instead of  $h$  in Eq.(39).

### 3.10. The Franck-Hertz experiment

We conclude this chapter with a brief discussion of the Franck-Hertz experiment. In 1914 James Franck and Gustav Hertz (nephew of Heinrich Hertz) performed a beautiful experiment demonstrating conclusively the quantized nature of the energy levels of atoms—the quantized energy states of the atom was predicted by Niels Bohr<sup>8</sup> in 1913. Indeed while introducing Franck and Hertz for receiving the Nobel Prize, it was mentioned “...Bohr’s hypotheses of 1913—that the atom can exist in different states, each of which is characterized by a given energy level and that these energy levels govern the spectral lines emitted by the atoms—are no longer mere hypotheses but experimentally proved facts. The methods of verifying these hypotheses are the work of James Franck and Gustav Hertz, for which they have been awarded the Physics Nobel Prize for 1925”. The Nobel Prize was awarded “for their discovery of the laws governing the impact of an electron upon an atom”.

The experimental setup of Franck and Hertz is shown in Fig. 3.19. The electrons are produced by a heated tungsten filament. These electrons are accelerated by a wire mesh  $G$  kept at a distance of a few centimeters from the filament. The wire mesh is kept at a positive potential  $V$  which can be varied. There is a plate  $P$  behind the wire mesh which was kept at a small negative potential so that very low energy electrons {after passing through  $G$ } would not reach the plate  $P$ . A typical variation of the plate current (as obtained by Franck and Hertz) with the voltage  $V$  is shown in Fig. 3.20. As can be seen when  $V$  reaches 4.9V (or a multiple of that) there is a sudden drop in the current. This was due to the fact that the electrons attaining 4.9 eV of energy excite the Hg atom and lose its entire energy and are no more collected by the plate  $P$ . Indeed when the Hg atom de-excites itself, it produces a photon of wavelength 2536 Å for which

$$\begin{aligned} h\nu &= \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{2.536 \times 10^{-7}} \text{ J} \\ &= 4.9 \text{ eV} \end{aligned} \tag{47}$$

Thus the Franck-Hertz experiment confirms the discrete energy states of the Hg-atom. Similarly, The Franck-Hertz experiment was performed using other atoms.

### 3.11. Problems

**Problem 3.1** An electron of energy 200 eV is passed through a circular hole of radius  $10^{-4}$  cm. What is the uncertainty introduced in the angle of emergence?

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<sup>8</sup> Niels Bohr was awarded the 1922 Nobel Prize in Physics “for his services in the investigation of the structure of atoms, and of the radiation emanating from them”.

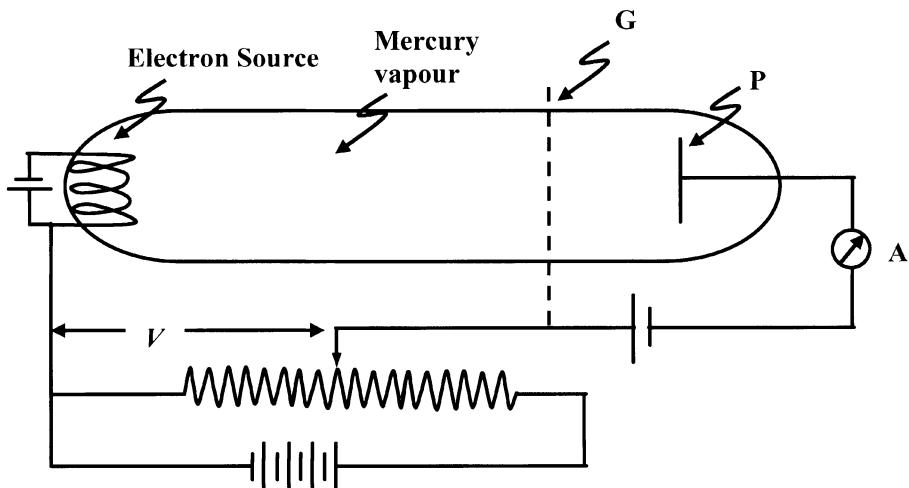


Figure 3.19. The schematic of the experimental set-up of Franck and Hertz.

**Problem 3.2** In continuation of the previous problem, what would be the corresponding uncertainty for a 0.1 g lead ball thrown with a velocity  $10^3$  cm/sec through a hole 1 cm in radius?

**Problem 3.3** Use the uncertainty principle to estimate the energy of the ground state of a two-electron atom of nuclear charge  $Ze$ .

[Hint: Use a method similar to that used in Example 3.1.]

**Problem 3.4** Calculate the uncertainty in the momentum of a proton which is confined to a nucleus of radius equal to  $10^{-13}$  cm. From this result, estimate the kinetic energy of the proton inside the nucleus and the strength of the nuclear interaction. What would be the kinetic energy for an electron if it had to be confined within a similar nucleus?

**Problem 3.5** Let a source (with  $\lambda = 5 \times 10^{-5}$  cm) of power 1 watt be used in the experimental arrangement shown in Fig. 3.17.

- Calculate the number of photons that are being emitted by the source per second.
- Assume that the radii of the holes  $S$ ,  $S_1$  and  $S_2$  to be 0.02 cm and  $S_0 S = SS_1 = SS_2 = 100$  cm and the distance between the planes  $AB$  and  $PP'$  to be also 100 cm. Show that in the region between the planes  $AB$  and  $PP'$  one can almost never find two photons.

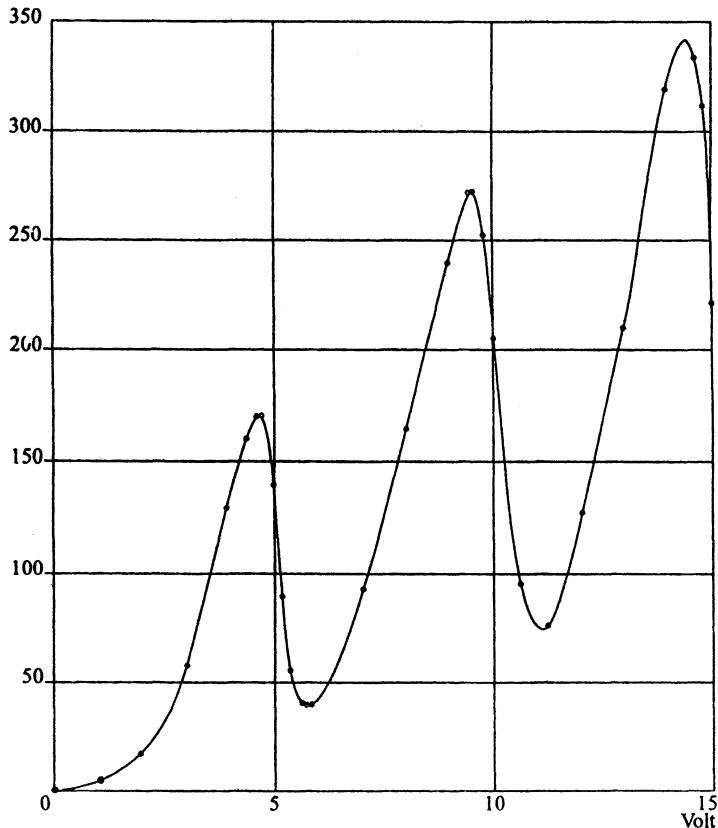


Figure 3.20. The variation of the plate current with voltage  $V$  as measured in the original experiment of Franck and Hertz (adapted from Ref. 15).

### 3.12. Solutions

#### Solution 3.1

$$p \approx \sqrt{2mE} = [2 \times 0.9 \times 10^{-27} \times 3.2 \times 10^{-10}]^{1/2} \cong 8 \times 10^{-19} \text{ g cm/sec}$$

Now

$$\Delta p \sim \frac{\hbar}{\Delta x} \cong \frac{10^{-27} \text{ erg sec}}{2 \times 10^{-4} \text{ cm}} = 5 \times 10^{-24} \text{ g cm/sec.}$$

$$\theta \sim \frac{\Delta p_x}{p} \approx 6 \times 10^{-6} \text{ radians} \cong 1 \text{ sec of arc}$$

#### Solution 3.2

$$p \approx 10^2 \text{ cm g/sec}, \quad \Delta p \approx \frac{\hbar}{\Delta x} \approx 5 \times 10^{-28} \text{ g cm/sec.}$$

$$\theta \sim 5 \times 10^{-30} \text{ radians} \approx 10^{-34} \text{ sec of arc}$$

**Solution 3.3** Let the dimensions of the region of localization for the first and second electrons be  $a_1$  and  $a_2$ . Then the spread in momenta (and therefore the momenta themselves) would be given by

$$p_1 \sim \frac{\hbar}{a_1}, \quad p_2 \sim \frac{\hbar}{a_2}$$

Thus

$$\text{Kinetic Energy} \sim \frac{\hbar^2}{2m} \left[ \frac{1}{a_1^2} + \frac{1}{a_2^2} \right] \quad (48)$$

The potential energy of the interaction of the electrons with a nucleus of charge  $Ze$  is

$$-Ze^2 \left( \frac{1}{a_1} + \frac{1}{a_2} \right)$$

and the interaction energy between the electrons is  $\sim e^2/(a_1 + a_2)$  because the separation between the two electrons is  $\sim (a_1 + a_2)$ ; for convenience, we are using cgs units so that  $q^2/(4\pi\epsilon_0)$  is replaced by  $e^2$ . The total energy is, therefore, given by

$$E(a_1, a_2) = \frac{\hbar^2}{2m} \left( \frac{1}{a_1^2} + \frac{1}{a_2^2} \right) - Ze^2 \left( \frac{1}{a_1} + \frac{1}{a_2} \right) + \frac{e^2}{a_1 + a_2} \quad (49)$$

For  $E$  to be minimum

$$\begin{aligned} \frac{dE}{da_1} &= -\frac{\hbar^2}{ma_1^3} + \frac{Ze^2}{a_1^2} - \frac{e^2}{(a_1 + a_2)^2} = 0 \\ \frac{dE}{da_2} &= -\frac{\hbar^2}{ma_2^3} + \frac{Ze^2}{a_2^2} - \frac{e^2}{(a_1 + a_2)^2} = 0 \end{aligned}$$

The solution would be

$$\begin{aligned} a_1 = a_2 &= \frac{\hbar^2}{me^2} \cdot \frac{1}{Z - \frac{1}{4}} \\ E &\cong - \left( Z - \frac{1}{4} \right)^2 \frac{me^4}{\hbar^2} = - \left( Z - \frac{1}{4} \right)^2 \times 27.2 \text{ eV} \end{aligned} \quad (50)$$

The values of  $E$  calculated using the above equation compare rather well with the experimental data as shown in Table 3.1. The energy is in units of  $me^4/2\hbar^2 = 13.6$  eV, the ionization potential of the hydrogen atom.

**Solution 3.4** The proton is confined within a sphere of radius  $r_0 \approx 10^{-13}$  cm. Thus the uncertainty in the momentum must be at least of the order of  $\hbar/r_0$ , or

$$p \sim \frac{\hbar}{r_0}$$

Table 3.1. Ground state energy (in units of  $me^4/2\nabla^2$ ) of various two electron atoms.  
[Adapted from Ref. 16]

	He	Li <sup>+</sup>	Be <sup>++</sup>	B <sup>+++</sup>	C <sup>++++</sup>
Experimental value -5.807	-14.56	-27.31	-44.06	-64.80	
Calculated value using Eq.(50)	-6.125	-15.12	-28.12	-45.12	-66.12

Therefore, the kinetic energy of the proton will be given by

$$E = \frac{p^2}{2m_p} \sim \frac{\hbar^2}{2m_p r_0^2}$$

where  $m_p$  is the mass of the proton. On substitution, we get

$$\begin{aligned} E &\sim \frac{(1.05 \times 10^{-27} \text{ erg-sec})^2}{2 \times 1.67 \times 10^{-24} \text{ g} \times (10^{-13} \text{ cm})^2} \\ &\cong 3 \times 10^{-5} \text{ ergs} \cong 20 \text{ MeV} \end{aligned}$$

Since the proton is bound inside the nucleus, the average of the potential energy,  $\langle V \rangle$ , must be negative and greater in magnitude than the kinetic energy. Therefore

$$-\langle V \rangle \gtrsim 20 \text{ MeV}$$

which indeed gives the correct order of the potential energy. The uncertainty in momentum for the electron is again  $\hbar/r_0$ ; however, since the rest mass of the electron is very much smaller than that of the proton, the velocity of the electron is very close to c and we have to use the extreme relativistic formula for the energy,

$$E = cp = \frac{c\hbar}{r_0} \cong \frac{(3 \times 10^{10})(1.05 \times 10^{-27})}{10^{-13} \times 1.6 \times 10^{-6}} \text{ MeV} \sim 200 \text{ MeV}$$

Although electrons do emerge from nuclei in  $\beta$ -decay, they seldom have energies exceeding a few million electron volts. Thus one does not expect the electron to be a basic constituent of the nucleus; the rare occasions when  $\beta$ -decay occurs may be attributed to the transformation of a neutron into a proton and an electron (and the neutrino) so that the electron is in fact created at the instant the decay occurs.

**Solution 3.5** (a) The energy of each photon will be

$$h\nu = \frac{hc}{\lambda} \cong \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{5 \times 10^{-5}} \cong 4 \times 10^{-12} \text{ ergs} = 4 \times 10^{-19} \text{ J}$$

Thus the number of photons emitted per second will be

$$\frac{1 \text{ Watt}}{4 \times 10^{-19} \text{ J}} = 2.5 \times 10^{18}$$

Similarly, the number of photons passing through either  $S_1$  or  $S_2$  will approximately be

$$\frac{2.5 \times 10^{10} \times 2 \times \pi \times (0.02)^2}{2\pi \times (100)^2} = 1000 \text{ per second}$$

where we have assumed that after passing through  $S$ , the photons are evenly distributed in the hemisphere; this is strictly not correct because the diffraction pattern is actually an Airy pattern—nevertheless, the above calculations would be qualitatively correct. The distance between the planes  $AB$  and  $PP'$  is 100 cm [see Fig. 3.17] which will be traversed by a photon in a time  $3 \times 10^{-9}$  sec. Thus, approximately every thousandth of a second a photon enters the region and the space is traversed much before the second photon enters. Therefore, in the region between  $AB$  and  $PP'$  one will (almost) never find two photons. This is somewhat similar to the case when, on an average, 100 persons pass through a room in one year and the time that each person takes to cross the room is  $\approx 1$  second, thus it will be highly improbable to have two persons simultaneously in the room.

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# Chapter 4

## Time Dependent Schrödinger Equation

*The scientist builds his theories as much with a kind of inspired artistry as with the strict procedures of logic. A great theory can no more be put together entirely with straightforward reasoning processes than a great symphony can be written with textbook principles of composition. The composer must have a finely tuned ear; the scientist must have a finely tuned insight. Just as the composer “hears” his incomplete symphony as if it were being played by a full orchestra, the scientist must “see” his theory extending far beyond its early, primitive limitations. In the beginning the work has a strange, complex sound; its beauty is subtle and few are able to understand and appreciate it. But gradually, with patience and faith and mastery of technique, the artist-scientist manages to bring the essential elements of his art together and to weave them into a powerful and moving whole (in music this is the creation of a single artist, but in science it finally requires the efforts of many). Eventually, sometimes much later, the work plays to larger audiences and is accepted into the standard repertoire.*

— W.H. CROPPER in *The Quantum Physicists*,  
Oxford University Press, New York (1970), p. 179.

### 4.1. Introduction

In the previous chapter we discussed some experiments which showed that particles like electrons, protons, neutrons, atoms, etc., exhibit wavelike properties. Indeed the wavelength is related to the momentum through the de Broglie relation:

$$\lambda = \frac{h}{p} \quad (1)$$

or

$$p = \hbar k \quad (2)$$

where  $k = 2\pi/\lambda$  and  $\hbar = h/2\pi$ ,  $h$  being the Planck's constant. Thus we write

$$\mathbf{p} = \hbar \mathbf{k} \quad (3)$$

where  $\mathbf{k}$  denotes the wave vector. Further, as established by Einstein's explanation of the photoelectric effect, the energy  $E$  of the particle is related to the frequency

through the relation

$$E = \hbar \omega \quad (4)$$

In this chapter we would like to obtain an equation, the solution of which would describe the behaviour of particles like the electron and the proton.<sup>1</sup> The corresponding solutions should describe the corpuscular and wavelike behaviour of the particle and should also be consistent with the uncertainty principle. Thus we assume that the trajectory of a particle should be describable by a wave function  $\Psi(\mathbf{r}, t)$  whose magnitude is large in regions where the probability of the occurrence of the particle is large; in other regions where the particle is less likely to be found, the magnitude of  $\Psi$  should be small. Indeed we will show that  $|\Psi|^2 d\tau$  can be interpreted to represent the probability of finding the particle in the volume element  $d\tau$ .

In Sec. 4.2 we will obtain an equation (known as the Schrödinger equation) satisfied by  $\Psi$  and will show that in quantum mechanics the dynamical variables like position, momentum, energy, etc., are represented by linear operators which, in general, do not commute with each other (see Sec. 4.3). In Sec. 4.4 we will give a physical interpretation of the wave function and in Sec. 4.5 we will give formulae which will enable us to calculate the expectation values of various observables (like position, momentum, energy, etc.); these will lead to the relation between classical and quantum motions (Ehrenfest's theorem) and also to the uncertainty principle which will be quantitatively discussed in Sec. 4.6. In the next chapter we will discuss the motion of a wave packet which will describe the trajectory of a free particle; the wave function describing the motion of the wave packet will obviously be a solution of the Schrödinger equation and will be shown to be consistent with the uncertainty principle. In Chapters 6, 7, 8 and 10 we will obtain exact solutions of the Schrödinger equation corresponding to problems of physical interest.

## 4.2. The Schrödinger equation

The simplest type of wave is a plane monochromatic wave described by the wave function

$$\Psi(\mathbf{r}, t) = A e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (5)$$

which represents a disturbance of amplitude  $A$  and of wavelength  $\lambda = 2\pi/k$  travelling in the direction of its wave vector  $\mathbf{k}$  with phase velocity  $\omega/k$ . If we assume the propagation to be along the  $x$ -axis, then

$$\mathbf{k} = k \hat{\mathbf{x}} \quad (6)$$

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<sup>1</sup> As discussed in the previous chapter, radiation also exhibits wave and particle like properties. The quantum theory of radiation is discussed in Chapter 27.

and we have

$$\Psi(x, t) = A e^{i(kx - \omega t)} \quad (7)$$

which on using Eqs (2) and (4) takes the form

$$\Psi(x, t) = A \exp \left[ \frac{i}{\hbar} (px - Et) \right] \quad (8)$$

Successive differentiation of Eq. (8) gives us

$$i \hbar \frac{\partial \Psi}{\partial t} = E \Psi(x, t) \quad (9)$$

$$-i \hbar \frac{\partial \Psi}{\partial x} = p \Psi(x, t) \quad (10)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m} \Psi(x, t) \quad (11)$$

Now for a free non-relativistic particle

$$E = \frac{p^2}{2m} \quad (12)$$

and therefore from Eqs (9) and (11) we get

$$i \hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \quad (13)$$

which is the one-dimensional time dependent Schrödinger equation for a free particle. In the next chapter we will discuss the most general solution of Eq. (13).

Equations (9) and (10) suggest that  $E$  and  $p$  can be represented by the operators  $i \hbar \frac{\partial}{\partial t}$  and  $-i \hbar \frac{\partial}{\partial x}$  respectively:

$$E \rightarrow i \hbar \frac{\partial}{\partial t}, \quad p \rightarrow -i \hbar \frac{\partial}{\partial x} \quad (14)$$

Thus Eq. (13) can also be written in the form

$$E \Psi = \frac{p^2}{2m} \Psi(x, t) \quad (15)$$

where it is implied that  $E$  and  $p$  are to be replaced by their operator representations.

The three-dimensional generalization is very straightforward. Instead of Eq. (8) we have

$$\begin{aligned}\Psi(\mathbf{r}, t) &= A \exp \left[ \frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - Et) \right] \\ &= A \exp \left[ \frac{i}{\hbar} (p_x x + p_y y + p_z z - Et) \right]\end{aligned}\quad (16)$$

Thus

$$\begin{aligned}i \hbar \frac{\partial \Psi}{\partial t} &= E \Psi \\ -i \hbar \frac{\partial \Psi}{\partial x} &= p_x \Psi \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} &= \frac{p_x^2}{2m} \Psi\end{aligned}$$

etc. Since

$$E = \frac{p^2}{2m} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

we immediately have

$$i \hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right] = -\frac{\hbar^2}{2m} \nabla^2 \Psi \quad (17)$$

which is the three-dimensional Schrödinger equation for a free particle. Once again the operator representation of  $E$  and components of  $\mathbf{p}$  would be

$$E \rightarrow i \hbar \frac{\partial}{\partial t} ; \quad \mathbf{p} \rightarrow -i \hbar \nabla \quad (18)$$

where the last step implies<sup>2</sup>

<sup>2</sup> At this point it is necessary to mention that the entire theory could have been equally well developed if we had assumed

$$\Psi = \exp \left[ -\frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - Et) \right]$$

to represent a plane wave propagating in the direction of  $\mathbf{p}$ . The operator representations of  $E$  and  $p$  would then have been  $E \rightarrow -i \hbar \frac{\partial}{\partial t}$  and  $\mathbf{p} \rightarrow +i \hbar \nabla$  and the Schrödinger equation for a free particle would have been [cf. Eq. (17)]

$$-i \hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi$$

The later analysis and the various solutions could have been obtained in a similar manner. However the sine and cosine functions of the type  $\sin \left[ \frac{1}{\hbar} (px - Et) \right]$ , which also represent plane waves, are quite unsuitable because then the operator representation of the type given by Eqs (18) and (19) would not have been possible.

$$\left. \begin{aligned} p_x &\rightarrow -i\hbar \frac{\partial}{\partial x} \\ p_y &\rightarrow -i\hbar \frac{\partial}{\partial y} \\ p_z &\rightarrow -i\hbar \frac{\partial}{\partial z} \end{aligned} \right\} \quad (19)$$

Further, Eq. (17) can be written in the form

$$E\Psi = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \Psi = \frac{p^2}{2m} \Psi \quad (20)$$

Till now we have assumed the particle to be free. If we now assume the particle to be in a field characterised by the potential energy function  $V(\mathbf{r}, t)$  then according to classical mechanics, the total energy would be given by

$$E = \frac{p^2}{2m} + V(\mathbf{r}, t) \quad (21)$$

Since the potential energy function does not depend on  $p$  and  $E$ , Eqs (18)–(21) suggest that the wave function should satisfy

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[ \frac{p^2}{2m} + V(\mathbf{r}, t) \right] \Psi = \left[ -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi \right] \quad (22)$$

which is the time dependent Schrödinger equation for a particle in a field characterised by the potential energy function  $V(\mathbf{r}, t)$ . Equation (22) is usually written in the form

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (23)$$

where

$$H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m} \nabla^2 + V \quad (24)$$

is known as the Hamiltonian operator. The corresponding one-dimensional equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi \quad (25)$$

It should be mentioned that the method for obtaining the Schrödinger equation is far from rigorous. We have tried to put together the corpuscular and wave characteristics of the particle and have assumed that the particle can be described by a wave function  $\Psi$  which, in general, is complex, and satisfies Eq. (22). To quote Feynman

*Where did we get that [equation] from? Nowhere. It is not possible to derive it from anything you know. It came out of the mind of Schrödinger.*

By solving Eq. (22) (under appropriate boundary and initial conditions) one can predict the results of various measurements which we will do in this and the following chapters. Indeed the validity of the Schrödinger equation comes from the agreement of the theoretical results (obtained by solving the Schrödinger equation) with experimental data.

### 4.3. The commutator

Because of the operator representation of  $p_x$  [see Eq. (19)] we have

$$[xp_x - p_xx] \Psi = -i \hbar \left[ x \frac{\partial \Psi}{\partial x} - \frac{\partial}{\partial x} (x\Psi) \right]$$

or

$$[xp_x - p_xx] \Psi = i \hbar \Psi$$

Since  $\Psi$  is an arbitrary function, the operator  $[xp_x - p_xx] / i \hbar$  is simply the unit operator. We write

$$[xp_x - p_xx] \equiv [x, p_x] = i \hbar \quad (26)$$

which is known as the commutation relation. The quantity

$$[\alpha, \beta] = \alpha\beta - \beta\alpha = -[\beta, \alpha] \quad (27)$$

is said to be the commutator of the two operators  $\alpha$  and  $\beta$ . It is easy to show that

$$\begin{aligned} [x, y] &= [y, z] = [z, x] = 0 \\ [x, p_y] &= [y, p_z] = [z, p_x] = 0 \\ [p_x, p_y] &= [p_y, p_z] = [p_z, p_x] = 0 \end{aligned}$$

But

$$[y, p_y] = [z, p_z] = i \hbar$$

Commutation relations play a very important role in quantum mechanics and we will use them in later chapters.

#### 4.4. Physical interpretation of $\Psi$ and the probability current density

We rewrite the Schrödinger equation [Eq. (22)]:

$$+i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \quad (28)$$

and its complex conjugate

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \quad (29)$$

where  $V(\mathbf{r}, t)$  is assumed to be real. If we multiply Eq. (28) by  $\Psi^*$  and Eq. (29) by  $\Psi$  and subtract we would obtain

$$i\hbar \left[ \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \right] = -\frac{\hbar^2}{2m} [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] \quad (30)$$

Since

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

we can rewrite Eq. (30) in the form

$$\frac{\partial}{\partial t} (\Psi^* \Psi) + \left[ \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} \right] = 0 \quad (31)$$

where

$$\begin{aligned} J_x &= \frac{i\hbar}{2m} \left[ \Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right] \\ J_y &= \frac{i\hbar}{2m} \left[ \Psi \frac{\partial \Psi^*}{\partial y} - \Psi^* \frac{\partial \Psi}{\partial y} \right] \\ J_z &= \frac{i\hbar}{2m} \left[ \Psi \frac{\partial \Psi^*}{\partial z} - \Psi^* \frac{\partial \Psi}{\partial z} \right] \end{aligned}$$

Equation (31) can be written in the form<sup>3</sup>

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad (32)$$

where

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<sup>3</sup> Equation (32) could have been directly written by using vector algebra as

$$\begin{aligned} \frac{i\hbar}{2m} \left[ \Psi^* \nabla^2 \Psi + \Psi \nabla^2 \Psi^* \right] &= \frac{i\hbar}{2m} \nabla \cdot [\Psi^* \nabla \Psi + \Psi \nabla \Psi^*] \\ &= \nabla \cdot \mathbf{J} \end{aligned}$$

$$\rho = \Psi^* \Psi \quad (33)$$

and

$$\mathbf{J} = \frac{i \hbar}{2m} [\Psi \nabla \Psi^* - \Psi^* \nabla \Psi] \quad (34)$$

Equation (32) is nothing but the equation of continuity in fluid dynamics (see Appendix B) where  $\rho$  represents the number of particles per unit volume and  $\mathbf{J}$  the current density. Thus we may associate  $\Psi^* \Psi$  with *position probability density* in the sense that  $\Psi^* \Psi d\tau$  will be proportional to the probability of finding the particle in volume element  $d\tau$ . Now, since the Schrödinger equation is a linear equation, a multiple of  $\Psi$  would also be a solution and we may choose the multiplicative constant such that

$$\iiint |\Psi|^2 d\tau = 1 \quad (35)$$

where the integration is over the entire space. Equation (35) is known as the normalization condition. If the wave function is normalized [i.e. if it satisfies Eq. (35)] then  $|\Psi|^2 d\tau$  can be interpreted to represent the probability of finding the particle in the volume element  $d\tau$  and Eq. (35) implies the fact that the particle has to be found somewhere in space. Further,

$$\mathbf{J} = \frac{i \hbar}{2m} [\Psi \nabla \Psi^* - \Psi^* \nabla \Psi] = \operatorname{Re} \left[ \Psi^* \frac{\hbar}{im} \nabla \Psi \right] \quad (36)$$

can be associated with *probability current density* (see Appendix B); here  $\operatorname{Re}$  stands for the real part of the quantity inside the bracket. It is of interest to mention that the quantity  $\frac{\hbar}{i} \nabla$  represents the momentum operator  $\mathbf{p}$  [(see Eq. (19)] and therefore we may write

$$\mathbf{J} = \operatorname{Re} [\Psi^* \mathbf{v} \Psi] \quad (37)$$

where  $\mathbf{v} = \mathbf{p}/m$  represents the velocity operator. Equations (33) and (37) are consistent with the fact that in fluid dynamics

$$\mathbf{J} = \rho \mathbf{v} \quad (38)$$

As an example we consider the wave function

$$\Psi = \exp \left[ \frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - Et) \right] \quad (39)$$

which, however, cannot be normalized as the position probability density is constant everywhere.<sup>4</sup> But

$$\mathbf{J} = \operatorname{Re} \left[ \Psi^* \frac{\hbar}{im} \nabla \Psi \right] = \frac{\mathbf{p}}{m} = \mathbf{v} \quad (40)$$

which is consistent with Eq. (38) because  $\rho = 1$ . It may be noted that in Eqs (39) and (40),  $\mathbf{p}$  and  $E$  are numbers.

We conclude this section by noting that

$$\begin{aligned} \frac{\partial}{\partial t} \int_{\Omega} \Psi^* \Psi \, d\tau &= \int_{\Omega} \frac{\partial \rho}{\partial t} \, d\tau = - \int_{\Omega} \nabla \cdot \mathbf{J} \, d\tau \\ &= - \int_S \mathbf{J} \cdot \hat{\mathbf{n}} \, dS \end{aligned} \quad (41)$$

where  $\Omega$  represents an arbitrary volume bounded by the surface  $S$  with  $\hat{\mathbf{n}}$  representing the outward unit normal on the surface, and in the last step we have used Gauss's theorem. Thus if the integration is carried over entire space and if the wave function vanishes at infinity, then

$$\frac{\partial}{\partial t} \iiint |\Psi|^2 \, d\tau = 0 \quad (42)$$

which is essentially a conservation condition.

## 4.5. Expectation values

By associating  $\Psi^* \Psi$  with position probability density we can calculate the expectation or average values of the position of the particle. Thus the expectation value of the  $x$ -coordinate would be given by

$$\langle x \rangle = \frac{\iiint x \Psi^* \Psi \, d\tau}{\iiint \Psi^* \Psi \, d\tau} \quad (43)$$

where the integration is over the entire space. If we assume the wave function to be normalized [see Eq. (35)], then

$$\langle x \rangle = \int \Psi^* x \Psi \, d\tau \quad (44)$$

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<sup>4</sup> A realistic wave function will be a wave packet which will be discussed in the next chapter.

where for the sake of convenience we are replacing the triple integral sign by a single integral. We have also put  $x$  between  $\Psi^*$  and  $\Psi$  for reasons which will become clear later in this section. In a similar manner we can write for  $\langle y \rangle$  and  $\langle z \rangle$ . In general, for any function  $f(\mathbf{r})$ , the expectation value will be given by

$$\langle f(\mathbf{r}) \rangle = \int \Psi^* f(\mathbf{r}) \Psi d\tau \quad (45)$$

In particular

$$\langle V(\mathbf{r}, t) \rangle = \int \Psi^* V(\mathbf{r}, t) \Psi d\tau \quad (46)$$

Now since  $E = p^2/2m + V$ , we should have

$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle \quad (47)$$

Further, if we multiply the Schrödinger equation [Eq. (22)] by  $\Psi^*$  and integrate over all space, we would get

$$\int \Psi^* \left( i \hbar \frac{\partial}{\partial t} \right) \Psi d\tau = \int \Psi^* \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \Psi d\tau + \int \Psi^* V(\mathbf{r}, t) \Psi d\tau \quad (48)$$

The last term in this equation is simply  $\langle V \rangle$  [see Eq. (46)] and therefore Eqs (46), (47) and (48) will be consistent only if we assume

$$\langle E \rangle = \int \Psi^* i \hbar \frac{\partial}{\partial t} \Psi d\tau \quad (49)$$

and

$$\left\langle \frac{p^2}{2m} \right\rangle = \int \Psi^* \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \Psi d\tau \quad (50)$$

Since  $i \hbar \frac{\partial}{\partial t}$  and  $-\frac{\hbar^2}{2m} \nabla^2$  are the operator representations of  $E$  and  $p^2/2m$ , we can say that the general recipe of determining the expectation value of any quantity is to replace it by its operator representation, operate it on  $\Psi$  and premultiply by  $\Psi^*$  and then integrate. Thus

$$\langle p_x \rangle = \iiint \Psi^* \left( -i \hbar \frac{\partial \Psi}{\partial x} \right) d\tau \quad (51)$$

$$\langle p_x^2 \rangle = \iiint \Psi^* \left( -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \right) d\tau \quad (52)$$

$$\langle p_y \rangle = \iiint \Psi^* \left( -i \hbar \frac{\partial \Psi}{\partial y} \right) d\tau \quad (53)$$

etc. Using the above recipe for calculation of the expectation values and also using the Schrödinger equation one can show that (see Problem 4.5)

$$\frac{d}{dt}\langle x \rangle = \frac{1}{m}\langle p_x \rangle \quad (54)$$

$$\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle \quad (55)$$

The above equations show that there is agreement between quantum and classical motions in the sense that in quantum theory the expectation values satisfy Newton's laws of motion. Equations (54) and (55) were first derived by Ehrenfest and the general relationship (between classical and quantum motions) is known as Ehrenfest's theorem.

In the next section we will use various expressions for the expectation values to give an exact statement of the uncertainty principle.

#### 4.6. Exact statement and proof of the uncertainty principle

In the previous chapter we had discussed experiments which showed that it is not possible to measure simultaneously the position of a particle along a particular (say  $x$ ) direction and also the corresponding momentum  $p_x$  with unlimited accuracy. Indeed we showed that  $\Delta x \Delta p_x \geq h$ , where  $\Delta x$  and  $\Delta p_x$  were uncertainties in the measurement of  $x$  and  $p_x$  respectively. In this section we will give precise definitions of  $\Delta x$  and  $\Delta p_x$  and using the results of the previous section, we will make an exact statement of the uncertainty principle. First, in analogy with the definition of standard deviation in statistics, we define the uncertainties in  $x$  and  $p_x$  as:

$$\Delta x = \langle (x - \langle x \rangle)^2 \rangle^{\frac{1}{2}} = [\langle x^2 \rangle - \langle x \rangle^2]^{\frac{1}{2}} \quad (56)$$

$$\Delta p = \langle (p - \langle p \rangle)^2 \rangle^{\frac{1}{2}} = [\langle p^2 \rangle - \langle p \rangle^2]^{\frac{1}{2}} \quad (57)$$

where, for the sake of convenience, we have dropped the subscript on  $p$ . We will establish that

$$\Delta x \Delta p \geq \frac{1}{2}\hbar \quad (58)$$

with the equality sign only for a Gaussian wave function. Equation (58) represents the exact statement of the uncertainty principle. In order to prove Eq. (58) we would use the following inequality

$$\int f^* f \, d\tau \int g^* g \, d\tau \geq \frac{1}{4} \left[ \int (f^* g + f g^*) \, d\tau \right]^2 \quad (59)$$

where  $f$  and  $g$  are arbitrary functions of the space coordinates; however, they must be single valued and all the integrals in Eq. (59) must exist. The proof of Eq. (59) is quite simple. We define three integrals

$$a = \int f^* f \, d\tau , \quad b = \int f^* g \, d\tau , \quad c = \int g^* g \, d\tau$$

Now

$$\int |\lambda f + g|^2 \, d\tau = a\lambda^2 + (b + b^*)\lambda + c \geq 0$$

because  $|\lambda f + g|^2 \geq 0$  everywhere; we have assumed  $\lambda$  to be a real quantity. Obviously for the above inequality to be satisfied we must have

$$4ac \geq (b + b^*)^2$$

which proves Eq. (59); the equality sign in Eq. (59) will occur when  $f$  is a multiple of  $g$ .

We will consider the special case<sup>5</sup> of  $\langle x \rangle = 0$  and  $\langle p \rangle = 0$  and assume

$$f = p\Psi = -i\hbar \frac{\partial \Psi}{\partial x} \quad (60)$$

$$g = ix\Psi \quad (61)$$

Thus

$$\begin{aligned} \int f^* f \, d\tau &= \hbar^2 \iint dy dz \int \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \, dx \\ &= \hbar^2 \iint dy dz \left[ \Psi^* \frac{\partial \Psi}{\partial x} \Big|_{-\infty}^{+\infty} - \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \, dx \right] \\ &= \iiint \Psi^* \left( -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \right) \, dx dy dz = \langle p_x^2 \rangle \end{aligned}$$

where we have used Eq. (52) and the fact that  $\Psi$  vanishes at infinity. Further,

$$\int g^* g \, d\tau = \int \Psi^* x^2 \Psi \, d\tau = \langle x^2 \rangle$$

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<sup>5</sup> For  $\langle x \rangle \neq 0$  and  $\langle p \rangle \neq 0$ , we must choose

$$f = (p - \langle p \rangle) \Psi$$

and

$$g = (x - \langle x \rangle) \Psi$$

and

$$\begin{aligned} \int (f^*g + fg^*) d\tau &= -\hbar \int \frac{\partial \Psi^*}{\partial x} x\Psi d\tau - \hbar \int \frac{\partial \Psi}{\partial x} x\Psi^* d\tau \\ &= -\hbar \int \frac{\partial}{\partial x} (\Psi^* x\Psi) d\tau + \hbar \int \Psi^* \Psi d\tau \\ &= \hbar \end{aligned}$$

because  $\Psi$  is normalized and  $\Psi^* x\Psi$  would vanish at  $x = \pm\infty$ . On substitution in Eq. (59), we immediately get the uncertainty relation given by Eq. (58). The uncertainty product is a minimum for a Gaussian wave function (see Problem 4.8).

#### 4.7. The eigenfunctions of the operator $p_x$

For an arbitrary operator  $\alpha$ , the equation

$$\alpha\psi = \lambda\psi \quad (62)$$

represents an eigenvalue equation; in the above equation,  $\lambda$  is a number which may, in general, be complex. We consider the eigenvalue equation of the momentum operator

$$p_{\text{op}} \psi = -i \hbar \frac{\partial}{\partial x} \psi = p\psi \quad (63)$$

where  $p_{\text{op}}$  ( $= -i \hbar \frac{\partial}{\partial x}$ ) is the operator representation of  $p_x$  (we are dropping the subscript  $x$ ) and  $p$  (a number) represents the eigenvalue. For the time being, we assume  $\psi$  to be a function of  $x$  alone so that Eq. (63) can be written in the form

$$\frac{1}{\psi(x)} \frac{d\psi}{dx} = \frac{i}{\hbar} p$$

The integration is simple and we get

$$\psi(x) = \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i p x / \hbar} \quad (64)$$

which are known as the momentum eigenfunctions. Obviously  $p$  has to be real, otherwise  $\psi_p(x)$  will blow up either as  $x \rightarrow +\infty$  or as  $x \rightarrow -\infty$ ;  $p$  can take any real value between  $-\infty$  and  $+\infty$ . The factor  $1/\sqrt{2\pi\hbar}$  makes the wave function normalized; thus (see Sec. 1.3):

$$\int_{-\infty}^{+\infty} \psi_{p'}^*(x) \psi_p(x) dx = \delta(p - p') \quad (65)$$

The functions  $\psi_p(x)$  also form a complete set of functions because of which we have

$$\int_{-\infty}^{+\infty} \psi_p^*(x) \psi_p(x') dp = \delta(x - x') \quad (66)$$

The above equation is said to represent the fact that  $\psi_p(x)$  (with  $-\infty < p < +\infty$ ) represents a complete set of functions because an arbitrary “well behaved” function  $f(x)$  can always be expanded in terms of  $\psi_p(x)$ :

$$\begin{aligned} f(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) e^{ipx/\hbar} dp \\ &= \int_{-\infty}^{+\infty} a(p) \psi_p(x) dp \end{aligned} \quad (67)$$

where (see Sec. 2.2)

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} f(x) e^{-ipx/\hbar} dx \quad (68)$$

In Sec. 5.2 we will show that the wave function  $\psi_p(x)$  [as given by Eq. (63)] is also an eigenfunction of the operator

$$H = \frac{1}{2m} p_x^2 \quad (69)$$

Thus  $\psi_p(x)$  is said to represent a simultaneous set of eigenfunctions of the operators  $p_x$  and  $p_x^2/2m$ .

It can easily be seen that the wave function

$$\psi_p(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \exp\left[\frac{i}{\hbar}(p_x x + p_y y + p_z z)\right] \quad (70)$$

(where  $p_x$ ,  $p_y$  and  $p_z$  are numbers) represents a complete set of simultaneous eigenfunctions of the operators corresponding to the  $x$ -,  $y$ - and  $z$ -components of the momentum. They are also eigenfunctions of the Hamiltonian operator corresponding to a free particle:

$$H = \frac{1}{2m} p^2 = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

Furthermore,

$$\iiint \psi_{\mathbf{p}'}^*(\mathbf{r}) \psi_{\mathbf{p}}(\mathbf{r}) d\mathbf{r} = \delta(\mathbf{p} - \mathbf{p}') \quad (71)$$

and

$$\iiint \psi_{\mathbf{p}}^*(\mathbf{r}') \psi_{\mathbf{p}}(\mathbf{r}) d\mathbf{p} = \delta(\mathbf{r} - \mathbf{r}') \quad (72)$$

which respectively represent the orthonormality and the completeness conditions.

---

#### 4.8. Problems

**Problem 4.1** Using the operator representations of  $p_x$ ,  $p_y$  and  $p_z$  prove that

$$\left. \begin{aligned} [x, p_y] &= 0 = [y, p_z] \\ [p_x, p_y] &= 0 = [p_z, p_x] \\ [y, p_y] &= i\hbar = [z, p_z] \end{aligned} \right\} \quad (73)$$

**Problem 4.2** Consider a Gaussian wave packet given by (see Example 5.1):

$$\psi(x) = \frac{1}{(\pi\sigma^2)^{\frac{1}{4}}} \exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right] \exp\left(\frac{i}{\hbar} p_0 x\right) \quad (74)$$

Show that it is normalized and that

$$\mathbf{J} = \frac{1}{\sqrt{\pi\sigma^2}} \exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right] \frac{p_0}{m} \hat{\mathbf{x}} \quad (75)$$

Interpret the result physically.

**Problem 4.3** Assume

$$\psi(r) = \frac{1}{r} e^{ikr} \quad (76)$$

where

$$r = \sqrt{x^2 + y^2 + z^2}$$

Calculate  $\mathbf{J}$  and interpret the result physically.

**Problem 4.4** Show by partial integration of Eq. (51) that  $\langle p_x \rangle$  is real.

**Problem 4.5** Using the general recipe that the expectation value of an observable characterised by the operator  $\mathcal{O}$  is given by

$$\langle \mathcal{O} \rangle = \int \Psi^* \mathcal{O} \Psi d\tau \quad (77)$$

prove that

$$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle \quad (78)$$

and

$$\frac{d}{dt} \langle p_x \rangle = - \left\langle \frac{\partial V}{\partial x} \right\rangle \quad (79)$$

These equations are referred to as Ehrenfest's theorem.

**Problem 4.6** Using Eq. (77) prove that

$$\frac{d}{dt} \langle \mathcal{O} \rangle = \frac{i}{\hbar} \int \Psi^* [H, \mathcal{O}] \Psi d\tau + \int \Psi^* \frac{\partial \mathcal{O}}{\partial t} \Psi d\tau \quad (80)$$

where  $[H, \mathcal{O}] = H\mathcal{O} - \mathcal{O}H$  represents the commutator of  $H$  and  $\mathcal{O}$  and  $\frac{\partial \mathcal{O}}{\partial t}$  is due to the explicit time dependence of the operator  $\mathcal{O}$ .

[Hint: Differentiate Eq. (77) inside the integral sign and use Eq. (24). You may use the Hermitian nature of  $H$  (see Problem 6.1) or else substitute for  $H$  and integrate by parts as in the solution of Problem 4.5.]

**Problem 4.7** For the ground state and the first excited state of the harmonic oscillator the wave functions are:

$$\exp \left[ -\frac{m\omega}{2\hbar} x^2 \right] \quad \text{and} \quad x \exp \left[ -\frac{m\omega}{2\hbar} x^2 \right]$$

respectively (see Sec. 7.3). Show that the values of the uncertainty product  $\Delta x \Delta p$  are  $\frac{1}{2}\hbar$  and  $\frac{3}{2}\hbar$  (see also Sec. 12.3).

**Problem 4.8** Show that the uncertainty product  $\Delta x \Delta p$  is minimum ( $= \frac{1}{2}\hbar$ ) for a Gaussian wave function.

---

## 4.9. Solutions

**Solution 4.3** Using Eq. (34), we get

$$\mathbf{J} = \frac{\hbar k}{m} \frac{1}{r^2} \hat{\mathbf{r}} = \frac{v}{r^2} \hat{\mathbf{r}} \quad (81)$$

which corresponds to a spherical wave whose intensity decreases according to the inverse square law.

**Solution 4.4**

$$\begin{aligned}
\langle p_x \rangle &= -i \hbar \int \Psi^* \frac{\partial \Psi}{\partial x} d\tau \\
&= -i \hbar \iint dy dz \left[ \Psi^* \Psi \Big|_{x=-\infty}^{x=+\infty} - \int_{-\infty}^{+\infty} \Psi \frac{\partial \Psi^*}{\partial x} dx \right] \\
&= i \hbar \int \Psi \frac{\partial \Psi^*}{\partial x} d\tau \\
&= \langle p_x \rangle^*
\end{aligned} \tag{82}$$

**Solution 4.5** Differentiating Eq. (44) we get

$$\begin{aligned}
\frac{d}{dt} \langle x \rangle &= \int \left[ \Psi^* x \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} x \Psi \right] d\tau \\
&= \frac{i \hbar}{2m} \int [\Psi^* x \nabla^2 \Psi - (\nabla^2 \Psi^*) x \Psi] d\tau
\end{aligned} \tag{83}$$

where use has been made of Eqs (28) and (29). Now

$$\int (\nabla^2 \Psi^*) x \Psi d\tau = \int \nabla \cdot (x \Psi \nabla \Psi^*) d\tau - \int (\nabla \Psi^*) \cdot \nabla (x \Psi) d\tau$$

The first integral on the right can be transformed to a surface integral by use of Gauss theorem and this integral would vanish because a wave packet vanishes at infinity. Thus

$$\begin{aligned}
\int (\nabla^2 \Psi^*) x \Psi d\tau &= - \int (\nabla \Psi^*) \cdot \nabla (x \Psi) d\tau \\
&= - \int \nabla (\Psi^* \nabla x \Psi) d\tau + \int \Psi^* \nabla^2 (x \Psi) d\tau
\end{aligned}$$

The first integral on the right again vanishes. On substitution in Eq. (83) we get

$$\begin{aligned}
\frac{d}{dt} \langle x \rangle &= \frac{i \hbar}{2m} \int \Psi^* [x \nabla^2 \Psi - \nabla^2 (x \Psi)] d\tau \\
&= \frac{1}{m} \int \Psi^* \left( -i \hbar \frac{\partial \Psi}{\partial x} \right) d\tau = \frac{1}{m} \langle p_x \rangle
\end{aligned} \tag{84}$$

Using a method similar to that used above one gets

$$\begin{aligned}
\frac{d}{dt} \langle p_x \rangle &= -i \hbar \int \left[ \frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial}{\partial x} \frac{\partial \Psi}{\partial t} \right] d\tau \\
&= \int \Psi^* \left[ V \frac{\partial \Psi}{\partial x} - \frac{\partial}{\partial x} (V \Psi) \right] d\tau = \left\langle -\frac{\partial V}{\partial x} \right\rangle
\end{aligned} \tag{85}$$

**Solution 4.8** The uncertainty product is minimum when  $f$  is a multiple of  $g$  (see Sec. 4.6); thus

$$-i \hbar \frac{\partial \Psi}{\partial x} = C i x \Psi$$

or

$$\frac{1}{\Psi} \frac{\partial \Psi}{\partial x} = (\text{const}) x$$

The integration of the above equation gives a Gaussian function.

---

#### 4.10. Sample questions

Q. 1 a) What are the normalized eigenfunctions of the operator

$$p_x = -i \hbar \frac{d}{dx}$$

b) Derive the orthonormality and completeness condition for these eigenfunctions.

Q. 2 Consider the Hamiltonian corresponding to a free particle in one-dimension

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

What are the corresponding eigenvalues and normalized eigenfunctions? Is there any degeneracy?

# Chapter 5

## Propagation of Wave Packets and Concept of Group Velocity

*Quantum mechanics allows us in principle to predict nearly everything around us, within the limits set by the uncertainty principle ...*

— STEPHEN HAWKING in *A Brief History of Time*,  
Bantam Books, New York (1988).

### 5.1. Introduction

We will devote this chapter to the solution of the time dependent Schrödinger equation for a free particle. In quantum mechanics, a free particle is described by a wave packet (which is nothing but a superposition of plane waves) and the solution of the time dependent Schrödinger equation will allow us to study the time evolution of the packet and how it would disperse in free space. We will also show how the uncertainty principle is contained in the solution of the Schrödinger equation.

### 5.2. The general solution of the one-dimensional Schrödinger equation for a free particle

We start with the one-dimensional time dependent Schrödinger equation [see Eq. (25) of the previous chapter]

$$i \hbar \frac{\partial \Psi}{\partial t} = H \Psi \quad (1)$$

with the Hamiltonian  $H$  given by

$$H = \frac{p^2}{2m} + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (2)$$

For a free particle

$$V(x) = 0 \quad (3)$$

and Eq. (1) becomes

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} \quad (4)$$

which represents the one-dimensional time dependent Schrödinger equation for a free particle. In order to solve the above equation we use the method of separation of variables:

$$\Psi(x, t) = \psi(x) T(t) \quad (5)$$

Substituting in Eq. (4) and subsequent division by  $\psi(x) T(t)$  gives us

$$i\hbar \frac{1}{T(t)} \frac{dT}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} = E \quad (6)$$

Since the LHS is a function of  $t$  alone and the RHS is a function of  $x$  alone, we have set them equal to a constant ( $= E$ ) which represents the total energy of the particle. From Eq. (6) we readily have

$$\frac{dT}{dt} = -\frac{iE}{\hbar} T(t) \quad (7)$$

the solution of which is given by

$$T(t) = (\text{constant}) e^{-iEt/\hbar} \quad (8)$$

Obviously  $E$  has to be real; if  $E$  is complex, the solution will blow up as  $t \rightarrow +\infty$  or as  $t \rightarrow -\infty$ . From Eq. (6) we also have

$$\frac{d^2\psi}{dx^2} + \frac{p^2}{\hbar^2} \psi(x) = 0 \quad (9)$$

where

$$p = \sqrt{2mE} \quad (10)$$

represents the momentum of the particle. The solution of Eq. (9) will be of the form

$$e^{ipx/\hbar}$$

Obviously  $E$  cannot be negative because then  $p$  would be imaginary and the solutions will blow up as  $x \rightarrow +\infty$  or  $-\infty$ . Thus we must have

- (i)  $E$  real and positive, and
- (ii)  $p$  can take any real value between  $-\infty$  and  $+\infty$ .

We write the solution of Eq. (9) as<sup>1</sup>

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}; \quad -\infty < p < +\infty \quad (11)$$

---

<sup>1</sup> The functions  $\psi_p(x)$  are simultaneous eigenfunctions of the momentum operator  $p$  and the Hamiltonian  $H$  (see Sec. 4.7).

where the factor  $1/\sqrt{2\pi\hbar}$  makes it normalized:

$$\int_{-\infty}^{+\infty} \psi_p^*(x) \psi_{p'}(x) dx = \delta(p - p') \quad (12)$$

The functions  $\psi_p(x)$  also satisfy the completeness condition [see Eq. (66) of the previous chapter].

The complete solution is therefore given by [see Eq. (5)]:

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2\pi\hbar}} \exp\left[\frac{i}{\hbar}(px - Et)\right] \\ &= \frac{1}{\sqrt{2\pi\hbar}} \exp\left[\frac{i}{\hbar}\left(px - \frac{p^2}{2m}t\right)\right] \end{aligned} \quad (13)$$

For positive values of  $p$ , the above equation represents a plane wave propagating along the  $+x$  direction; similarly, for negative values of  $p$ , it represents a plane wave propagating along the  $-x$  direction. Since  $p$  can take any value from  $-\infty$  to  $+\infty$ , the most general solution of Eq. (4) (i.e. of the time dependent Schrödinger equation for a free particle) is given by

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) \exp\left[\frac{i}{\hbar}\left(px - \frac{p^2}{2m}t\right)\right] dp \quad (14)$$

which is essentially a superposition of plane waves. Equation (14) describes the time evolution of a one-dimensional wave packet. In Example 5.1 we will discuss the time evolution of a Gaussian wave packet; however, we will first discuss some general properties of the solution given by Eq. (14):

If  $\Psi(x, 0)$  is normalized, i.e. if

$$\int_{-\infty}^{+\infty} |\Psi(x, 0)|^2 dx = 1 \quad (15)$$

then one can readily show that (see Problem 5.1)

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad (16)$$

Physically, this is obvious because  $|\Psi(x, 0)|^2 dx$  represents the probability of finding the particle between  $x$  and  $x + dx$  at time  $t$ .

The time evolution of the centre of the wave packet (i.e. the trajectory of the particle) is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx \quad (17)$$

The spatial spread of the wave packet is given by

$$\Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{\frac{1}{2}} \quad (18)$$

where

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 |\Psi(x, t)|^2 dx \quad (19)$$

Furthermore (see Problems 5.1 and 5.2),

$$\int_{-\infty}^{+\infty} |a(p)|^2 dp = 1 \quad (20)$$

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) \left[ -i \hbar \frac{\partial \Psi(x, t)}{\partial x} \right] dx = \int_{-\infty}^{+\infty} p |a(p)|^2 dp \quad (21)$$

$$\langle p^2 \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) \left[ -\hbar^2 \frac{\partial^2 \Psi(x, t)}{\partial x^2} \right] dx = \int_{-\infty}^{+\infty} p^2 |a(p)|^2 dp \quad (22)$$

Equations (20)–(22) clearly show that the quantity  $|a(p)|^2 dp$  can be interpreted as the probability of the momentum lying between  $p$  and  $p + dp$ .

### 5.3. The time evolution of a wave packet

Let us suppose that at  $t = 0$ , a particle is described by the wave function  $\Psi(x, 0)$ . Knowing  $\Psi(x, 0)$  we wish to determine the time evolution of the wave function  $\Psi(x, t)$  from which we would obtain the trajectory of the particle.

From Eq. (14) we have

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) \exp \left[ \frac{i}{\hbar} px \right] dp \quad (23)$$

Thus using the inverse Fourier transform relation [see Sec. 2.2]:

$$a(p) = \frac{1}{\sqrt{2\pi}\hbar} \int_{-\infty}^{+\infty} \Psi(x, 0) \exp\left[-\frac{i}{\hbar} px\right] dx \quad (24)$$

Therefore, the *recipe* is as follows:

Using the known expression for  $\Psi(x, 0)$ , we first determine  $a(p)$  by carrying out the integration in Eq. (24); we then substitute  $a(p)$  in Eq. (14) and carry out the integration over  $p$  to obtain  $\Psi(x, t)$  and hence the time evolution of the wave packet.

**Example 5.1 The Gaussian wave packet** We assume that at  $t = 0$ , a free particle is described by the Gaussian wave function:

$$\Psi(x, 0) = \frac{1}{(\pi\sigma_0^2)^{\frac{1}{4}}} e^{-x^2/2\sigma_0^2} \exp\left(\frac{i}{\hbar} p_0 x\right) \quad (25)$$

The wave function is normalized, i.e.

$$\int_{-\infty}^{+\infty} |\Psi(x, 0)|^2 dx = 1 \quad (26)$$

Thus

$$P(x) dx = |\Psi(x, 0)|^2 dx = \frac{1}{\sqrt{\pi}\sigma_0} e^{-x^2/\sigma_0^2} dx \quad (27)$$

would represent the probability of finding the particle between  $x$  and  $x + dx$  (at  $t = 0$ ). The following average values are readily obtained (see Problem 5.4):

$$\langle x \rangle = 0 \quad (28)$$

$$\Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{\frac{1}{2}} = \frac{\sigma_0}{\sqrt{2}} \quad (29)$$

$$\langle p \rangle = p_0 \quad (30)$$

$$\Delta p = [\langle p^2 \rangle - \langle p \rangle^2]^{\frac{1}{2}} = \frac{\hbar}{\sqrt{2}\sigma_0} \quad (31)$$

Thus (at  $t = 0$ ) the wave function given by Eq. (25) describes a particle which is localized within a distance  $\sim \sigma_0$  around  $x = 0$  and moving with an average momentum of  $p_0$  (in the  $+x$  direction) with a momentum spread approximately equal to  $\hbar/\sigma_0$ . Thus the uncertainty principle is contained in Eq. (25)!

In order to study the time evolution of the wave packet, we use Eq. (24) to calculate  $a(p)$ :

$$\begin{aligned} a(p) &= \frac{1}{\sqrt{2\pi\hbar}} \frac{1}{(\pi\sigma_0^2)^{\frac{1}{4}}} \int_{-\infty}^{+\infty} e^{-x^2/2\sigma_0^2} \exp\left[-\frac{i}{\hbar}(p-p_0)x\right] dx \\ &= \left(\frac{\sigma_0^2}{\pi\hbar^2}\right)^{\frac{1}{4}} \exp\left[-\frac{(p-p_0)^2\sigma_0^2}{2\hbar^2}\right] \end{aligned} \quad (32)$$

where we have used the relation (see Appendix A)

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2 + \beta x} dx = \sqrt{\frac{\pi}{\alpha}} \exp\left(\frac{\beta^2}{4\alpha}\right) \quad (33)$$

The momentum probability distribution is given by

$$|a(p)|^2 = \frac{\sigma_0}{\sqrt{\pi\hbar}} \exp\left[-\frac{\sigma_0^2}{\hbar^2}(p-p_0)^2\right] \quad (34)$$

The above equation shows that the average momentum is  $p_0$  with a spread  $\sim \hbar/\sigma_0$ . In Fig. 5.1 we have plotted  $|\Psi(x, 0)|^2$  and  $|a(p)|^2$  for

$$\sigma_0 = 5 \text{ nm} \quad \text{and} \quad 1 \text{ nm}$$

It may be seen that as we decrease the value of  $\sigma$  (i.e. as the wave function becomes more localized), the value of the momentum spread  $\Delta p$  decreases.

We next substitute for  $a(p)$  from Eq. (32) in Eq. (14) and carry out the straightforward integration to obtain

$$\begin{aligned} \Psi(X, \tau) &= \frac{1}{\pi^{\frac{1}{4}} [\sigma_0(1+i\tau)]^{\frac{1}{2}}} \exp\left[-\frac{(X-\alpha\tau)^2}{2(1+\tau^2)}\right. \\ &\quad \left. + \frac{i}{2(1+\tau^2)} [2\alpha X + \tau(X^2 - \alpha^2)]\right] \end{aligned} \quad (35)$$

where we have introduced the following dimensionless variables:

$$\left. \begin{aligned} X &= \frac{x}{\sigma_0} \\ \tau &= \frac{\hbar}{m\sigma_0^2} t \\ \alpha &= \frac{p_0\sigma_0}{\hbar} \end{aligned} \right\} \quad (36)$$

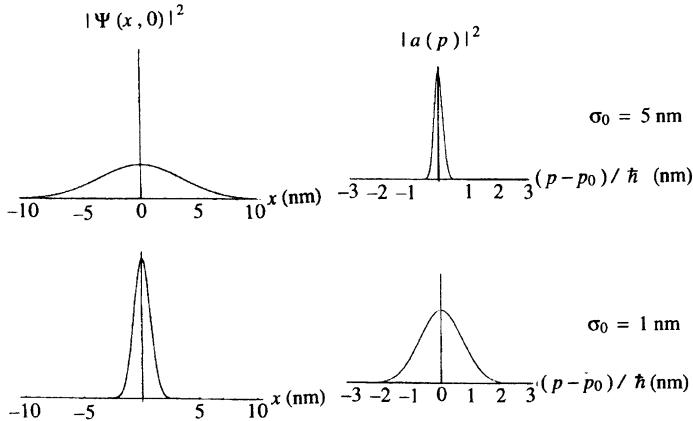


Figure 5.1. Plots of  $|\Psi(x, 0)|^2$  and  $|a(p)|^2$  for  $\sigma_0 = 5 \text{ nm}$  and  $1 \text{ nm}$ .

The corresponding probability distribution is given by

$$|\Psi(X, \tau)|^2 = \frac{1}{\sqrt{\pi}\sigma(\tau)} \exp \left[ -\frac{(X - \alpha\tau)^2}{(1 + \tau^2)} \right] \quad (37)$$

or,

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{\pi}\sigma(t)} \exp \left[ -\frac{(x - \frac{p_0}{m}t)^2}{\sigma^2(t)} \right] \quad (38)$$

where

$$\sigma(t) = \sigma_0 \left[ 1 + \frac{\hbar^2}{m^2\sigma_0^4} t^2 \right]^{\frac{1}{2}} \quad (39)$$

which represents the spatial broadening of the wave packet with time. In Fig. 5.2 we have plotted the  $x$  dependence of the real part of the wave function [given by Eq. (35)] at

$$\tau = 0, 0.5 \text{ and } 1.0$$

with  $\alpha = 15$ . In Fig. 5.3 we have plotted the  $x$  dependence of the probability distribution function at

$$\tau = 0, 0.5, 1.0 \text{ and } 1.5$$

Figures 5.2 and 5.3 show that the centre of the wave packet moves with the velocity  $p_0/m$  which is the group velocity of the wave packet (see Sec. 5.5). One can readily verify that

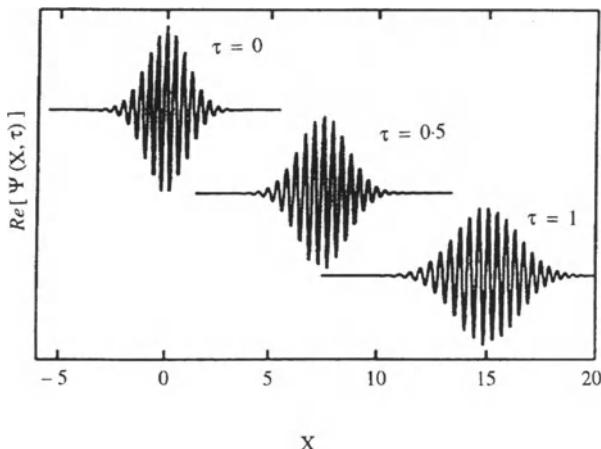


Figure 5.2. The variation of  $\text{Re}[\Psi(X, \tau)]$  with  $X$  for  $\tau = 0, 0.5$  and  $1.0$ ;  $\alpha = 15$ .

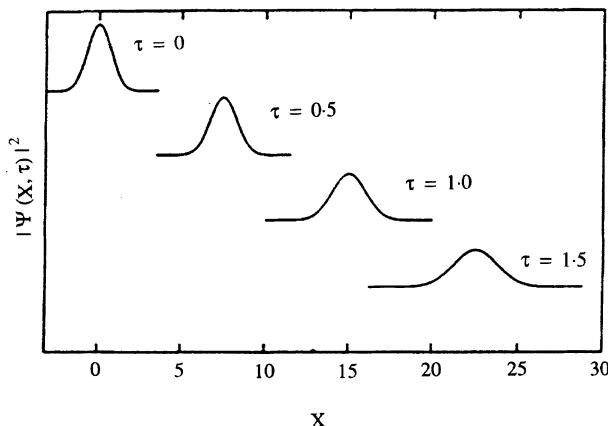


Figure 5.3. The variation of the probability distribution  $|\Psi(X, \tau)|^2$  with  $X$  for  $\tau = 0, 0.5, 1.0$  and  $1.5$ ;  $\alpha = 15$ . Notice the spreading of the wave packet.

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad (40)$$

for all values of time as it indeed should be. It may also be noted that using Eq. (35) we readily get

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x, t) x \Psi(x, t) dx \\ &= \frac{p_0}{m} t \end{aligned} \quad (41)$$

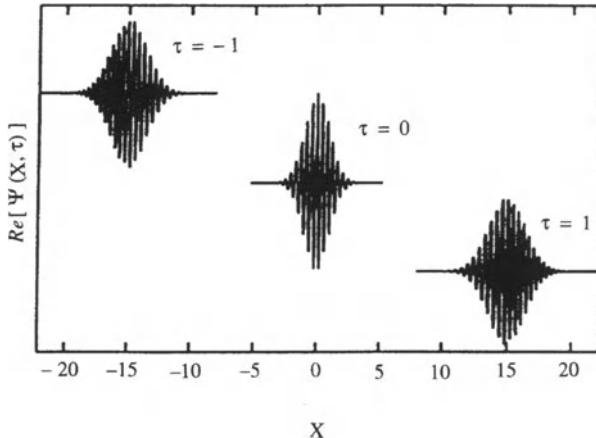


Figure 5.4. The spatial variation of  $\text{Re}[\Psi(X, \tau)]$  for  $\tau = -1, 0$  and  $+1$ ;  $\alpha = 15$ . Notice that if the wave packet initially corresponds to the top curve, it will first undergo spatial compression.

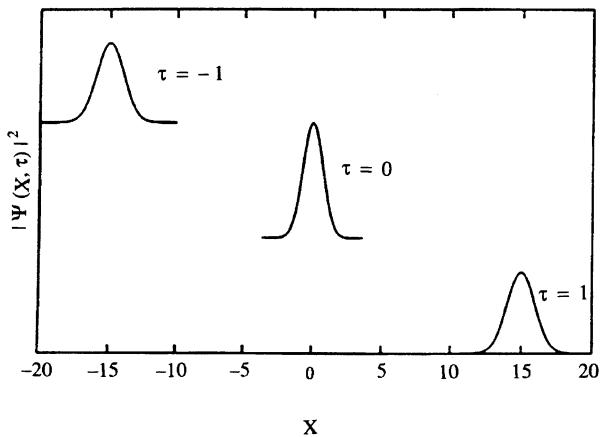


Figure 5.5. The spatial variation of  $|\Psi(X, \tau)|^2$  for  $\tau = -1, 0$  and  $+1$ ;  $\alpha = 15$ . Notice the spatial compression of the wave packet.

and

$$\begin{aligned}\langle x^2 \rangle &= \int_{-\infty}^{+\infty} x^2 |\Psi(x, t)|^2 dx \\ &= \frac{1}{2} \sigma^2(t) + \left( \frac{p_0}{m} \right)^2 t^2\end{aligned}\quad (42)$$

giving

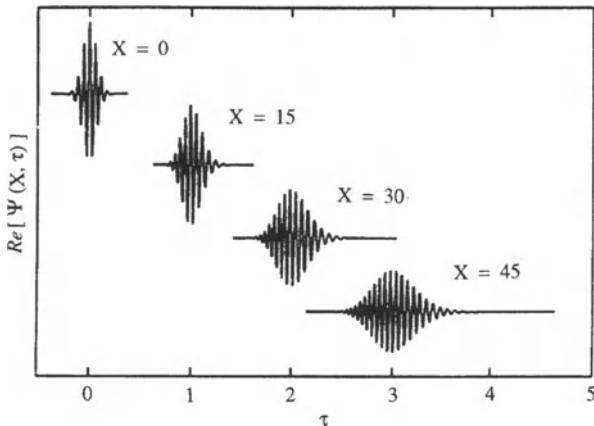


Figure 5.6. The temporal variation of  $\text{Re}[\Psi(X, \tau)]$  for  $X = 0, 15, 30$  and  $45$ ;  $\alpha = 15$ . Notice the temporal dispersion of the wave packet.

*Spatial spread of the wave packet*

$$\begin{aligned}\Delta x &= [\langle x^2 \rangle - \langle x \rangle^2]^{\frac{1}{2}} \\ &= \frac{\sigma_0}{\sqrt{2}} \left[ 1 + \frac{\hbar^2 t^2}{m^2 \sigma_0^4} \right]^{\frac{1}{2}}\end{aligned}\quad (43)$$

The momentum distribution [as given by Eq. (32)] remains the same at all times and therefore

$$\Delta p = \frac{\hbar}{\sqrt{2}\sigma_0} \quad \text{for all values of } t \quad (44)$$

Thus

$$\Delta p \Delta x = \frac{1}{2} \hbar \left[ 1 + \frac{\hbar^2 t^2}{m^2 \sigma_0^4} \right]^{\frac{1}{2}} \quad (45)$$

showing that the uncertainty product is minimum at  $t = 0$ .

In Figs 5.4 and 5.5 we have plotted  $\text{Re}[\Psi(X, \tau)]$  and  $|\Psi(X, \tau)|^2$  for negative values of time. Thus, if at  $t = 0$ , the wave function corresponds to the top curve of Fig. 5.4, then it will first undergo compression.

In Fig. 5.6 we have shown the temporal variation of the wave function at different values of  $X$ . The temporal dispersion may be noted.

## 5.4. The free particle propagator

In the previous section we have shown that if  $\Psi(x, 0)$  is known then  $\Psi(x, t)$  can be calculated by first calculating  $a(p)$  [using Eq. (24)] and then calculating  $\Psi(x, t)$  [using Eq. (14)]. Indeed, one can directly determine  $\Psi(x, t)$  by using the relation

$$\Psi(x, t) = \left( \frac{m}{2\pi i \hbar t} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \Psi(x', 0) \exp \left[ \frac{im(x - x')^2}{2\hbar t} \right] dx' \quad (46)$$

without making any explicit calculation of  $a(p)$ . Thus all one has to do is to substitute the form of the wave function at  $t = 0$  and carry out the above integration to obtain  $\Psi(x, t)$ . The proof of Eq. (46) is very simple: We substitute for  $a(p)$  from Eq. (24) in Eq. (14) to obtain

$$\begin{aligned} \Psi(x, t) &= \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} dx' \int_{-\infty}^{+\infty} dp \Psi(x', 0) \exp \left[ -\frac{i}{\hbar} px' \right] \\ &\quad \times \exp \left[ \frac{i}{\hbar} \left( px - \frac{p^2}{2m} t \right) \right] \end{aligned}$$

or

$$\Psi(x, t) = \int_{-\infty}^{+\infty} dx' \Psi(x', 0) K(x, x', t) \quad (47)$$

where

$$\begin{aligned} K(x, x', t) &= \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} \exp \left[ \frac{i}{\hbar} p(x - x') \right] \exp \left[ -\frac{i}{\hbar} \frac{p^2}{2m} t \right] dp \\ &= \left( \frac{m}{2\pi i \hbar t} \right)^{\frac{1}{2}} \exp \left[ \frac{im(x - x')^2}{2\hbar t} \right] \end{aligned} \quad (48)$$

where we have used Eq. (33). The quantity  $K(x, x', t)$  is known as the free particle propagator. As a simple example, if we assume  $\Psi(x, 0)$  to be given by Eq. (25), then carrying out the integration in Eq. (46) we would readily obtain Eq. (35). Often it is more convenient to use Eq. (46) to obtain  $\Psi(x, t)$ . The two- and three-dimensional generalization of Eq. (46) is discussed in Sec. 5.6.

## 5.5. Group velocity of a wave packet

In wave theory a (one-dimensional) wave packet is formed by the superposition of plane waves:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} A(k) e^{i(kx - \omega t)} dk \quad (49)$$

where the frequency  $\omega$  is a known function of  $k$ :

$$\omega = \omega(k) \quad (50)$$

Equation (50) is known as the dispersion relation. For example, for a free (non-relativistic) particle

$$E = \frac{p^2}{2m} \quad (51)$$

implying

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}$$

or,

$$\omega(k) = \frac{\hbar}{2m} k^2 \quad (52)$$

Now, for a purely monochromatic wave

$$A(k) = A_0 \delta(k - k_0) \quad (53)$$

If we substitute the above expression for  $A(k)$  in Eq. (49) we would get

$$\Psi(x, t) = \frac{A_0}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \quad (54)$$

where

$$\omega_0 = \omega(k_0) \quad (55)$$

Equation (54) is never achieved in practice. Usually  $A(k)$  is a very sharply peaked function around  $k = k_0$ ; see, e.g. Fig. 5.1. In all of what follows we will assume that there exists only a small range  $\Delta k$  (around  $k = k_0$ ) where the amplitudes of the component waves  $A(k)$  have significant values; beyond  $k = k_0 \pm \Delta k$ ,  $A(k)$  is assumed to be negligible. Under such an assumption, it is possible to assign an average velocity of the wave packet provided  $\omega(k)$  is a smoothly varying function in the domain  $k_0 - \Delta k \leq k \leq k_0 + \Delta k$ . This average velocity is known as the group velocity. We write

$$A(k) = |A(k)| e^{i\phi(k)} \quad (56)$$

and assume that  $|A(k)|$  is very sharply peaked when  $k$  lies in a small interval  $\Delta k$  around  $k = k_0$  and negligible everywhere else so that we may write

$$\Psi(x, t) \approx \frac{1}{\sqrt{2\pi}} \int_{\Delta k} dk |A(k)| e^{i[kx - \omega(k)t + \phi(k)]} \quad (57)$$

where the integration extends over the domain  $\Delta k$  where  $|A(k)|$  has appreciable values. Next, we make Taylor expansions of  $\omega(k)$  and  $\phi(k)$  around  $k = k_0$ :

$$\omega(k) = \omega(k_0) + \left. \frac{d\omega}{dk} \right|_{k=k_0} (k - k_0) + \frac{1}{2} \left. \frac{d^2\omega}{dk^2} \right|_{k=k_0} (k - k_0)^2 + \dots \quad (58)$$

$$\phi(k) = \phi(k_0) + \left. \frac{d\phi}{dk} \right|_{k=k_0} (k - k_0) + \frac{1}{2} \left. \frac{d^2\phi}{dk^2} \right|_{k=k_0} (k - k_0)^2 + \dots \quad (59)$$

We substitute the above expansion in Eq. (57) and assume that in the domain of integration  $\Delta k$ ,  $\omega(k)$  and  $\phi(k)$  do not vary significantly so that the terms involving quadratic and higher powers of  $(k - k_0)$  can be neglected; under such an approximation one obtains

$$\Psi(x, t) \approx f(x, t) e^{i(k_0 x - \omega_0 t + \phi_0)} \quad (60)$$

where  $\omega_0 \equiv \omega(k_0)$ ,  $\phi_0 \equiv \phi(k_0)$  and  $f(x, t)$ , which represents the envelope of the wave packet, is given by

$$f(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\Delta k} dk |A(k)| e^{i(k - k_0)(x - x_0 - v_g t)} \quad (61)$$

where

$$x_0 = - \left. \frac{d\phi}{dk} \right|_{k=k_0}$$

and

$$v_g = \left. \frac{d\omega}{dk} \right|_{k=k_0} \quad (62)$$

Since the function  $f(x, t)$  depends on  $x$  and  $t$  only through the combination  $x - v_g t$ , the wave packet propagates without any distortion with velocity  $v_g$  which is known as the *group velocity* of the packet. It should be pointed out that the packet remains undistorted as long as the neglect of second and higher order terms in Eqs (58) and (59) is justified (see Problem 5.9 and Example 5.1). However, if the  $\omega$ - $k$  relation is strictly linear, the packet will never undergo any distortion<sup>2</sup>.

---

<sup>2</sup> A medium is said to be non-dispersive when the  $\omega$ - $k$  relation is linear. For example, for electromagnetic waves in free space

$$\omega(k) = ck$$

Now, from Eq. (61) we have

$$f(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{\Delta k} |A(k)| e^{i(k-k_0)(x-x_0)} dk \quad (63)$$

It is immediately seen that at  $x = x_0$ , the integrand is everywhere positive and the value of the integral is maximum. For  $|x - x_0| > \sim 1/\Delta k$  the exponential function oscillates rapidly in the domain of integration and the value of the integral is very small. This immediately leads to the relation

$$\Delta k \Delta x \geq 1 \quad (64)$$

which when multiplied by  $\hbar$  gives the uncertainty relation:

$$\Delta p \Delta x \geq \hbar \quad (65)$$

Thus, at  $t = 0$  the wave packet is sharply peaked at  $x = x_0$  and as  $t$  increases, the centre of the packet,  $x_c(t)$ , moves according to the equation

$$x_c(t) = x_0 + v_g t \quad (66)$$

This was explicitly seen in Example 5.1 where we discussed the spreading of a Gaussian wave packet. Now, since (see Sec. 4.1)

$$E = \hbar\omega \quad (67)$$

and

$$p = \hbar k \quad (68)$$

we get

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp} \quad (69)$$

Thus for a non-relativistic particle for which  $E = p^2/2m$ , we have

$$v_g = \frac{dE}{dp} = \frac{p}{m} = v \quad (70)$$

---

where  $c$  represents the speed of light in free space. For such a case, Eq. (49) becomes

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk A(k) e^{ik(x-ct)} \\ &= f(x - ct) \end{aligned}$$

implying that the packet travels undistorted with speed  $c$ . Thus the free space is a non-dispersive medium for electromagnetic waves. On the other hand, whenever the  $\omega$ - $k$  relationship is not linear [see, e.g. Eq. (52)] the medium is said to be dispersive and a wave packet undergoes distortion (see Example 5.1).

Further, for a relativistic particle

$$E^2 = p^2 c^2 + m^2 c^4 \quad (71)$$

(where  $m$  represents the rest mass) we have

$$\frac{dE}{dp} = \frac{pc^2}{E} \quad (72)$$

But

$$E = \frac{mc^2}{\sqrt{1 - v^2/c^2}} \quad \text{and} \quad p = \frac{mv}{\sqrt{1 - v^2/c^2}}$$

giving

$$\frac{pc^2}{E} = v$$

Thus

$$v_g = v \quad (73)$$

Equations (70) and (73) tell us that the group velocity of the packet is to be associated with the velocity of the particle.

The phase velocity  $v_p$  is defined through the relation

$$v_p = \frac{\omega}{k} \quad (74)$$

and represents the velocity of propagation of an infinitely long monochromatic plane wave. Only when  $\omega$  is proportional to  $k$  are  $v_p$  and  $v_g$  equal. In general, it is the group velocity of a packet which is of physical significance.

## 5.6. Free particle propagator for the two- and three-dimensional Schrödinger equation

The two- and three-dimensional generalization of Eq. (46) is obvious:

The general solution of the two-dimensional Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \Psi(x, y, t) \quad (75)$$

is given by

$$\Psi(x, y, t) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Psi(x', y', 0) K_2(x, y, x', y'; t) dx' dy' \quad (76)$$

where

$$K_2(x, y, x', y'; t) = \left( \frac{m}{2\pi i \hbar t} \right) \exp \left[ \frac{im}{2\hbar t} \left[ (x - x')^2 + (y - y')^2 \right] \right] \quad (77)$$

Similarly, the general solution of the three-dimensional Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(x, y, z, t) \quad (78)$$

is given by

$$\Psi(x, y, z, t) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Psi(x', y', z', 0) K_3(x, y, z, x', y', z'; t) dx' dy' dz' \quad (79)$$

where

$$K_3(x, y, z, x', y', z'; t) = \left( \frac{m}{2\pi i \hbar t} \right)^{\frac{3}{2}} \exp \left[ \frac{im}{2\hbar t} \left[ (x - x')^2 + (y - y')^2 + (z - z')^2 \right] \right] \quad (80)$$


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## 5.7. Problems

**Problem 5.1** Using Eq. (14) show that if

$$\int_{-\infty}^{+\infty} |\Psi(x, 0)|^2 dx = 1 \quad (81)$$

then

$$\int_{-\infty}^{+\infty} |a(p)|^2 dp = 1 \quad (82)$$

and

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad (83)$$

Give physical interpretations of the above equations.

**Problem 5.2** For an arbitrary (normalized) wave function  $\Psi(x)$ , we define

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x) \exp \left[ -\frac{i}{\hbar} px \right] dx \quad (84)$$

Show that

$$\langle p \rangle = \int_{-\infty}^{+\infty} a^*(p) p a(p) dp \quad (85)$$

and

$$\langle p^2 \rangle = \int_{-\infty}^{+\infty} a^*(p) p^2 a(p) dp \quad (86)$$

**Problem 5.3** Using Eq. (84) show that

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x) x \Psi(x) dx \\ &= i \hbar \int_{-\infty}^{+\infty} a^*(p) \frac{\partial a(p)}{\partial p} dp \end{aligned} \quad (87)$$

Comparison of Eqs. (85) and (87) with Eqs. (44) and (51) of the previous chapter shows that  $a(p)$  plays the same role in momentum space as  $x$  does in ordinary space. Further, Eq. (87) tells us that the operator representation of  $x$  in momentum space is  $i \hbar \frac{\partial}{\partial p}$ .

**Problem 5.4 (a)** For the Gaussian wave packet given by Eq. (25) evaluate  $\langle x \rangle$ ,  $\langle x^2 \rangle$ ,  $\langle p \rangle$ ,  $\langle p^2 \rangle$  and show that

$$\Delta x \Delta p = \frac{1}{2} \hbar \quad (88)$$

**(b)** Repeat the calculation for  $\Psi(x, t)$  given by Eq. (35) and derive Eqs (43)–(45).

**Problem 5.5** Assume  $\Psi(x, 0)$  to be given by Eq. (25). Use Eq. (46) to derive Eq. (35).

**Problem 5.6** Consider a two-dimensional wave packet given by

$$\Psi(x, y, 0) = \left[ \left( \frac{1}{\pi \sigma_{x0}^2} \right)^{\frac{1}{4}} \exp \left[ -\frac{x^2}{2\sigma_{x0}^2} \right] e^{i \hbar p_0 x} \right] \left[ \left( \frac{1}{\pi \sigma_{y0}^2} \right)^{\frac{1}{4}} \exp \left[ -\frac{y^2}{2\sigma_{y0}^2} \right] \right] \quad (89)$$

**(a)** Determine  $a(p_x, p_y)$  and then evaluate the probability distribution  $|\Psi(x, y, t)|^2$ . Interpret the results physically.

**(b)** Substitute Eq. (89) directly in Eq. (76) and obtain  $|\Psi(x, y, t)|^2$  and show that one obtains the same result.

**Problem 5.7 Single Slit Diffraction Pattern** Consider again a two-dimensional wave packet given by

$$\Psi(x, y, 0) = \left[ \left( \frac{1}{\pi \sigma_{x0}^2} \right)^{\frac{1}{4}} \exp \left[ -\frac{x^2}{2\sigma_{x0}^2} \right] e^{\frac{i}{\hbar} p_0 x} \right] \psi_b(y) \quad (90)$$

where

$$\begin{aligned} \psi_b(y) &= \frac{1}{\sqrt{b}} & |y| < b/2 \\ &= 0 & |y| > b/2 \end{aligned} \quad (91)$$

(a) Determine  $a(p_x, p_y)$  and interpret it physically. Show that the subsequent evaluation of  $\Psi(x, t)$  is difficult to carry out.

(b) Use Eq. (76) to evaluate  $|\Psi(x, y, t)|^2$  and interpret it physically.

**Problem 5.8 Double Slit Diffraction Pattern** In the previous problem assume

$$\psi_b(y) = \begin{cases} \frac{1}{\sqrt{2b}} & \text{for } (d-b)/2 < |y| < (d+b)/2 \\ 0 & \text{elsewhere} \end{cases} \quad (92)$$

which corresponds to a double slit (each of width  $b$ ) separated by a distance  $d$ . Calculate  $|a(p_y)|^2 dp_y$  and interpret the result physically.

**Problem 5.9 (a)** For the wave packet given by Eq. (57) show that it remains undistorted for  $t \ll t_0$  where

$$t_0 = \frac{2}{(\Delta k)^2 \frac{d^2\omega}{dk^2}} = \frac{2\hbar}{(\Delta p)^2 \frac{d^2E}{dp^2}} \simeq \frac{2m (\Delta x)^2}{\hbar} \quad (93)$$

where use has to be made of Eqs (67) and (68) and the uncertainty relation.

(b) For a particle of mass  $10^{-4}$  g and localized within  $\Delta x \sim 10^{-3}$  cm calculate  $t_0$  and compare its value for an electron localized in a distance of  $10^{-8}$  cm. Interpret the two results physically.

(c) Calculate  $t_0$  for the Gaussian wave packet and show that the exact results obtained in Example 5.1 are consistent with Eq. (93).

**Problem 5.10** Consider the three-dimensional wave packet describing the motion of a free particle

$$\Psi(x, y, z, 0) = N \exp \left[ -\frac{x^2}{2\sigma_1^2} - \frac{y^2}{2\sigma_2^2} - \frac{z^2}{2\sigma_3^2} \right] \exp \left[ \frac{i}{\hbar} p_0 x \right] \quad (94)$$

Discuss physically the motion of such a wave packet. Calculate the value of  $a(p_x, p_y, p_z)$  and then  $\Psi(x, y, z, t)$ .

**Problem 5.11** Consider the three-dimensional momentum space wave function

$$a(\mathbf{p}) = N \exp\left[-\frac{p}{\Delta p}\right] \quad (95)$$

Calculate  $\Psi(\mathbf{r}, 0)$ .

**Problem 5.12 (a)** From Eq. (14) show that

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \exp\left[\frac{i}{\hbar} \frac{p^2}{2m} t\right] \int_{-\infty}^{+\infty} \Psi(x, t) \exp\left[-\frac{i}{\hbar} px\right] dx \quad (96)$$

which is independent of time.

(b) Substitute the expression for  $\Psi(x, t)$  from Eq. (35) and show that after evaluating the above integral one obtains Eq. (32) (obviously!).

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## 5.8. Solutions

**Solution 5.1** Equation (82) follows directly from Parseval's theorem (see Sec. 2.3). In order to prove Eq. (83), we take the complex conjugate of Eq. (14) and obtain

$$\begin{aligned} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx &= \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dp' a^*(p') a(p) \\ &\times \exp\left[-\frac{i}{\hbar} \left(p'x - \frac{p'^2}{2m}t\right) + \frac{i}{\hbar} \left(px - \frac{p^2}{2m}t\right)\right] \end{aligned}$$

Since

$$\frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \exp\left[\frac{i}{\hbar}(p-p')x\right] dx = \delta(p-p') \quad (97)$$

[see Eq. (9) of Chapter 1], after carrying out the integration over  $p'$  we readily get

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} |a(p)|^2 dp = 1 \quad (98)$$

**Solution 5.2**

$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) \exp\left[\frac{i}{\hbar} px\right] dp \quad (99)$$

Thus

$$\begin{aligned}
 \langle p \rangle &= -i \hbar \int \Psi^* \frac{\partial \Psi}{\partial x} dx \\
 &= -i \hbar \int_{-\infty}^{+\infty} \Psi^*(x) \left[ \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \frac{i}{\hbar} p' a(p') \exp\left(\frac{i}{\hbar} p' x\right) dp' \right] dx \\
 &= \int_{-\infty}^{+\infty} dp a^*(p) \left[ \int_{-\infty}^{+\infty} dp' p' a(p') \delta(p - p') \right] \\
 &= \int_{-\infty}^{+\infty} a^*(p) p a(p) dp
 \end{aligned} \tag{100}$$

Similarly, one can calculate for  $\langle p^2 \rangle$ .

**Solution 5.3** Use Eq. (84) to evaluate  $a^*(p)$  and  $\frac{\partial a}{\partial p}$  and substitute in the RHS of Eq. (87). Alternatively, we can substitute the expression

$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) \exp\left[\frac{i}{\hbar} px\right] dp$$

and its complex conjugate in the integral

$$\int_{-\infty}^{+\infty} \Psi^*(x) x \Psi(x) dx$$

and carry out the integration over  $p$  by parts.

**Solution 5.4**

$$\begin{aligned}
 \langle x \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x, 0) x \Psi(x, 0) dx \\
 &= \frac{1}{\sqrt{\pi\sigma_0^2}} \int_{-\infty}^{+\infty} x e^{-x^2/\sigma_0^2} dx \\
 &= 0 \\
 \langle x^2 \rangle &= \frac{1}{\sqrt{\pi\sigma_0^2}} \int_{-\infty}^{+\infty} x^2 e^{-x^2/\sigma_0^2} dx \\
 &= \frac{1}{2} \sigma_0^2
 \end{aligned}$$

(see Appendix A). Further  $\langle p \rangle = 0$  because the integrand would be an odd function. Finally

$$\begin{aligned}\langle p^2 \rangle &= -\frac{\hbar^2}{\sqrt{\pi \sigma_0^2}} \int_{-\infty}^{+\infty} e^{-x^2/2\sigma_0^2} \frac{d^2}{dx^2} \left( e^{-x^2/2\sigma_0^2} \right) dx \\ &= \frac{\hbar^2}{2\sigma_0^2}\end{aligned}$$

### Solution 5.6

**(a)** We define the two-dimensional Fourier transform

$$a(p_x, p_y) = \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Psi(x, y, 0) \exp \left[ \frac{i}{\hbar} (p_x x + p_y y) \right] dx dy \quad (101)$$

and

$$\Psi(x, y, t) = \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} a(p_x, p_y) \exp \left[ -\frac{i}{\hbar} (p_x x + p_y y) \right] dp_x dp_y \quad (102)$$

Since  $\Psi(x, y, 0)$  is a product of a function of  $x$  and of  $y$ , the integrals over  $x$  and  $y$  in Eq. (101) separate out and we obtain

$$a(p_x, p_y) = a(p_x) a(p_y) \quad (103)$$

where

$$a(p_x) = \left( \frac{\sigma_{x0}^2}{\pi \hbar^2} \right)^{\frac{1}{4}} \exp \left[ -\frac{\sigma_{x0}^2}{2\hbar^2} (p_x - p_0)^2 \right] \quad (104)$$

and

$$a(p_y) = \left( \frac{\sigma_{y0}^2}{\pi \hbar^2} \right)^{\frac{1}{4}} \exp \left[ -\frac{\sigma_{y0}^2}{2\hbar^2} p_y^2 \right] \quad (105)$$

Obviously, the quantity

$$|a(p_y)|^2 dp_y = \left( \frac{\sigma_{y0}^2}{\pi \hbar^2} \right)^{\frac{1}{2}} \exp \left[ -\frac{\sigma_{y0}^2 p_y^2}{\hbar^2} \right] dp_y \quad (106)$$

represents the probability of finding  $p_y$  in the interval  $dp_y$ ; this is nothing but the diffraction of a Gaussian beam.

**(b)** We substitute Eqs (104) and (105) in Eq. (102) and carry out the integration to obtain

$$|\Psi(x, y, t)|^2 = \left\{ \frac{1}{\sqrt{\pi}\sigma_x(t)} \exp \left[ -\frac{(x - \frac{p_0}{m}t)^2}{\sigma_x^2(t)} \right] \right\} \\ \times \left\{ \frac{1}{\sqrt{\pi}\sigma_y(t)} \exp \left[ -\frac{y^2}{\sigma_y^2(t)} \right] \right\} \quad (107)$$

where

$$\sigma_x(t) = \sigma_{x0} \left[ 1 + \frac{\hbar^2 t^2}{m^2 \sigma_{x0}^4} \right]^{\frac{1}{2}} \quad (108)$$

$$\sigma_y(t) = \sigma_{y0} \left[ 1 + \frac{\hbar^2 t^2}{m^2 \sigma_{y0}^4} \right]^{\frac{1}{2}}$$

Equation (107) shows the diffraction broadening along the  $y$ -direction.

**Solution 5.7** Equation (103) still remains valid with

$$a(p_y) = \sqrt{\frac{b}{\pi \hbar}} \frac{\sin(p_y b)/2\hbar}{p_y b/2\hbar} \quad (109)$$

Thus the probability that (after passing through the slit) the  $y$ -component of the momentum lies between  $p_y$  and  $p_y + dp_y$  would be given by

$$|a(p_y)|^2 dp_y = \frac{b}{\pi \hbar} \frac{\sin^2 \beta}{\beta^2} dp_y \quad (110)$$

where

$$\beta = \frac{p_y b}{2\hbar} = \frac{p \sin \theta b}{2\hbar} = \frac{\pi b \sin \theta}{\lambda} \quad (111)$$

and use has been made of the de Broglie relation

$$\lambda = \frac{h}{p} \quad (112)$$

Thus, far away from the slit, we will observe the intensity distribution given by

$$I = I_0 \frac{\sin^2 \beta}{\beta^2} \quad (113)$$

which is nothing but the single slit Fraunhofer diffraction pattern.

In order to get  $\Psi(x, y, t)$  we must substitute for  $a(p_x, p_y)$  in Eq. (102); however, the  $y$  integral would be difficult to carry out. Instead we must directly evaluate

$\Psi(x, y, t)$  by using Eq. (76). The final result can be expressed in terms of Fresnel integrals (see Appendix C).

### Solution 5.8

$$a(p_y) = \frac{1}{\sqrt{2\pi\hbar}} \frac{1}{\sqrt{2b}} \left[ \int_{-\frac{d}{2}-\frac{b}{2}}^{-\frac{d}{2}+\frac{b}{2}} + \int_{\frac{d}{2}-\frac{b}{2}}^{\frac{d}{2}+\frac{b}{2}} \right] e^{i p_y y / \hbar} dy$$

Thus

$$|a(p_y)|^2 = \frac{4b}{\pi\hbar} \left[ \frac{\sin^2 \beta}{\beta^2} \right] \cos^2 \gamma \quad (114)$$

where

$$\beta = \frac{b p_y}{2\hbar} = \frac{\pi b \sin \theta}{\lambda} \quad (115)$$

and

$$\gamma = \frac{d p_y}{2\hbar} = \frac{\pi d \sin \theta}{\lambda} \quad (116)$$

Equation (114) is nothing but the double slit Fraunhofer diffraction pattern.

**Solution 5.9 (a)** If we substitute for  $\omega(k)$  from Eq. (58) in Eq. (57) we would get

$$\begin{aligned} \Psi(x, t) &= \frac{e^{i(k_0 x - \omega t)}}{\sqrt{2\pi}} \int_{\Delta k} A(k) e^{i\phi(k)} \\ &\quad \times \exp [i(x - v_g t)(k - k_0) - i\alpha(k - k_0)^2 t] dk \end{aligned}$$

where

$$\alpha = \frac{1}{2} \left. \frac{d^2 \omega}{dk^2} \right|_{k=k_0}$$

Since  $|A(k)|$  is assumed to have a negligible value for  $|k - k_0| \gtrsim \Delta k$ , the term involving  $\alpha$  would make a negligible contribution for  $t \ll t_0$  where  $t_0$  is given by Eq. (93).

In order to understand Eq. (93) physically, we notice that there is a spread  $\sim \Delta p$  in the momentum associated with the packet. Thus if we consider two portions of the packet, one corresponding to  $p_0 - \frac{\Delta p}{2} < p < p_0$  and the other corresponding to  $p_0 < p < p_0 + \frac{\Delta p}{2}$ , then the velocity of the two packets will differ by  $\frac{\Delta p}{2m}$ . Thus there will be distortion in the packet when

$$\frac{t \Delta p}{2m} \approx \Delta x \quad (\text{the initial width of the packet})$$

The above condition is consistent with Eq. (93).

(b) For  $m \approx 10^{-4}$  g,  $\Delta x \approx 10^{-3}$  cm,  $t_0 \sim 2 \times 10^{17}$  s  $\sim 10^{10}$  years. On the other hand, for an electron with  $\Delta x \approx 10^{-8}$  cm,  $t_0 \approx 10^{-16}$  sec. Thus for a macroscopic particle the distortion is negligible and hence a classical description is adequate.

**Solution 5.10** For a three-dimensional wave packet describing a free particle

$$\Psi(\mathbf{r}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \iiint a(\mathbf{p}) \exp\left[\frac{i}{\hbar}(\mathbf{p} \cdot \mathbf{r} - Et)\right] d\mathbf{p} \quad (117)$$

and

$$a(\mathbf{p}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \iiint \Psi(\mathbf{r}, t) \exp\left[-\frac{i}{\hbar}(\mathbf{p} \cdot \mathbf{r} - Et)\right] d\mathbf{r} \quad (118)$$

where

$$\mathbf{p} \cdot \mathbf{r} = p_x x + p_y y + p_z z, \quad d\mathbf{r} = dx dy dz, \quad d\mathbf{p} = dp_x dp_y dp_z$$

and

$$E = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

On substitution of Eq. (94) in Eq. (118), the three-dimensional integral becomes a product of three one-dimensional integrals giving

$$a(\mathbf{p}) = a(p_x, p_y, p_z) = \left(\frac{\sigma_1 \sigma_2 \sigma_3}{\hbar^3}\right)^{\frac{1}{2}} \frac{1}{\pi^{3/4}} \times \exp\left[-\frac{\sigma_1^2}{2\hbar^2}(p_x - p_0)^2 - \frac{\sigma_2^2}{\hbar^2}p_y^2 - \frac{\sigma_3^2}{\hbar^2}p_z^2\right]$$

where we have used the fact that the normalization constant  $N = \pi^{-3/4}/(\sigma_1 \sigma_2 \sigma_3)^{1/2}$ . If we substitute for  $a(\mathbf{p})$  in Eq. (117) we would get

$$|\Psi(\mathbf{r}, t)|^2 = \frac{1}{\pi^{3/2} [\sigma_1(t) \sigma_2(t) \sigma_3(t)]} \exp\left[-\frac{\left\{x - \frac{p_0}{m}t\right\}^2}{\sigma_1^2(t)}\right] \times \exp\left[-\frac{y^2}{\sigma_2^2(t)}\right] \exp\left[-\frac{z^2}{\sigma_3^2(t)}\right]$$

where

$$\sigma_i(t) = \sigma_i \left[1 + \frac{\hbar^2 t^2}{m^2 \sigma_i^4}\right]^{1/2}$$

If we assume  $\sigma_1$  to be very large then there is propagation along the  $x$ -axis and diffraction along the  $y$ - and  $z$ -directions.

**Solution 5.11** In order to calculate  $N$  we use spherical polar coordinates to get

$$1 = |N|^2 \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \int_0^\infty e^{-2p/\Delta p} p^2 \, dp$$

which gives  $N = (\Delta p)^{3/2} / \sqrt{\pi}$ . Thus

$$\Psi(\mathbf{r}, 0) = \frac{|N|^2}{(2\pi\hbar)^{3/2}} \int_0^{2\pi} d\phi \int_0^\infty p^2 \, dp \exp\left[-\frac{p}{\Delta p}\right] \int_0^\pi \exp\left[-\frac{i pr \cos \theta}{\hbar}\right] \sin \theta \, d\theta$$

where we have assumed  $p_z$  along  $\mathbf{r}$ . On carrying out the integration we get

$$\Psi(\mathbf{r}, 0) = \frac{1}{\pi} (2r_0)^{3/2} \frac{r_0}{(r^2 + r_0^2)^2}$$

where  $r_0 = \hbar/\Delta p$ .

---

## 5.9. Sample questions

- Q. 1 a) Write the one-dimensional time dependent Schrödinger equation for a free particle.  
 b) Write the general solution of the above equation.  
 c) If we know  $\Psi(x, 0)$ , write the recipe for determining  $\Psi(x, t)$ .
- Q. 2 Starting from the one-dimensional Schrödinger equation for a free particle show that the solution can be written in the form

$$\Psi(x, t) = \int_{-\infty}^{+\infty} \Psi(x', 0) K(x, x'; t) \, dx'$$

Derive the expression for  $K(x, x'; t)$ . What will be the form of  $K(x, x'; 0)$ ?

- Q. 3 Given

$$\Psi(x, y, 0) = e^{-x^2/2\sigma^2} e^{\frac{i}{\hbar} p_0 x} \psi(y)$$

where

$$\begin{aligned} \psi(y) &= 1 \quad |y| < b/2 \\ &= 0 \quad |y| > b/2 \end{aligned}$$

- a) What is the probability of finding the particle between  $x$  and  $x + dx$  and  $y$  and  $y + dy$ ?
- b) Calculate the probability for the  $x$ -component of the momentum to lie between  $p_x$  and  $p_x + dp_x$  and  $y$ -component of the momentum to lie between  $p_y$  and  $p_y + dp_y$ . Give a physical interpretation in terms of the single slit diffraction pattern.

# Chapter 6

## Bound State Solutions of the Schrödinger Equation

*Only questions about the results of experiments have a real significance and it is only such questions that theoretical physics has to consider.*

— P.A.M. DIRAC  
in *The Principles of Quantum Mechanics*

### 6.1. Stationary states

When the Hamiltonian for a system is independent of time, there is an essential simplification in that the general solution of the Schrödinger equation can be expressed as a function of spatial coordinates and a function of time. Thus, assuming the potential energy function to be independent of time, the one-dimensional time dependent Schrödinger equation [see Eq. (25) of Chapter 4] is given by

$$i \hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi(x, t) \quad (1)$$

where  $\mu$  represents the mass of the particle. The above equation can be solved by using the method of separation of variables

$$\Psi(x, t) = \psi(x) T(t) \quad (2)$$

Substituting in Eq. (1) and dividing by  $\Psi(x, t)$ , we obtain

$$\frac{i \hbar}{T(t)} \frac{dT}{dt} = \frac{1}{\psi(x)} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2 \psi}{dx^2} + V(x) \psi(x) \right] \quad (3)$$

The variables have indeed separated out in the sense that the LHS is a function of time alone while the RHS is a function of space alone; thus each side must be equal to a constant, say  $E$ . We have therefore

$$\frac{i \hbar}{T} \frac{dT}{dt} = \frac{1}{\psi} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2 \psi}{dx^2} + V(x) \psi \right] = E \quad (4)$$

or

$$T(t) = e^{-iEt/\hbar} \quad (5)$$

and

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x) \quad (6)$$

so that the solution can be written as

$$\Psi(x, t) = \psi(x) e^{-iEt/\hbar} \quad (7)$$

Now, Eq. (6) can be written as

$$H\psi(x) = E\psi(x) \quad (8)$$

where

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V(x) = \frac{p^2}{2\mu} + V(x) \quad (9)$$

represents the Hamiltonian operator and  $E$  is a *number*. Equation (8) is an eigenvalue equation and  $E$  is the energy eigenvalue. In general, the eigenvalues can have a discrete set along with a continuous range of eigenvalues and the general solution of Eq. (1) is of the form

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar} \quad (10)$$

where  $\psi_n(x)$  are the eigenfunctions of  $H$  and  $E_n$  are the corresponding energy eigenvalues;  $c_n$  are constants which can be determined from the form of  $\Psi(x, 0)$ . In Eq. (10),  $\sum$  denotes a summation over the discrete states and integration over the continuum states<sup>1</sup>.

Equation (6) is usually written in the form

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (11)$$

which is known as the one-dimensional time independent Schrödinger equation.

In Sec. 6.2 we will discuss two theorems regarding the boundary and continuity conditions of the wave function. In Secs 6.3 and 6.4 we will discuss the degeneracy of a state and the orthogonality of the eigenfunctions and in Sec. 6.5 we will discuss the parity of the eigenfunctions. In Sec. 6.6 we will give the solution of

<sup>1</sup> In Chapter 5 we had solved Eq. (1) for a free particle for which  $V(x) = 0$ . There the eigenvalues formed a continuum ( $0 < E < \infty$ ) and the  $\sum$  in Eq. (10) was indeed an integral over the continuum states [see Eq. (14) of Chapter 5].

the eigenvalue equation [Eq. (8)] for some simple problems. In Sec. 6.7 we will discuss the properties of the wave function associated with the three-dimensional Schrödinger equation and in Sec. 6.8 we will obtain solutions of the Schrödinger equation for a particle in a three-dimensional box. In Secs 6.9 and 6.10 we will discuss applications of the particle in a box problem to free electrons inside a metal and also inside a white dwarf star.

## 6.2. Boundary and continuity conditions

In Sec. 4.4 we have interpreted the wave function  $\psi$  as the probability amplitude, therefore  $\psi$  should be single-valued and  $|\psi(x)|^2 dx$  has to be finite for finite values of  $dx$ . Thus

$$\lim_{dx \rightarrow 0} |\psi|^2 dx = 0$$

In practice this is satisfied by demanding that  $\psi$  be finite everywhere. We also have the following theorems.

**THEOREM 1.** *The derivative of the wave function  $d\psi/dx$  is always continuous as long as the potential energy  $V(x)$  is finite, whether or not it is continuous<sup>2</sup>.*

**Proof** We integrate the Schrödinger equation [Eq. (11)] from  $x - \epsilon$  to  $x + \epsilon$  to obtain

$$\int_{x-\epsilon}^{x+\epsilon} \frac{d^2\psi}{dx^2} dx = -\frac{2\mu}{\hbar^2} \int_{x-\epsilon}^{x+\epsilon} [E - V(x)] \psi(x) dx$$

or

$$\psi'(x + \epsilon) - \psi'(x - \epsilon) = -\frac{2\mu}{\hbar^2} \int_{x-\epsilon}^{x+\epsilon} [E - V(x)] \psi(x) dx \quad (12)$$

Since  $V(x)$  is assumed to be finite (it could, however, be discontinuous), the RHS tends to zero as  $\epsilon \rightarrow 0$ . Thus  $\psi'$  is continuous at any value of  $x$ . It is obvious that  $\psi$  has to be necessarily continuous everywhere.

Alternatively one may argue that if  $d\psi/dx$  is discontinuous, then  $d^2\psi/dx^2$  must be a delta function (see Sec. 1.3); this will be inconsistent with Eq. (12) as long as  $V(x)$  does not become infinite.

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<sup>2</sup> It may be mentioned that in many texts the continuity of  $\psi$  and  $d\psi/dx$  is taken to be an axiom. This is not correct because it follows from the fact that  $\psi(x)$  satisfies a second order differential equation [see Eq. (11)]. Indeed, when  $V(x)$  becomes infinite,  $d\psi/dx$  is *not* continuous (see Sec. 6.6.1).

**THEOREM 2.** *If the potential energy function  $V(x)$  is infinite anywhere, the proper boundary condition is obtained by assuming  $V(x)$  to be finite at that point and carrying out a limiting process making  $V(x)$  tend to infinity. Such a limiting process makes the wave function vanish at a point where  $V(x) = \infty$  (see Problem 6.2).*

### 6.3. Degeneracy

If there is more than one linearly independent wave function belonging to the same energy eigenvalue  $E$ , the energy level is said to be degenerate. If there are  $g$  linearly independent wave functions ( $\psi_1, \psi_2, \dots, \psi_g$ ) belonging to the same energy state, then the energy level is said to be  $g$ -fold degenerate. It can be easily shown that any linear combination of the degenerate wave functions

$$\psi = c_1 \psi_1 + c_2 \psi_2 + \dots + c_g \psi_g$$

is also an eigenfunction belonging to the same energy eigenvalue. We will prove this for  $g = 2$ , the generalization is straightforward. Since  $\psi_1$  and  $\psi_2$  are eigenfunctions belonging to same eigenvalue  $E_1$ , we have [see Eq. (6)]:

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_1}{dx^2} + V(x) \psi_1 = E_1 \psi_1$$

and

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_2}{dx^2} + V(x) \psi_2 = E_1 \psi_2$$

If we multiply the first equation by  $c_1$  and the second equation by  $c_2$  and add, we would get

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} (c_1 \psi_1 + c_2 \psi_2) + V(x) (c_1 \psi_1 + c_2 \psi_2) = E_1 (c_1 \psi_1 + c_2 \psi_2) \quad (13)$$

which shows that the linear combination  $c_1 \psi_1 + c_2 \psi_2$  is also an eigenfunction belonging to the *same* eigenvalue  $E_1$ .

### 6.4. Orthogonality of eigenfunctions

We shall first prove that *all energy eigenvalues  $E_n$  are real and that if  $E_n \neq E_k$ , the corresponding eigenfunctions are necessarily orthogonal*. We write the one-dimensional Schrödinger equation for the two states corresponding to the eigenvalues  $E_n$  and  $E_k$ :

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_n}{dx^2} + V(x) \psi_n = E_n \psi_n \quad (14)$$

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_k}{dx^2} + V(x) \psi_k = E_k \psi_k \quad (15)$$

If we multiply Eq. (14) by  $\psi_k^*$  and multiply the complex conjugate of Eq. (15) by  $\psi_n$  and subtract, we would get

$$-\frac{\hbar^2}{2\mu} \left[ \psi_k^* \frac{d^2\psi_n}{dx^2} - \psi_n \frac{d^2\psi_k^*}{dx^2} \right] = (E_n - E_k^*) \psi_k^* \psi_n$$

or,

$$-\frac{\hbar^2}{2\mu} \int_{-\infty}^{\infty} \frac{d}{dx} \left[ \psi_k^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_k^*}{dx} \right] dx = (E_n - E_k^*) \int_{-\infty}^{\infty} \psi_k^* \psi_n dx \quad (16)$$

The left-hand side is simply

$$-\frac{\hbar^2}{2\mu} \left[ \psi_k^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_k^*}{dx} \right] \Big|_{-\infty}^{+\infty}$$

which would vanish if the wave functions are assumed to vanish at infinity. Thus we get

$$(E_n - E_k^*) \int_{-\infty}^{\infty} \psi_k^* \psi_n dx = 0 \quad (17)$$

If  $k = n$ , then since  $\int_{-\infty}^{\infty} |\psi_n|^2 dx$  is necessarily positive<sup>3</sup>, we must have

$$E_n = E_n^* \quad (18)$$

proving that *all eigenvalues are real*. Further, for  $E_n \neq E_k$ ,

$$\int_{-\infty}^{\infty} \psi_k^* \psi_n dx = 0 \quad (19)$$

which represents the *orthogonality condition*.

If  $E_k = E_n$ , i.e. if there are two (or more) wave functions belonging to the same eigenvalue, then the corresponding wave functions are not necessarily orthogonal. Since any linear combination of degenerate state wave functions is also a possible eigenfunction (see Sec. 6.3) one can *always* construct suitable linear combinations which are mutually orthogonal (see Problems 6.3 and 6.4).

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<sup>3</sup> Except in the trivial case when the wave function vanishes everywhere.

Since the Schrödinger equation is a linear equation, if  $\psi$  is a solution,  $c\psi$  is also a solution where  $c$  is an arbitrary complex number. One can always choose the constant such that

$$\int_{-\infty}^{\infty} |\psi_n|^2 dx = 1 \quad (20)$$

which is known as the normalization condition. Equations (19) and (20) can be combined in the form

$$\int_{-\infty}^{\infty} \psi_k^* \psi_n dx = \delta_{kn} \quad (21)$$

where  $\delta_{kn}$  is the Kronecker delta function defined through the equation

$$\delta_{kn} = \begin{cases} 0 & k \neq n \\ 1 & k = n \end{cases} \quad (22)$$

Equation (21) is known as the orthonormality condition.

## 6.5. Parity

In this section we will show that if

$$V(x) = V(-x) \quad (23)$$

i.e. if the potential energy function is symmetric about  $x = 0$ , then the eigenfunctions of the Schrödinger equation are either symmetric functions of  $x$  [ $\psi(x) = \psi(-x)$ ] or antisymmetric functions<sup>4</sup> of  $x$  [ $\psi(x) = -\psi(-x)$ ]. In order to prove this, we first write the Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x) \quad (24)$$

Making the transformation  $x \rightarrow -x$  we get

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi(-x)}{dx^2} + V(x) \psi(-x) = E \psi(-x) \quad (25)$$

<sup>4</sup> The theorem is strictly true for non-degenerate states only. For degenerate states the wave functions need not be symmetric or antisymmetric functions of  $x$ . However, even for degenerate states one can always construct appropriate linear combinations which are either symmetric or antisymmetric functions of  $x$ .

where we have used the fact that  $V(-x) = V(x)$ . Comparing Eqs (24) and (25) we see that  $\psi(x)$  and  $\psi(-x)$  are eigenfunctions belonging to the same energy  $E$ . Thus, if the state is non-degenerate, then  $\psi(-x)$  must be a multiple of  $\psi(x)$ :

$$\psi(-x) = \lambda \psi(x)$$

Clearly

$$\psi(x) = \lambda \psi(-x) = \lambda^2 \psi(x)$$

so that  $\lambda^2 = 1$  or  $\lambda = \pm 1$ . Hence

$$\psi(-x) = \pm \psi(x) \quad (26)$$

proving the theorem. The eigenfunctions which belong to the class  $\lambda = +1$  are said to have *even parity* and those with  $\lambda = -1$  to have *odd parity*.

For a degenerate state  $\psi(-x)$  need not be a multiple of  $\psi(x)$ . Indeed, if  $\psi(-x)$  is not a multiple of  $\psi(x)$  then, from Eqs (24) and (25), it immediately follows that  $\psi(-x)$  must be another independent solution corresponding to the same energy level. Further any linear combination of  $\psi(x)$  and  $\psi(-x)$  could also be a possible eigenfunction (see Sec. 6.3) and we can always choose linear combinations

$$[\psi(x) + \psi(-x)] \quad \text{and} \quad [\psi(x) - \psi(-x)]$$

which are symmetric and antisymmetric functions of  $x$  respectively. Thus even for degenerate states one can always choose appropriate linear combinations which are either symmetric or antisymmetric functions of  $x$ .

## 6.6. Some exact solutions of the one-dimensional Schrödinger equation

In this section we will consider two potential energy distributions for which an exact solution of the one-dimensional Schrödinger equation will be obtained. In Sec. 6.6.1 we will consider a particle inside an infinitely deep potential well which will be followed by considering the effects of the potential well of finite depth. In the next chapter we will consider the linear harmonic oscillator problem and in Chapter 16 we will consider the double well problem.

### 6.6.1. PARTICLE IN A ONE-DIMENSIONAL INFINITELY DEEP POTENTIAL WELL

We will determine the energy levels and the corresponding eigenfunctions of a particle of mass  $\mu$  in a one-dimensional infinitely deep potential well characterised by the potential energy variation of the form

$$\begin{aligned} V(x) &= 0 \text{ for } 0 < x < a \\ &= \infty \text{ for } x < 0 \text{ and for } x > a \end{aligned} \quad (27)$$

(The corresponding three-dimensional problem is discussed in Sec. 6.8). For  $0 < x < a$ , the one-dimensional Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} + k^2 \psi(x) = 0 \quad (28)$$

where

$$k^2 = \frac{2\mu E}{\hbar^2} \quad (29)$$

The general solution of this equation is

$$\psi = A \sin kx + B \cos kx$$

Since the boundary condition at a surface at which there is an infinite potential step is that  $\psi$  is zero (see Sec. 6.2, Theorem 2), we must have

$$\psi(x=0) = \psi(x=a) = 0 \quad (30)$$

The above condition also follows from the fact that since the particle is inside an infinitely deep potential well, it is always confined in the region  $0 < x < a$  and therefore  $\psi$  must vanish for  $x < 0$  and  $x > a$ ; and for  $\psi$  to be continuous, Eq. (30) must be satisfied. Using the boundary condition given by Eq. (30), we get

$$\psi(x=0) = B = 0$$

and

$$\psi(x=a) = A \sin ka = 0$$

Thus, either

$$A = 0$$

or

$$ka = n\pi ; \quad n = 1, 2, \dots \quad (31)$$

The condition  $A = 0$  leads to the trivial solution of  $\psi$  vanishing everywhere, the same is the case for  $n = 0$ . Thus the allowed energy levels are given by

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2\mu a^2} ; \quad n = 1, 2, 3, \dots \quad (32)$$

The corresponding eigenfunctions are

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad (0 < x < a) \quad (33)$$

where the factor  $\sqrt{2/a}$  is such that the wave functions form an orthonormal set [cf. Eq. (21)]:

$$\int_0^a \psi_m^*(x) \psi_n(x) dx = \delta_{mn} \quad (34)$$

It may be noted that whereas  $\psi_n(x)$  is continuous everywhere,  $d\psi_n(x)/dx$  is discontinuous at  $x = 0$  and at  $x = a$ . This is because of  $V(x)$  becoming infinite at  $x = 0$  and at  $x = a$  (see Sec. 6.2). Figure 6.1 gives a plot of the first three eigenfunctions and one can see that the eigenfunctions are either symmetric or antisymmetric about the line  $x = a/2$ ; this follows from the fact that  $V(x)$  is symmetric about  $x = a/2$  (see Sec. 6.5).

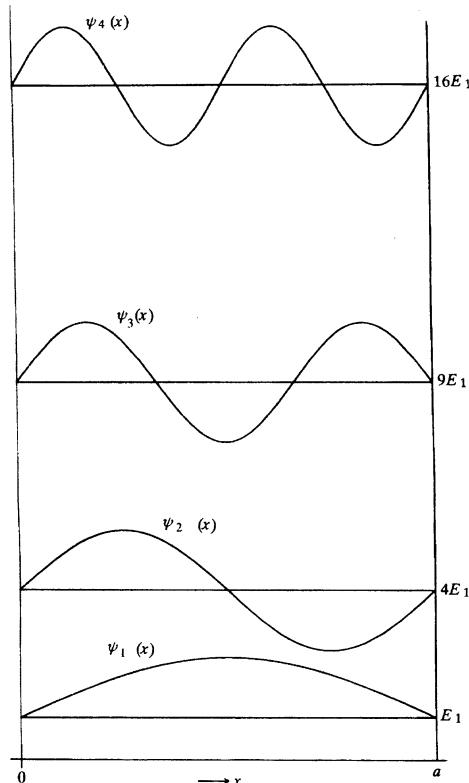


Figure 6.1. The energy eigenvalues and eigenfunctions for a particle in an infinitely deep potential well. Notice that the eigenfunctions are either symmetric or antisymmetric about  $x = a/2$ .

The following points are also to be noted.

- (i)  $E$  cannot be negative because if we assume  $E$  to be negative then the boundary conditions at  $x = 0$  and at  $x = a$  cannot be simultaneously satisfied (see also Problem 7.1).
- (ii) The eigenvalues form a discrete set.
- (iii) The eigenfunctions given by Eq. (33) form a complete set, i.e. an arbitrary (well-behaved) function which satisfies the same boundary conditions (viz., vanishing at  $x = 0$  and at  $x = a$ ) can be expanded in terms of the eigenfunction of  $H$ :

$$f(x) = \sum_n c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1,2,\dots}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right) \quad (35)$$

where  $f(x)$  is an arbitrary well-behaved function (with  $f(0) = f(a) = 0$ ) and  $c_n$  are constants which can be determined by multiplying both sides of the above equation by  $\psi_m^*(x)$  and integrating from 0 to  $a$  to obtain

$$\int_0^a \psi_m^*(x) f(x) dx = \sum_n c_n \int_0^a \psi_m^* \psi_n(x) dx = \sum_n c_n \delta_{mn} = c_m \quad (36)$$

where we have used the orthonormality condition given by Eq. (34). Substituting for  $c_m$  in Eq. (35) we would readily get (cf. Sec. 1.5):

$$\sum_n \psi_n^*(x') \psi_n(x) = \frac{2}{a} \sum_{n=1,2,\dots}^{\infty} \sin\left(\frac{n\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x'\right) = \delta(x - x') \quad 0 < x, x' < a \quad (37)$$

which represents the completeness condition.

- (iv) The most general solution of the time dependent Schrödinger equation [Eq. (1)] with  $V(x)$  given by Eq. (27) would be

$$\Psi(x, t) = \sum_n^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \quad (38)$$

Substituting for  $\psi_n(x)$  and  $E_n$  we get

$$\Psi(x, t) = \sum_{n=1,2,\dots}^{\infty} c_n \left( \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right) \exp \left[ -i \frac{n^2 \pi^2 \hbar}{2 \mu a^2} t \right] \quad (39)$$

Since

$$\Psi(x, 0) = \sum_n c_n \psi_n(x) \quad (40)$$

the coefficients  $c_n$  can be determined from the initial form of the wave function:

$$c_n = \int_0^a \psi_n^*(x) \Psi(x, 0) dx \quad (41)$$

(v) We assume  $\Psi(x, 0)$  to be normalized:

$$\int_0^a |\Psi(x, 0)|^2 dx = 1 \quad (42)$$

This would imply

$$\begin{aligned} 1 &= \int_0^a \sum_n c_n^* \psi_n^*(x) \sum_m c_m \psi_m(x) dx \\ &= \sum_n \sum_m c_n^* c_m \int_0^a \psi_n^*(x) \psi_m(x) dx \\ &= \sum_n \sum_m c_n^* c_m \delta_{mn} \\ &= \sum_n |c_n|^2 \end{aligned} \quad (43)$$

where we have used the orthonormality condition given by Eq. (34). Now, using Eq. (38)

$$\begin{aligned} \int_0^a |\Psi(x, t)|^2 dx &= \sum_n \sum_m c_n^* c_m e^{i(E_n - E_m)t/\hbar} \int_0^a \psi_n^*(x) \psi_m(x) dx \\ &= \sum_n \sum_m c_n^* c_m e^{i(E_n - E_m)t/\hbar} \delta_{mn} \\ &= \sum_n |c_n|^2 \end{aligned} \quad (44)$$

Thus, if the wave function is normalized at  $t = 0$ , then it will remain normalized at all times. Further, we can interpret Eq. (44) by saying that  $|c_n|^2$  represents the probability of finding the system in the  $n^{\text{th}}$  state which remains

the same at all times. Thus there are no transitions. Indeed, whenever the potential energy function is time-independent, we obtain what are known as *stationary states* and there is no transition between states.<sup>5</sup>

- (vi) As a simple example, let us assume that the particle is described by the following wave function (at  $t = 0$ ):

$$\Psi(x, 0) = \sqrt{\frac{1}{6}} \psi_1(x) + \frac{i}{\sqrt{2}} \psi_2(x) + \sqrt{\frac{1}{3}} \psi_3(x) \quad (45)$$

Thus, if we carry out a measurement of energy, the probabilities of obtaining the values  $E_1$ ,  $E_2$  and  $E_3$  would be  $\frac{1}{6}$ ,  $\frac{1}{2}$ , and  $\frac{1}{3}$  respectively. How will such a state evolve with time? Well, we just multiply each term by the appropriate time dependent factor to obtain  $\Psi(x, t)$  [see Eq. (10)].

$$\begin{aligned} \Psi(x, t) &= \sqrt{\frac{1}{6}} \psi_1(x) e^{-it/t_0} + \frac{i}{\sqrt{2}} \psi_2(x) e^{-4it/t_0} \\ &\quad + \sqrt{\frac{1}{3}} \psi_3(x) e^{-9it/t_0} \end{aligned} \quad (46)$$

where

$$t_0 = \frac{2\mu a^2}{\pi^2 \hbar}$$

Obviously

$$\int_0^a |\Psi(x, t)|^2 dx = 1$$

for all values of  $t$ . In Fig. 6.2 we have shown the time evolution of the probability distribution

$$P(x, t) = |\Psi(x, t)|^2$$

for  $\Psi(x, t)$  given by Eq. (46) at

$$\frac{t}{t_0} = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2} \text{ and } 2\pi$$

---

<sup>5</sup> A simple solution of the Schrödinger equation corresponding to a time dependent Hamiltonian is discussed in Sec. 14.6.

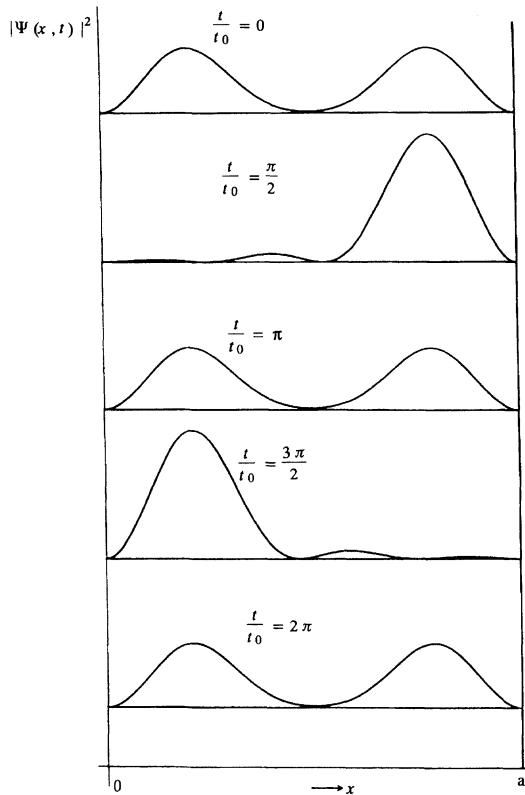


Figure 6.2. The time evolution of the probability distribution  $|\Psi(x, t)|^2$  corresponding to Eq. (46) at  $t/t_0 = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}$  and  $2\pi$ .

At all values of time, the probability of finding the system in a particular state remains the same. Further, the average value of the energy is given by

$$\begin{aligned}
 \langle E \rangle &= \frac{1}{6} E_1 + \frac{1}{2} E_2 + \frac{1}{3} E_3 \\
 &= \left[ \frac{1}{6} + 2 + 3 \right] \frac{\pi^2 \hbar^2}{2\mu a^2} \\
 &= \frac{31}{6} \frac{\pi^2 \hbar^2}{2\mu a^2}
 \end{aligned} \tag{47}$$

Thus, if one carries out a large number of measurements (of energy) on identical systems characterized by the same wave function as given by Eq. (46), then the average value of the energy would be given by Eq. (47).

- (vii) What happens to the wave function if  $E \neq E_n$ ; i.e. if  $E$  is not one of the eigenvalues? For such a case the boundary conditions cannot be satisfied and

therefore it cannot be an allowed value of energy. For example, if

$$E = \frac{0.81\pi^2\hbar^2}{2\mu a^2}$$

then for the wave function to vanish at  $x = 0$  we must have

$$\psi(x) = A \sin \frac{0.9\pi x}{a}$$

which cannot vanish at  $x = a$ .

### 6.6.2. PARTICLE IN A ONE-DIMENSIONAL POTENTIAL WELL OF FINITE DEPTH

We next consider the square well potential (Fig. 6.3)

$$\begin{aligned} V(x) &= 0 \quad \text{for } -\frac{a}{2} < x < \frac{a}{2} \\ &= V_0 \quad \text{for } |x| > \frac{a}{2} \end{aligned} \tag{48}$$

We first look for solutions corresponding to  $E < V_0$ . The Schrödinger equation can be written in the form

$$\begin{aligned} \frac{d^2\psi}{dx^2} + k^2 \psi(x) &= 0 \quad \text{for } |x| < \frac{a}{2} \\ \frac{d^2\psi}{dx^2} - \kappa^2 \psi(x) &= 0 \quad \text{for } |x| > \frac{a}{2} \end{aligned} \tag{49}$$

where

$$k^2 = \frac{2\mu E}{\hbar^2} \quad \text{and} \quad \kappa^2 = \frac{2\mu}{\hbar^2} (V_0 - E) \tag{50}$$

Since  $V(-x) = V(x)$ , the solutions are either symmetric or antisymmetric in  $x$ . Corresponding to the symmetric solution we may write

$$\begin{aligned} \psi(x) &= A \cos kx \quad |x| < \frac{a}{2} \\ &= B \exp[-\kappa|x|] \quad |x| > \frac{a}{2} \end{aligned} \tag{51}$$

where in the region  $|x| > a/2$ , we have rejected the solution  $\exp(\kappa|x|)$  because then  $\psi(x)$  will go to infinity as  $|x| \rightarrow \infty$ . Continuity of  $\psi(x)$  and  $d\psi/dx$  (see Sec. 6.2) at  $x = a/2$  leads to

$$A \cos \frac{ka}{2} = B \exp \left[ -\frac{\kappa a}{2} \right] \tag{52}$$

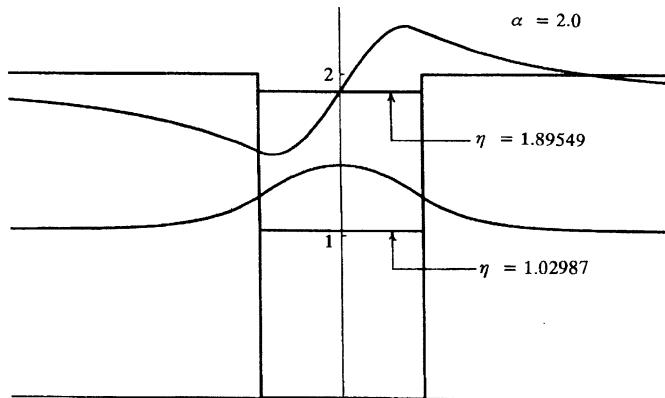


Figure 6.3. A potential well of finite depth. The eigenvalues and eigenfunctions correspond to  $\alpha = 2.0$ .

and

$$-Ak \sin \frac{ka}{2} = -B\kappa \exp \left[ -\frac{\kappa a}{2} \right] \quad (53)$$

For non-trivial solutions one gets

$$\tan \frac{ka}{2} = \frac{\kappa}{k} = \left[ \frac{V_0 - E}{E} \right]^{\frac{1}{2}} \quad (54)$$

The roots of the transcendental equation (54) determine the discrete values of  $E$  (for given values of  $\mu$ ,  $a$  and  $V_0$ ) and one has to use numerical or graphical methods to obtain the energy levels. For a particular value of  $E$ , the ratio  $A/B$  can be determined by using either Eq. (52) or Eq. (53) using which one can determine  $\psi(x)$  within a multiplicative constant. The value of  $A$  (and hence of  $B$ ) can be determined by using the normalization condition (see Problem 6.7).

It is of interest to point out that for  $V_0 \gg E$ , the RHS of Eq. (54) tends to  $\infty$  so that one obtains

$$\frac{ka}{2} = \left( p + \frac{1}{2} \right) \pi ; \quad p = 0, 1, 2, \dots$$

or

$$E = \frac{(2p+1)^2 \pi^2 \hbar^2}{2\mu a^2} ; \quad p = 0, 1, 2, \dots \quad (55)$$

which is the same as Eq. (32) with  $n$  now restricted to odd values because we have considered only the symmetric solution. Further for  $V_0 \rightarrow \infty$ ,  $\kappa$  will tend to  $\infty$  and the wave function would vanish in the region  $|x| > a/2$ .

For the antisymmetric solution (for which  $\psi$  is proportional to  $\sin kx$  inside the well and to  $\exp(-\kappa|x|)$  outside the well) the transcendental equation determining

the energy eigenvalues would be [cf. Eq. (54)].

$$\cot \frac{ka}{2} = -\frac{\kappa}{k} = -\left(\frac{V_0 - E}{E}\right)^{\frac{1}{2}} \quad (56)$$

which for  $V_0 \rightarrow \infty$  would give

$$E = \frac{(2p)^2 \pi^2 \hbar^2}{2\mu a^2}; \quad p = 1, 2, 3, \dots \quad (57)$$

Equations (54) and (56) can be put in the more convenient form

$$\eta \tan \eta = (\alpha^2 - \eta^2)^{\frac{1}{2}} \quad (\text{Symmetric case}) \quad (58)$$

$$-\eta \cot \eta = (\alpha^2 - \eta^2)^{\frac{1}{2}} \quad (\text{Antisymmetric case}) \quad (59)$$

where

$$\eta = \frac{ka}{2} = \left(\frac{2\mu E a^2}{4\hbar^2}\right)^{\frac{1}{2}}$$

and

$$\alpha = \left(\frac{2\mu V_0 a^2}{4\hbar^2}\right)^{\frac{1}{2}}$$

For a given value of  $\alpha$ , the right-hand sides of Eqs (58) and (59) are a portion of a circle and therefore the roots can easily be determined using numerical methods. In Fig. 6.4 we have plotted the functions  $\eta \tan \eta$  (solid curve) and  $-\eta \cot \eta$  (dotted curve) as a function of  $\eta$ . Their points of intersection with the portion of the circle determines the eigenvalues. It is easy to see that

for  $0 < \alpha < \pi/2$ , there will be only one symmetric state;

for  $\pi/2 < \alpha < \pi$ , there will be one symmetric and one antisymmetric state;

for  $\pi < \alpha < 3\pi/2$ , there will be two symmetric and one antisymmetric state;

etc.

**Example 6.1** As an example, we consider a proton (of mass  $1.67 \times 10^{-27}$  kg) inside a one-dimensional well with  $V_0 \simeq 25$  MeV  $\simeq 4 \times 10^{-12}$  J and  $a \simeq 3.65 \times 10^{-15}$  m. Thus

$$\alpha = \left(\frac{2\mu V_0 a^2}{4\hbar^2}\right)^{\frac{1}{2}} \simeq 2.0 \quad (60)$$

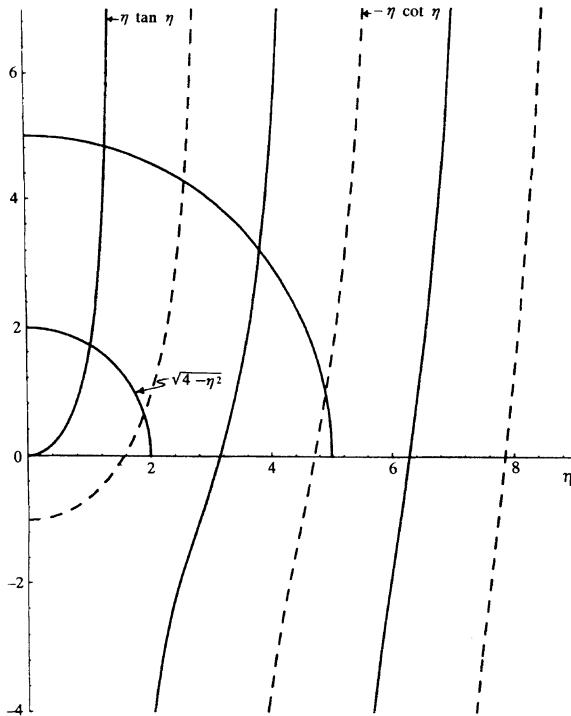


Figure 6.4. The variation of  $\eta \tan \eta$  (solid curve) and  $-\eta \cot \eta$  (dotted curve) as a function of  $\eta$ . The points of intersection of these curves with the quadrant of a circle of radius  $\alpha$  determine the discrete eigenvalues corresponding to the potential well of finite depth.

Since  $\alpha < \pi$ , there will be one symmetric state and one antisymmetric state; the roots of Eqs (58) and (59) for  $\alpha = 2$  are given by (see Fig. 6.3)

$$\begin{aligned} \eta &= 1.02987 \quad (\Rightarrow E \simeq 6.63 \text{ MeV}) \\ &\text{for the symmetric state and} \end{aligned}$$

$$\begin{aligned} \eta &= 1.89549 \quad (\Rightarrow E \simeq 22.45 \text{ MeV}) \\ &\text{for the antisymmetric state} \end{aligned}$$

Till now we have assumed  $E < V_0$ ; had we considered values of  $E > V_0$ , we would have found that all values of  $E$  (greater than  $V_0$ ) could be possible, i.e. the energy eigenvalues would be continuously distributed in the domain  $V_0 < E < \infty$ . However, the wave function would not have vanished at large distances from the origin (see Chapter 8). Such solutions are of great importance in connection with the scattering of a particle by a force field where the energy is specified in advance and the behaviour of the wave function at great distances is found in terms of energy.

## 6.7. Three-dimensional Schrödinger equation

In previous sections we had discussed the stationary states of the one-dimensional Schrödinger equation; the corresponding considerations for the three-dimensional equation are very straightforward. For example, by using the method of separation of variables, the solution of the time dependent Schrödinger equation

$$i \hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2\mu} \nabla^2 \Psi + V(\mathbf{r}) \Psi(\mathbf{r}, t) \quad (61)$$

is of the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp[-iEt/\hbar] \quad (62)$$

where  $\psi(\mathbf{r})$  is the solution of the eigenvalue equation [cf. Eq. (8)]

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (63)$$

and

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r}) = \frac{1}{2\mu} [p_x^2 + p_y^2 + p_z^2] + V(\mathbf{r}) \quad (64)$$

represents the Hamiltonian operator and  $E$  the energy eigenvalue. The potential energy function has been assumed to be independent of time. In general, the eigenvalues can have a discrete set along with a continuous range of eigenvalues and the general solution of Eq. (61) is of the form

$$\Psi(\mathbf{r}, t) = \sum_n c_n \psi_n(\mathbf{r}) \exp[-iEt/\hbar] \quad (65)$$

where  $\sum_n$  denotes a sum over the discrete states and an integration over the continuum.

Equation (64) is usually written in the form

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2} [E - V(\mathbf{r})] \psi(\mathbf{r}) = 0 \quad (66)$$

which is known as the three-dimensional time independent Schrödinger equation.

As in Sec. 6.2, the wave function satisfies continuity and boundary conditions. Thus

- (i) The wave function and its gradient are continuous everywhere as long as the potential energy function is finite.
- (ii) The wave function should also be single-valued everywhere so that it corresponds to a definite physical situation.

- (iii) For a degenerate state any linear combination of the degenerate eigenfunctions is also a possible eigenfunction.

The orthogonality of the wave functions can be proved by using a method similar to the one used in Sec. 6.4. Indeed, instead of Eqs (14) and (15), we will have

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi_n + V(\mathbf{r}) \psi_n = E_n \psi_n \quad (67)$$

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi_k + V(\mathbf{r}) \psi_k = E_k \psi_k \quad (68)$$

If we multiply Eq. (67) by  $\psi_k^*$  and multiply the complex conjugate of Eq. (68) by  $\psi_n$  and subtract, we would get

$$-\frac{\hbar^2}{2\mu} \int \nabla \cdot [\psi_k^* \nabla \psi_n - \psi_n \nabla \psi_k^*] d\tau = (E_n - E_k^*) \int \psi_k^* \psi_n d\tau$$

By using the Gauss theorem, the LHS becomes a surface integral

$$-\frac{\hbar^2}{2\mu} \int [\psi_k^* \nabla \psi_n - \psi_n \nabla \psi_k^*] \cdot \hat{\mathbf{n}} dS$$

where  $\hat{\mathbf{n}}$  represents the unit outward normal on the surface. The surface integral would vanish if the volume integral is over the entire space. Thus, as in Sec. 6.4, we will have

$$E_n = E_n^* \quad (69)$$

proving that all eigenvalues are real and the wave functions belonging to different energy levels are orthogonal. By appropriate normalization we can always have

$$\int \psi_k^* \psi_n d\tau = \delta_{kn} \quad (70)$$

which is the orthonormality condition. For degenerate states one can always construct appropriate linear combinations so that the orthonormality condition is satisfied (see Problem 6.3).

As a simple example, we will, in the next section, solve the three-dimensional Schrödinger equation for a particle inside a cube of length  $L$ .

## 6.8. Particle in a three-dimensional box

In this section we will solve the Schrödinger equation for a potential energy variation of the form

$$\begin{aligned} V(x, y, z) &= 0 \quad \text{for } 0 < x < L, 0 < y < L, 0 < z < L \\ &= \infty \quad \text{everywhere else} \end{aligned} \quad (71)$$

which represents a particle in an infinitely deep potential well inside a cube of side  $L$ . This problem has an important applications in many areas. For example, in the free electron theory of metals, the valence electrons can be approximately assumed to be free and confined inside a box (see Sec. 6.9). Similarly, the free electron theory allows us to understand the basic physics behind the white dwarf stars (see Sec. 6.10). The free electron theory is also the basis of the Thomas-Fermi model of the atom (see Sec. 23.6).

Now, the Schrödinger equation is given by

$$\nabla^2 \psi + \frac{2\mu E}{\hbar^2} \psi = 0 \quad \left\{ \begin{array}{l} 0 < x < L \\ 0 < y < L \\ 0 < z < L \end{array} \right. \quad (72)$$

with the boundary condition that  $\psi$  should vanish everywhere on the surface of the cube. We use the method of separation of variables and write  $\psi = X(x) Y(y) Z(z)$  to obtain

$$\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} = -\frac{2\mu E}{\hbar^2} \quad (73)$$

The first term is a function of  $x$  alone, the second term of  $y$  alone, etc., so that each term has to be set equal to a constant. We write

$$\frac{1}{X} \frac{d^2 X}{dx^2} = -k_x^2 \quad (74)$$

and similar Equations for  $Y(y)$  and  $Z(z)$  with

$$k_x^2 + k_y^2 + k_z^2 = \frac{2\mu E}{\hbar^2} \quad (75)$$

We have set each term equal to a negative constant; otherwise the boundary conditions cannot be satisfied. The solution of Eq. (74) is

$$X(x) = A \sin k_x x + B \cos k_x x \quad (76)$$

and since  $\psi$  has to vanish on all points on the surfaces  $x = 0$  and  $x = L$  we must have  $B = 0$  and  $k_x = n_x \pi / L$  with  $n_x = 1, 2, \dots$  (cf. Sec. 6.6.1). Similarly for  $k_y$

and  $k_z$ . Using Eq. (75) we get

$$E = \frac{\pi^2 \hbar^2}{2\mu L^2} (n_x^2 + n_y^2 + n_z^2) ; \quad n_x, n_y, n_z = 1, 2, 3, \dots \quad (77)$$

The corresponding normalized wave functions are

$$\psi(x, y, z) = \left(\frac{8}{L^3}\right)^{1/2} \sin \frac{n_x \pi}{L} x \sin \frac{n_y \pi}{L} y \sin \frac{n_z \pi}{L} z \quad (78)$$

#### 6.8.1. THE DENSITY OF STATES

If  $g(E)dE$  represents the number of states whose energy lies between  $E$  and  $E + dE$  then  $g(E)$  is known as the density of states and it represents a very important quantity in the theory of solids. In order to calculate  $g(E)$  we first calculate  $N(E)$  which represents the total number of states whose energies are less than  $E$ . Obviously

$$N(E) = \int_0^E g(E) dE \quad (79)$$

and therefore

$$g(E) = \frac{dN(E)}{dE} \quad (80)$$

Now,

$$n_x^2 + n_y^2 + n_z^2 = \frac{2\mu L^2 E}{\pi^2 \hbar^2} = R^2 \text{ (say)} \quad (81)$$

Thus  $N(E)$  will be the number of sets of integers whose sum of squares is less than  $R^2$ . In the  $n_x, n_y, n_z$  space each point corresponds to a unit volume and if we draw a sphere of radius  $R$  then the volume of the positive octant will approximately represent<sup>6</sup>  $N(E)$ ; we have to take the positive octant because  $n_x, n_y$  and  $n_z$  take positive values. Thus

$$N(E) = 2 \times \frac{1}{8} \times \frac{4\pi}{3} R^3 = \frac{(2\mu)^{3/2} L^3}{3\pi^2 \hbar^3} E^{3/2} \quad (82)$$

<sup>6</sup> If the reader finds it difficult to understand he may first try to make the corresponding two-dimensional calculations in which one is interested in finding the number of sets of integers such that  $n_x^2 + n_y^2 < R^2$ . If one takes a graph paper then each corner corresponds to a set of integers and each point can be associated with a unit area. Thus the number of sets of integers would be  $\pi R^2/4$  where the factor 1/4 is because of the fact that we are interested in the positive quadrant.

where an additional factor of 2 has been introduced as a state can be occupied by two electrons. Using Eq. (80) we get

$$g(E) = \frac{(2\mu)^{3/2} V}{2\pi^2 \hbar^3} E^{1/2} \quad (83)$$

where  $V (= L^3)$  represents the volume of the box.

Often it is more convenient to express the density of states in momentum space. Now for a free non-relativistic particle

$$E = \frac{p^2}{2\mu} \quad (84)$$

Thus the equation

$$g(p) dp = g(E) dE \quad (85)$$

would readily give

$$g(p) = \frac{V}{\pi^2 \hbar^3} p^2 \quad (86)$$

### 6.8.2. RELATIVISTIC CONSIDERATIONS

Equation (84) represents the non-relativistic relation between energy and momentum. The corresponding relativistic relation is given by

$$E^2 = p^2 c^2 + \mu^2 c^4 \quad (87)$$

where  $\mu$  represents the rest mass of the particle. Now, it so happens that if one solves Dirac's relativistic equation then the density of states in the momentum space is still given by Eq. (86) (see, e.g. Ref. 2). Since

$$E dE = c^2 p dp$$

we get

$$g(E) = \begin{cases} \frac{V}{\pi^2 \hbar^3 c^3} E(E^2 - \mu^2 c^4)^{1/2} & E \geq \mu c^2 \\ 0 & E < \mu c^2 \end{cases} \quad (88)$$

In the extreme relativistic limit

$$E \gg \mu c^2$$

we obtain

$$g(E) = \frac{V}{\pi^2 \hbar^3 c^3} E^2 \quad E \gg \mu c^2 \quad (89)$$

## 6.9. Free electrons in a metal

The problem corresponding to a particle in a box has a very important application in the free electron theory of metals where the valence electrons can be approximately assumed to be free and confined inside the metal. Now, the probability of finding an electron with energy  $E$  is given by the Fermi-Dirac function

$$F(E) = \frac{1}{1 + e^{(E-E_F)/kT}} \quad (90)$$

The quantity  $E_F$  is referred to as the Fermi energy. At absolute zero ( $T = 0$ ), we have

$$F(E) = \begin{cases} 1 & E < E_{F_0} \\ 0 & E > E_{F_0} \end{cases} \quad (91)$$

where the subscript zero implies that we are calculating the Fermi energy at  $T = 0$ . Equation (91) tells us that all states below the Fermi level are filled up and all states above the Fermi level are empty. For such a situation (when all the lowest quantum states are occupied), the electron gas is said to be *completely degenerate*. Now the total number of electrons (inside the box) is given by

$$N = \int_0^{\infty} g(E) F(E) dE \quad (92)$$

which at  $T = 0$  becomes

$$\begin{aligned} N &= \int_0^{E_{F_0}} g(E) dE \\ &= (2\mu)^{3/2} \frac{V}{2\pi^2 \hbar^3} \int_0^{E_{F_0}} E^{1/2} dE \\ &= (2\mu)^{3/2} \frac{V}{3\pi^2 \hbar^3} E_{F_0}^{3/2} \end{aligned} \quad (93)$$

Simple manipulations give us

$$E_{F_0} = \frac{\hbar^2}{2\mu} (3\pi^2 n)^{2/3} \quad (94)$$

where  $n (= N/V)$  represents the number of free electrons per unit volume. Substituting the numerical values of various constants we get

$$\begin{aligned} E_{F_0} &\approx 5.84 \times 10^{-27} n^{2/3} \text{ erg} \\ &\approx 3.65 \times 10^{-15} n^{2/3} \text{ eV} \end{aligned} \quad (95)$$

where  $n$  is measured in  $\text{cm}^{-3}$ . For example, for sodium with one free electron per atom and having a density of  $0.97 \text{ g/cm}^3$  we get

$$n \approx \frac{6.023 \times 10^{23} \times 0.97}{23} \simeq 2.54 \times 10^{22} \text{ electrons/cm}^3$$

Thus

$$E_{F_0} \approx 3.2 \text{ eV}$$

The total energy of the gas at absolute zero will be given by

$$\begin{aligned} \mathcal{E} &= \int_0^{E_{F_0}} E g(E) F(E) dE \\ &= \frac{(2\mu)^{3/2} V}{5\pi^2 \hbar^3} E_{F_0}^{5/2} \end{aligned} \quad (96)$$

If we use Eq. (93) we would get the following expression for average energy per particle

$$\langle E \rangle = \frac{\mathcal{E}}{N} = \frac{3}{5} E_{F_0} \quad (97)$$

In general, the Fermi energy  $E_F$  is dependent on temperature. However, when  $kT \ll E_{F_0}$ , we say that the electron gas is *strongly degenerate*—or, *almost completely degenerate*. In Problem 6.13 we will discuss the variation of  $E$  with temperature for a strongly degenerate gas and we will show

$$E_F(T) = E_F(T) = E_{F_0} \left[ 1 - \frac{\pi^2}{12} \left( \frac{kT}{E_{F_0}} \right)^2 + \frac{\pi^4}{720} \left( \frac{kT}{E_{F_0}} \right)^4 \dots \right] \quad (98)$$

and the average energy per electron is

$$\langle E \rangle = \frac{3}{5} E_{F_0} \left[ 1 + \frac{5\pi^2}{12} \left( \frac{kT}{E_{F_0}} \right)^2 \dots \right] \quad (99)$$

In order to get numerical appreciation of the corrections, we consider sodium for which  $E_{F_0} \approx 3.15$  eV. Thus, at  $T = 300^\circ\text{K}$  ( $kT \approx 0.0259$  eV)

$$\frac{kT}{E_{F_0}} \approx 8.2 \times 10^{-3}$$

and the correction terms in Eqs. (98) and (99) are very small. Indeed

$$E_F(300^\circ\text{K}) \approx E_{F_0}[1 - 5.5 \times 10^{-5} + 6 \times 10^{-10}]$$

and

$$\langle E \rangle \approx \frac{3}{5} E_{F_0}[1 - 2.8 \times 10^{-4} + \Lambda]$$

Even for  $T \approx 5000^\circ\text{K}$

$$\frac{kT}{E_{F_0}} \approx 0.137$$

and

$$E_F \approx 3.10 \text{ eV}$$

Thus even at such high temperatures, the corrections are very small. In Fig. 6.5 we

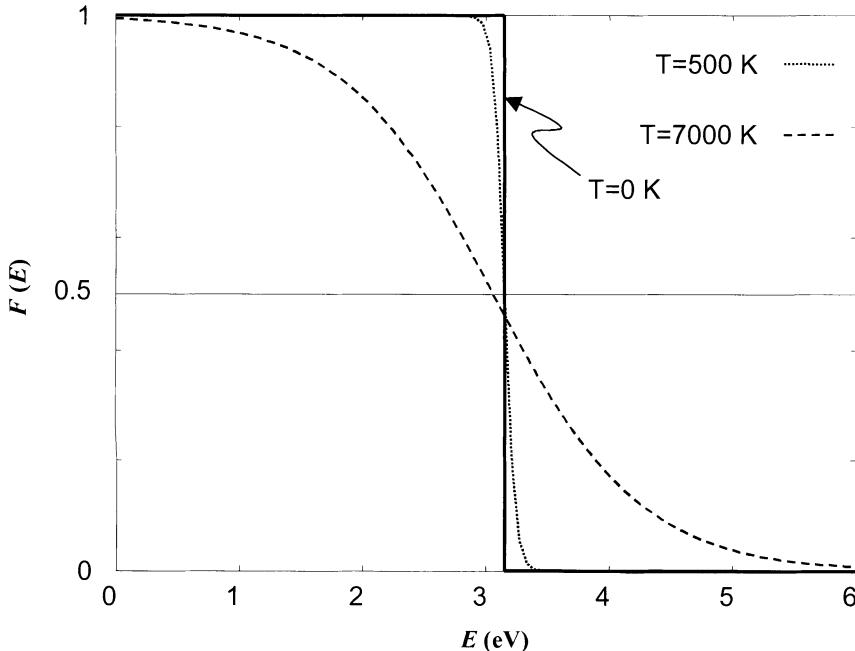


Figure 6.5. The Fermi-Dirac distribution function for sodium ( $E_{F_0} = 3.15$  eV) at  $0^\circ\text{K}$ ,  $50^\circ\text{K}$  and  $7000^\circ\text{K}$ .

have plotted the Fermi-Dirac distribution function for sodium at  $T = 0^\circ\text{K}$ ,  $500^\circ\text{K}$

and  $7000^{\circ}\text{K}$ . At  $T = 0^{\circ}\text{K}$ , the electron gas is in the lowest energy state and all states below are occupied. At  $T = 500^{\circ}\text{K}$ , the probability of occupancy remains very close to that at  $T = 0^{\circ}\text{K}$  except in the close vicinity of  $E = E_F$ . Because of this, it is extremely unlikely that the low energy electrons will get excited to higher energy states. Thus, when the temperature is raised, only those electrons which are within  $kT$  of  $E_F$  get excited to higher energy states. It is for this reason that the specific heat for the electron gas is much below the classical value. We will explicitly show this below. On the other hand, at  $T = 7000^{\circ}\text{K}$ , the occupancy probability is significantly different from that at  $T = 0^{\circ}\text{K}$ . Also, one can see that  $E_F$  (at which  $F(E) = \frac{1}{2}$ ) is visibly smaller than  $E_{F_0}$ ; at  $T = 500^{\circ}\text{K}$ , this difference is extremely small.

#### 6.9.1. THE SPECIFIC HEAT OF THE ELECTRON GAS

Assuming 1 free electron per atom, we will have  $N_0$  free electrons per kmol of the metal where

$$N_0 \approx 6.023 \times 10^{26} \text{ kmole}^{-1}$$

represents the Avagadro's number. Thus [using Eq. (99)] the total energy of the electron gas per kilomole of the metal would be

$$\varepsilon = N_0 \langle E \rangle \approx \frac{3}{5} N_0 E_{F_0} \left[ 1 + \frac{5\pi^2}{12} \left( \frac{kT}{E_{F_0}} \right)^2 + \Lambda \right] \quad (100)$$

The specific heat (at constant volume) of the electron gas would therefore be given by

$$\begin{aligned} (C_V)_{\text{electronic}} &= \left( \frac{\partial \varepsilon}{\partial T} \right)_V \\ &= \frac{\pi^2 N_0 k^2 T}{2 E_{F_0}} \end{aligned} \quad (101)$$

On the other hand, if electrons are assumed to behave like a classical gas, the average energy per electron would be

$$\langle E \rangle_{\text{cl}} = \frac{3}{2} kT \quad (102)$$

where the subscript 'cl' refers to the fact that we are considering a classical gas. Thus the total energy of the electron gas (per kilomole of the metal) would be given by

$$\varepsilon_{\text{cl}} = \frac{3}{2} RT \quad (103)$$

where  $R = N_0 k \approx 8.316 \times 10^3 \text{ J/kmol.K}$  represents the universal gas constant. From Eq. (103) we readily obtain

$$(C_V)_{\text{cl}} = \frac{3}{2}R = \frac{3}{2}N_0k \quad (104)$$

Thus

$$(C_V)_{\text{electronic}} = (C_V)_{\text{cl}} \left[ \frac{\pi^2 k T}{3E_{F_0}} \right] \quad (105)$$

Now for sodium at  $T \approx 300^\circ\text{K}$ ,

$$\frac{kT}{E_{F_0}} \approx 8.2 \times 10^{-3}$$

and therefore

$$(C_V)_{\text{electronic}} \approx \frac{1}{37}(C_V)_{\text{cl}}$$

In general, at normal temperatures since

$$\frac{kT}{E_{F_0}} \ll 1$$

the electronic contribution to the specific heat is much less than what would be expected if we had assumed the electrons to behave like a classical gas. This is indeed borne out by experimental data. The physical reason for this has been discussed at the end of the previous section. We may mention here that at high temperatures when  $kT \gg E_{F_0}$ , the Fermi energy EF becomes negative and we may neglect the unity in the denominator of Eq. (90) to obtain

$$F(E) \approx e^{E_F/kT} e^{-E/kT} \quad (106)$$

Thus if  $N(E)dE$  represents the number of electrons whose energies lie between  $E$  and  $E + dE$  then

$$\begin{aligned} N(E)dE &= g(E)F(E)dE \\ &= \text{const. } E^{1/2}e^{-E/kT}dE \end{aligned}$$

which corresponds to the classical Maxwellian distribution; using the above equation we would readily get Eq. (102). The total number of electrons would be given by

$$N = (2\mu)^{3/2} \frac{V}{2\pi^2\hbar^3} e^{E_F/kT} \int_0^\infty E^{1/2}e^{-E/kT}dE$$

Simple algebra and use of Eq. (94) would give

$$E_F = -kT \ln \left[ \frac{3\sqrt{\pi}}{4} \left( \frac{kT}{E_{F_0}} \right)^{3/2} \right] \quad (107)$$

showing that the Fermi energy becomes negative.

## 6.10. White dwarf stars

Another example of a highly degenerate electron gas is the inside of a white dwarf star where the electron densities are so high that the electron gas is in a highly degenerate state. In this section, we will discuss the basic physics associated with a white dwarf star. However, before we discuss the details, we should mention that in astrophysics almost everyone uses the cgs units and in these units, the values of some important constants (which we will be using) are given in Table 6.1.

*Table 6.1.* Values of some physical constants

Quantity	Symbol	Value
Mass of the hydrogen atom	$m_H$	$1.673 \times 10^{-24}$ g
Mass of the electron	$m_e$	$9.110 \times 10^{-28}$ g
Speed of light in vacuum	$c$	$2.998 \times 10^{10}$ cm/s
Planck's constant	$\hbar$	$1.055 \times 10^{-27}$ erg s
Gravitational constant	$G$	$6.672 \times 10^{-8}$ cm <sup>3</sup> s <sup>-2</sup> g <sup>-1</sup>
Mass of the sun	$M_S$	$1.989 \times 10^{33}$ g
Radius of the sun	$R_S$	$6.960 \times 10^{10}$ cm

We assume that the star to be in hydrostatic equilibrium under its own gravitation, i.e., the inward directed gravitational force exactly balances the outward directed force due to the gas pressure. We also assume the star to be of uniform density  $\rho$  (this is quite a drastic assumption; however, it allows us to obtain analytical results for important parameters associated with the star). Thus the mass of the spherical shell whose inner and outer radii are  $r$  and  $r + dr$  will be given by

$$dM = \rho 4\pi r^2 dr \quad (108)$$

We next consider the gravitational force acting on this spherical shell. Obviously, the mass lying outside the shell does not contribute and the gravitational force due to the sphere of radius  $r$  would be given by

$$\frac{G \left[ \rho \frac{4\pi}{3} r^3 \right] dM}{r^2} \quad (109)$$

where  $G$  represents the gravitational constant. The gravitational force will be directed inwards and if  $dP$  represents the increment in pressure over the distance  $dr$  then for the star to be in hydrostatic equilibrium we must have

$$-4\pi r^2 dP(r) = \frac{G [\rho \frac{4\pi}{3} r^3] dM}{r^2} \quad (110)$$

Using Eq. (108) we get

$$\frac{dP}{dr} = -\frac{4\pi}{3} G \rho^2 r \quad (111)$$

The above equation is the basic equation in understanding stellar structures—of course, under the assumption of the constancy of density inside the star. Carrying out the straightforward integration we get

$$P(r) = \frac{2\pi}{3} G \rho^2 (R^2 - r^2) \quad (112)$$

where  $R$  represents the radius of the star where the pressure vanishes. Thus the pressure at the center of the star is approximately given by

$$P_c = \frac{2\pi}{3} G \rho^2 R^2 \quad (113)$$

Now, for Sirius B (which is a white dwarf star)

$$\left. \begin{array}{l} M \approx 1.05 M_s \approx 2.1 \times 10^{33} \text{ g} \\ R \approx 5.5 \times 10^8 \text{ cm} \end{array} \right\} \quad (114)$$

where  $M_s$  and  $R_s$  represent the mass and radius of the sun; the corresponding values are given in Table 6.1. Equation (114) gives the following value for the average density of Sirius B

$$\rho \approx 3 \times 10^6 \text{ g/cm}^3 \quad (115)$$

Notice that the radius of the star is about 5500 km (which is slightly smaller than that of the earth) whereas the mass is about the same as that of the sun leading to extremely high densities (about  $3000 \text{ kg/cm}^3$ ). At such high densities, inspite of very high temperatures, the electrons may form a degenerate gas. We may mention that in a white dwarf star the densities are such that whereas the electron gas is in a degenerate state, the gas consisting of protons and other nuclei is in a non-degenerate state so that the perfect gas law is applicable to these nuclei. However, the pressure due to the gas formed by these nuclei is usually negligible in comparison to the pressure due to the degenerate electron gas and therefore we need only consider the pressure due to the degenerate electron gas.

Returning to Eq. (113) if we substitute the values of  $R$  and  $\rho$  (for Sirius B) we would get

$$P_c \approx 4 \times 10^{23} \text{ dynes/cm}^2 \quad (116)$$

The above expression may be compared with the pressure at the center of the sun which is about  $1.2 \times 10^{17}$  dynes/cm<sup>2</sup>. Thus the pressure at the center of the white dwarf star Sirius B is about 3 million times more than the pressure at the center of the sun! Further, because of very high temperatures, the stellar matter is in a completely ionized state; thus, if we assume the atoms are of atomic number  $Z$  and atomic weight  $A$ , the number of electrons per unit volume will be given by

$$n_e = \frac{Z}{A} \frac{\rho}{m_H} \quad (117)$$

where  $m_H$  represents the mass of the (neutral) hydrogen atom. Assuming that the stellar matter contains primarily heavy elements (which is indeed true for white dwarf stars), we may write  $A/Z \approx 2$ ; thus, for  $\rho \approx 3 \times 10^6$  g/cm<sup>3</sup>, we get

$$n_e \approx 9 \times 10^{29} \text{ cm}^{-3}$$

For the above value of  $n_e$ , Eq.(94) would give

$$E_{F_0} \approx 0.3 \text{ MeV}$$

We may note two points:

1. At  $T \approx 10^7$  K

$$\frac{E_{F_0}}{kT} \approx 400 \gg 1$$

Thus even at such high temperatures, the electron gas can be assumed to be almost completely degenerate.

2. The value of  $E_{F_0}$  ( $\approx 0.3$  MeV) may be compared with the rest mass energy of the electron which is about 0.5 MeV. Thus we should use relativistic expressions relating energy and mass. Nevertheless, we will use non-relativistic formulae and hope that their use should at least give us values which will be of the right order.

Now, in the non-relativistic theory, the pressure due to the degenerate electron gas is given by<sup>7</sup>

$$P = \frac{2}{5} n_e E_{F_0} = \frac{\hbar^2}{5\mu} (3\pi^2)^{2/3} n_e^{5/3} \quad (118)$$

<sup>7</sup> In the elementary kinetic theory of a gas, the pressure is given by (see, e.g., Sec. 23.5 of Ref. 1)

$$P = \frac{2}{3} n \langle E \rangle$$

where  $\langle E \rangle$  represents the average kinetic energy of the gas particles. If we now use Eqs. (94) and (97), we would get Eq. (118).

Thus

$$P = \frac{\hbar^2}{5\mu} (3\pi^2)^{2/3} \left[ \frac{Z}{A} \frac{\rho}{m_H} \right]^{5/3} \quad (119)$$

Assuming the pressure is primarily due to the degenerate electron gas, we will have

$$\frac{2\pi}{3} G \rho^2 R^2 = \frac{\hbar^2}{5\mu} (3\pi^2)^{2/3} \left[ \frac{Z}{A} \frac{\rho}{m_H} \right]^{5/3} \quad (120)$$

Since

$$\rho = \frac{M}{\frac{4\pi}{3} R^3} \quad (121)$$

We get after simple manipulations

$$R_{wd} = \frac{3}{5} \left( \frac{3\pi^2}{2} \right)^{1/3} \frac{\hbar^2}{\mu G} \left( \frac{Z}{Am_H} \right)^{5/3} \frac{1}{M_{wd}^{1/3}} \quad (122)$$

where the subscript *wd* stands for white dwarf. If we substitute the numerical values of various constants (see Table 6.1), and assume  $A/Z \approx 2$ , we would get

$$R_{wd} = \frac{3.6 \times 10^{19}}{M_{wd}^{1/3}} \text{ cgs units} \quad (123)$$

where  $R_{wd}$  is in centimeters and  $M_{wd}$  is in grams. For Sirius B,  $M \approx 2.1 \times 10^{33}$  g, and Eq. (123) would give us  $R \approx 2.8 \times 10^8$  cm; although it is much smaller than the actual value of  $R$ , we do get the correct order. The discrepancy is due to neglect of relativistic effects and the assumption of constancy of density of stellar matter.

Equation (123) gives the very important result that higher the mass of the white dwarf star, smaller will be the radius—leading to higher densities. Although, this is borne out by experimental data on white-dwarf stars, Eq.(122) predicts that as the mass tends to become extremely large, the radius of the star approaches zero! This is incorrect because as the densities become higher, relativistic effects become more important. Indeed, in the extreme relativistic limit, one gets the following expression for the pressure [see, e.g., Ref. 2]

$$P \approx \frac{(3\pi^2)^{1/3}}{4} \hbar c \left[ \frac{Z}{A} \frac{\rho}{m_H} \right]^{4/3} \quad (124)$$

If we equate this to the gravitational pressure given by Eq.(113) we would get

$$M \approx \frac{3}{4} \sqrt{\frac{\pi}{2}} \left( \frac{\hbar c}{G} \right)^{3/2} \left( \frac{Z}{Am_H} \right)^2 \quad (125)$$

The above is indeed a remarkable result—in the sense that the limiting mass depends mainly only on the values of some universal constants. If we substitute the values of various constants, and assume  $A/Z \approx 2$ , we would get

$$M = 0.87 \times 10^{33} \text{ g} \approx 0.44M_s \quad (126)$$

In fact, if one carries out a more careful analysis (in particular, if one takes into account the density variation inside the star) one gets

$$M = M_{Ch} = 2.86 \times 10^{33} \text{ g} \approx 1.44M_s \quad (127)$$

This limiting mass is known as the *Chandrasekhar limit* [and hence the subscript ‘Ch’]—after the famous Indian physicist S. Chandrasekhar who had derived this result [for a detailed account of Chandrasekhar’s work on white dwarf stars we refer the reader to his classic treatise entitled *Introduction to the Study of Stellar Structures* (Ref. 2)]. Equation (127) is consistent with experimental data on white-dwarf stars.

## 6.11. Neutron stars

While collapsing, if the mass of the degenerate core (of the star) is close to the Chandrasekhar limit ( $\approx 1.44M_s$ ), the electron energy becomes so large that the following capture process takes place



resulting in the formation of a neutron star in which the gravitational pressure is balanced by the pressure due to the degenerate neutron gas. Assuming that a neutron star consists only of neutrons, the neutron density would be given by [cf. Eq. (117)]

$$n_n = \frac{\rho}{m_n} \quad (129)$$

where  $m_n$  represents the mass of the neutron. Thus Eq. (120) takes the form

$$\frac{2\pi}{3} G \rho^2 R^2 = \frac{\hbar^2}{5m_n} (3\pi^2)^{2/3} \left[ \frac{\rho}{m_n} \right]^{5/3} \quad (130)$$

If we now use Eq. (121) and simplify we would get

$$R_{ns} = \frac{3}{5} \left( \frac{3\pi^2}{2} \right)^{1/3} \frac{\hbar^2}{G} \left( \frac{1}{m_n} \right)^{8/3} \frac{1}{M_{ns}^{1/3}} \quad (131)$$

where  $R_{ns}$  and  $M_{ns}$  represent respectively the mass and the radius of the neutron star. For  $M_{ns} \approx 1.4M_s \approx 2.78 \times 10^{33} \text{ g}$ , we obtain

$$R_{ns} \approx 4.4 \text{ km} \quad (132)$$

Because of the assumption of constancy of density, the above value of the radius may be an underestimate by a factor of about 2 or 3—so assuming

$$R_{ns} \approx 10 \text{ km} \quad (133)$$

we obtain the following value for the average density.

$$\rho \approx 7 \times 10^{14} \text{ g/cm}^3$$

which is indeed an enormous number—even greater than the density of nuclear matter.

## 6.12. Conclusions

In this chapter we have obtained bound state solutions of the one- and three-dimensional Schrödinger equations for some specific potential energy distributions. In the next chapter we will obtain solutions of the one-dimensional Schrödinger equation for the linear harmonic oscillator problem and discuss the relation with the classical oscillator.

In chapter 10 we will show that as long as the potential is spherically symmetric (i.e. as long as the potential depends only on the magnitude of the distance from a fixed point), the angular part of the wave function is a spherical harmonic and the potential energy function enters only in the radial part of the equation. In the same chapter we will solve the hydrogen atom problem and obtain the discrete states for the Coulomb potential and will show that the results are consistent with the experimental data.

## 6.13. Problems

**Problem 6.1 (a)** Show that the eigenvectors of the Hermitian matrix

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

are orthogonal to each other. Normalize these vectors to form a complete set of orthonormal vectors.

**(b)** Repeat the calculation for the matrices

$$\begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

and

$$\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

**Problem 6.2** In order to determine the boundary condition of  $V(x)$  going to infinity at a particular value of  $x$  (say  $x = 0$ ), we consider the following limiting process: assume  $V(x) = 0$  for  $x < 0$  and  $V(x) = V_0$  for  $x > 0$ ; in the limit of  $V_0 \rightarrow \infty$ , show that  $\psi$  vanishes in the region  $x > 0$ .

**Problem 6.3** Let  $\phi_1, \phi_2, \dots, \phi_g$  represent a set of linearly independent eigenfunctions corresponding to a degenerate state. Construct appropriate linear combinations so that the wave functions form an orthonormal set.

**Problem 6.4** Discuss the eigenvalues and eigenfunctions of the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

Show that the vectors

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

belong to the degenerate state but do not form an orthonormal set. Use the results of the previous problem to obtain an orthonormal set.

**Problem 6.5** Consider the potential energy variation given by

$$V(x) = \begin{cases} \infty & x \leq 0 \\ 0 & 0 < x < b \\ V_0 & x \geq b \end{cases} \quad (134)$$

(a) Derive the transcendental equation determining the energy eigenvalues for the bounded states. Show that they correspond to the antisymmetric states for the potential energy distribution given by Eq. (48) with  $b = a/2$ .

(b) Obtain the normalized wave function.

(c) Assuming

$$\frac{2\mu V_0 b^2}{\hbar^2} = 9\pi^2$$

show that there will be three bound states with

$$\xi = 2.83595, 5.64146 \text{ and } 8.33877$$

where

$$\xi = \sqrt{\frac{2\mu E b^2}{\eta^2}}$$

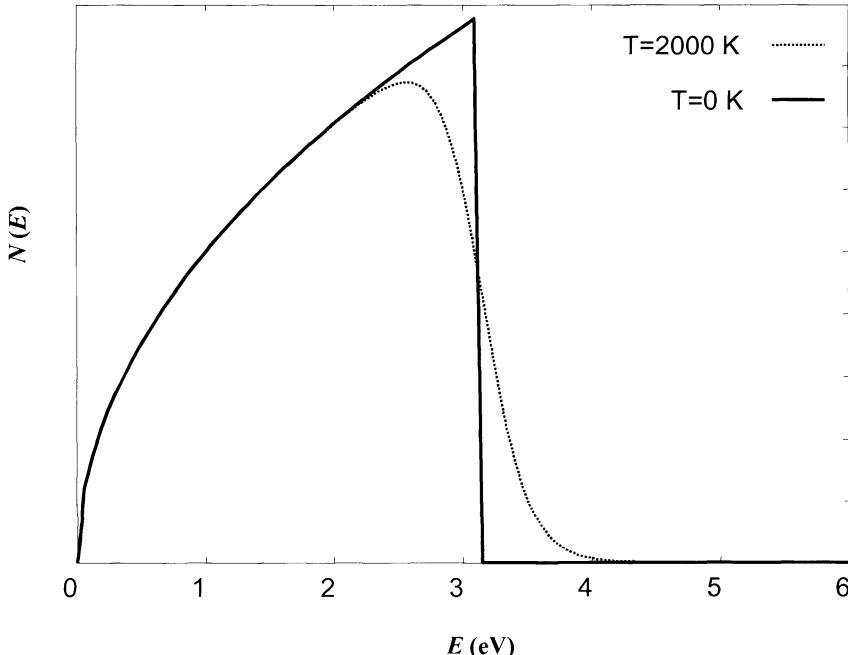


Figure 6.6. A plot of  $N(E)$  for sodium at  $T = 0^\circ\text{K}$  and  $2000^\circ\text{K}$ .

**Problem 6.6** For the one-dimensional potential well (see Sec. 6.6.2) derive the transcendental equations determining the discrete eigenvalues [i.e., Eqs. (58) and (59)] without making the assumption that the wave functions have to be symmetric and antisymmetric functions of  $x$ .

**Problem 6.7** Use the normalization condition to determine the values of  $A$  and  $B$  in Eq. (51).

**Problem 6.8** For copper we may assume one free electron per atom. Its density is about  $8.94 \text{ g/cm}^3$  and its atomic mass is 63.5. Calculate  $E_{F_0}$  and show that at room temperatures ( $T \approx 300^\circ\text{K}$ ), the electron gas is almost completely degenerate.

[Ans:  $E_{F_0} \approx 7.0 \text{ eV}$ ]

**Problem 6.9 (a)** In the free electron theory if  $N(E)dE$  represents the number of electrons/unit volume whose energy lie between  $E$  and  $E + dE$ , show that it is given by

$$N(E) = \frac{3n/2}{e^{(E-E_F)/kT} + 1} E_{F_0}^{-3/2} E^{1/2} \quad (135)$$

where  $n$  represents the total number of electrons per unit volume.

**(b)** For sodium plot  $N(E)$  as a function of  $E$  for  $T = 0^\circ\text{K}$  and  $2000^\circ\text{K}$  (see Fig. 6.6). Assume  $E_F(T) \approx E_{F_0} \approx 3.15 \text{ eV}$ . Justify this assumption.

**Problem 6.10 (a)** Assume the sun to consist only of free electrons and protons. Using the data given in Table 6.1, calculate for proton gas and for the electron gas.

(b) Inside the sun we may assume  $T \approx 10^7^\circ\text{K}$  calculate  $E_{F_0}/kT$  in each case.

[Ans: 0.018 eV and 33 eV for the proton and electron gas.]

**Problem 6.11** Assuming the density of the neutron star to be  $7 \times 10^{14} \text{ g/cm}^3$ , calculate and compare with rest mass energy.

[Ans:  $E_{F_0} \approx 100 \text{ MeV}$ ]

**Problem 6.12 (a)** Using the data given in Problem 6.8 calculate  $E_F$  for copper at  $1000^\circ\text{K}$ .

(b) Evaluate  $dF/dE$  and plot it for  $T = 1000^\circ\text{K}$ . Show that it is a very sharply peaked function around  $E = E_F$ .

(c) At  $T = 0$ , show that  $dF/dE$  is a delta function.

**Problem 6.13** Assuming  $E_{F_0}/kT \gg 1$ , derive Eqs.(98) and (99).

[Hint: Integrate Eq. (92) (and a similar equation for  $\varepsilon$ ) by parts and use the previous problem].

**Problem 6.14** Consider the potential energy variations given by

$$\begin{aligned} V(x) &= \infty \quad x < 0 \\ &= \gamma x \quad x > 0 \end{aligned} \quad (136)$$

Show that the solution of the Schrödinger equation can be written in terms of Airy function (see Appendix D) and that the energy eigenvalues are given by

$$E_n = \left( \frac{\hbar^2 \gamma^2}{2m} \right)^{1/3} \varepsilon_n \quad (137)$$

where

$$\varepsilon_1 = 2.33811; \quad \varepsilon_2 = 4.08795; \quad \varepsilon_3 = 5.52056; \quad \text{etc.} \quad (138)$$

**Problem 6.15** Show that for

$$V(x) = -S\delta(x) \quad (139)$$

there is only one bound state with

$$E = -\frac{\mu S^2}{2\hbar^2} \quad (140)$$

What is the corresponding eigenfunction?

**Problem 6.16 (a)** Solve the one-dimensional Schrödinger equation for

$$\begin{aligned} V(x) &= -V_0 \quad |x| < \frac{a}{2} \\ &= 0 \quad |x| > \frac{a}{2} \end{aligned} \quad (141)$$

and derive the transcendental equation which would determine the energy eigenvalues.

(b) Show that if we let  $a \rightarrow 0$  and  $V_0 \rightarrow \infty$  such that

$$aV_0 \rightarrow S$$

we would obtain only one bound state with energy as given in the previous problem.

## 6.14. Solutions

**Solution 6.1 (a)** The eigenvalues are  $+1$ ,  $-1$  and  $2$ ; the corresponding normalized eigenvectors are

$$\psi_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}; \quad \psi_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}; \quad \psi_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Further

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \frac{(a+b)}{\sqrt{2}}\psi_1 + \frac{(a-b)}{\sqrt{2}}\psi_2 + c\psi_3$$

showing that an arbitrary vector can be written as a linear combination of  $\psi_1$ ,  $\psi_2$  and  $\psi_3$ .

**Solution 6.2** Since  $V(x) = 0$  for  $x < 0$  and  $V = V_0$  for  $x > 0$  the solution of the Schrödinger equation is

$$\begin{aligned} \psi(x) &= A \sin kx + B \cos kx \quad \text{for } x < 0 \\ &= C e^{-\kappa x} \quad \text{for } x > 0 \end{aligned}$$

where  $k = (2\mu E/\hbar^2)^{1/2}$  and  $\kappa = [2\mu(V_0 - E)/\hbar^2]^{1/2}$ ; we have assumed  $V_0 > E$  and rejected the solution  $e^{\kappa x}$  which goes to  $\infty$  as  $x \rightarrow \infty$ . Continuity of  $\psi$  and  $d\psi/dx$  at  $x = 0$  gives

$$\begin{aligned} C &= B \\ C &= -\frac{k}{\kappa}A = -\left(\frac{1}{\frac{V_0}{E} - 1}\right)^{1/2} A \end{aligned}$$

Thus as  $V_0 \rightarrow \infty$ ,  $C \rightarrow 0$  (and hence  $B \rightarrow 0$ ) implying that  $\psi = 0$  for  $x \geq 0$ .

**Solution 6.3** Let

$$v_1 = \phi_1, \quad \psi_1 = \frac{v_1}{l_1}, \quad l_1 = \left[ \int v_1^* v_1 dx \right]^{1/2} \quad (142)$$

$v_1$  is known as the length of the vector  $v_1$ . We next define

$$v_2 = \phi_2 - c_{21}\psi_1, \quad \psi_2 = \frac{v_2}{l_2}, \quad l_2 = \left[ \int v_2^* v_2 dx \right]^{1/2} \quad (143)$$

$c_{21}$  is such that  $v_2$  is orthogonal to  $\psi_1$ .

$$0 = \int v_2 \psi_1^* dx = \int \phi_2 \psi_1^* dx - c_{21}$$

or

$$c_{21} = \int \phi_2 \psi_1^* dx$$

similarly

$$v_3 = \phi_3 - c_{31}\psi_1 - c_{32}\psi_2, \quad \psi_3 = \frac{v_3}{l_3}, \quad l_3 = \left[ \int v_3^* v_3 dx \right]^{1/2} \quad (144)$$

$$c_{31} = \int \psi_1^* \phi_3 dx \quad \text{and} \quad c_{32} = \int \psi_2^* \phi_3 dx$$

are such that  $v_3$  is orthogonal to  $\psi_1$  and  $\psi_2$ . In general

$$v_{n+1} = \phi_{n+1} - \sum_{m=1}^n \left[ \int \psi_m^* \phi_{n+1} dx \right] \psi_m$$

$$\psi_{n+1} = \frac{v_{n+1}}{l_{n+1}}, \quad l_{n+1} = \left[ \int v_{n+1}^* v_{n+1} dx \right]^{1/2}$$

Thus  $v_1, v_2, \dots$  form an orthonormal set. This is known as *Schmidt's orthogonalization procedure*.

**Solution 6.4** We choose

$$\psi_1 = v_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

then

$$c_{21} = (1 \ 1 \ 0) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 1$$

so that

$$v_2 = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} - \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \psi_2$$

$\psi_1$  and  $\psi_2$  form an orthonormal set correspond to the degenerate eigenvalue. It may be mentioned that

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}$$

also form an orthonormal set. Thus there can be infinite number of orthonormal sets.

### Solution 6.5

$$\begin{aligned}\psi(x) &= A \sin kx \\ &= A \sin kbe^{-\kappa(x-b)}\end{aligned}$$

Continuity of  $d\psi/dx$  at  $x = b$  will give us

$$-\xi \cot \xi = \sqrt{\alpha^2 - \xi^2} \quad (145)$$

where

$$\alpha^2 = \frac{2\mu V_0 b^2}{\hbar^2}$$

and

$$\xi^2 = \frac{2\mu E b^2}{\hbar^2}$$

The normalization condition will give us

$$A = \frac{1}{\sqrt{b}} \left[ \frac{1}{2} - \frac{\sin 2\xi}{4\xi} + \frac{\sin^2 \xi}{2\sqrt{\alpha^2 - \xi^2}} \right]^{-1/2} \quad (146)$$

**Solution 6.6** The wave function which would not blow up as  $x \rightarrow \pm\infty$  would be given by

$$\psi = \begin{cases} Ae^{\kappa x} & \text{for } x < -a/2 \\ B \sin kx + C \cos kx & \text{for } -a/2 < x < a/2 \\ De^{-\kappa x} & \text{for } x > a/2 \end{cases} \quad (147)$$

Continuity of  $\psi$  and  $d\psi/dx$  at  $x = \pm a/2$  will give us four equations from which we may obtain

$$\begin{aligned}2B \sin \eta &= (D - A)e^{-\xi}, \quad 2kB \cos \eta = \kappa(-D + A)e^{-\xi} \\ 2C \cos \eta &= (D + A)e^{-\xi}, \quad 2kC \sin \eta = \kappa(D + A)e^{-\xi}\end{aligned}$$

where  $\eta = ka/2$  and  $\xi = \kappa a/2$ . From this we immediately see that either  $B = 0$  and  $D = A$  (the symmetric solution) and one obtains Eq. (58), or  $C = 0$  and  $D = -A$  (the antisymmetric solution) and one obtains Eq. (59).

**Solution 6.7** For the symmetric mode

$$B = \left[ \exp\left(\frac{\kappa a}{2}\right) \cos\left(\frac{\kappa a}{2}\right) \right] a$$

and the normalization condition gives us

$$|A| = \left( \frac{2}{a} \right)^{1/2} \left[ 1 + \frac{\sin ka}{ka} + \frac{2 \cos^2(ka/2)}{\kappa a} \right]^{-1/2}$$

**Solution 6.13** For metals like Na, Cu, etc.,  $E_{F_0} \approx$  few eV, since  $kT \approx 0.025$  eV (at  $T \approx 300K$ ).  $E_{F_0}/kT \gg 1$ . Now

$$\begin{aligned} N &= \int_0^\infty g(E) F(E) dE \\ &= \frac{(2\mu)^{3/2} V}{2\pi^2 \hbar^3} \left[ \frac{2}{3} E^{3/2} F(E) \Big|_0^\infty - \frac{2}{3} \int_0^\infty E^{3/2} \frac{dF}{dE} dE \right] \\ &= -\frac{(2\mu)^{3/2} V E_F^{3/2}}{3\pi^2 \hbar^3} \int_{-E_F/kT}^\infty \left( 1 + \frac{xkT}{E_F} \right)^{3/2} \frac{dF}{dx} dx \end{aligned}$$

where  $x = (E - E_F)/kT$ . Assuming  $E_{F_0}/kT \gg 1$  and since  $dF/dx$  is very sharply peaked around  $x = 0$ , we replace the lower limit by  $-\infty$ , expand  $(1 + xkT/E_F)^{3/2}$  in a binomial series and integrate term by term to obtain<sup>8</sup>

$$\begin{aligned} N &= -\frac{(2\mu)^{3/2} V E_F^{3/2}}{3\pi^2 \hbar^3} \left[ [F(x)]_{-\infty}^{+\infty} + 0 - \frac{3}{8} \left( \frac{kT}{E_F} \right)^2 \int_{-\infty}^{+\infty} \frac{x^2 e^x}{(1 + e^x)^2} + \Lambda \right] \\ &= \frac{(2\mu)^{3/2} V E_F^{3/2}}{3\pi^2 \hbar^3} \left[ 1 + \frac{\pi^2}{8} \left( \frac{kT}{E_F} \right)^2 \right] \end{aligned}$$

8

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{x^2 e^x}{(1 + e^x)^2} dx &= 2 \int_{-\infty}^{\infty} x^2 e^{-x} (1 + e^{-x})^{-2} dx \\ &= 2 \left[ \int_{-\infty}^{\infty} x^2 (e^{-x} - 2e^{-2x} + \Lambda) dx \right] \\ &= 4 \left[ 1 - \frac{1}{2^2} + \frac{1}{3^2} - \Lambda \right] = \frac{\pi^2}{3} \end{aligned}$$

or,

$$E_F = E_{F_0} \left[ 1 + \frac{\pi^2}{8} \left( \frac{kT}{E_F} \right)^2 \right]^{-2/3}$$

Thus

$$E_F(T) \approx E_{F_0} \left[ 1 - \frac{\pi^2}{12} \left( \frac{kT}{E_{F_0}} \right)^2 + \Lambda \right]$$

Similarly

$$\begin{aligned} \langle E \rangle &= \int_0^\infty Eg(E)F(E)dE \\ &\approx \frac{(2m)^{3/2}VE_F^{5/2}}{3\pi^2\hbar^3} \int_{-\infty}^{+\infty} \left[ 1 + \frac{xkT}{E_F} \right]^{5/2} F(x)dx \end{aligned}$$

from which we get

$$\langle E \rangle \approx \frac{3}{5}nE_{F_0} \left[ 1 + \frac{5\pi^2}{12} \left( \frac{kT}{E_{F_0}} \right)^2 + \Lambda \right]$$

**Solution 6.14** In the region  $0 < x < \infty$ , the Schrödinger equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} [E - \gamma x]\psi(x) = 0 \quad (148)$$

which can be written in the form

$$\frac{d^2\psi}{d\xi^2} - \xi\psi(\xi) = 0 \quad (149)$$

where

$$\xi = X - \varepsilon \quad (150)$$

with

$$X = \frac{\gamma}{\alpha}x, \quad \varepsilon = \frac{E}{\alpha} \quad \text{and} \quad \alpha = \left( \frac{\hbar^2\gamma^2}{2\mu} \right)^{1/3}$$

The solution of Eq. (149) is given by

$$\psi(\xi) = C_1Ai(\xi) + C_2Bi(\xi) \quad (151)$$

Since  $Bi(\xi) \rightarrow \infty$  as  $\xi \rightarrow \infty$  (see Fig. 2 of Appendix D), we must choose  $C_2 = 0$ . Further, since  $V(x) = \infty$  for  $x < 0$ , we must have

$$\psi(x = 0) = 0 \quad (152)$$

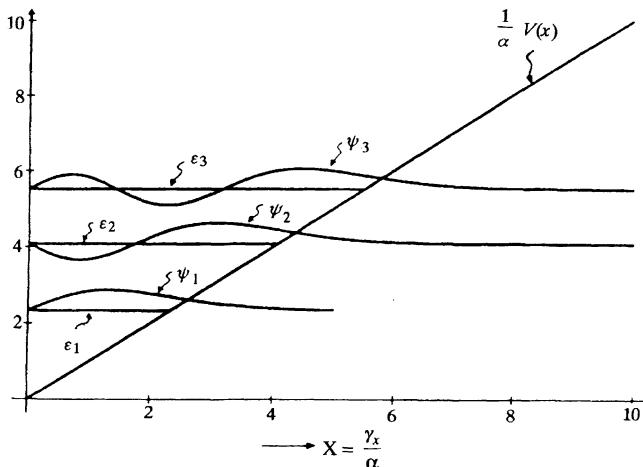


Figure 6.7. The potential energy distribution as given by Eq. (136). The first three eigenvalues and the corresponding eigenfunctions are also shown.

implying

$$\psi(\xi = -\varepsilon) = 0 \quad (153)$$

or,

$$Ai(-\varepsilon) = 0 \quad (154)$$

Now  $Ai(\xi) = 0$  for

$$\xi = a_n = -2.33811, -4.08795, -5.52056, \dots \quad (155)$$

using which we readily get Eq. (137), the corresponding eigenfunctions being

$$\psi_n(x) = (\text{const})Ai(\xi) = (\text{const})Ai(X + a_n) \quad (156)$$

where  $a_n$  represent the zeros of the Airy function [see Eq. (155) and Table 1 of Appendix D]. The energy eigenvalues are shown as horizontal lines in Fig. 6.7 along with the corresponding eigenfunctions.

**Solution 6.15** The Schrödinger equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}[E + S\delta(x)]\psi(x) = 0 \quad (157)$$

Thus for  $x < 0$  and  $x > 0$ ,  $\psi(x)$  will satisfy the equation

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi(x) = 0 \quad x < 0 \text{ and } x > 0 \quad (158)$$

where

$$\kappa^2 = -\frac{2\mu E}{\hbar^2} \quad (159)$$

For bound states  $E$  is negative and therefore  $\kappa^2$  is a positive quantity. The solution of Eq. (158) which vanishes as  $x \rightarrow +\infty$  and  $x \rightarrow -\infty$  would be given by

$$\begin{aligned}\psi(x) &= Ae^{-\kappa x} \quad x > 0 \\ &= Ae^{\kappa x} \quad x < 0\end{aligned}\quad (160)$$

which takes into account the continuity of  $\psi(x)$  at  $x = 0$ . Now, integrating Eq. (157) we obtain

$$\int_{-\varepsilon}^{+\varepsilon} \frac{d^2\psi}{dx^2} dx = -\frac{2\mu E}{\hbar^2} \int_{-\infty}^{+\infty} \psi(x) dx - \frac{2\mu S}{\hbar^2} \int_{-\varepsilon}^{+\varepsilon} \delta(x)\psi(x) dx$$

where  $\varepsilon$  is an infinitesimally small quantity. Since  $\psi(x)$  is continuous at  $x = 0$ , the first term on the RHS of the above equation would vanish and we would get

$$\left. \frac{d\psi}{dx} \right|_{x=\varepsilon} - \left. \frac{d\psi}{dx} \right|_{x=-\varepsilon} = -\frac{2\mu S}{\hbar^2} \psi(0) = -\frac{2\mu SA}{\hbar^2} \quad (161)$$

From Eq. (160), we would get

$$\left. \frac{d\psi}{dx} \right|_{x=\varepsilon} - \left. \frac{d\psi}{dx} \right|_{x=-\varepsilon} = -2A\kappa \quad (162)$$

Thus

$$\kappa = \frac{\mu S}{\hbar^2} \quad (163)$$

or

$$E = -\frac{\mu S^2}{2\hbar^2} \quad (164)$$

The corresponding normalized eigenfunction is given by (see also Example 1.1)

$$\psi(x) = \sqrt{\frac{\mu S}{\hbar^2}} \exp\left[-\frac{\mu S}{\hbar^2}|x|\right] \quad (165)$$

**Solution 6.16** The transcendental equation determining the energy eigenvalues corresponding to symmetric states is given by

$$\xi \tan \xi = \sqrt{\sigma^2 - \xi^2} \quad (166)$$

where

$$\xi = \left[ \frac{\mu}{2\hbar^2} (V_0 + E) a^2 \right]^{1/2} \quad (167)$$

and

$$\sigma^2 = \frac{\mu}{2\hbar^2} V_0 a^2 \quad (168)$$

Notice that for bound states  $E$  is negative with  $|E| < V_0$ . When  $V_0 \rightarrow \infty$  and  $a \rightarrow 0$  such that  $V_0 a \rightarrow S$  we obtain

$$\sigma^2 = \frac{\mu S}{2\hbar^2} a^2 \quad (169)$$

which tends to zero. Thus the root of Eq. (166) will correspond to a very small value of  $\xi$  (see Fig. 6.4) so that we may replace  $\tan \xi$  by  $\xi$  to obtain

$$\xi^2 = \sqrt{\sigma^2 - \xi^2}$$

or

$$\xi^4 + \xi^2 - \sigma^2 = 0$$

or

$$\xi^2 = \frac{1}{2} \left[ -1 \pm \sqrt{1 + 4\sigma^2} \right]$$

We neglect the minus sign and make a binomial expansion to obtain

$$\xi^2 \approx \sigma^2 - \sigma^4 \quad (170)$$

or

$$\frac{\mu}{2\hbar^2} [V_0 + E] a^2 \approx \frac{\mu V_0 a^2}{2\hbar^2} - \frac{\mu V_0^2 a^4}{4\hbar^4}$$

or

$$E \approx -\frac{\mu S^2}{2\hbar^2} \quad (171)$$

## 6.15. References

1. D. Halliday and R. Resnick, *Physics Parts I & II*, John Wiley, New York (1978).
2. S. Chandrasekhar, *Introduction to the Study of Stellar Structure*, Dover Publications, New York (1957).

## Chapter 7

# Linear Harmonic Oscillator: I Solution of the Schrödinger Equation and Relationship with the Classical Oscillator

*In 1924 Niels Bohr wrote<sup>1</sup>: “As frequently emphasized, these principles, although they are formulated by the help of classical conceptions, are to be regarded purely as laws of the quantum theory, which gives us, notwithstanding the formal nature of the quantum theory, a hope in the future of a consistent theory, which at the same time reproduces the characteristic features of the quantum theory, important for its applicability, and, nevertheless, can be regarded as a rational generalization of classical electrodynamics.” About three years later this consistent theory was accomplished. In fact, there was rarely in the history of physics a comprehensive theory which owed so much to one principle as quantum mechanics owed to Bohr’s correspondence principle.*

— MAX JAMMER in *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York (1966), p. 118.

### 7.1. Introduction

The linear harmonic oscillator problem is one of the most fascinating problems in quantum mechanics. It allows us to understand the basic features of a quantum system along with its transition to the classical domain. It has applications in many problems in physics; e.g. in studying the vibrational spectra of molecules, quantum theory of radiation, etc. In this chapter, we will first obtain solutions of the one-dimensional Schrödinger equation corresponding to the linear harmonic oscillator and then discuss the time evolution of the *coherent states* of the oscillator which represent the quantum mechanical analogs of the classical oscillator.

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<sup>1</sup> N. Bohr, “On the application of the quantum theory to atomic structure,” *Proceedings of the Cambridge Philosophical Society (Supplement)*, Part I (Cambridge University Press, 1924), p. 42.

## 7.2. Solution of the time dependent Schrödinger equation

The one-dimensional time dependent Schrödinger equation is given by

$$i \hbar \frac{\partial \Psi}{\partial t} = H \Psi (x, t) \quad (1)$$

where

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V(x) \quad (2)$$

represents the Hamiltonian and

*Potential energy function*

$$V(x) = \frac{1}{2} \mu \omega^2 x^2 \quad (3)$$

represents the potential energy of the one-dimensional harmonic oscillator<sup>2</sup>; in the above equation  $\mu$  represents the mass of the oscillator and  $\omega$  represents the *classical frequency* of the oscillator. Thus Eq. (1) takes the form

*Time dependent Schrödinger equation*

$$i \hbar \frac{\partial \Psi}{\partial t} = \left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} \mu \omega^2 x^2 \right] \Psi (x, t) \quad (4)$$

which represents the time dependent Schrödinger equation for the linear harmonic oscillator problem. We try to solve the above equation by using the method of separation of variables:

$$\Psi(x, t) = \psi(x) T(t) \quad (5)$$

Substituting in Eq. (4) and dividing by  $\psi(x) T(t)$  we obtain

$$\frac{i \hbar}{T(t)} \frac{dT}{dt} = \frac{1}{\psi(x)} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu \omega^2 x^2 \right] \psi(x)$$

---

<sup>2</sup> The restoring force of a linear oscillator is given by

$$F = -kx$$

where  $k (= \mu \omega^2)$  represents the force constant and  $x$  represents the displacement from the equilibrium position. The potential energy is the work done to bring it to the position  $x$  from the equilibrium position  $x = 0$  and is given by

$$V(x) = \int_0^x F dx = \frac{1}{2} kx^2$$

or

$$V(x) = \frac{1}{2} \mu \omega^2 x^2$$

The left-hand side of the above equation is a function of  $t$  alone and the right-hand side is a function of  $x$  alone; therefore both sides must be set equal to a constant which we represent by  $E$  (the total energy of the oscillator<sup>3</sup>)

$$\frac{i \hbar}{T(t)} \frac{dT}{dt} = \frac{1}{\psi(x)} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu \omega^2 x^2 \right] \psi(x) = E \quad (6)$$

The solution of the equation

$$\frac{i \hbar}{T(t)} \frac{dT}{dt} = E \quad (7)$$

is given by

$$T(t) = (\text{constant}) \exp \left[ -\frac{i E t}{\hbar} \right] \quad (8)$$

Equation (6) also gives us

$$H \psi = \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu \omega^2 x^2 \right] \psi(x) = E \psi(x) \quad (9)$$

which represents an eigenvalue equation; i.e. (as we will show later) only for some specific values of  $E$  will we have “well-behaved” solutions of Eq. (9). We rewrite Eq. (9) in the form

$$\frac{d^2 \psi}{dx^2} + \frac{2\mu}{\hbar^2} \left[ E - \frac{1}{2} \mu \omega^2 x^2 \right] \psi(x) = 0 \quad (10)$$

We may mention that the (time independent) Schrödinger equation is often written in the form

$$H \psi(x) = E \psi(x) \quad (11)$$

where  $H$  is the operator corresponding to the Hamiltonian of the system [see Eq. (2)] and the eigenvalue  $E$  is simply a number.

In order to solve Eq. (10) we introduce the variable

$$\xi = \gamma x$$

<sup>3</sup> As mentioned in Chapter 4

$$\begin{aligned} H &= \frac{p^2}{2\mu} + V(x) \\ &= -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V(x) \end{aligned}$$

represents the operator corresponding to the total energy of the system and is known as the Hamiltonian of the system. The eigenvalues  $E_n$  [see Eq. (28)] are the allowed values of the total energy.

where the parameter  $\gamma$  will be chosen so that Eq. (10) reduces to a convenient form. Now

$$\frac{d\psi}{dx} = \frac{d\psi}{d\xi} \frac{d\xi}{dx} = \gamma \frac{d\psi}{d\xi}$$

and

$$\frac{d^2\psi}{dx^2} = \gamma^2 \frac{d^2\psi}{d\xi^2}$$

Thus, Eq. (10) becomes

$$\frac{d^2\psi}{d\xi^2} + \left[ \frac{2\mu E}{\hbar^2 \gamma^2} - \frac{\mu^2 \omega^2 \xi^2}{\hbar^2 \gamma^4} \right] \psi(\xi) = 0$$

We choose  $\gamma$  such that the coefficient of  $\xi^2$  is unity, thus

$$\gamma = \left( \frac{\mu \omega}{\hbar} \right)^{\frac{1}{2}} \quad (12)$$

Thus, the Schrödinger equation takes the form

$$\frac{d^2\psi}{d\xi^2} + (\Lambda - \xi^2) \psi(\xi) = 0 \quad (13)$$

where

$$\Lambda = \frac{2\mu E}{\hbar^2 \gamma^2} = \frac{2E}{\hbar \omega} \quad (14)$$

In order to solve Eq. (13) we make the transformation<sup>4</sup>

$$\psi(\xi) = u(\xi) e^{-\frac{1}{2}\xi^2} \quad (15)$$

Thus

$$\frac{d\psi}{d\xi} = \left[ \frac{du}{d\xi} - \xi u(\xi) \right] e^{-\frac{1}{2}\xi^2}$$

<sup>4</sup> The transformation given by Eq. (15) is suggested from the fact that in the region  $\xi^2 \gg \Lambda$ , the function

$$\psi(\xi) \sim \xi^n \exp\left(\pm \frac{1}{2}\xi^2\right)$$

indeed satisfies Eq. (13) because

$$\frac{d^2\psi}{d\xi^2} = \left[ 1 \pm \frac{2n+1}{\xi^2} + \frac{n(n-1)}{\xi^4} \right] \xi^{n+2} \exp\left(\pm \frac{1}{2}\xi^2\right) \longrightarrow \xi^2 \psi(\xi)$$

for large  $\xi$ . This suggests that it might be possible to find an exact solution of Eq. (13) of the form given by Eq. (15). We reject the solution with positive exponent because then the solution would diverge as  $\xi \rightarrow \pm\infty$ .

and

$$\frac{d^2\psi}{d\xi^2} = \left[ \frac{d^2u}{d\xi^2} - 2\xi \frac{du}{d\xi} + (\xi^2 - 1) u(\xi) \right] e^{-\frac{1}{2}\xi^2}$$

Substituting in Eq. (13) we get

*Hermite equation*

$$\frac{d^2u}{d\xi^2} - 2\xi \frac{du}{d\xi} + (\Lambda - 1) u(\xi) = 0 \quad (16)$$

which is known as the Hermite equation. We will solve the above equation by assuming a power series solution

$$u(\xi) = \sum_{r=0,1,2,\dots}^{\infty} c_r \xi^{s+r} \quad (17)$$

Substituting in Eq. (16) we get

$$\sum_{r=0,1,2,\dots}^{\infty} c_r (s+r)(s+r-1) \xi^{s+r-2}$$

$$-2 \sum_{r=0,1,2,\dots}^{\infty} c_r (s+r) \xi^{s+r} + (\Lambda - 1) \sum_{0,1,2,\dots} c_r \xi^{s+r} = 0$$

or

$$\sum_{r=0,1,2,\dots}^{\infty} c_r (s+r)(s+r-1) \xi^r$$

$$- \sum_{r=0,1,2,\dots}^{\infty} c_r (2s+2r-\Lambda+1) \xi^{r+2} = 0$$

or

$$c_0 s(s-1) + c_1 (s+1)s \xi$$

$$+ \sum_{r=2,3,\dots}^{\infty} [c_r (s+r)(s+r-1) - c_{r-2} (2s+2r-3-\Lambda)] \xi^r = 0$$

Since, the above equation has to be valid for all values of  $\xi$ , the coefficients of various powers of  $\xi$  must be equal to zero giving

$$s(s-1) = 0 \quad (18)$$

$$c_1 s(s+1) = 0 \quad (19)$$

$$c_r = \frac{2s + 2r - 3 - \Lambda}{(s+r)(s+r-1)} c_{r-2}; \quad r \geq 2 \quad (20)$$

Equation (18) is known as the Indicial Equation and we must have

$$s = 0 \quad \text{or} \quad 1$$

The root  $s = 0$  makes  $c_1$  indeterminate and therefore the root  $s = 0$  would determine both the independent solutions (see also Problem 7.6). Substituting  $s = 0$  in Eq. (20) we get

$$c_r = \frac{2r - 3 - \Lambda}{r(r-1)} c_{r-2}, \quad r \geq 2 \quad (21)$$

which gives

$$\begin{aligned} c_2 &= \frac{1 - \Lambda}{2!} c_0, & c_3 &= \frac{3 - \Lambda}{3!} c_1 \\ c_4 &= \frac{(1 - \Lambda)(5 - \Lambda)}{4!} c_0, & c_5 &= \frac{(3 - \Lambda)(7 - \Lambda)}{5!} c_1, \quad \text{etc.} \end{aligned} \quad (22)$$

Because  $c_2, c_4, \dots$  are related to  $c_0$ ; and  $c_3, c_5, \dots$  are related to  $c_1$ , we can split the solution in even and odd series. Thus we may write

$$\begin{aligned} u(\xi) &= [c_0 + c_2 \xi^2 + c_4 \xi^4 + \dots] \\ &\quad + [c_1 \xi + c_3 \xi^3 + \dots] \end{aligned}$$

or

$$\begin{aligned} u(\xi) &= c_0 \left[ 1 + \frac{1 - \Lambda}{2!} \xi^2 + \frac{(1 - \Lambda)(5 - \Lambda)}{4!} \xi^4 + \dots \right] \\ &\quad + c_1 \left[ \xi + \frac{3 - \Lambda}{3!} \xi^3 + \frac{(3 - \Lambda)(7 - \Lambda)}{5!} \xi^5 + \dots \right] \end{aligned} \quad (23)$$

Since the values of  $c_0$  and  $c_1$  can be arbitrary we have obtained two independent solutions of Eq. (16) and therefore the above equation represents the most general solution of Eq. (16). It may be readily seen that when

$$\Lambda = 1, 5, 9, \dots$$

the even series becomes a polynomial and the odd series remains an infinite series. Similarly, for

$$\Lambda = 3, 7, 11, \dots$$

the odd series becomes a polynomial and the even series remains an infinite series. Thus when

$$\Lambda = 2n + 1; \quad n = 0, 1, 2, \dots$$

one of the solutions becomes a polynomial. Returning to Eq. (21) we have

$$\frac{c_r}{c_{r-2}} = \frac{2r-3-\Lambda}{r(r-1)} \rightarrow \frac{2}{r} \quad \text{for large } r \quad (24)$$

Thus

$$\lim_{r \rightarrow \infty} \frac{c_r}{c_{r-2}} = 0$$

which shows that both the infinite series in Eq. (23) will converge for all values of  $\xi$ . We next consider the expansion of  $e^{\xi^2}$ :

$$e^{\xi^2} = \sum_{r=0,2,4,\dots}^{\infty} b_r \xi^r ; \quad b_r = \frac{1}{\left(\frac{r}{2}\right)!}$$

implying

$$\frac{b_r}{b_{r-2}} = \frac{\left(\frac{r}{2}-1\right)!}{\frac{r}{2}!} = \frac{2}{r} \quad (25)$$

Thus the ratio  $c_r/c_{r-2}$  (in the limit of large  $r$ ) is the same as that of the coefficients of  $\xi^r$  and  $\xi^{r-2}$  in the expansion of  $e^{\xi^2}$ . Consequently, if the series in Eq. (23) is not terminated,  $u(\xi)$  will behave as  $e^{\xi^2}$  for large<sup>5</sup>  $\xi$ ; therefore  $\psi(\xi)$  will behave as  $e^{\frac{1}{2}\xi^2}$  [see Eq. (15)]. Thus the boundary condition

$$\psi(\xi) \rightarrow 0 \quad \text{as} \quad \xi \rightarrow \pm\infty \quad (26)$$

will not be satisfied. For the wave function to satisfy the boundary condition given by Eq. (26), the infinite series must be terminated to a polynomial and as mentioned earlier, this can happen only when  $\Lambda$  is an odd integer, i.e. when

$$\Lambda = 2n + 1 ; \quad n = 0, 1, 2, \dots \quad (27)$$

Substituting in Eq. (14) we get

*Energy eigenvalues*

$$E = E_n = \left(n + \frac{1}{2}\right) \hbar \omega ; \quad n = 0, 1, 2, \dots \quad (28)$$

which represent the (discrete) energy eigenvalues of the operator  $H$ .

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<sup>5</sup> This is because of the fact that only for large values of  $\xi$  will the large  $r$  terms dominate in the expansion and only then will the infinite series behave as  $\exp(\xi^2)$ .

### 7.3. The eigenfunctions

In order to determine the corresponding eigenfunctions we rewrite Eq. (23):

$$\begin{aligned} u(\xi) = & c_0 \left[ 1 + \frac{1 - \Lambda}{2!} \xi^2 + \frac{(1 - \Lambda)(5 - \Lambda)}{4!} \xi^4 + \dots \right] \\ & + c_1 \left[ \xi + \frac{3 - \Lambda}{3!} \xi^3 + \frac{(3 - \Lambda)(7 - \Lambda)}{5!} \xi^5 + \dots \right] \end{aligned} \quad (29)$$

For example, for  $\Lambda = 9$  ( $n = 4$ ), the even series becomes a polynomial and the odd series remains an infinite series. We must therefore choose  $c_1 = 0$ ; the polynomial solution is given by

$$u(\xi) = c_0 \left[ 1 - 4\xi^2 + \frac{4}{3}\xi^4 \right]$$

Similarly, for  $\Lambda = 7$  ( $n = 3$ ), the odd series becomes a polynomial and the even series remains an infinite series. We must therefore choose  $c_0 = 0$ ; the polynomial solution is given by

$$u(\xi) = c_1 \left[ \xi - \frac{2}{3}\xi^3 \right]$$

Now, if the multiplication constant  $c_0$  or  $c_1$  is chosen such that the coefficient of the highest power of  $\xi$  in the polynomial becomes  $2^n$ , then these polynomials are known as Hermite polynomials which are denoted by  $H_n(\xi)$ . For example, for  $\Lambda = 9$  ( $n = 4$ ), if we choose

$$c_0 = 12$$

the coefficient of  $\xi^4$  becomes  $2^4$  and therefore,

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$$

Similarly, for  $\Lambda = 7$  ( $n = 3$ ), we choose

$$c_1 = -12$$

giving

$$H_3(\xi) = 8\xi^3 - 12\xi$$

#### *Hermite polynomials*

The first few Hermite polynomials are given by

$$\begin{aligned} H_0(\xi) &= 1; & H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2; & H_3(\xi) &= 8\xi^3 - 12\xi \end{aligned} \quad (30)$$

Higher order Hermite polynomials can be determined from the following recurrence relation

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2n H_{n-1}(\xi) \quad (31)$$

Returning to Eq. (15) we therefore have

$$\psi_n(x) = N_n H_n(\xi) e^{-\frac{1}{2}\xi^2}; \quad n = 0, 1, 2, \dots$$

where  $N_n$  represents a multiplicative constant. If we impose the normalization condition

$$\int_{-\infty}^{+\infty} |\psi_n(x)|^2 dx = 1$$

we would get (see Appendix E)

$$N_n = \left[ \frac{\gamma}{2^n n! \sqrt{\pi}} \right]^{\frac{1}{2}}$$

which is usually referred to as the normalization constant. The normalized eigenfunctions are given by (see also Sec. 7.8):

$$\psi_n(x) = \left[ \frac{\gamma}{2^n n! \sqrt{\pi}} \right]^{\frac{1}{2}} H_n(\xi) e^{-\frac{1}{2}\xi^2}; \quad n = 0, 1, 2, \dots \quad (32)$$

### Normalized eigenfunctions

The first four normalized eigenfunctions are given by

$$\left. \begin{aligned} \psi_0(x) &= \left( \frac{\gamma}{\sqrt{\pi}} \right)^{\frac{1}{2}} \exp \left[ -\frac{1}{2} \gamma^2 x^2 \right] \\ \psi_1(x) &= \left( \frac{\gamma}{2\sqrt{\pi}} \right)^{\frac{1}{2}} (2\gamma x) \exp \left[ -\frac{1}{2} \gamma^2 x^2 \right] \\ \psi_2(x) &= \left( \frac{\gamma}{8\sqrt{\pi}} \right)^{\frac{1}{2}} (4\gamma^2 x^2 - 2) \exp \left[ -\frac{1}{2} \gamma^2 x^2 \right] \\ \psi_3(x) &= \left( \frac{\gamma}{48\sqrt{\pi}} \right)^{\frac{1}{2}} (8\gamma^3 x^3 - 12\gamma x) \exp \left[ -\frac{1}{2} \gamma^2 x^2 \right] \end{aligned} \right\} \quad (33)$$

and are plotted in Fig. 7.1. The horizontal lines correspond to the eigenvalues

### Eigenvalues

$$E = \frac{1}{2} \hbar\omega, \quad \frac{3}{2} \hbar\omega, \quad \frac{5}{2} \hbar\omega, \quad \text{and} \quad \frac{7}{2} \hbar\omega$$

For a given value of  $E$  the classically allowed region of the oscillator corresponds to

$$|x| \leq x_0$$

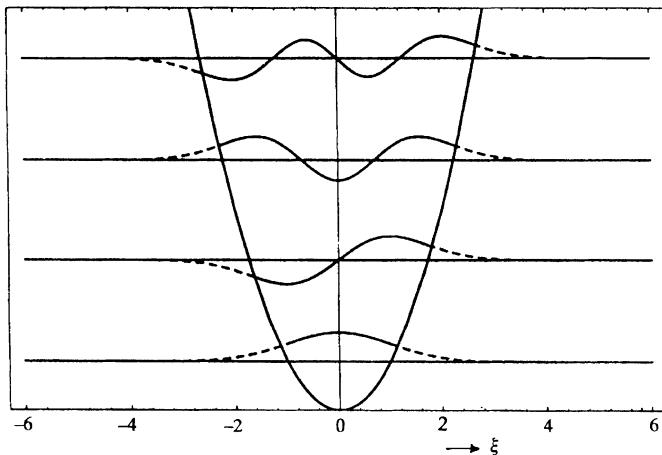
Normalized Harmonic Oscillator Wave Functions for  $n = 0, 1, 2, 3$ 

Figure 7.1. The harmonic oscillator potential and the first four eigenfunctions. The horizontal lines correspond to the eigenvalues  $\frac{1}{2}\hbar\omega$ ,  $\frac{3}{2}\hbar\omega$ ,  $\frac{5}{2}\hbar\omega$  and  $\frac{7}{2}\hbar\omega$ . The dashed portions of the curves correspond to the classically forbidden regions.

where

$$x_0 = \left[ \frac{2E}{\mu\omega^2} \right]^{\frac{1}{2}} \quad (34)$$

represents the classical turning point of the oscillator. The corresponding value of  $\xi$  will be given by

$$\xi_0 = \gamma x_0 = \left( \frac{\mu\omega}{\hbar} \right)^{\frac{1}{2}} \left( \frac{2E}{\mu\omega^2} \right)^{\frac{1}{2}}$$

or

$$\xi_0 = \sqrt{(2n+1)} ; \quad n = 0, 1, 2, \dots \quad (35)$$

where we have used Eq. (28). Thus the classically allowed region would be given by

$$|\xi| < \sqrt{2n+1} ; \quad n = 0, 1, 2, \dots$$

In Fig. 7.1, the dashed portions of the curves correspond to the classically forbidden regions and as can be seen, this is consistent with the above equation.

In Figs 7.2 and 7.3 we have plotted  $|\psi_0(x)|^2$  and  $|\psi_{12}(x)|^2$  as a function of  $\xi$ . Obviously if the oscillator is in the  $n^{th}$  state,  $|\psi_n(x)|^2 dx$  would represent the probability of finding the particle between  $x$  and  $x + dx$ . The corresponding classical distribution function is given by (see Problem 7.3)

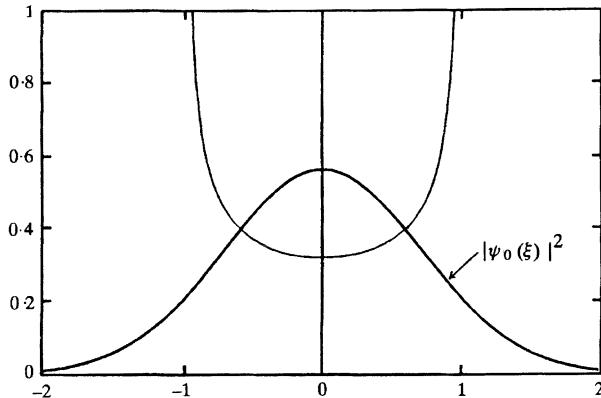


Figure 7.2. The dark curve represents the probability distribution function  $|\psi_0(\xi)|^2$  for the ground state of the harmonic oscillator; the corresponding classical distribution as given by Eq. (36) is also shown.

### *Classical distribution function*

$$P_{cl}(x) = \frac{1}{\pi \sqrt{x_0^2 - x^2}} \quad |x| < x_0 \quad (36)$$

$P_{cl}(x) dx$  represents the probability of finding the particle between  $x$  and  $x + dx$  and represents the fractional time that it spends in the interval  $dx$ . Although  $P_{cl}(x)$  blows up at  $|x| = x_0$ ,

$$\int_{-x_0}^{+x_0} P_{cl}(x) dx = 1 \quad (37)$$

In Figs 7.2 and 7.3 we have shown the probability distributions as predicted by the classical and quantum mechanical theories. For large values of  $n$ ,  $|\psi_n(x)|^2$  undergoes very rapid oscillations and the average value is in good agreement with the corresponding classical value. Obviously, larger the value of  $n$  better will be the agreement—this is what is predicted by Bohr's Correspondence Principle.

The wave functions given by Eq. (32) form an orthonormal set (see Sec. 6.4):

### *Orthonormality condition*

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx = \delta_{mn} = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases} \quad (38)$$

The eigenfunctions and the eigenvalues form a discrete set and there are no continuum eigenfunctions. The infinite number of discrete eigenfunctions form

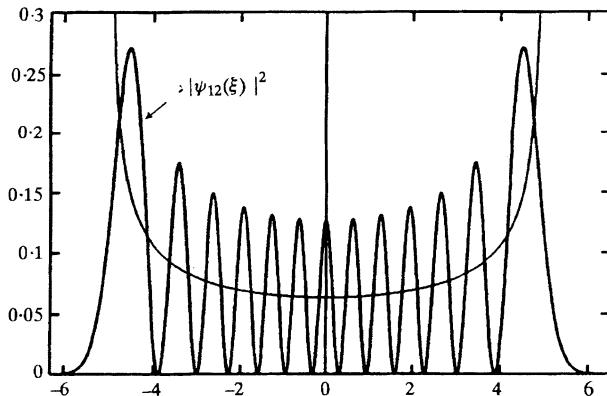


Figure 7.3. The dark curve represents the probability distribution function  $|\psi_{12}(\xi)|^2$  for the  $n = 12$  state of the harmonic oscillator; the average of this distribution closely resembles the classical distribution given by Eq. (36) which has also been shown.

a complete set in the sense that an arbitrary “well-behaved” square integrable<sup>6</sup> function  $\phi(x)$  (defined in the interval  $-\infty < x < \infty$ ) can be expanded in terms of  $\psi_n(x)$ :

$$\phi(x) = \sum_{n=0}^{\infty} c_n \psi_n(x) \quad (39)$$

In order to determine  $c_n$ , we multiply the above equation by  $\psi_m^*(x)$  and integrate to obtain

$$\begin{aligned} \int_{-\infty}^{+\infty} \psi_m^*(x) \phi(x) dx &= \sum_{n=0,1,2,\dots}^{\infty} c_n \int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx \\ &= \sum_{n=0,1,2,\dots}^{\infty} c_n \delta_{mn} \\ &= c_m \end{aligned}$$

Thus

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x) \phi(x) dx \quad (40)$$

---

<sup>6</sup> By square integrable we imply

$$\int_{-\infty}^{+\infty} |\phi(x)|^2 dx \quad \text{to be finite}$$

If we substitute the above expression for  $c_n$  in Eq. (39) we would obtain

$$\phi(x) = \int_{-\infty}^{+\infty} \phi(x') \left[ \sum_n \psi_n^*(x') \psi_n(x) \right] dx'$$

Thus (see Sec. 1.5):

*Completeness condition*

$$\sum_{n=0}^{\infty} \psi_n^*(x') \psi_n(x) = \delta(x - x') \quad (41)$$

which represents the completeness condition of the Hermite-Gauss functions.

#### 7.4. The most general solution of the time dependent Schrödinger equation

Using Eqs (5) and (8) we can write the solution of Eq. (4) in the form

$$\Psi(x, t) = \psi(x) \exp\left[-\frac{iE}{\hbar}t\right]$$

Since the allowed values of  $E$  are given by Eq. (28) [with the corresponding eigenfunctions given by Eq. (32)], the most general solution of Eq. (4) would be given by

$$\Psi(x, t) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) \exp\left[-\frac{iE_n}{\hbar}t\right] \quad (42)$$

or

$$\Psi(x, t) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) e^{-i(n+\frac{1}{2})\omega t} \quad (43)$$

*Determination of  $\Psi(x, t)$*

Thus if we know  $\Psi(x, 0)$ , i.e. if we know the state of the oscillator at  $t = 0$ ,  $\Psi(x, t)$  can be determined as follows:

(i) Since

$$\Psi(x, 0) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x)$$

we get

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x) \Psi(x, 0) dx \quad (44)$$

(ii) We substitute the calculated value of  $c_n$  in Eq. (43) and sum the series to obtain<sup>7</sup>  $\Psi(x, t)$ . This will describe the time evolution of the wave packet. Obviously if

$$\int_{-\infty}^{+\infty} |\Psi(x, 0)|^2 dx = 1 \quad (45)$$

then

$$\sum_n |c_n|^2 = 1 \quad (46)$$

implying (see Problem 7.9)

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad (47)$$

The quantity  $|c_n|^2$  can be interpreted to represent the probability of finding the oscillator in the  $n^{th}$  state which does not change with time. As can be seen from Eq. (43), the wave functions superpose with different phases at different times.

As a simple example, let

$$\Psi(x, 0) = \frac{1}{\sqrt{3}} \psi_0(x) + i\sqrt{\frac{2}{3}} \psi_2(x) \quad (48)$$

Obviously

$$\int_{-\infty}^{+\infty} |\Psi(x, 0)|^2 dx = 1$$

and the time evolution of the wave function would be given by

$$\Psi(x, t) = \frac{1}{\sqrt{3}} \psi_0(x) e^{-i\omega t/2} + i\sqrt{\frac{2}{3}} \psi_2(x) e^{-5i\omega t/2} \quad (49)$$

If we make a measurement of energy, there will be  $\frac{1}{3}^{rd}$  probability of finding it in the ground state (with  $E = \frac{1}{2}\hbar\omega$ ) and  $\frac{2}{3}^{rd}$  probability of finding it in the second excited state (with  $E = \frac{5}{2}\hbar\omega$ ). These probabilities do not change with time; however, once the measurement is made, the oscillator will jump to one of the eigenstates of the system.

---

<sup>7</sup>  $\Psi(x, t)$  will describe the time evolution of the wave packet. The method is quite similar to the one we used for a free particle (see Sec. 5.3).

For the oscillator described by Eq. (48), the average energy will be given by

$$\begin{aligned}\langle E \rangle &= \frac{1}{3} \left( \frac{1}{2} \hbar\omega \right) + \frac{2}{3} \left( \frac{5}{2} \hbar\omega \right) \\ &= \frac{11}{6} \hbar\omega\end{aligned}$$

which will never be measured!

## 7.5. The coherent state

In this section we will define the coherent state and in the following section we will consider its time evolution. We first define the *annihilation operator*<sup>8</sup>  $a$ :

*Annihilation operator*

$$a = \frac{\mu \omega x + i p}{\sqrt{2 \mu \hbar \omega}} \quad (50)$$

Replacing  $p$  by  $-i \hbar d/dx$  we get

$$a = \sqrt{\frac{\mu \omega}{2 \hbar}} x + \sqrt{\frac{\hbar}{2 \mu \omega}} \frac{d}{dx} \quad (51)$$

We next write the eigenvalue equation for the operator  $a$ :

$$a \psi_\alpha(x) = \alpha \psi_\alpha(x) \quad (52)$$

*Coherent states*

where  $\alpha$  represents the eigenvalue of the operator  $a$ . The eigenfunctions  $\psi_\alpha(x)$  describe what are known as *coherent states*. In order to solve the eigenvalue equation Eq. (52), we substitute for  $a$  from Eq. (51) to obtain

$$\sqrt{\frac{\mu \omega}{2 \hbar}} x \psi_\alpha(x) + \sqrt{\frac{\hbar}{2 \mu \omega}} \frac{d \psi_\alpha}{dx} = \alpha \psi_\alpha(x)$$

or

$$\frac{1}{\psi_\alpha(x)} \frac{d \psi_\alpha(x)}{dx} = -\frac{\mu \omega}{\hbar} x + \alpha \sqrt{\frac{2 \mu \omega}{\hbar}}$$

---

<sup>8</sup> The properties of creation and annihilation operators  $a$  and  $\bar{a}$  are discussed in Chapter 12 while solving the harmonic oscillator problem using Dirac's bra and ket algebra.

Carrying out the integration, we get

$$\begin{aligned}\ln \psi_\alpha(x) &= -\frac{\mu\omega}{2\hbar}x^2 + \alpha\sqrt{\frac{2\mu\omega}{\hbar}}x + \text{constant} \\ &= -\frac{1}{2}(\xi - \xi_0)^2 + \text{constant}\end{aligned}$$

where

$$\xi = \gamma x = \sqrt{\frac{\mu\omega}{\hbar}}x$$

and

$$\xi_0 = \sqrt{2}\alpha$$

Thus

$$\psi_\alpha(x) = \text{const } e^{-\frac{1}{2}(\xi - \xi_0)^2}$$

or

$$\psi_\alpha(x) = \left(\frac{\gamma}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}(\xi - \xi_0)^2} \quad (53)$$

where the constant factor has been chosen such that the wave function is normalized. Obviously, the ground state wave function  $\psi_0(x)$  is a coherent state corresponding to  $\xi_0 = 0$ .

## 7.6. Time evolution of a coherent state: relationship with the classical oscillator

Let us assume that at  $t = 0$ , the oscillator is in the coherent state, i.e.

$$\Psi(x, 0) = \psi_\alpha(x) = \left(\frac{\gamma}{\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}(\xi - \xi_0)^2} \quad (54)$$

We wish to study its time evolution; i.e. if  $\Psi(x, 0)$  is given by the above equation then what is  $\Psi(x, t)$ ? Since for the harmonic oscillator problem

$$\Psi(x, t) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) e^{-i(n+\frac{1}{2})\omega t} \quad (55)$$

we have

$$\Psi(x, 0) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) \quad (56)$$

Thus [see Eq. (40)]

$$\begin{aligned}
 c_n &= \int_{-\infty}^{+\infty} \psi_n^*(x) \Psi(x, 0) dx \\
 &= \left( \frac{\gamma^2}{2^n n! \pi} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \left[ H_n(\xi) e^{-\frac{1}{2}\xi^2} \right] e^{-\frac{1}{2}(\xi - \xi_0)^2} dx \\
 &= \frac{1}{\sqrt{n!}} \left( \frac{1}{2} \xi_0^2 \right)^{n/2} \exp \left( -\frac{1}{4} \xi_0^2 \right)
 \end{aligned} \tag{57}$$

where the explicit evaluation of the integral has been carried out in Appendix E. Substituting for  $c_n$  in Eq. (55) we get

$$\begin{aligned}
 \Psi(x, t) &= \sum_{n=0,1,2,\dots} \left[ \frac{1}{\sqrt{n!}} \left( \frac{1}{2} \xi_0^2 \right)^{n/2} \exp \left( -\frac{1}{4} \xi_0^2 \right) \right] \\
 &\quad \times \left[ N_n H_n(\xi) e^{-\frac{1}{2}\xi^2} \right] e^{-i(n+\frac{1}{2})\omega t}
 \end{aligned} \tag{58}$$

Indeed one can obtain an analytical expression for the sum; the final result is (the details are given in Appendix E):

$$\begin{aligned}
 \Psi(x, t) &= \frac{\gamma^{\frac{1}{2}}}{\pi^{\frac{1}{4}}} \exp \left[ -\frac{1}{2} (\xi - \xi_0 \cos \omega t)^2 \right. \\
 &\quad \left. -i \left( \frac{1}{2} \omega t + \xi \xi_0 \sin \omega t - \frac{1}{4} \xi_0^2 \sin 2\omega t \right) \right]
 \end{aligned} \tag{59}$$

The probability distribution is therefore given by

$$|\Psi(x, t)|^2 = \frac{\gamma}{\sqrt{\pi}} \exp \left[ -(\xi - \xi_0 \cos \omega t)^2 \right] \tag{60}$$

Notice that

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \tag{61}$$

for all values of  $t$ , as it indeed should be. The time evolution of the coherent state is described by Eq. (59)

In Figs 7.4 and 7.5 we have plotted  $|\Psi(x, t)|^2$  as a function of  $\xi$  for different values of time and as can be seen, the centre of the wave packet executes simple harmonic motion like a classical harmonic oscillator. The average energy of the

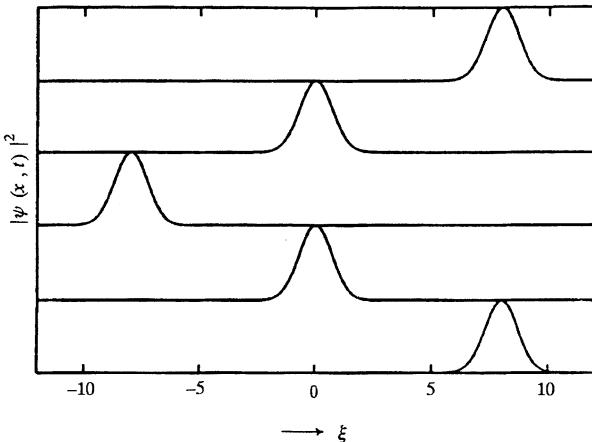


Figure 7.4. The  $\xi$ -dependence of  $|\Psi(x, t)|^2$  for  $\xi_0 = 8$  ( $\langle n \rangle = 32$ ) at  $\omega t = 0, \pi/2, \pi, 3\pi/2, 2\pi$  and  $5\pi/2$ . Notice that the centre of the wave packet executes simple harmonic motion.

oscillator is given by

*Average energy*

$$\langle E \rangle = \left[ \langle n \rangle + \frac{1}{2} \right] \hbar \omega$$

Thus a large (average) energy of the oscillator will imply a large value of  $\langle n \rangle$ . Later in this section we will show that

$$\langle n \rangle = \sum_{n=1,2,\dots} n |c_n|^2 = \frac{1}{2} \xi_0^2$$

Figures 7.4 and 7.5 correspond to

$$\langle n \rangle = 32 \quad (\xi_0 = 8)$$

and

$$\langle n \rangle = 2048 \quad (\xi_0 = 64)$$

respectively. Obviously, as we increase the value of  $\langle n \rangle$ , the wave packet becomes more and more localized. We may mention that for a classical oscillator with  $\mu = 0.1$  g,  $\omega = 1$  s<sup>-1</sup>,  $x_0 = 1$  cm

$$\xi_0 = \sqrt{\frac{\mu \omega}{\hbar}} x_0 \approx 10^{13}$$

so that

$$\langle n \rangle = 5 \times 10^{25}$$

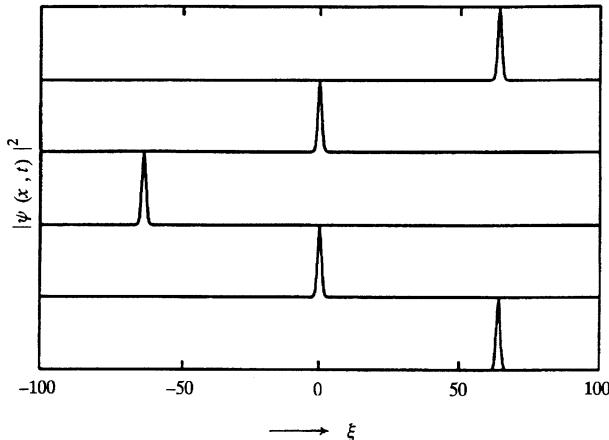


Figure 7.5. The  $\xi$ -dependence of  $|\Psi(x, t)|^2$  for  $\xi_0 = 64$  ( $\langle n \rangle = 2048$ ) at  $\omega t = 0, \pi/2, \pi, 3\pi/2, 2\pi$  and  $5\pi/2$ . Notice that the centre of the wave packet executes simple harmonic motion.

which is an enormously large number. The particle would then be very localized and a classical description would be very accurate.

Using Eq. (58) one can readily calculate the various expectation values, e.g.,

$$\begin{aligned}
 \langle x \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x, t) x \Psi(x, t) dx \\
 &= \frac{1}{\gamma \sqrt{\pi}} \int_{-\infty}^{+\infty} \xi e^{-(\xi - \xi_0 \cos \omega t)^2} d\xi \\
 &= \frac{1}{\gamma \sqrt{\pi}} \int_{-\infty}^{+\infty} (\eta + \xi_0 \cos \omega t) e^{-\eta^2} d\eta \quad [\eta \equiv \xi - \xi_0 \cos \omega t] \\
 &= \frac{1}{\gamma} \xi_0 \cos \omega t = x_0 \cos \omega t
 \end{aligned}$$

where

$$x_0 = \frac{\xi}{\gamma_0}$$

represents the amplitude of the classical oscillator. Other integrals can be similarly evaluated, but the evalution is much easier using bra and ket algebra which we will discuss in Chapter 12. The final results are given below:

$$\langle x \rangle = x_0 \cos \omega t \tag{62}$$

$$\begin{aligned}\langle p \rangle &= -\mu\omega x_0 \sin \omega t \\ &= -p_0 \sin \omega t\end{aligned}\quad (63)$$

where

$$p_0 = \mu\omega x_0$$

The above equations imply

$$\langle p \rangle = \mu \frac{d}{dt} \langle x \rangle \quad (64)$$

This is nothing but the manifestation of Ehrenfest's theorem (see Sec. 4.5) according to which the expectation values satisfy Newton's laws of motion.

From Eqs (62) and (63) we find that  $\langle x \rangle$  lags  $\langle p \rangle$  by a phase  $\frac{\pi}{2}$  just as we have for a classical oscillator. Furthermore (see Problem 12.6),

$$\langle x^2 \rangle = x_0^2 \cos^2 \omega t + \frac{1}{2\gamma^2} \quad (65)$$

$$\langle p^2 \rangle = p_0^2 \sin^2 \omega t + \frac{\gamma^2 \hbar^2}{2} \quad (66)$$

Thus

$$\Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{\frac{1}{2}} = \frac{1}{\sqrt{2}\gamma} = \left( \frac{\hbar}{2\mu\omega} \right)^{\frac{1}{2}} \quad (67)$$

$$\Delta p = [\langle p^2 \rangle - \langle p \rangle^2]^{\frac{1}{2}} = \frac{\gamma\hbar}{\sqrt{2}} = \left( \frac{\mu\omega\hbar}{2} \right)^{\frac{1}{2}} \quad (68)$$

giving

$$\Delta x \Delta p = \frac{1}{2} \hbar \quad (69)$$

which represents the minimum uncertainty product<sup>9</sup>. Further,

$$\begin{aligned}\langle E \rangle &= \frac{1}{2\mu} \langle p^2 \rangle + \frac{1}{2} \mu\omega^2 \langle x^2 \rangle \\ &= \frac{1}{2\mu} \left( p_0^2 \sin^2 \omega t + \frac{\gamma^2 \hbar^2}{2} \right) + \frac{1}{2} \mu\omega^2 \left( x_0^2 \cos^2 \omega t + \frac{1}{2\gamma^2} \right)\end{aligned}$$

Thus

$$\langle E \rangle = \frac{1}{2} \mu\omega^2 x_0^2 + \frac{1}{2} \hbar\omega \quad (70)$$

---

<sup>9</sup> The values for  $\Delta x$  and  $\Delta p$  remain the same for all values of time and are the same for the ground state wave function  $\psi_0(x)$ . Indeed, the ground state wave function  $\psi_0(x)$  is also a coherent state corresponding to  $\alpha = 0$  (i.e. zero eigenvalue).

Notice the appearance of the zero point energy  $\frac{1}{2}\hbar\omega$ . For a classical oscillator the total energy is just  $\frac{1}{2}\mu\omega^2x_0^2$ .

In order to have a physical understanding of  $\langle E \rangle$  we recall that energy eigenstates of the harmonic oscillator are given by [see Eq. (28)]

$$E = \left( n + \frac{1}{2} \right) \hbar\omega$$

Thus

$$\langle E \rangle = \left[ \langle n \rangle + \frac{1}{2} \right] \hbar\omega \quad (71)$$

Comparing the above equation with Eq. (70) we get

$$\langle n \rangle = \frac{1}{2} \gamma^2 x_0^2 = \frac{1}{2} \xi_0^2 \quad (72)$$

Now

$$\Psi(x, t) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) e^{-i(n+\frac{1}{2})\omega t}$$

Thus, the quantity

$$\begin{aligned} P_n &= \left| c_n e^{-i(n+\frac{1}{2})\omega t} \right|^2 \\ &= |c_n|^2 = \frac{1}{n!} \left( \frac{1}{2} \xi_0^2 \right)^n e^{-\frac{1}{2} \xi_0^2} \end{aligned} \quad (73)$$

represents the probability of finding the oscillator in the  $n^{th}$  state<sup>10</sup>. This implies that if the oscillator is in a coherent state and if we make a measurement of energy then  $|c_n|^2$  would represent the probability of obtaining the value  $(n + \frac{1}{2})\hbar\omega$ . The average value of  $n$  is given by

$$\begin{aligned} \langle n \rangle &= \sum_{n=0,1,2,\dots}^{\infty} n |c_n|^2 \\ &= e^{-\frac{1}{2}\xi_0^2} \left( \frac{1}{2} \xi_0^2 \right) \sum_{n=1,2,\dots}^{\infty} \frac{1}{(n-1)!} \left( \frac{1}{2} \xi_0^2 \right)^{n-1} \\ &= e^{-\frac{1}{2}\xi_0^2} \left( \frac{1}{2} \xi_0^2 \right) e^{\frac{1}{2}\xi_0^2} \\ &= \frac{1}{2} \xi_0^2 = \frac{1}{2} \gamma^2 x_0^2 \end{aligned}$$

---

<sup>10</sup> It may be seen that the probability of finding the oscillator in the  $n^{th}$  state does not change with time. At different times, the states superpose with different phases which results in the time variation of the probability distribution  $|\Psi(x, t)|^2$ .

consistent with Eq. (72). Similarly

$$\begin{aligned}\langle n^2 \rangle &= \sum_{n=0,1,2,\dots}^{\infty} n^2 |c_n|^2 \\ &= e^{-\frac{1}{2}\xi_0^2} \left(\frac{1}{2}\xi_0^2\right) \sum_{n=1,2,\dots}^{\infty} (n-1+1) \frac{1}{(n-1)!} \left(\frac{1}{2}\xi_0^2 2\right)^{n-1} \\ &= \left(\frac{1}{2}\xi_0^2\right)^2 + \frac{1}{2}\xi_0^2\end{aligned}$$

Thus

$$\Delta n = [\langle n^2 \rangle - \langle n \rangle^2]^{\frac{1}{2}} = \frac{1}{\sqrt{2}}\xi_0 = \sqrt{\langle n \rangle}$$

We summarize the above results:

$$\langle n \rangle = \frac{1}{2}\xi_0^2 = \frac{1}{2}\gamma^2 x_0^2 \quad (74)$$

$$\langle n^2 \rangle = \langle n \rangle^2 + \langle n \rangle \quad (75)$$

$$\Delta n = [\langle n^2 \rangle - \langle n \rangle^2]^{\frac{1}{2}} = \sqrt{\langle n \rangle} \quad (76)$$

$$\frac{\Delta n}{\langle n \rangle} = \frac{1}{\sqrt{\langle n \rangle}} \quad (77)$$

the last equation implying that the fractional uncertainty in  $n$  decreases as  $\langle n \rangle$  increases. The probability of finding the oscillator in the  $n^{th}$  state is therefore given by

$$P_n = |c_n|^2 = e^{-\langle n \rangle} \frac{\langle n \rangle^n}{n!} \quad (78)$$

which is known as a Poisson distribution. In terms of  $\langle n \rangle$ , we express the various expectation values

*Expectation values in terms of  $\langle n \rangle$*

$$\langle x \rangle = x_0 \cos \omega t = \frac{1}{\gamma} \sqrt{2\langle n \rangle} \cos \omega t \quad (79)$$

$$\langle p \rangle = -\frac{\mu \omega}{\gamma} \sqrt{2\langle n \rangle} \sin \omega t = \mu \frac{d}{dt} \langle x \rangle \quad (80)$$

$$\langle x^2 \rangle = \frac{1}{\gamma^2} \left[ 2\langle n \rangle \cos^2 \omega t + \frac{1}{2} \right] \quad (81)$$

$$\langle p^2 \rangle = \frac{\mu^2 \omega^2}{\gamma^2} \left[ 2\langle n \rangle \sin^2 \omega t + \frac{1}{2} \right] \quad (82)$$

$$\langle E \rangle = \frac{1}{2\mu} \langle p^2 \rangle + \frac{1}{2} \mu \omega^2 \langle x^2 \rangle = \left[ \langle n \rangle + \frac{1}{2} \right] \hbar \omega \quad (83)$$

$$\frac{\Delta x}{x_0} = \frac{\sqrt{\langle x^2 \rangle - \langle x \rangle^2}}{x_0} = \frac{1}{\sqrt{\langle n \rangle}} \quad (84)$$

$$\frac{\Delta p}{p_0} = \frac{\sqrt{\langle p^2 \rangle - \langle p \rangle^2}}{p_0} = \frac{1}{\sqrt{\langle n \rangle}} \quad (85)$$

$$\langle E^2 \rangle = \left[ \langle n^2 \rangle + \langle n \rangle + \frac{1}{4} \right] \hbar^2 \omega^2 \quad (86)$$

$$\frac{\Delta E}{\langle E \rangle} = \frac{[\langle E^2 \rangle - \langle E \rangle^2]^{\frac{1}{2}}}{\langle E \rangle} = \frac{\Delta n}{\langle n \rangle + \frac{1}{2}} = \frac{\sqrt{\langle n \rangle}}{\langle n \rangle + \frac{1}{2}} \quad (87)$$

In Figs 7.6, 7.7 and 7.8 we have plotted  $|c_n|^2$  as a function of  $n$  for

$$\langle n \rangle = 10 \left( \Delta n \simeq 3.1, \frac{\Delta n}{\langle n \rangle} \simeq 0.31 \right); \quad (88)$$

$$\langle n \rangle = 100 \left( \Delta n = 10, \frac{\Delta n}{\langle n \rangle} = 0.1 \right) \quad (89)$$

and

$$\langle n \rangle = 10^6 \left( \Delta n = 10^3, \frac{\Delta n}{\langle n \rangle} = 0.001 \right) \quad (90)$$

We find that as the value of  $\langle n \rangle$  increases the value of  $\Delta n$  also increases implying that a large number of states get excited; however, the value of  $\Delta n/\langle n \rangle$  (and hence of  $\Delta E/\langle E \rangle$ ) decreases implying that the fractional spread in energy becomes very small.

#### *Relation with a classical oscillator*

In order to relate the above analysis to a classical oscillator, we consider a small mass ( $\mu \approx 0.002$  g) executing simple harmonic motion with  $\omega = 1 \text{ s}^{-1}$  (implying a time period of  $2\pi$  seconds). If the amplitude of motion ( $= x_0$ ) is 1 cm then

$$\langle x \rangle = \cos t \quad (91)$$

$$\langle p \rangle = -0.002 \sin t \quad (92)$$

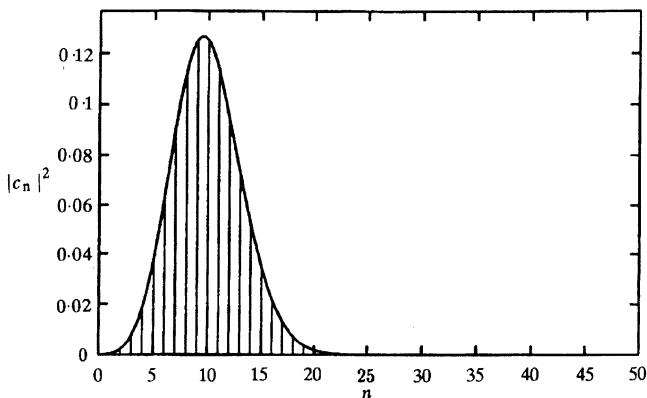


Figure 7.6. The variation of  $|c_n|^2$  with  $n$  for  $\langle n \rangle = 10$ . Notice that although only about 20 states are excited,  $\frac{\Delta x}{x_0}$ ,  $\frac{\Delta p}{p_0}$  have an appreciable value ( $\approx 0.316$ ).

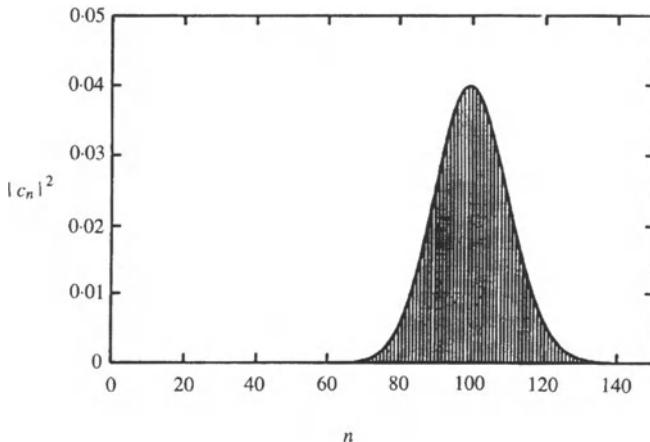


Figure 7.7. The variation of  $|c_n|^2$  with  $n$  for  $\langle n \rangle = 100$ .

where  $\langle x \rangle$ ,  $t$  and  $\langle p \rangle$  are measured in cm, s and g cm/s respectively. Further

$$\langle n \rangle = \frac{1}{2} \gamma^2 x_0^2 = \frac{\mu\omega}{2\hbar} x_0^2$$

$$\approx 10^{24}$$

implying

$$\Delta n = \sqrt{\langle n \rangle} \approx 10^{12} \quad (93)$$

and

$$\frac{\Delta E}{\langle E \rangle} = \frac{\sqrt{\langle n \rangle}}{\langle n \rangle + \frac{1}{2}} \approx 10^{-12} \quad (94)$$

Thus although a very large number of states ( $\approx 10^{12}$ ) get excited, the fractional spread in energy is extremely small and a classical description should be very accurate. Also

$$\frac{\Delta p}{p_0} = \frac{\Delta x}{x_0} = \frac{1}{\sqrt{\langle n \rangle}} \approx 10^{-12} \quad (95)$$

#### *Bohr's correspondence principle*

implying that both position and momentum can be determined with tremendous precision. This is the domain of classical physics and is a consequence of **Bohr's correspondence principle** according to which *the results from quantum theory must go over to results from classical mechanics when very large number of quanta are involved.*

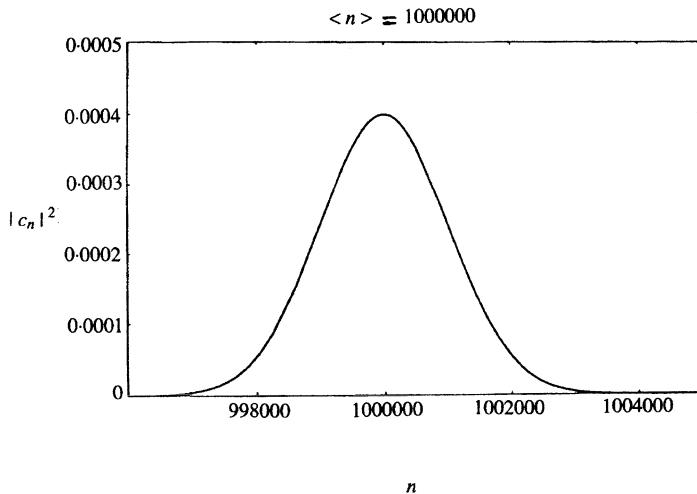


Figure 7.8. The variation of  $|c_n|^2$  with  $n$  for  $\langle n \rangle = 10^6$ . Although a very large number of states are excited ( $\approx 10^6$ ), the values of  $\frac{\Delta x}{x_0}$ ,  $\frac{\Delta p}{p_0}$  and  $\frac{\Delta E}{E_0}$ , are extremely small.

On the other hand, if the mass of the particle is so small that

$$\langle n \rangle = 10$$

then

$$\frac{\Delta E}{E_0} \approx 0.301$$

$$\frac{\Delta p}{p_0} = \frac{\Delta x}{x_0} \simeq 0.316$$

and a quantum mechanical description would be necessary.

We may mention here that when a laser is operated much beyond the threshold, it generates a coherent state excitation of the cavity mode. Thus, for such a beam if

one carries out a photon counting experiment one should find that the probability of measuring  $n$  quanta in a certain interval of time is given by [see Eq. (73)]

$$P_n = e^{-\langle n \rangle} \frac{\langle n \rangle^n}{n!} \quad (96)$$

where  $\langle n \rangle$  represents the average number of counts measured in that time interval. Equation (96) is known as the Poisson distribution and is indeed verified through experiments (see, e.g. Ref. 1 and 2).

## 7.7. The propagator

The general solution of the time dependent Schrödinger equation for the linear harmonic oscillator problem is given by [see Eq. (42)]:

$$\Psi(x, t) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) e^{-i(n+\frac{1}{2})\omega t} \quad (97)$$

Thus

$$\Psi(x, 0) = \sum_{n=0,1,2,\dots}^{\infty} c_n \psi_n(x) \quad (98)$$

from which we obtain

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x') \Psi(x', 0) dx' \quad (99)$$

where we have put a prime on  $x$  so that the integration variable does not get confused with  $x$  in Eq. (97). We substitute for  $c_n$  from Eq. (99) in Eq. (97) to obtain

$$\Psi(x, t) = \int_{-\infty}^{+\infty} \left[ \sum_{n=0,1,2,\dots}^{\infty} \psi_n^*(x') \psi_n(x) e^{-i(n+\frac{1}{2})\omega t} \right] \Psi(x', 0) dx' \quad (100)$$

Thus we may write

$$\Psi(x, t) = \int_{-\infty}^{+\infty} K(x, x', t) \Psi(x', 0) dx' \quad (101)$$

where

$$K(x, x', t) = \sum_{n=0,1,2,\dots}^{\infty} \psi_n^*(x') \psi_n(x) e^{-i(n+\frac{1}{2})\omega t} \quad (102)$$

represents the propagator. The above equation may be compared with the results obtained in Sec. 5.4. If we substitute for  $\psi_n(x)$  from Eq. (32) then it is possible to sum the infinite series (see, e.g., Chapter 6 of Ref. 3); the final result is

$$K(x, x', t) = \frac{\gamma}{(2\pi i \sin \omega t)^{\frac{1}{2}}} \exp \left[ -\frac{\gamma^2}{2i \sin \omega t} \left\{ (x^2 + x'^2) \right. \right. \\ \left. \left. \times \cos \omega t - 2x x' \right\} \right] \quad (103)$$

Thus for the linear harmonic oscillator problem, the time evolution of an arbitrary wave packet can easily be carried out by substituting for  $\Psi(x, 0)$  in Eq. (101) and carrying out the integration. Indeed, if we substitute Eq. (54) for  $\Psi(x, 0)$  and carry out the integration in Eq. (101) we would get Eq. (59).

## 7.8. Solutions in terms of the confluent hypergeometric function

The equation

$$x \frac{d^2y}{dx^2} + (c - x) \frac{dy}{dx} - ay(x) = 0 \quad (104)$$

is known as the confluent hypergeometric equation. For  $c \neq 0, \pm 1, \pm 2, \dots$  the general solution of Eq. (104) is given by [see Appendix F]

$$y(x) = C_1 {}_1F_1(a, c, x) + C_2 x^{1-c} {}_1F_1(a - c + 1, 2 - c, x) \quad (105)$$

where

$${}_1F_1(a, c, x) = 1 + \frac{a}{c} \frac{x}{1!} + \frac{a(a+1)}{(c+c_1)} \frac{x^2}{2!} + \dots \quad (106)$$

is known as the confluent hypergeometric function. Obviously, for  $a = c$

$${}_1F_1(a, a, x) = 1 + x + \frac{x^2}{2!} + \dots = e^x$$

Thus although the series is convergent for all values of  $x$ , it blows up at infinity. Indeed the asymptotic form of  ${}_1F_1(a, c, x)$  is given by

$${}_1F_1(a, c, x) \xrightarrow[x \rightarrow \infty]{} x^{a-c} e^x \quad (107)$$

We go back to the Schrödinger equation for the harmonic oscillator problem and rewrite Eq. (16)

$$\frac{d^2u}{d\xi^2} - 2\xi \frac{du}{d\xi} + (\Lambda - 1)u(\xi) = 0 \quad (108)$$

We define

$$\eta = \xi^2$$

Thus

$$\frac{du}{d\xi} = \frac{du}{d\eta} 2\xi \text{ and } \frac{d^2u}{d\xi^2} = \frac{d^2u}{d\eta^2} 4\eta + 2 \frac{du}{d\eta}$$

and Eq. (18) becomes

$$\frac{d^2u}{d\eta^2} + \left(\frac{1}{2} - \eta\right) \frac{du}{d\eta} + \frac{\Lambda - 1}{4} u(\eta) = 0 \quad (109)$$

which is the confluent hypergeometric equation with

$$c = \frac{1}{2} \quad \text{and} \quad a = -\frac{\Lambda - 1}{4} \quad (110)$$

Thus for any given value of  $\Lambda$

$$\psi_1(\xi) = {}_1F_1\left(\frac{1-\Lambda}{4}, \frac{1}{2}, \xi^2\right) e^{-\frac{1}{2}\xi^2} \quad (111)$$

and

$$\psi_2(\xi) = \xi {}_1F_1\left(\frac{3-\Lambda}{4}, \frac{3}{2}, \xi^2\right) e^{-\frac{1}{2}\xi^2} \quad (112)$$

will represent the two independent solutions of the Schrödinger equation [Eq. (13)]. Now, as mentioned earlier, if the infinite series given by Eq. (106) is not made into a polynomial, it will diverge as  $x^{a-c} e^x$  and therefore  $\psi_1(\xi)$  and  $\psi_2(\xi)$  will behave<sup>11</sup> as  $\exp(1/2\xi^2)$  for  $\xi \rightarrow \pm\infty$ . The even solution becomes a polynomial for

$$\Lambda = 1, 5, 9, \dots$$

and the odd solution becomes a polynomial for

$$\Lambda = 3, 7, 11, \dots$$

The results are the same as derived in Sec. 7.2. Indeed

$$H_n(\xi) = \begin{cases} (-1)^{n-2} \frac{n!}{\frac{n}{2}!} {}_1F_1\left(-\frac{n}{2}, \frac{1}{2}, \xi^2\right) & \text{for } n = 0, 2, 4, \dots \\ (-1)^{(n-1)/2} \frac{n!}{\left(\frac{n-1}{2}\right)!} 2\xi {}_1F_1\left(-\frac{n-1}{2}, \frac{3}{2}, \xi^2\right) & \text{for } n = 1, 3, 5, \dots \end{cases} \quad (113)$$

---

<sup>11</sup> We may mention here that we can always choose appropriate linear combinations of  $\psi_1(\xi)$  and  $\psi_2(\xi)$  so that they decay as  $\xi \rightarrow +\infty$  or as  $\xi \rightarrow -\infty$ . In fact such linear combinations are the  $D_\nu$  functions (see Solution 17.6); however, we cannot have a linear combination which will decay as  $\xi \rightarrow +\infty$  as well as for  $\xi \rightarrow -\infty$ , unless of course,  $\Lambda$  is one of the eigenvalues. This is somewhat similar to the functions  $\cosh x$  and  $\sinh x$  which diverge as  $x \rightarrow \pm\infty$ ; however, the linear combination  $\cosh x + \sinh x$  decays as  $x \rightarrow -\infty$  but diverges as  $x \rightarrow +\infty$ .

The solutions expressed by Eq. (113) are very convenient to use for a bounded parabolic potential (Problem 7.15), double oscillator (Problem 17.6), etc.

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## 7.9. Problems

**Problem 7.1** Show that the energy eigenvalues of the one-dimensional Schrödinger equation can never be less than the absolute minimum of  $V(x)$ .

**Problem 7.2** For a wave packet [see Eq. (51) of Chapter 4]

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) \left( -i \hbar \frac{\partial}{\partial x} \right) \Psi(x, t) dx$$

Use Eq. (59) for  $\Psi(x, t)$  to derive Eq. (63).

**Problem 7.3 (a)** Derive Eq. (36) for the probability distribution function for a classical oscillator. **(b)** Using the asymptotic form of the Hermite polynomials for large values of  $n$ , show that the quantum mechanical probability distribution function agrees with the corresponding classical result. (This is a consequence of the Bohr's correspondence principle.)

**Problem 7.4** For the harmonic oscillator in its ground state, show that the probability of finding it beyond the classical turning points is approximately 0.16.

**Problem 7.5 (a)** Substitute the function

$$\psi(x) = A e^{-bx^2}$$

in Eq. (10) to show that it indeed satisfies the equation only if

$$E = \frac{1}{2} \hbar \omega$$

and

$$b = \frac{1}{2} \frac{\mu \omega}{\hbar}$$

**(b)** Substitute the function

$$\psi(x) = A e^{-cx^4}$$

in Eq. (10) and show that it can never satisfy the equation.

**Problem 7.6 (a)** The ground state wave function

$$\psi_0(\xi) = N e^{-\frac{1}{2} \xi^2}$$

is one of the solutions of Eq. (13) for  $\Lambda = 1$ . Obtain the other solution in the form of an integral and show that it would behave as  $\exp\left[\frac{1}{2}\xi^2\right]$  for large values of  $x$ .

[Hint: Write  $\psi(x) = \psi_0(x)\phi(x)$  and obtain the differential equation satisfied by  $\phi(x)$ ]

(b) Repeat the above analysis for  $\psi_1(\xi)$  and  $\psi_2(\xi)$ .

**Problem 7.7** A harmonic oscillator is in a state described by the wave function

$$\Psi(x, 0) = \frac{1}{2} \psi_0(x) + \frac{i}{\sqrt{2}} \psi_1(x) + \frac{1}{\sqrt{2}} e^{i\pi/3} \psi_2(x)$$

where  $\psi_n(x)$  are the normalized Hermite-Gauss wave functions [see Eq. (32)].

(a) Is the wave function normalized?

(b) What is  $\Psi(x, t)$ ?

**Problem 7.8 (a)** Assume

$$\Psi(x, 0) = \psi_\alpha(x)$$

with  $\langle n \rangle = 400$ . Evaluate

$$\frac{\Delta x}{x_0}, \frac{\Delta p}{p_0}, \frac{\Delta E}{E_0} \quad \text{and} \quad P_n$$

(b) Repeat the analysis for  $\langle n \rangle = 10^8$  and physically interpret the results.

**Problem 7.9** Assuming the normalization condition given by Eq. (45), derive Eqs. (46) and (47).

**Problem 7.10** Assuming  $\Psi(x, 0)$  to be given by Eq. (54), use Eq. (101) to derive Eq. (59).

**Problem 7.11** Using Eqs (32) and (51) show that

$$\begin{aligned} a\psi_0(x) &= 0 \\ a\psi_1(x) &= \psi_0(x) \\ a\psi_2(x) &= \sqrt{2}\psi_1(x) \end{aligned}$$

In general

$$a\psi_n(x) = \sqrt{n}\psi_{n-1}(x) \tag{114}$$

**Problem 7.12** Equations (50) and (51) define the operator  $a$ . The adjoint of this operator is defined by the equation

$$\bar{a} = \frac{1}{\sqrt{2\mu\hbar\omega}} (\mu\omega x - ip) \tag{115}$$

or

$$\bar{a} = \sqrt{\frac{\mu\omega}{2\hbar}} x - \sqrt{\frac{\hbar}{2\mu\omega}} \frac{d}{dx}$$

Show that

$$\bar{a}\psi_0(x) = \psi_1(x) \quad (116)$$

$$\bar{a}\psi_1(x) = \sqrt{2}\psi_2(x) \quad (117)$$

and

$$\bar{a}\psi_2(x) = \sqrt{3}\psi_3(x) \quad (118)$$

**Problem 7.13** In this and the following problem replace  $\mu$  by  $m$  in the definitions of  $a$  and  $\bar{a}$ .

Solve the eigenvalue equation

$$(\mu a + \nu \bar{a})\psi_\beta(x) = \beta \psi_\beta(x)$$

to obtain

$$\psi_\beta(x) = \left( \frac{1}{\sqrt{\pi} \sigma_0} \right)^{\frac{1}{2}} \exp \left[ -\frac{(x - x_0)^2}{2 \sigma_0^2} \right] \quad (119)$$

where

$$\sigma_0 = \frac{1}{\gamma} \sqrt{\frac{\mu - \nu}{\mu + \nu}} \quad (120)$$

and

$$x_0 = \frac{1}{\gamma} \frac{\sqrt{2}\beta}{\mu + \nu} \quad (121)$$

Obviously we must choose  $\mu > \nu$ ; for  $\mu = 1$  and  $\nu = 0$  we get the coherent states.  $\psi_\beta(x)$  describes what is known as a *squeezed state*.

**Problem 7.14 (a)** Assuming  $\Psi(x, 0)$  to be  $\psi_\beta(x)$  as given in the previous problem, show by using Eq. (101) that

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{\pi} \sigma(t)} \exp \left[ -\frac{(x - x_0 \cos \omega t)^2}{\sigma^2(t)} \right] \quad (122)$$

where

$$\sigma(t) = \frac{1}{\sqrt{2} \gamma^2 \sigma_0} \left[ (\gamma \sigma_0)^4 + 1 + \{(\gamma \sigma_0)^4 - 1\} \cos 2\omega t \right]^{\frac{1}{2}} \quad (123)$$

Discuss the time evolution of  $\sigma(t)$ .

**(b)** Show that

$$\langle x \rangle = x_0 \cos \omega t \quad (124)$$

$$\langle x^2 \rangle = \langle x \rangle^2 + \frac{1}{2} \sigma^2(t) \quad (125)$$

and

$$\Delta x = \frac{1}{\sqrt{2}} \sigma(t) \quad (126)$$

**Problem 7.15** *Bounded Harmonic Potential*<sup>12</sup>

1. Consider the bounded linear harmonic potential given by

$$V(x) = \begin{cases} \frac{1}{2}\mu\omega^2x^2 & |x| < l/2 \\ \infty & |x| > l/2 \end{cases} \quad (127)$$

where  $x = \pm l/2$  represent the two boundaries of the potential. Show that the eigenvalues  $\Lambda$  are obtained by solving the following transcendental equations

$${}_1F_1\left(\frac{1-\Lambda}{4}, \frac{1}{2}, \xi_0^2\right) = 0 \text{ for even solutions} \quad (128)$$

$${}_1F_1\left(\frac{3-\Lambda}{4}, \frac{3}{2}, \xi_0^2\right) = 0 \text{ for odd solutions}$$

where  $\xi_0 = \gamma l/2$ .

2. For  $\xi_0^2 = 0.5$  and 2, solve the above equations numerically to obtain the first few eigenvalues  $\Lambda$ .

[Ans: The eigenvalues are (5.00, 19.88, 44.57, 79.12, ...) and (1.49, 5.49, 11.73, 20.38, ...) for  $\xi_0^2 = 0.5$  and 2.0 respectively, one could have guessed the eigenvalue 5.0 directly—how?].

**Problem 7.16** Consider the bounded linear harmonic potential given by

$$V(x) = \begin{cases} \infty & x = 0 \\ \frac{1}{2}\mu\omega^2x^2 & x > 0 \end{cases} \quad (129)$$

Show that the eigenvalues are

$$\Lambda = 3, 7, 11, \dots$$

What are the corresponding eigenfunctions?

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## 7.10. Solutions

**Solution 7.1** We write the Schrödinger equation in the form

<sup>12</sup> One of the very early works on the bounded harmonic oscillator was by D.S. Kothari and F.C. Auluck, Science and Culture, **6**, pp 370-1, 1940.

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} [V(x) - E] \psi(x)$$

If  $V(x) > E$  for all values of  $x$  then everywhere  $\psi''(x)$  has the same sign as  $\psi(x)$ . We assume  $\psi$  to be positive at some value of  $x$ ; then  $\psi''(x)$  will also be positive. Hence if  $\psi'$  is positive, then  $\psi \rightarrow \infty$  as  $x \rightarrow \infty$  and if  $\psi'$  is negative,  $\psi$  will tend to  $\infty$  as  $x \rightarrow -\infty$ . In either case,  $\psi(x)$  will blow up either at  $+\infty$  or at  $-\infty$ . We can have a similar argument if we assume  $\psi$  to be negative at some value of  $x$ .

**Solution 7.3** For the classical oscillator we may assume

$$x = x_0 \sin \omega t$$

where  $x_0$  represents the amplitude of motion. For  $0 < t < T/2$ , the velocity is everywhere positive and we may write

$$v = \omega x_0 \cos \omega t = \omega \sqrt{x_0^2 - x^2}$$

If  $P(x) dx$  represents the probability of finding the particle between  $x$  and  $x+dx$ , then

$$\begin{aligned} P(x) dx &= \text{Fractional time spent} \\ &\quad \text{between } x \text{ and } x+dx \\ &= \frac{dx/v}{T/2} \end{aligned}$$

Thus

$$P(x) dx = \frac{1}{\pi \sqrt{x_0^2 - x^2}} dx \quad (130)$$

According to quantum theory (see Eq. (32))

$$P(x) = |\psi_n(x)|^2 = \frac{\gamma}{2^n n! \sqrt{\pi}} \exp(-\xi^2) H_n^2(\xi) \quad (131)$$

For large values of  $n$ , the asymptotic expression is given by (see, eg. Reference 4)

$$H_n(\xi) \sim \frac{2^{(n+2)/2}}{\sqrt{2 \cos \beta}} \sqrt{\frac{n!}{\sqrt{2n\pi}}} e^{n\beta^2} \cos \left[ \left(2n + \frac{1}{2}\right)\beta - \frac{n\pi}{2} \right] \quad (132)$$

where  $\beta$  is the smallest positive angle whose sine is  $(\xi/\sqrt{2n})$ . For large values of  $n$ , we may take the average value of the  $\cos^2$  term as  $\frac{1}{2}$ . Further,

$$x_0 = \left( \frac{2E}{\mu\omega} \right)^{\frac{1}{2}} = \frac{\sqrt{2n+1}}{\gamma} \sim \frac{\sqrt{2n}}{\gamma}$$

Thus

$$\begin{aligned}\cos \beta &= \sqrt{1 - \sin^2 \beta} = \sqrt{1 - \frac{1}{2n} \xi^2} \\ &\simeq \frac{1}{\xi_0} \sqrt{\xi_0^2 - \xi^2}\end{aligned}$$

Elementary algebra gives

$$P(x) \simeq \frac{1}{\pi \sqrt{x_0^2 - x^2}}$$

**Solution 7.4** The required probability is

$$\begin{aligned}2 \int_{x_0}^{\infty} |\Psi_0(x)|^2 dx &= \frac{2}{\sqrt{\pi}} \int_1^{\infty} e^{-\xi^2} d\xi \\ &\simeq 0.16\end{aligned}$$

**Solution 7.6**  $\psi_n(\xi)$  [as given by Eq. (32)] is one of the solutions of the equation

$$\frac{d^2\psi}{d\xi^2} + [(2n+1) - \xi^2] \psi(\xi) = 0 \quad (133)$$

In order to obtain the other solution, we write

$$\psi(\xi) = \psi_n(\xi) \phi(\xi)$$

Thus

$$\psi''(\xi) = \psi''_n(\xi) \phi(\xi) + 2\psi'_n(\xi) \phi'(\xi) + \psi_n(\xi) \phi''(\xi)$$

Substituting in Eq. (133) we get

$$\begin{aligned}\left[ \frac{d^2\psi_n}{d\xi^2} + [(2n+1) - \xi^2] \psi_n(\xi) \right] \phi(\xi) \\ + 2\psi'_n(\xi) \phi'(\xi) + \psi_n(\xi) \phi''(\xi) = 0 \quad (134)\end{aligned}$$

Since  $\psi_n(\xi)$  is a solution of Eq. (133) the first term in the LHS vanishes and we obtain

$$2 \frac{\psi'_n(\xi)}{\psi_n(\xi)} + \frac{\phi''(\xi)}{\phi'(\xi)} = 0$$

or

$$\frac{d}{d\xi} [2 \ln \psi_n(\xi) + \ln \phi'(\xi)] = 0$$

or

$$\ln [\psi_n^2(\xi) \phi'(\xi)] = \text{constant}$$

Thus

$$\phi'(\xi) = \frac{\text{constant}}{\psi_n^2(\xi)}$$

For  $n = 0$ , we therefore have

$$\frac{d\phi}{d\xi} = C_1 e^{\xi^2}$$

or

$$\phi(\xi) = C_1 \int_{-\infty}^{\xi} e^{\xi'^2} d\xi' + C_2$$

Thus

$$\psi(\xi) = C_1 e^{-\frac{1}{2}\xi^2} \int_{-\infty}^{\xi} e^{\xi'^2} d\xi' + C_2 e^{-\frac{1}{2}\xi^2}$$

which represents the general solution of Eq. (133). The last term is nothing but  $\psi_0(\xi)$ . Since the integral behaves as  $\exp(\xi^2)$ , the first term would behave as  $e^{\frac{1}{2}\xi^2}$ . Indeed

$$\begin{aligned} e^{-\frac{1}{2}\xi^2} \int_{-\infty}^{\xi} e^{\xi'^2} d\xi' &= e^{-\frac{1}{2}\xi^2} \int \left[ 1 + \xi'^2 + \frac{(\xi'^4)}{2!} + \frac{(\xi'^6)}{3!} + \dots \right] d\xi' \\ &= e^{-\frac{1}{2}\xi^2} \left[ \xi + \frac{(\xi^3)}{3} + \frac{(\xi^5)}{10} + \frac{(\xi^7)}{42} + \dots \right] \end{aligned}$$

The quantity within the brackets is the term proportional to  $c_1$  in Eq. (29)—as it indeed should be.

**Solution 7.14** From Eq. (123) we may note the following

(a) If

$$\gamma \sigma_0 = 1 \Rightarrow \sigma_0 = \frac{1}{\gamma}$$

i.e. if the initial width is the same as the ground state width, then

$$\sigma^2(t) = \sigma_0^2 = \frac{1}{\gamma} \quad (\text{independent of time})$$

Thus the width does not change and we have the coherent state.

(b) In Fig. 7.9 we have plotted the time evolution of the wave packet for a squeezed state corresponding to  $\gamma\sigma_0 = 1.5$  with  $\xi_0 = 5$ ; the corresponding variation of  $\Delta x$  with time is shown in Fig. 7.10. As can be seen, we find that the width of the wave

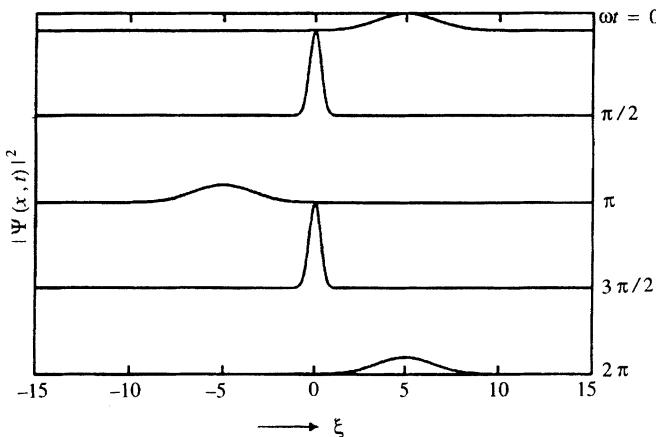


Figure 7.9. The variation of  $|\Psi(x, t)|^2$  at  $\omega t = 0, \pi/2, \pi, 3\pi/2, 2\pi$  for a squeezed state ( $\gamma \sigma_0 = 1.5; \xi_0 = 5$ ).

packet decreases below the ground state width; this is known as “squeezing” which has important applications.

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{+\infty} x |\Psi(x)|^2 dx = \frac{1}{\sqrt{\pi} \sigma(t)} \int_{-\infty}^{+\infty} x e^{-(x - x_0 \cos \omega t)^2 / \sigma^2(t)} dx \\ &= x_0 \cos \omega t \end{aligned}$$

and

$$\begin{aligned} \langle x^2 \rangle &= \frac{1}{\sqrt{\pi} \sigma(t)} \int_{-\infty}^{+\infty} x^2 e^{-(x - x_0 \cos \omega t)^2 / \sigma^2(t)} dx \\ &= x_0^2 \cos^2 \omega t + \frac{1}{2} \sigma^2(t) \end{aligned}$$

Thus

$$\Delta x = \frac{1}{\sqrt{2}} \sigma(t)$$

showing that  $\Delta x$  oscillates with time (see Fig. 7.10) with its value becoming smaller than the ground state value.

## 7.11. Sample questions

- Q. 1    a) Write the Hamiltonian  $H$  for the linear harmonic oscillator problem.

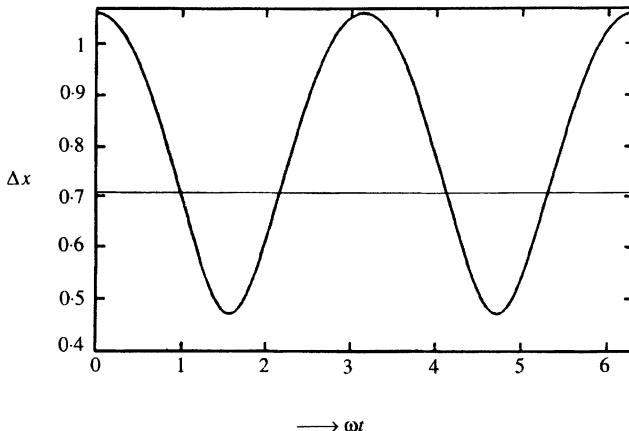


Figure 7.10. The variation of  $\Delta x$  with  $\omega t$  for a squeezed state ( $\gamma\sigma_0 = 1.5$ ;  $\xi_0 = 5$ ). The horizontal line corresponds to the ground state.

- b) For what value of  $g$ , would the function  $xe^{-gx^2}$  be an eigenfunction of  $H$ ? What is the corresponding eigenvalue?
- c) For what values of  $\alpha$  and  $\beta$  would the function  $(1 + \alpha x^2)e^{-\beta x^2}$  be an eigenfunction of  $H$ ? What is the corresponding eigenvalue?

Q. 2 In the linear harmonic oscillator problem we assume

$$\psi(x) = \left( \sum_{r=0}^{\infty} c_r \xi^{r+s} \right) \exp \left[ -\frac{1}{2} \xi^2 \right] \quad (135)$$

and obtain

$$c_r = \frac{2s + 2r - 3 - \Lambda}{(s+r)(s+r-1)} c_{r-2} \quad r \geq 2$$

where  $\Lambda = 2E/\hbar\omega$ . We use  $s = 0$  as the root of the indicial equation.

- a) Why should the infinite series in Eq. (135) be made into a polynomial?
- b) For what values of  $\lambda$  will the infinite series become a polynomial?
- c) Determine the normalized eigenfunction for the first excited state.
  
- a) Consider the operator

$$a = \frac{\mu\omega x + ip}{\sqrt{2\mu\hbar\omega}}$$

where symbols have their usual meaning. Replace  $p$  by the corresponding differential operator and obtain the eigenfunctions and eigenvalues of the operator  $a$ . Normalize the eigenfunction.

- b) Discuss the solution of the eigenvalue equation for  $\bar{a}$ .

### 7.12. References and suggested reading

1. F.T. Arechi, *Quantum Optics and Photon Statistics*, in *Lasers and Their Applications*, A. Sona (ed.), Gorden and Breach, New York, p. 497.
2. R. Loudon, *The Quantum Theory of Light*, Clarendon Press, Oxford (1973).
3. A.K. Ghatak, I.C. Goyal and S.J. Chua, *Mathematical Physics*, Macmillan India Limited, New Delhi (1995).
4. J.L. Powell and B. Craseman, *Quantum Mechanics*, Addison-Wesley (1961).

## One-Dimensional Barrier Transmission Problems

*It is possible in quantum mechanics to sneak quickly across a region which is illegal energetically.*

— RICHARD FEYNMAN<sup>1</sup>

### 8.1. Introduction

In the previous two chapters we considered the bound states corresponding to one-dimensional potentials. For example, we showed that for a particle in a one-dimensional potential well of finite depth (see Sec. 6.6.2 and Fig. 6.3) there exist a number of discrete states (for  $E < V_0$ ), the corresponding wave functions vanishing at large distances from the origin. In this chapter we will consider solutions for  $E > V_0$  and will show that the corresponding wave functions in the region  $|x| > a/2$  do not vanish at large distances from the origin and  $E$  can have any arbitrary value (greater than  $V_0$ ). Thus, for such a potential well there exists a finite number of bound states (with  $E < V_0$ ) and a continuum of states for which  $E > V_0$ . A good example is the neutron-proton problem. For  $E < 0$  we have the deuteron nucleus (see Example 10.6) and for  $E > 0$  we have the neutron-proton scattering problem (see, e.g. Sec. 24.5.3).

It may be mentioned that there are situations where the continuous spectrum does not exist at all; e.g. for the infinitely deep potential well (see Sec. 6.6.1), the linear harmonic oscillator (see Sec. 7.3), etc. On the other hand, there may be situations where the discrete spectrum may not exist at all and one may have only the continuous spectrum; examples of such a situation are the potential step and the rectangular potential barrier discussed in Secs 8.2 and 8.3, the free particle discussed in Sec. 5.2, etc. Further, there may be a continuum along with an infinite number of discrete states as in the hydrogen atom problem.

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<sup>1</sup> The author found this quotation in *The Quantum Universe* by T. Hey and P. Walters, Cambridge University Press, Cambridge (1987).

The solutions corresponding to the continuous spectrum are of great importance in connection with the scattering of a particle by a potential field. For example, in Secs. 8.2 and 8.3 we will consider the incidence of a particle (of specified energy) on a potential step and on a rectangular potential barrier respectively and in each case we will calculate the reflection and transmission coefficients<sup>2</sup>. Such barrier transmission problems have many practical applications, e.g. in Esaki tunnelling (see Problems 8.8 and 17.11), field emission (see Problem 17.9),  $\alpha$ -decay (see Sec. 17.7), etc. However, unfortunately for most practical cases the exact solution is very difficult and one usually resorts to approximate techniques; one such technique is the JWKB approximation which will be discussed in Chapter 17 along with some practical applications.

## 8.2. The potential step

We first consider a potential step (see Fig. 8.1) for which

$$\begin{aligned} V(x) &= 0 \quad \text{for } x < 0 \\ &= V_0 \quad \text{for } x > 0 \end{aligned} \tag{1}$$

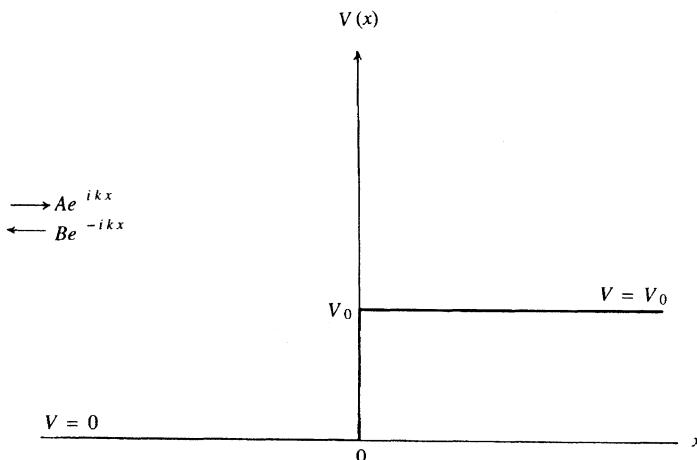


Figure 8.1. The reflection of a wave by a potential step at  $x = 0$ .

We consider the incidence of a particle (of energy  $E$ ) from the left of the barrier. Classically, if  $E > V_0$ , the particle penetrates the barrier and keeps on moving

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<sup>2</sup> In the corresponding three-dimensional situation, the scattering occurs into a solid angle  $d\Omega$ ; see Chapter 19 of Ref. 1.

(with reduced kinetic energy) in the positive  $x$ -direction; on the other hand, if  $E < V_0$  the particle is reflected back at  $x = 0$  because the particle does not have sufficient energy to be in the region  $x > 0$ . Quantum mechanically, we will show that for  $E > V_0$ , the particle may undergo reflection and for  $E < V_0$ , although the reflection coefficient is unity, the wave function is non-zero in the region  $x > 0$  implying that there is a finite probability of finding the particle in the region  $x > 0$ .

$$E > V_0$$

We will first discuss the case  $E > V_0$ . The Schrödinger equation is

$$\frac{d^2\psi(x)}{dx^2} + k^2 \psi(x) = 0 \quad \text{for } x < 0 \quad (2)$$

and

$$\frac{d^2\psi(x)}{dx^2} + k_1^2 \psi(x) = 0 \quad \text{for } x > 0$$

where

$$k = \left[ \frac{2mE}{\hbar^2} \right]^{1/2} \quad \text{and} \quad k_1 = \left[ \frac{2m}{\hbar^2} (E - V_0) \right]^{1/2} \quad (3)$$

The solutions are

$$\begin{aligned} \psi(x) &= A e^{ikx} + B e^{-ikx} \quad \text{for } x < 0 \\ &= C e^{ik_1 x} + D e^{-ik_1 x} \quad \text{for } x > 0 \end{aligned} \quad (4)$$

If we multiply the wave functions by the time dependent factor  $\exp(-iEt/\hbar)$ , we can interpret the terms  $A e^{ikx}$  and  $C e^{ik_1 x}$  as waves propagating in the  $+x$  direction and the terms  $B e^{-ikx}$  and  $D e^{-ik_1 x}$  as waves propagating in the  $-x$  direction. Since we are considering the incidence of a particle from the left of the barrier at  $x = 0$ , there cannot be a wave propagating in the  $-x$  direction in the region  $x > 0$  and hence we must put  $D = 0$ . Continuity of  $\psi$  and  $d\psi/dx$  at  $x = 0$  gives us

$$A + B = C$$

and

$$ik(A - B) = ik_1 C$$

from which we readily obtain

$$B = \frac{k - k_1}{k + k_1} A \quad (5)$$

$$C = \frac{2k}{k + k_1} A \quad (6)$$

Now, the current density is given by [see Eq. (36) of Chapter 5]

$$\mathbf{J} = \operatorname{Re} \left[ \psi^* \frac{\hbar}{im} \frac{\partial \psi}{\partial x} \right] \hat{\mathbf{x}} \quad (7)$$

If  $J_i$ ,  $J_r$  and  $J_t$  represent the magnitude of the current densities associated with the incident wave (corresponding to  $A e^{ikx}$ ), reflected wave (corresponding to  $B e^{-ikx}$ ) and the transmitted wave (corresponding to  $C e^{ik_1 x}$ ) respectively then use of Eq. (7) would readily give

$$J_i = \frac{\hbar k}{m} |A|^2 \quad (8)$$

$$J_r = \frac{\hbar k}{m} |B|^2 \quad (9)$$

and

$$J_t = \frac{\hbar k_1}{m} |C|^2 \quad (10)$$

#### *Reflection and transmission coefficients*

Thus the reflection and transmission coefficients are given by

$$R = \frac{J_r}{J_i} = \frac{|B|^2}{|A|^2} = \frac{(k - k_1)^2}{(k + k_1)^2} \quad (11)$$

and

$$T = \frac{J_t}{J_i} = \frac{k_1 |C|^2}{k |A|^2} = \frac{4kk_1}{(k + k_1)^2} \quad (12)$$

It is easy to see that  $R + T = 1$  as it indeed should be.

$$E < V_0$$

For  $E < V_0$ , the analysis remains similar except that  $k_1$  has to be replaced by  $i\kappa$ :

$$k_1 \rightarrow i\kappa = i \left[ \frac{2m}{\hbar^2} (V_0 - E) \right]^{1/2} \quad (13)$$

In the region  $x > 0$  we now have solutions  $C e^{-\kappa x}$  and  $D e^{\kappa x}$ ; the latter we have to reject because it increases indefinitely with  $x$ . Continuity of  $\psi$  and  $d\psi/dx$  leads to:

$$B = \frac{k - i\kappa}{k + i\kappa} A = e^{-2i\alpha} A \quad (14)$$

where

$$\tan \alpha = \frac{\kappa}{k} \quad (15)$$

Equation (14) tells us that there is a phase change on reflection but the amplitude of the reflected wave is the same as that of the incident wave. In the region  $x > 0$ , since the wave function is now real, the transmitted current vanishes and one has

$$R = 1 \text{ and } T = 0 \quad (16)$$

It may be noted that although the transmission coefficient vanishes, the wave function is not zero in the region  $x > 0$ , i.e. there is a finite probability of finding the particle in the *classically-forbidden* region. However, in order to observe the particle in the region  $x > 0$ ,  $\Delta x \sim 1/\kappa$  (see Problem 8.7) and therefore the uncertainty in the momentum should be given by

$$\Delta p \gtrsim \frac{\hbar}{\Delta x} \sim \hbar\kappa \sim \sqrt{2m(V_0 - E)} \quad (17)$$

The uncertainty in the kinetic energy will be  $\sim \frac{(\Delta p)^2}{2m} \sim (V_0 - E)$  which should be sufficient to raise it to the classically-allowed region. Thus, if we try to observe the particle in the region  $x > 0$ , we necessarily impart so much of kinetic energy to it that the total energy is greater than  $V_0$ .

In order to get a better physical insight, we should consider the reflection (and transmission) of a wave packet. This is discussed in Sec. 8.4 (see also Problem 8.6).

### 8.3. The rectangular potential barrier

We next consider a potential barrier of the type shown in Fig. 8.2. Classically, for

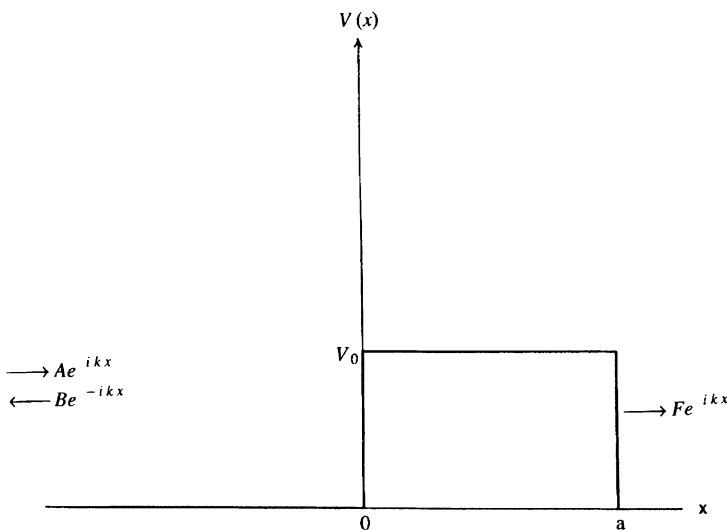


Figure 8.2. The reflection and transmission of a wave by a rectangular potential barrier.

a particle of energy  $E$  incident on the barrier, if  $E < V_0$  the particle gets reflected by the barrier and if  $E > V_0$ , the particle gets transmitted through the barrier. We will see that according to quantum mechanics, even for  $E < V_0$  there is a finite probability of the particle *tunnelling* through the barrier. This is entirely a quantum

mechanical effect and field emission of electrons (see Problem 17.9), emission of  $\alpha$ -particles from the nucleus (see Sec. 17.7) are examples of this *tunnelling* phenomenon. Further, for  $E > V_0$ , there may be a finite probability for reflection.

$$E < V_0$$

We first consider  $E < V_0$ . For such a case the solutions of the Schrödinger equation in the three regions are given by:

$$\begin{aligned}\psi &= A e^{ikx} + B e^{-ikx} & x < 0 \\ &= C e^{\kappa x} + D e^{-\kappa x} & 0 < x < a \\ &= F e^{ikx} + G e^{-ikx} & x > a\end{aligned}\quad (18)$$

where

$$k = \left( \frac{2mE}{\hbar^2} \right)^{1/2} \quad \text{and} \quad \kappa = \left( \frac{2m(V_0 - E)}{\hbar^2} \right)^{1/2} \quad (19)$$

As in Sec. 8.2 we set  $G = 0$  because there cannot be a wave propagating in the  $-x$  direction in the region  $x > a$ . Continuity of  $\psi$  and  $d\psi/dx$  at  $x = 0$  and at  $x = a$  gives us

$$\begin{aligned}A + B &= C + D \\ \frac{ik}{\kappa} (A - B) &= C - D\end{aligned}$$

Thus

$$C = \frac{1}{2} \left( 1 + \frac{ik}{\kappa} \right) A + \frac{1}{2} \left( 1 - \frac{ik}{\kappa} \right) B \quad (20)$$

and

$$D = \frac{1}{2} \left( 1 - \frac{ik}{\kappa} \right) A + \frac{1}{2} \left( 1 + \frac{ik}{\kappa} \right) B \quad (21)$$

Continuity conditions at  $x = a$  give us

$$C e^{\kappa a} + D e^{-\kappa a} = F e^{ika} \quad (22)$$

and

$$C e^{\kappa a} - D e^{-\kappa a} = \frac{ik}{\kappa} F e^{ika} \quad (23)$$

Thus

$$\begin{aligned}C &= \frac{1}{2} \left( 1 + \frac{ik}{\kappa} \right) F e^{-\kappa a} e^{ika} \\ D &= \frac{1}{2} \left( 1 - \frac{ik}{\kappa} \right) F e^{\kappa a} e^{ika}\end{aligned}$$

and

$$\frac{C}{D} = \frac{\left( 1 + \frac{ik}{\kappa} \right)}{\left( 1 - \frac{ik}{\kappa} \right)} e^{-2\kappa a} = \frac{\left( 1 + \frac{ik}{\kappa} \right) A + \left( 1 - \frac{ik}{\kappa} \right) B}{\left( 1 - \frac{ik}{\kappa} \right) A + \left( 1 + \frac{ik}{\kappa} \right) B}$$

where in the last step we have used Eqs. (20) and (21). Simple manipulations give us

$$\frac{B}{A} = \frac{(k^2 + \kappa^2) \sinh \kappa a}{(k^2 - \kappa^2) \sinh \kappa a + 2ik\kappa \cosh \kappa a} \quad (24)$$

We also have

$$\frac{F}{A} = \frac{2ik\kappa e^{-ika}}{(k^2 - \kappa^2) \sinh \kappa a + 2ik\kappa \cosh \kappa a} \quad (25)$$

### Reflection and transmission coefficients

The above equations will lead to the following expressions for the reflection and transmission coefficients:

$$R = \frac{J_r}{J_i} = \frac{\frac{\hbar k}{m} |B|^2}{\frac{\hbar k}{m} |A|^2} = \left[ 1 + \frac{4\epsilon (1-\epsilon)}{\sinh^2(\alpha\sqrt{1-\epsilon})} \right]^{-1} \quad (26)$$

$$T = \frac{J_t}{J_i} = \frac{\frac{\hbar k}{m} |C|^2}{\frac{\hbar k}{m} |A|^2} = \left[ 1 + \frac{\sinh^2(\alpha\sqrt{1-\epsilon})}{4\epsilon (1-\epsilon)} \right]^{-1} \quad (27)$$

where

$$\epsilon = \frac{E}{V_0} \quad (28)$$

and

$$\alpha = \left( \frac{2mV_0a^2}{\hbar^2} \right)^{1/2} \quad (29)$$

is a dimensionless variable characterising the potential. In writing Eqs. (26) and (27) we have used the fact that

$$\kappa a = \alpha \sqrt{1 - \epsilon}$$

Notice that

$$R + T = 1$$

Further for  $\kappa a \gg 1$

$$T \approx 16\epsilon(1-\epsilon)e^{-2\kappa a} \quad (30)$$

$$E > V_0$$

For  $E > V_0$ , the analysis is very similar, excepting that, in the region  $0 < x < a$ , instead of the solutions  $e^{\pm\kappa x}$  we will have solutions  $e^{\pm ik_1 x}$  where

$$k_1 = \left[ \frac{2m(E-V_0)}{\hbar^2} \right]^{1/2} \quad (31)$$

Thus we have to replace  $\kappa$  by  $ik_1$ , everywhere. The final results are

$$R = \left[ 1 + \frac{4\epsilon(\epsilon-1)}{\sin^2(\alpha\sqrt{\epsilon-1})} \right]^{-1} \quad (32)$$

$$T = \left[ 1 + \frac{\sin^2(\alpha\sqrt{\epsilon-1})}{4\epsilon(\epsilon-1)} \right]^{-1} \quad (33)$$

Once again  $R + T = 1$ . In writing Eqs (32) and (33) we have used the fact that

$$k_1 a = \alpha\sqrt{\epsilon - 1}$$

In Fig. 8.3 we have plotted variations of the reflection and transmission coef-

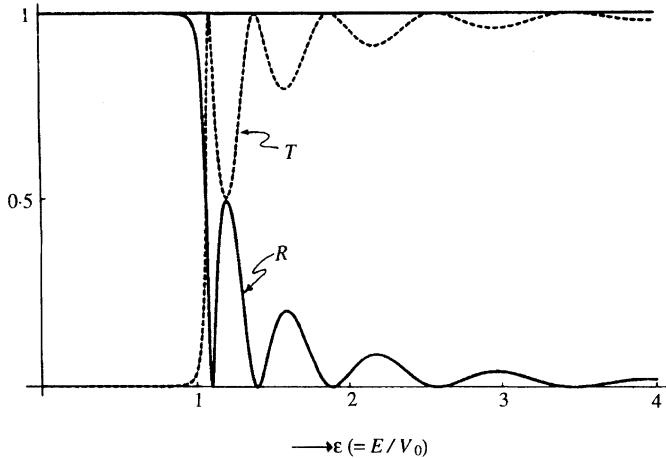


Figure 8.3. The solid and dotted curves correspond respectively to the variation of the reflection and transmission coefficients with  $\epsilon = (E / V_0)$  for a rectangular potential barrier (see Fig. 8.2) with  $\alpha = 10.0$ .

ficients with  $\epsilon (= E / V_0)$  for  $\alpha = 10.0$ . It may be noticed that the transmission coefficient is unity for

$$k_1 a = \pi, 2\pi, \dots \quad (34)$$

or

$$a = \frac{\lambda_1}{2}, 2\left(\frac{\lambda_1}{2}\right), 3\left(\frac{\lambda_1}{2}\right), \dots \quad (35)$$

where  $\lambda_1 = 2\pi/k_1$ . Thus whenever the barrier width is a multiple of  $\lambda_1/2$ , perfect transmission occurs; this is similar to the interference pattern observed in a Fabry-Perot etalon. This is also observed for a potential well as discussed in Problem 8.1.

#### 8.4. The reflection and transmission of a wave packet

In the analysis discussed in Secs 8.2 and 8.3 we obtained expressions for reflection and transmission coefficients by considering the time independent solutions of the

Schrödinger equation. However, in order to get a better physical insight we consider the incidence of a wave packet on a potential barrier. For the sake of simplicity we consider the reflection of a wave packet by a potential step, similar analysis can be carried out for other potential barriers also.

We will assume  $E < V_0$  so that the solutions of the Schrödinger equation are given by

$$\begin{aligned}\psi(x) &= A e^{ikx} + B e^{-ikx} & x < 0 \\ &= C e^{-\kappa x} & x > 0\end{aligned}\quad (36)$$

Continuity conditions would give us [cf. Eqs (5) and (6)]:

$$B = \frac{k - i\kappa}{k + i\kappa} A \quad (37)$$

$$C = \frac{2k}{k + i\kappa} A \quad (38)$$

Thus the solution in the region  $x < 0$  can be written in the form

$$\psi(x) = A \left[ e^{ikx} + e^{-2i\alpha(k)} e^{-ikx} \right] \quad (39)$$

where

$$\alpha(k) = \tan^{-1} \left( \frac{\kappa}{k} \right) = \tan^{-1} \sqrt{\frac{V_0 - E}{E}} \quad (40)$$

Since all values of  $E$  are possible, we can construct a wave packet formed by the superposition of plane waves (cf. Sec. 5.5):

$$\Psi(x, t) = \frac{1}{2\pi} \int_0^\beta A(k) \left[ e^{ikx} + e^{-2i\alpha(k)} e^{-ikx} \right] e^{-i\omega(k)t} dk \quad (41)$$

where

$$\omega(k) = \frac{\hbar k^2}{2m} \quad (42)$$

and the upper limit  $\beta$  corresponds to  $E = V_0$ :

$$\beta = \sqrt{\frac{2mV_0}{\hbar^2}} \quad (43)$$

We write Eq. (41) as a superposition of incident and reflected wave packets

$$\Psi(x, t) = \Psi_i(x, t) + \Psi_r(x, t) \quad (44)$$

where

*Incident wave packet*

$$\Psi_i(x, t) = \frac{1}{\sqrt{2\pi}} \int_0^\beta |A(k)| e^{i[kx - \omega(k)t + \phi(k)]} dk \quad (45)$$

*Reflected wave packet*

$$\Psi_r(x, t) = \frac{1}{\sqrt{2\pi}} \int_0^\beta |A(k)| e^{-i[kx + \omega(k)t + 2\alpha(k) - \phi(k)]} dk \quad (46)$$

and

$$A(k) = |A(k)| e^{i\phi(k)} \quad (47)$$

If we assume  $|A(k)|$  to be a sharply peaked function around  $k = k_0$  and carry out an analysis similar to that given in Sec. 5.5, we would readily obtain the following expressions for the centre of the wave packet associated with the incident and reflected waves

$$x_c^{\text{inc}}(t) = x_0 + v_g t \quad (48)$$

$$x_c^{\text{refl}}(t) = -x_0 - v_g t + \tau \quad (49)$$

where

$$x_0 = -\left. \frac{d\phi}{dk} \right|_{k=k_0} \quad (50)$$

$$v_g = \left. \frac{d\omega}{dk} \right|_{k=k_0} = \frac{\hbar k_0}{m} \quad (51)$$

and

*Time delay*

$$\tau = -2 \left. \frac{d\alpha}{dk} \right|_{k=k_0} = \frac{2}{\sqrt{\beta^2 - k_0^2}} \quad (52)$$

represents the time delay<sup>3</sup> introduced during the reflection of the wave packet. Obviously,  $x_0$  is negative; further, both  $x_c^{\text{inc}}(t)$  and  $x_c^{\text{refl}}(t)$  should be negative because the solution given by Eq. (41) corresponds to the region  $x < 0$ . Now at  $t = 0$  we assume the packet to be far away from the barrier (see Fig. 8.4) and as  $t$  increases the packet moves towards the barrier. At a much later time the reflected

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<sup>3</sup> This can be physically understood from the fact that since the wave function is finite in the region  $x > 0$  (see Sec. 8.2) the packet can be thought of as penetrating into the region  $x > 0$  for a certain distance and then coming back (see the discussion at the end of this section and Problem 8.5); the corresponding optical problem is discussed in Chapter 11 of Ref. 2.

packet moves towards the left (see Fig. 8.6) with the same group velocity  $v_g$ . At intermediate times the incident and reflected waves interfere near  $x = 0$  and the total wave function is quite complicated (see Fig. 8.5). Finally, the transmitted wave packet (in the region  $x > 0$ ) will be given by

*Transmitted wave packet*

$$\begin{aligned} \Psi_t = & \frac{1}{\sqrt{2\pi}} \int_0^\beta |A(k)| \frac{2k}{\sqrt{k^2 + \kappa^2}} \\ & \times \exp[-\kappa(k)x - i\{\omega(k)t + \alpha(k) - \phi(k)\}] dk \end{aligned} \quad (53)$$

where  $\omega(k)$  is given by Eq. (42) and use has been made of the fact that the amplitude of the transmitted wave packet is given by [see Eq. (6)]

$$C = \frac{2k}{k + i\kappa} A = \frac{2k}{(k^2 + \kappa^2)^{1/2}} e^{-i\alpha(k)} \quad (54)$$

As a simple example, we assume that at  $t = 0$ , the particle is described by a localized Gaussian wave packet given by the following equation (cf. Example 5.1)

$$\Psi(x, 0) = \frac{1}{(\pi\sigma^2)^{1/4}} e^{-(x-x_0)^2/2\sigma^2} e^{ik_0 x} \quad (55)$$

We assume  $x_0 \gg \sigma$  so that the particle is localized far away from the potential step. The quantity  $\hbar k_0$  represents the average momentum of the wave packet. Now

$$A(k) \approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x, 0) e^{-ikx} dx \quad (56)$$

where we have put the limits from  $-\infty$  to  $+\infty$  because for  $|x - x_0| \gtrsim 4\sigma$  the integrand has a negligible value. Carrying out the integration, we readily get

$$A(k) \approx \left(\frac{\sigma^2}{\pi}\right)^{1/4} \exp\left[-\frac{1}{2}\sigma^2(k - k_0)^2 - i(k - k_0)x_0\right] \quad (57)$$

Thus

$$\begin{aligned} \Psi(X, \tau) = & \text{const. } \int_0^\delta \exp\left[-\frac{1}{2}\alpha^2(K-1)^2 - i(K-1)\gamma\right] \\ & \times [e^{iKX} + r(K) e^{-iKX}] e^{-iK^2\tau/2} dK \end{aligned} \quad (58)$$

where we have introduced the following dimensionless variables

$$\begin{aligned} K &= \frac{k}{k_0}, \quad X = k_0 x, \quad \tau = \frac{t}{m/(\hbar k_0^2)} \\ \alpha &= k_0 \sigma, \quad \gamma = k_0 x_0, \quad \delta = \sqrt{\frac{V_0}{(\hbar^2 k_0^2 / 2m)}} \end{aligned} \quad (59)$$

Further

$$r(K) = \frac{1 - i\Gamma(K)}{1 + i\Gamma(K)} \quad (60)$$

where

$$\Gamma(K) = \frac{\kappa}{K} = \sqrt{\frac{\delta^2}{K^2} - 1} \quad (61)$$

Figure 8.4 shows the results of the numerical integration for

$$\alpha = 10, \beta = -100, \delta = 2$$

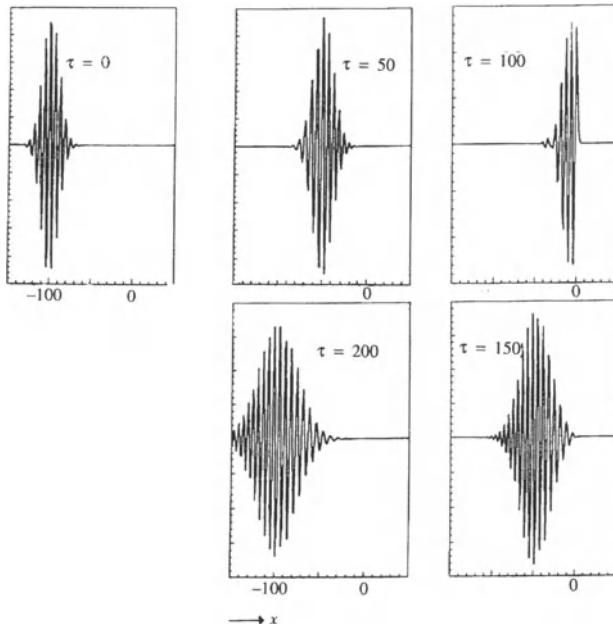


Figure 8.4. The reflection of a Gaussian wave packet by a potential step at  $\tau = 0, 50, 100, 150$  and  $250$ ;  $\alpha = 10, \beta = -100$  and  $\delta = 2$ . [Calculations courtesy Mr. Norman Lim]

at

$$\tau = 0, 50, 100, 150 \text{ and } 200$$

The figure shows the penetration of the wave packet inside the barrier and also the slight broadening of the reflected wave packet. Figure 8.5 shows the corresponding probability distributions at different values of  $\tau$ .

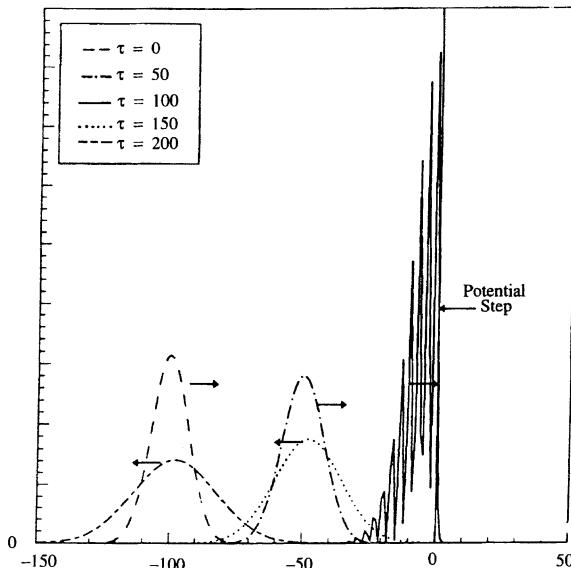
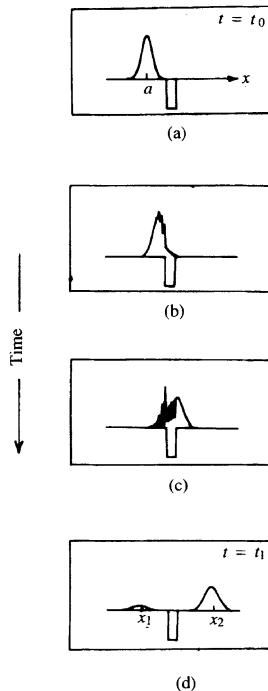


Figure 8.5. Variation of  $|\Psi(X, \tau)|^2$  for the Gaussian wave packet at different values of  $\tau$ ;  $\alpha = 10$ ,  $\beta = -100$  and  $\delta = 2$ . Note the broadening of the wave packet. [Calculations courtesy Mr. Norman Lim]

We conclude this section by noting that Goldberg *et al.* (Ref. 3) have obtained numerical solutions of the time dependent Schrödinger equation to study the reflection and transmission of a wave packet by a square well and by a rectangular barrier. One of their results is shown in Fig. 8.6. Figure 8.6(a) tells us that at  $t = t_0$  the particle (localized around  $x = a$ ) is described by a Gaussian wave packet and is approaching the square well potential. Figures 8.6(b), 8.6(c) and 8.6(d) give us the form of the wave packet at subsequent times. It is interesting to note that at  $t = t_1$  the particle is described by two packets one centered around  $x = x_1$  and the other around  $x = x_2$ . Thus at  $t = t_1$  the particle is at both the places in the sense that there are finite probabilities of finding the particle around  $x = x_1$  as well as around  $x = x_2$ ; however, if we try to determine the position of the particle then it will be found either near  $x = x_1$  or near  $x = x_2$ . A similar situation arises when a light wave gets partially reflected by a dielectric (like glass). In classical optics, we have a reflected beam and a transmitted beam. However, if we consider a single photon then it would be described by a wave function associated with the reflected



*Figure 8.6.* Reflection and transmission of a wave packet by a square well; the mean energy of the packet corresponds to the well depth [adapted from Ref. 3].

beam superposed by a wave function associated with the transmitted beam; thus it is present in the reflected beam as well as in the transmitted beam. If we make a measurement then it will be found either in the reflected beam or in the transmitted beam.

## 8.5. Problems

**Problem 8.1** Consider a square well potential given by

$$\begin{aligned} V(x) &= -V_0 & |x| < a/2 \\ &= 0 & |x| > a/2 \end{aligned} \tag{62}$$

(see Fig. 8.7). In Sec. 6.6.2 we had discussed the bound states for such a potential well. Discuss the solutions of the Schrödinger equation for  $E > 0$  and assuming the incidence of a particle of energy  $E$  from the left show that the transmission

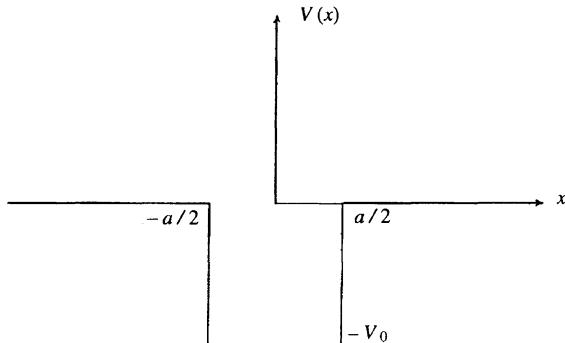


Figure 8.7. The square well potential

coefficient is given by

$$T = \left[ 1 + \frac{1}{4} \left( \frac{k}{k_2} - \frac{k_2}{k} \right)^2 \sin^2(k_2 a) \right]^{-1} \quad (63)$$

where

$$k = (2mE/\hbar^2)^{1/2}, \quad k_2 = [2m(E + V_0)/\hbar^2]^{1/2} \quad (64)$$

Notice that transmission resonance occurs when  $k_2 a = n\pi$ . Interpret the result physically. It may be mentioned that such transmission resonances occur in the scattering of electrons from noble gases such as argon and neon. This is known as the Ramsauer-Townsend effect (see also Sec. 24.5.2 and e.g. Ref. 4, p. 133).

**Problem 8.2** Consider a potential barrier of the form (see Fig. 8.8)

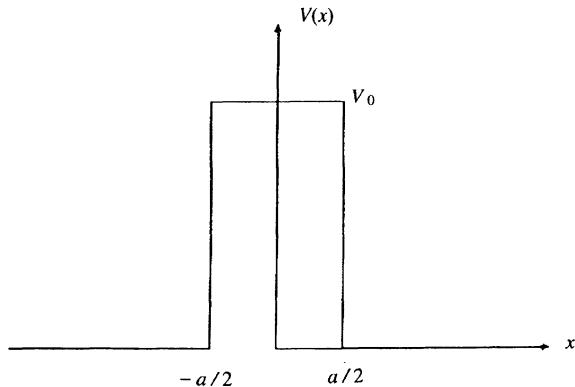


Figure 8.8. A rectangular potential barrier.

$$\begin{aligned} V(x) &= V_0 & |x| < a/2 \\ &= 0 & |x| > a/2 \end{aligned} \quad (65)$$

In the region  $|x| > a/2$ , the solution of the Schrödinger equation can be written as

$$\begin{aligned}\psi &= A e^{ikx} + B e^{-ikx} & x < -a/2 \\ &= F e^{ikx} + G e^{-ikx} & x > +a/2\end{aligned}\quad (66)$$

Using continuity conditions at  $x = \pm a/2$  show

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix} \quad (67)$$

where

$$\left. \begin{aligned}R_{11} &= \left[ \cosh \kappa a + \frac{i\sigma}{2} \sinh \kappa a \right] e^{ika} \\R_{22} &= \left[ \cosh \kappa a - \frac{i\sigma}{2} \sinh \kappa a \right] e^{-ika} \\R_{12} &= (i\tau/2) \sinh \kappa a = -R_{21} \\\sigma &= \frac{\kappa}{k} - \frac{k}{\kappa}, \quad \tau = \frac{\kappa}{k} + \frac{k}{\kappa}\end{aligned}\right\} \quad (68)$$

$k$  and  $\kappa$  are defined through Eq. (19). For  $E < V_0$ ,  $\kappa$  is real and for  $E > V_0$ ,  $\kappa$  is purely imaginary.

**Problem 8.3** In the previous problem if we set  $G = 0$  then it will physically correspond to the situation of a wave incident from the left of the barrier and getting partially reflected and partially transmitted by it. Calculate the transmission coefficient for the cases  $E < V_0$  and  $E > V_0$  and show that the results are the same as obtained in Sec. 8.3.

**Problem 8.4** Consider a periodic potential of the form<sup>4</sup> (see Fig. 8.9)

$$\begin{aligned}V(x) &= V_0 & -a/2 < x < +a/2 \\ &= 0 & a/2 < x < a/2 + b\end{aligned}\quad (69)$$

with

$$V(x+l) = V(x) \quad (70)$$

where  $l = a + b$  represents the periodicity of the potential. We label the  $n^{\text{th}}$  valley (of the periodic potential) as

$$(n-1)l + a/2 < x < nl - a/2 \quad (71)$$

with  $n = 0, \pm 1, \pm 2, \dots$  and write the solution of the Schrödinger equation in the  $n^{\text{th}}$  valley as

$$\psi(x) = A_n \exp[i\alpha(x-nl)] + B_n \exp[-i\alpha(x-nl)] \quad (72)$$

---

<sup>4</sup> Such a periodic potential is of great importance in band theory of solids (see, e.g., Ref. 5). The present method of solution for the periodic potential is adapted from Ref. 6; see also Sections 16.3 and 23.3.

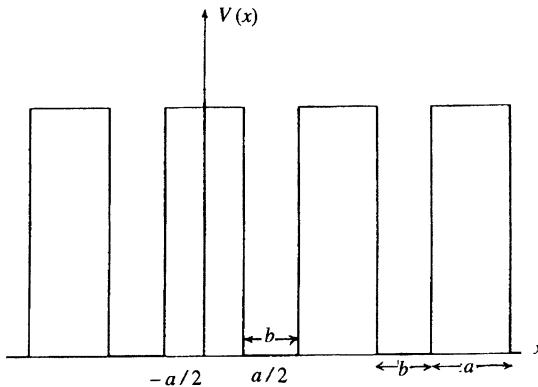


Figure 8.9. The periodic potential.

where we have defined

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} \quad (73)$$

so that the notation is consistent with that in Sec. 16.3. We write

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix} \quad (74)$$

Use continuity conditions to determine  $R_{11}$ ,  $R_{12}$ , ... and show that the matrix elements are independent of  $n$ . Thus it immediately follows that

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix}^n \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} \quad (75)$$

Using the boundary condition that the wave function must remain finite as  $x \rightarrow \pm\infty$ , obtain the equation which lead to the allowed and forbidden energy bands.

**Problem 8.5** Consider a potential barrier given by the following equation

$$\begin{aligned} V &= V_1 & z < 0 \\ &= V_2 & z > 0 \end{aligned} \quad (76)$$

with  $V_2 > V_1$ . Consider the incidence of a plane wave (at an angle) on the surface  $z = 0$ . Solve the three-dimensional Schrödinger equation in the two regions and using continuity conditions determine the laws of reflection and refraction.

[Hint: Without any loss of generality assume the  $x$ -axis to lie in the plane of incidence so that the  $y$ -dependence of the wave function can be neglected.]

**Problem 8.6** In Sec. 8.4 we had considered the reflection of a wave packet by a potential step and had assumed that the component waves, the superposition of

which gives the wave packet, correspond to  $E < V_0$ . Discuss the reflection (and) transmission of a wave packet whose component waves correspond to  $E > V_0$ .

**Problem 8.7** For the potential step problem (see Sec. 8.2) the wave function in the region  $x > 0$  is of the form  $e^{-\kappa x}$ . Calculate  $\langle x \rangle, \langle x^2 \rangle$  and show that  $\Delta x \sim 1/\kappa$ .

[Hint:  $\langle x \rangle = \int_0^\infty x e^{-2\kappa x} dx / \int_0^\infty e^{-2\kappa x} dx$ , etc.]

**Problem 8.8** Consider a potential energy variation given by

$$\begin{aligned} V(x) &= 0 & x < -d \text{ and } x > 0 \\ &= V_0 \left(1 + \frac{x}{d}\right) & -d < x < 0 \end{aligned} \quad (77)$$

Obtain an exact solution of the Schrödinger equation and obtain an expression for the transmission coefficient.

[Hint: In the region  $-d < x < 0$  write the solution in terms of  $Ai(x)$  and  $Bi(x)$  — see Appendix D and also Problems 6.8 and 17.9.]

**Problem 8.9** Consider a delta function potential of the form

$$V(x) = S \delta(x) \quad (78)$$

Show that the transmission amplitude ( $= F/A$ ) and the transmission coefficient ( $= |F/A|^2$ ) are

$$\frac{ik}{\left(ik - \frac{mS}{\hbar^2}\right)}$$

and

$$\frac{E}{\left(E + \frac{mS^2}{2\hbar^2}\right)}$$

respectively.

[Hint: In the results given in Sec. 8.3 take the limit of  $V_0 \rightarrow \infty$  and  $a \rightarrow 0$  such that the product  $V_0 a \rightarrow S$ .]

---

## 8.6. Solutions

**Solution 8.1** For a particle incident from the left, the solutions of the Schrödinger equation are:

$$\begin{aligned} \psi &= A e^{ikx} + B e^{-ikx} & x < -a/2 \\ &= C e^{ik_2 x} + D e^{-ik_2 x} & a/2 < x < -a/2 \\ &= F e^{ikx} & x > a/2 \end{aligned} \quad (79)$$

The continuity conditions at  $x = \pm a/2$  immediately lead to the transmission coefficient ( $= |F/A|^2$ ). For  $k_2 a = n\pi$  the transmission coefficient is unity and this is again similar to what happens in a Fabry-Perot etalon.

**Solution 8.4** The continuity conditions immediately give

$$\begin{aligned} R_{11} &= e^{i\alpha b} \left[ \cosh \kappa a - \frac{i\sigma}{2} \sinh \kappa a \right] \\ R_{12} &= -\frac{i\tau}{2} \sinh \kappa a e^{i\alpha(a+b)} \\ R_{22} &= R_{11}^*, \quad R_{21} = R_{12}^* \end{aligned} \quad (80)$$

where  $\sigma$  and  $\tau$  are defined through Eq. (68). Now the eigenvalues of  $R$  matrix are given by

$$\lambda_{\pm} = \frac{1}{2} \left[ \eta \pm \sqrt{\eta^2 - 4} \right] \quad (81)$$

where we have used the fact that  $R_{11}R_{22} - R_{12}R_{21} = 1$  and  $\eta = R_{11} + R_{22} = R_{11} + R_{11}^*$  which is a real quantity. Further, any column vector can also be written as a sum of two eigenvectors and therefore we may write

$$\begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} a_+ \\ b_+ \end{pmatrix} + \begin{pmatrix} a_- \\ b_- \end{pmatrix}$$

where

$$\begin{pmatrix} a_+ \\ b_+ \end{pmatrix} \text{ and } \begin{pmatrix} a_- \\ b_- \end{pmatrix}$$

are eigenvectors corresponding to the eigenvalues  $\lambda_+$  and  $\lambda_-$  respectively. Thus

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = R^n \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \lambda_+^n \begin{pmatrix} a_+ \\ b_+ \end{pmatrix} + \lambda_-^n \begin{pmatrix} a_- \\ b_- \end{pmatrix} \quad (82)$$

Clearly if  $|\eta| > 2$ , the two roots are real and the wave function will diverge either for  $x \rightarrow \infty$  or  $x \rightarrow -\infty$ . Thus we must have

$$\eta \leq 2 \quad (83)$$

for which  $|\lambda_+| = |\lambda_-| = 1$ . Since  $\eta$  is real we can always write

$$\frac{1}{2}\eta = \cos \phi \quad (84)$$

or

$$\cos \phi = \cosh \kappa a \cos \alpha b + \frac{\sigma}{2} \sinh \kappa a \sin \alpha b \quad (85)$$

For  $\alpha b = n\pi$ , it immediately follows that Eqs. (83) and (85) cannot be satisfied and hence such energy values are not allowed. By plotting  $\eta/2$  as a function of  $E$  one can readily obtain regions of allowed and forbidden energies—these are the energy bands and are discussed in any book on solid state physics.

For  $E > V_0$ , the corresponding equation becomes

$$\cos \phi = \cos k_1 a \cos \alpha b - \frac{k_1^2 + \alpha^2}{2\alpha k_1} \sin k_1 a \sin \alpha b \quad (86)$$

which again lead to allowed and forbidden energy bands.

In order to get a numerical appreciation, we consider the limiting case of  $V_0 \rightarrow \infty$  and  $a \rightarrow 0$  such that

$$\frac{mb}{\hbar^2} V_0 a \rightarrow P$$

(This is known as the Krönig-Penney model.) For such a case, Eq. (85) becomes

$$\cos \phi = \frac{P}{\alpha b} \sin \alpha b + \cos \alpha b \quad (87)$$

Equation (87) forms the basic equation of the Krönig-Penney model, the solution of which leads to the formation of energy bands (corresponding to a periodic potential). Using another method, we will rederive Eq. (87) in Sec. 16.3 where we will also discuss the physical implications, viz., the formation of energy bands.

**Solution 8.5** The three-dimensional Schrödinger equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V(z)] \psi(x, y, z) = 0 \quad (88)$$

with

$$\begin{aligned} V(z) &= V_1 & z < 0 \\ &= V_2 & z > 0 \end{aligned} \quad (89)$$

can easily be solved by using the method of separation of variables. The solution corresponding to the reflection and transmission of a particle is given by

$$\begin{aligned} \psi &= A \exp[i(k_{1x}x + k_{1z}z)] + B \exp[i(k_{2x}x - k_{2z}z)] & z < 0 \\ &= C \exp[i(k_{3x}x + k_{3z}z)] & z > 0 \end{aligned} \quad (90)$$

where we have assumed (without any loss of generality) that  $k_{1y} = 0$ , i.e. the  $x$ -axis is chosen to lie in the plane of incidence (see Fig. 8.10). Further,

$$k_{1x}^2 + k_{1z}^2 = k_{2x}^2 + k_{2z}^2 = \frac{2m}{\hbar^2} (E - V_1) \quad (91)$$

and

$$k_{3x}^2 + k_{3z}^2 = \frac{2m}{\hbar^2} (E - V_2) \quad (92)$$

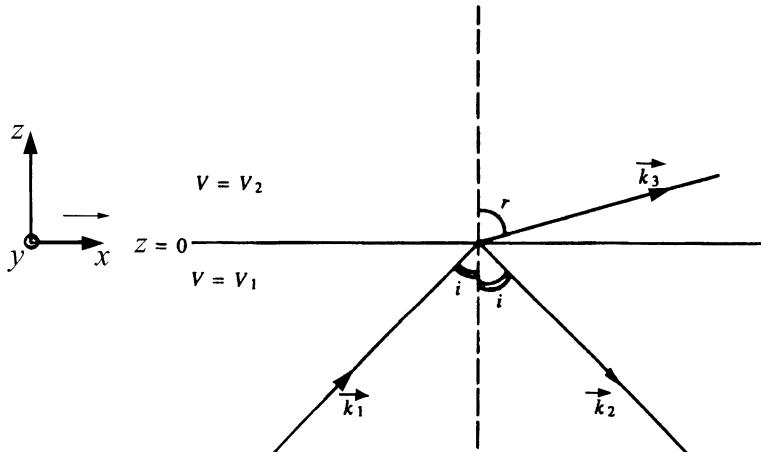


Figure 8.10. The reflection and refraction of a plane wave at the plane  $z = 0$ .

For the wave function to be continuous at  $z = 0$  (for all values of  $x$ ) we must have

$$k_{1x} = k_{2x} = k_{3x} \quad (93)$$

Thus  $k_{2z} = k_{1z}$  [see Eq. (91)] implying that the angles of incidence and reflection are equal. Further, if  $i$  and  $r$  represent the angles of incidence and refraction then

$$\sin i = \frac{k_{1x}}{(k_{1x}^2 + k_{1z}^2)^{1/2}} = \left( \frac{\hbar^2}{2m(E - V_1)} \right)^{1/2} k_{1x} \quad (94)$$

and a similar relation for  $\sin r$ , from which we immediately obtain

$$\frac{\sin i}{\sin r} = \left( \frac{E - V_2}{E - V_1} \right)^{1/2} \quad (95)$$

which is nothing but Snell's law. The critical angle is given by

$$\sin i_c = \left( \frac{E - V_2}{E - V_1} \right)^{1/2} \quad (96)$$

For  $i > i_c$ ,  $k_{3z}$  is purely imaginary and there is an exponentially decaying wave in the region  $z > 0$ .

Now, continuity of  $\psi$  and  $d\psi/dz$  at  $z = 0$  gives [cf. Eqs (5) and (6)]

$$\frac{B}{A} = \frac{k_{1z} - k_{3z}}{k_{1z} + k_{3z}} = \frac{\cos i - (\sin^2 i_c - \sin^2 i)^{1/2}}{\cos i + (\sin^2 i_c - \sin^2 i)^{1/2}} \quad (97)$$

and

$$\frac{C}{A} = \frac{2k_{1z}}{k_{1z} + k_{3z}} = \frac{2 \cos i}{\cos i + (\sin^2 i_c - \sin^2 i)^{1/2}} \quad (98)$$

For  $i > i_c$ ,  $|B/A| = 1$  and the reflection coefficient is unity. However, the wave function is given by

$$\psi = C \exp [i \kappa x \sin i] \exp \left[ -\kappa z \frac{(\sin^2 i - \sin^2 i_c)^{1/2}}{\sin i_c} \right] \quad (99)$$

where  $\kappa = [2m(E - V_2)/\hbar^2]^{1/2}$ . The above wave function gives the following expression for the current density:

$$J_x = \frac{\hbar \kappa}{m} \frac{\sin i}{\sin i_c} |C|^2 \exp \left[ -2\kappa \frac{(\sin^2 i - \sin^2 i_c)^{1/2}}{\sin i_c} z \right] \quad (100)$$

$$J_y = J_z = 0$$

Such a wave which is propagating in a particular direction and has an exponentially decreasing amplitude in another direction is known as an evanescent wave and is a subject of considerable importance in optics. Because of this evanescent wave, the beam (on reflection) undergoes a lateral shift which is known as the Goos-Hanchen effect (see, e.g. Chapter 11 of Ref. 2).

**Solution 8.6** For  $E > V_0$ , the incident, reflected and transmitted wave packets would be [cf. Eqs (45), (46) and (53)]

$$\psi_{\text{inc}}(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\beta}^{\infty} |A(k)| \times \exp [i(kx - \omega(k)t - \phi(k))] dk \quad (101)$$

$$\psi_{\text{refl}}(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\beta}^{\infty} |A(k)| \frac{k - \sqrt{k^2 - \beta^2}}{k + \sqrt{k^2 - \beta^2}} \times \exp [-i(kx - \omega(k)t + \phi(k))] dk \quad (102)$$

$$\psi_{\text{tr}}(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\beta}^{\infty} |A(k)| \frac{2k}{k + \sqrt{k^2 - \beta^2}} \times \exp \left[ i \left( \sqrt{k^2 - \beta^2} x - \omega(k)t + \phi(k) \right) \right] dk \quad (103)$$

where we have used Eqs. (5) and (6) and the fact that

$$k_1 = \left[ \frac{2m(E - V_0)}{\hbar^2} \right]^{1/2} = [k^2 - \beta^2]^{1/2} \quad (104)$$

Notice that since  $B/A$  and  $C/A$  are real [see Eqs. (5) and (6)], there are no additional phase factors appearing in the exponent. Thus the centre of the wave packet associated with the incident, reflected and transmitted waves would be [cf. Eqs (48) and (49)]

$$\left. \begin{aligned} x_c^{\text{inc}} &= x_0 + v_g t \\ x_c^{\text{ref}} &= -x_0 - v_g t \\ x_c^{\text{tr}} &= x_0 \frac{v'_g}{v_g} + v'_g t \end{aligned} \right\} \quad (105)$$

where

$$v'_g = \frac{\hbar \sqrt{k_0^2 - \beta^2}}{m} \quad (106)$$

which represents the group velocity in the region  $x > 0$ . The expression for  $v'_g$  follows from the fact that

$$\begin{aligned} (k^2 - \beta^2)^{1/2} x - \omega t &= \left[ (k_0^2 - \beta^2)^{1/2} + \frac{k_0}{(k_0^2 - \beta^2)^{1/2}} (k - k_0) + \dots \right] x \\ &\quad - \left[ \omega(k_0) + (k - k_0) \left. \frac{d\omega}{dk} \right|_{k=k_0} + \dots \right] t \\ &= \left[ (k_0^2 - \beta^2)^{1/2} x - \omega(k_0) t \right] + (k - k_0) \frac{k_0}{\sqrt{k_0^2 - \beta^2}} \\ &\quad \times \left\{ x - \frac{\sqrt{k_0^2 - \beta^2} \left. \frac{d\omega}{dk} \right|_{k=k_0}}{k_0} t \right\} + \dots \end{aligned}$$


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## 8.7. References and suggested reading

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# Chapter 9

## Angular Momentum I—The Spherical Harmonics

*The final criterion of truth is the agreement of a theory with experience, and it is only when all attempts to describe the facts in the frame of accepted ideas fail that new notions are formed, at first cautiously and reluctantly and then, if they are experimentally confirmed, with increasing confidence. In this way the classical philosophy of science was transformed into the modern one ...*

— From MAX BORN'S Preface in *Physics in My Generation*,  
Springer Verlag, New York (1969).

### 9.1. Introduction

In this chapter we will discuss the basic theory of angular momentum which plays an extremely important role in the study of quantum mechanics. We will first define the angular momentum operator through the classical relation  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$  and replace  $\mathbf{p}$  by its operator representation  $-i\hbar\nabla$  [see Eq. (18) of Chapter 4]. We will then show that the representations of  $L_z$  and  $L^2 (= L_x^2 + L_y^2 + L_z^2)$  in spherical polar coordinates  $(r, \theta, \phi)$  are given by the following differential operators

$$L_z = -i\hbar \frac{\partial}{\partial\phi} \quad (1)$$

and

$$L^2 = -\hbar^2 \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \quad (2)$$

In Sec. 9.3 we will solve the eigenvalue equation

$$L^2 Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi) \quad (3)$$

where  $\lambda \hbar^2$  represents the eigenvalues of the operator  $L^2$ . We will show that  $\lambda$  takes the values  $l(l+1)$  where  $l = 0, 1, 2, 3, \dots$  and for each value of  $l$  there is  $(2l+1)$ -fold degeneracy; i.e. there are  $(2l+1)$  eigenfunctions corresponding to the same eigenvalue  $l(l+1)\hbar^2$ —these eigenfunctions are known as spherical harmonics and

are denoted by  $Y_{lm}(\theta, \phi)$ . Thus the eigenvalue equation (3) can be written in the form

$$L^2 Y_{lm}(\theta, \phi) = l(l+1) \hbar^2 Y_{lm}(\theta, \phi) \quad (4)$$

where

$$l = 0, 1, 2, 3, \dots$$

and for each value of  $l$ , we have

$$m = -l, -l+1, \dots +l$$

The spherical harmonics are actually simultaneous eigenfunctions of  $L^2$  and  $L_z$ ; i.e.

$$L_z Y_{lm}(\theta, \phi) = m \hbar Y_{lm}(\theta, \phi) \quad (5)$$

These eigenfunctions will be used in the theory of the hydrogen atom (Chapter 10) – in fact, for any problem characterized by a spherically symmetric potential  $V(r)$ . In Sec. 9.4 the commutation relations between  $L_x$ ,  $L_y$  and  $L_z$  will be derived which will be the starting equations in Chapter 13. The relationship of angular momentum with rotations will be discussed in Sec. 9.5.

## 9.2. The angular momentum operator and its representations in spherical polar coordinates

In classical mechanics the angular momentum of a particle is defined through the relation

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (6)$$

where  $\mathbf{r}$  and  $\mathbf{p}$  represent the position and linear momentum of the particle. Thus

$$L_x = yp_z - zp_y \quad (7)$$

with similar relations for  $L_y$  and  $L_z$ . In quantum mechanics we replace  $p_x$ ,  $p_y$  and  $p_z$  by the corresponding operators [see Eq. (19) of Chapter 4] to obtain the following operator representations of  $L_x$ ,  $L_y$  and  $L_z$ :

*Operator representations of  $L_x$ ,  $L_y$ ,  $L_z$*

$$\left. \begin{aligned} L_x &= yp_z - zp_y = -i \hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ L_y &= zp_x - xp_z = -i \hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ L_z &= xp_y - yp_x = -i \hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \end{aligned} \right\} \quad (8)$$

In order to determine the eigenvalues and eigenfunctions of the operator  $L^2 (\equiv L_x^2 + L_y^2 + L_z^2)$  it is convenient to express  $L_x$ ,  $L_y$  and  $L_z$  in spherical polar coordinates which are defined through the following equations:

$$\left. \begin{array}{l} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{array} \right\} \quad (9)$$

Thus

$$r^2 = x^2 + y^2 + z^2 \quad (10)$$

$$\tan^2 \theta = \frac{(x^2 + y^2)}{z^2} \quad (11)$$

$$\tan \phi = \frac{y}{x} \quad (12)$$

Now<sup>1</sup>

$$2r \frac{\partial r}{\partial x} = 2x \quad (13)$$

$$2 \tan \theta \sec^2 \theta \frac{\partial \theta}{\partial x} = \frac{2x}{z^2} = \frac{2}{r} \tan \theta \sec \theta \cos \phi \quad (14)$$

$$\sec^2 \phi \frac{\partial \phi}{\partial x} = -\frac{y}{x^2} = -\frac{1}{r} \operatorname{cosec} \theta \sec \phi \tan \phi \quad (15)$$

giving

$$\frac{\partial r}{\partial x} = \sin \theta \cos \phi \quad (16)$$

$$\frac{\partial \theta}{\partial x} = \frac{1}{r} \cos \theta \cos \phi \quad (17)$$

$$\frac{\partial \phi}{\partial x} = -\frac{1}{r} \sin \phi \operatorname{cosec} \theta \quad (18)$$

---

<sup>1</sup> Notice that  $\frac{\partial x}{\partial r} = \sin \theta \cos \phi = \frac{x}{r}$ . Thus  $\left(\frac{\partial r}{\partial x}\right) \neq 1/\left(\frac{\partial x}{\partial r}\right)$ .

Similarly one can obtain  $\frac{\partial r}{\partial y}$ ,  $\frac{\partial \theta}{\partial y}$ , etc. Now

$$\begin{aligned} L_z \psi(r, \theta, \phi) &= -i \hbar \left[ x \frac{\partial \psi}{\partial y} - y \frac{\partial \psi}{\partial x} \right] \\ &= -i \hbar \left[ x \left( \frac{\partial \psi}{\partial r} \frac{\partial r}{\partial y} + \frac{\partial \psi}{\partial \theta} \frac{\partial \theta}{\partial y} + \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial y} \right) \right. \\ &\quad \left. - y \left( \frac{\partial \psi}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial \theta} \frac{\partial \theta}{\partial x} + \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial x} \right) \right] \\ &= -i \hbar \left[ r \sin \theta \cos \phi \left\{ \frac{\partial \psi}{\partial r} (\sin \theta \sin \phi) + \frac{\partial \psi}{\partial \theta} \left( \frac{1}{r} \cos \theta \sin \phi \right) \right. \right. \\ &\quad \left. \left. + \frac{\partial \psi}{\partial \phi} \left( \frac{1}{r} \cos \phi \operatorname{cosec} \theta \right) \right\} - r \sin \theta \sin \phi \left\{ \frac{\partial \psi}{\partial r} \right. \right. \\ &\quad \times (\sin \theta \cos \phi) + \frac{\partial \psi}{\partial \theta} \left( \frac{1}{r} \cos \theta \cos \phi \right) \\ &\quad \left. \left. + \frac{\partial \psi}{\partial \phi} \left( -\frac{1}{r} \sin \phi \operatorname{cosec} \theta \right) \right\} \right] \end{aligned}$$

or,

$$L_z \psi(r, \theta, \phi) = -i \hbar \frac{\partial \psi(r, \theta, \phi)}{\partial \phi} \quad (19)$$

*Operator representations of  $L_x$ ,  $L_y$  and  $L_z$  in spherical polar coordinates*

Since the above equation holds for arbitrary  $\psi(r, \theta, \phi)$ , we have the following operator representation for  $L_z$ :

$$L_z = -i \hbar \frac{\partial}{\partial \phi} \quad (20)$$

Similarly (see also Problem 9.5)

$$L_x = i \hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \quad (21)$$

$$L_y = i \hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \quad (22)$$

The operator  $L^2$  is defined through the following equation:

$$L^2 = L_x^2 + L_y^2 + L_z^2 \quad (23)$$

where the square of an operator is defined by

$$L_x^2 = L_x L_x$$

etc. Thus

$$L_z^2 \psi(r, \theta, \phi) = L_z L_z \psi = (-i \hbar)^2 \frac{\partial}{\partial \phi} \frac{\partial \psi}{\partial \phi} = -\hbar^2 \frac{\partial^2 \psi}{\partial \phi^2}$$

Hence, the operator representation of  $L_z^2$  is given by

$$L_z^2 = -\hbar^2 \frac{\partial^2}{\partial \phi^2} \quad (24)$$

Similarly one can obtain the operator representations of  $L_x^2$  and  $L_y^2$  (although the algebra is much more involved). Adding up, one obtains (see also Problem 9.7)

$$L^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (25)$$

It may be noted that (see Problem 9.8)

$$L^2 = -\hbar^2 \left[ \nabla^2 - \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right] \quad (26)$$

### 9.3. Eigenvalues and eigenfunctions of $L^2$

In this section we will solve the eigenvalue equation

$$L^2 Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi) \quad (27)$$

where  $\lambda \hbar^2$  represents the eigenvalues of  $L^2$  and  $Y(\theta, \phi)$  the corresponding eigenfunctions. We will show that  $\lambda$  takes the values  $l(l+1)$  where  $l = 0, 1, 2, \dots$  and the corresponding eigenfunctions are the spherical harmonics. For each value of  $l$  there will be  $(2l+1)$  fold degeneracy; i.e. there will be  $(2l+1)$  eigenfunctions belonging to the same eigenvalue  $l(l+1)\hbar^2$ .

Now, substituting for  $L^2$  from Eq. (25) in Eq. (27), we obtain

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \lambda Y(\theta, \phi) = 0 \quad (28)$$

In order to solve the above equation, we try the method of separation of variables and write

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \quad (29)$$

On substitution and subsequent multiplication by  $\sin^2 \theta / Y(\theta, \phi)$  we obtain

$$\frac{\sin^2 \theta}{\Theta} \left[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \lambda \Theta(\theta) \right] = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m^2 \quad (30)$$

The variables have indeed separated out and we have set each side equal to a positive constant  $m^2$ , the reason for which will shortly become clear. Equation (30) gives us

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi(\phi) = 0$$

the solution of which is given by

$$\Phi(\phi) \sim e^{im\phi}$$

For the wave function to be a single-valued, we must have

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (31)$$

or

$$e^{2\pi mi} = 1$$

giving<sup>2</sup>

$$m = 0, \pm 1, \pm 2, \dots$$

We label the functions by the subscript  $m$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}; \quad m = 0, \pm 1, \pm 2, \dots \quad (32)$$

where the factor  $1/\sqrt{2\pi}$  ensures that

$$\int_0^{2\pi} |\Phi_m(\phi)|^2 d\phi = 1$$

which is the normalization condition. Indeed

*Orthonormality condition*

$$\int_0^{2\pi} \Phi_{m'}^*(\phi) \Phi_m(\phi) d\phi = \delta_{mm'} \quad (33)$$

which represents the orthonormality condition for  $\Phi_m(\phi)$ .

The equation satisfied by  $\Theta(\theta)$  is [from Eq. (30)]

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( \lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta(\theta) = 0 \quad (34)$$

---

<sup>2</sup> It immediately follows that we could not have set  $\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}$  to a positive (or complex) constant for then the wave function would not have been single-valued.

Writing  $\cos \theta = \mu$  and  $\Theta(\theta) = F(\mu)$ , we obtain

$$\frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dF}{d\mu} \right] + \left[ \lambda - \frac{m^2}{1 - \mu^2} \right] F(\mu) = 0 \quad (35)$$

We first consider the case  $m = 0$  and then  $m \neq 0$ .

### 9.3.1. CASE I: $m = 0$

For  $m = 0$ , Eq. (35) reduces to

$$(1 - \mu^2) \frac{d^2 F}{d\mu^2} - 2\mu \frac{dF}{d\mu} + \lambda F(\mu) = 0 \quad (36)$$

As in the case of the linear harmonic oscillator problem, we try a power series solution

$$F(\mu) = \sum_{r=0,1,\dots}^{\infty} a_r \mu^{r+s} \quad (37)$$

Differentiating (37) term by term and substituting in (36), we obtain

$$\begin{aligned} & \sum_{r=0,1,2,\dots}^{\infty} [(r+s)(r+s-1)a_r \mu^{r+s-2} \\ & - \{(r+s)(r+s-1) + 2(r+s) - \lambda\} a_r \mu^{r+s}] = 0 \end{aligned}$$

Since the above equation is to be valid for all values of  $\mu$ , we equate the coefficients of each power of  $\mu$  to zero. Thus

$$s(s-1)a_0 = 0 \quad (38)$$

$$s(s+1)a_1 = 0 \quad (39)$$

and

$$\begin{aligned} (r+s+2)(r+s+1)a_{r+2} &= [(r+s)(r+s+1) - \lambda] a_r \\ r &= 0, 1, 2, \dots \end{aligned} \quad (40)$$

The roots of the indicial equation [Eq. (38)] are

$$s = 0 \quad \text{or} \quad s = 1 \quad (41)$$

For  $s = 0$ , the recurrence relation is<sup>3</sup>

$$\frac{a_{r+2}}{a_r} = \frac{r(r+1) - \lambda}{(r+1)(r+2)} \quad (42)$$

---

<sup>3</sup> Since the root  $s = 0$  makes  $a_1$  indeterminate, it provides all the necessary independent solutions. (see, e.g. Ref. 3); indeed, we do obtain two independent solutions [see Eq. (43)].

Since  $a_{r+2}$  is related to  $a_r$  we may write Eq. (37) as

$$\begin{aligned} F(\mu) &= \left[ 1 + \frac{a_2}{a_0} \mu^2 + \frac{a_4}{a_0} \mu^4 + \dots \right] \\ &\quad + a_1 \left[ \mu + \frac{a_3}{a_1} \mu^3 + \frac{a_5}{a_1} \mu^5 + \dots \right] \end{aligned} \quad (43)$$

The quantities inside the square brackets represent the two independent solutions of Eq. (36). From Eq. (42) it is readily seen that

$$\lim_{r \rightarrow \infty} \frac{a_{r+2}}{a_r} = 1 \quad (44)$$

Thus if the infinite series in Eq. (43) is not terminated, it will diverge at  $\mu = \pm 1$  (i.e. at  $\theta = 0$  and  $\theta = \pi$ ). Since that is not admissible, the series has to be terminated which can happen only if

$$\lambda = l(l+1); \quad l = 0, 1, 2, \dots \quad (45)$$

Thus when  $\lambda = 0, 2, 6, 12, \dots$  one of the series will terminate at  $a_l \mu^l$ . For example, for  $l = 4$

$$\frac{a_2}{a_0} = -10; \quad \frac{a_4}{a_2} = -\frac{14}{12}$$

and

$$a_6 = a_8 = \dots = 0$$

Thus the polynomial solution is given by

$$P_4(\mu) = \frac{1}{8} [3 - 30\mu^2 + 35\mu^4] \quad (46)$$

where the constant  $a_0$  has been chosen such that

$$P_l(1) = 1 \quad (47)$$

For even values of  $l$ , the odd series will not terminate (see Problem 9.2) and we must set  $a_1 = 0$ . Similarly, for an odd value of  $l$  the odd series will terminate at  $\mu^l$  and we must set  $a_0 = 0$ . The resulting polynomials are known as the Legendre polynomials  $P_l(\mu)$  which are assumed to satisfy Eq. (47). The first few Legendre polynomials are

### *Legendre polynomials*

$$\left. \begin{aligned} P_0(\mu) &= 1; & P_1(\mu) &= \mu; \\ P_2(\mu) &= \frac{1}{2} (3\mu^2 - 1); & P_3(\mu) &= \frac{1}{2} (5\mu^3 - 3\mu) \end{aligned} \right\} \quad (48)$$

The Legendre polynomials satisfy the following relation (see, e.g. Reference 4; see also Problem 9.10):

$$\int_{-1}^{+1} P_l(\mu) P_{l'}(\mu) d\mu = \frac{2}{2l+1} \delta_{ll'} \quad (49)$$

Higher order Legendre polynomials can be obtained from the following recurrence relation

$$P_l(\mu) = \frac{2l-1}{l} \mu P_{l-1}(\mu) - \frac{(l-1)}{l} P_{l-2}(\mu); \quad l \geq 2 \quad (50)$$

Thus for  $m = 0$ , the well-behaved orthonormal sets of solutions of Eqs (35) and (28) are

$$\Theta_l(\theta) = \left( \frac{2l+1}{2} \right)^{1/2} P_l(\cos \theta) \quad (51)$$

and

$$Y_{l,0}(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \Theta_l(\theta) = \left( \frac{2l+1}{4\pi} \right)^{1/2} P_l(\cos \theta) \quad (52)$$

respectively. The subscripts of  $Y(\theta, \phi)$  represent the values of  $l$  and  $m$ . The orthonormality condition is

$$\int \int Y_{l',0} Y_{l,0} \sin \theta \, d\theta \, d\phi = \left[ \frac{1}{2\pi} \int_0^{2\pi} d\phi \right] \left[ \int_0^\pi \Theta_{l'}(\theta) \Theta_l(\theta) \sin \theta \, d\theta \right] = \delta_{ll'} \quad (53)$$

### 9.3.2. CASE II: $m \neq 0$

The ‘brute force’ method for obtaining  $Y_{lm}(\theta, \phi)$  is to directly solve Eq. (35); this is done in Appendix G. However, the most straightforward and elegant way of obtaining the solutions is through the use of the ladder operators:

*Ladder operators*

$$L_+ = L_x + i L_y = \hbar e^{i\phi} \left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] \quad (54)$$

$$L_- = L_x - i L_y = \hbar e^{-i\phi} \left[ -\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] \quad (55)$$

Using operator algebra, in Chapter 13 we have shown that

$$L_+ Y_{l,m} = [(l-m)(l+m+1)]^{1/2} \hbar Y_{l,m+1} \quad (56)$$

and

$$L_- Y_{l,m} = [(l+m)(l-m+1)]^{1/2} \hbar Y_{l,m-1} \quad (57)$$

From very general considerations we have also shown that for a given value of  $l, m$  can only take values  $-l, -l + 1, \dots + l$ . From Eqs (56) and (57) we also see that

$$L_+ Y_{l,l} = 0 \quad (58)$$

and

$$L_- Y_{l,-l} = 0 \quad (59)$$

Now from Eqs (54) and (56) we can write

$$Y_{l,m+1} = [(l-m)(l+m+1)]^{-1/2} e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] Y_{l,m} \quad (60)$$

Thus if we start from  $m = 0$ , we can readily obtain  $Y_{l,1}; Y_{l,2}; \dots Y_{l,l}$ . As an example, we consider  $l = 2$ . Now, from Eqs. (52) and (48)

$$\begin{aligned} Y_{2,0}(\theta, \phi) &= \sqrt{\frac{5}{4\pi}} P_2(\cos\theta) \\ &= \sqrt{\frac{5}{16\pi}} [3\cos^2\theta - 1] \end{aligned} \quad (61)$$

Thus

$$\begin{aligned} Y_{2,1} &= \sqrt{\frac{5}{96\pi}} e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] (3\cos^2\theta - 1) \\ &= -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{i\phi} \end{aligned} \quad (62)$$

and

$$\begin{aligned} Y_{2,2} &= -\sqrt{\frac{15}{32\pi}} e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \left( \frac{1}{2} \sin 2\theta e^{i\phi} \right) \\ &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\phi} \end{aligned} \quad (63)$$

Similarly, using the relation

$$Y_{l,m-1} = [(l+m)(l-m+1)]^{-1/2} e^{-i\phi} \left[ -\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] Y_{l,m} \quad (64)$$

we can obtain  $Y_{l,-1}$  and  $Y_{l,-2}$ . The resulting wave functions are automatically normalized. Thus if one knows the expression of  $P_l(\cos\theta)$  then by repeated application of Eqs (60) and (64) one can explicitly determine  $Y_{lm}$  for all values of  $m$ . The expressions for spherical harmonics have been given in Sec. 15.3 and satisfy the following orthonormality condition:

### Orthonormality condition

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \, Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{mm'} \quad (65)$$

Thus the eigenvalue equation for  $L^2$  [see Eq. (24)] takes the form

$$L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \quad (66)$$

where  $l(l+1)\hbar^2$  (with  $l = 0, 1, 2, \dots$ ) represent the eigenvalues of  $L^2$ ;  $Y_{lm}(\theta, \phi)$  being the corresponding eigenfunctions. The eigenvalue  $l(l+1)\hbar^2$  is  $(2l+1)$  fold degenerate; i.e. corresponding to a particular value of  $l$  there will be  $(2l+1)$  values of  $m$  ( $= -l, -l+1, \dots, l-1, l$ ). Since the  $\phi$ -dependence of  $Y_{lm}(\theta, \phi)$  is of the form  $e^{im\phi}$ , one obtains

$$L_z Y_{lm}(\theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} \left[ \Theta_l(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi} \right]$$

or

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \quad (67)$$

where we have used Eq. (20). Thus  $Y_{lm}(\theta, \phi)$  are simultaneous eigenfunctions of  $L^2$  and  $L_z$ . It is easy to show that they are not eigenfunctions of  $L_x$  and  $L_y$  except for the case  $l = 0, m = 0$ . In fact, it is impossible to construct eigenfunctions of any but  $L^2$  and one of the three components of  $\mathbf{L}$ . However, by choosing appropriate linear combinations, it is possible to have simultaneous eigenfunctions of  $L^2$  and  $L_x$  and also of  $L^2$  and  $L_y$  (see Problems 15.5 and 15.6).

### 9.4. The commutation relations

In this section we will show that the components of the angular momentum operator do not commute. For example,

$$\begin{aligned} [L_x L_y] &= L_x L_y - L_y L_x \\ &= (yp_z - zp_y)(zp_x - xp_z) - (zp_x - xp_z)(yp_z - zp_y) \\ &= y p_z z p_x - y p_z x p_z - z p_y z p_x + z p_y x p_z \\ &\quad - z p_x y p_z + z p_x z p_y + x p_z y p_z - x p_z z p_y \\ &= y p_x (p_z z - z p_z) + p_y x (z p_z - p_z z) \\ &= i\hbar [x p_y - y p_x] = i\hbar L_z \end{aligned}$$

where we have used the commutation relations derived in Sec. 4.3. Thus

$$[L_x, L_y] = i\hbar L_z \quad (68)$$

Similarly,

$$[L_y, L_z] = i \hbar L_x \quad (69)$$

$$[L_z, L_y] = i \hbar L_y \quad (70)$$

These commutation relations will be the starting point in Chapter 13 where we will show that if we just use these commutation relations (and general axioms of quantum mechanics) then the angular momentum components can have values  $0, \frac{1}{2}\hbar, \hbar, \frac{3}{2}\hbar, 2\hbar$  etc.<sup>4</sup> The existence of systems having components of angular momenta taking the values which are half integral multiplies of  $\hbar$  lead to extremely important considerations. We will discuss these in Chapters 13 and 14.

## 9.5. Angular momentum and rotations

We now show that the angular momentum is related to the rotations of a system. In fact, each component of  $\mathbf{L}$  is related to an infinitesimal rotation about the corresponding axis. For example, the effect of a rotation about the  $z$ -axis through an angle  $\Delta\alpha$  results in the following transformations (see Fig. 9.1):

$$\left. \begin{array}{l} x' = x \cos(\Delta\alpha) + y \sin(\Delta\alpha) \\ y' = -x \sin(\Delta\alpha) + y \cos(\Delta\alpha) \\ z' = z \end{array} \right\} \quad (71)$$

If we assume  $\Delta\alpha$  to be infinitesimal, we may write

$$\left. \begin{array}{l} x' = x + y \Delta\alpha \\ y' = y - x \Delta\alpha \\ z' = z \end{array} \right\} \quad (72)$$

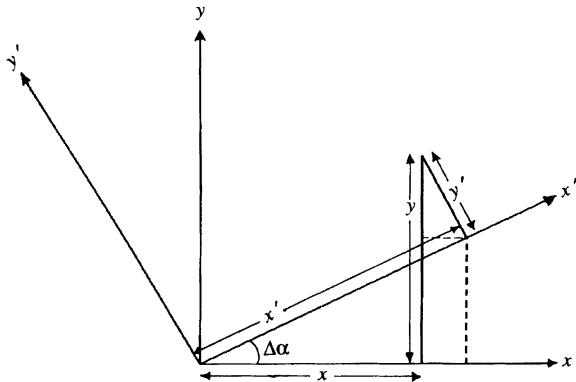
### *Rotational operator*

Thus, if  $R_z(\Delta\alpha)$  represents the rotational operator corresponding to a rotation about the  $z$ -axis through an infinitesimal angle  $\Delta\alpha$ , then the effect of this rotation on an arbitrary function  $\psi$  is given by

$$\begin{aligned} R_z(\Delta\alpha)\psi(x, y, z) &= \psi(x', y', z') \\ &= \psi(x + y\Delta\alpha, y - x\Delta\alpha, z) \\ &= \psi(x, y, z) + y\Delta\alpha \frac{\partial\psi}{\partial x} - x\Delta\alpha \frac{\partial\psi}{\partial y} \end{aligned}$$

---

<sup>4</sup> It may be noted that in this chapter we have shown that components of angular momenta, defined as  $\mathbf{r} \times \mathbf{p}$ , can only have eigenvalues  $0, \hbar, 2\hbar, \dots$

Figure 9.1. Rotation through an angle  $\Delta\alpha$  about  $z$ -axis.

where we have retained only the first term in the Taylor expansion because  $\Delta\alpha$  is infinitesimal. Thus,

$$R_z(\Delta\alpha)\psi(x, y, z) = \left[ 1 + \Delta\alpha \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \right] \psi(x, y, z)$$

Since

$$L_z = xp_y - yp_x = i\hbar \left[ y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right]$$

we may write

$$R_z(\Delta\alpha)\psi(x, y, z) = \left[ 1 + \frac{\Delta\alpha}{i\hbar} L_z \right] \psi(x, y, z)$$

Since  $\psi(x, y, z)$  is arbitrary, we can write

$$R_z(\Delta\alpha) = 1 + \frac{\Delta\alpha}{i\hbar} L_z \quad (73)$$

Similarly,

$$R_x(\Delta\alpha) = 1 + \frac{\Delta\alpha}{i\hbar} L_x \quad (74)$$

and

$$R_y(\Delta\alpha) = 1 + \frac{\Delta\alpha}{i\hbar} L_y \quad (75)$$

The operators  $L_x$ ,  $L_y$ , and  $L_z$  are called the *generators* of the infinitesimal rotations about the three coordinate axes.

In order to find  $R_z(\alpha)$  for some *finite* rotation  $\alpha$  about the  $z$ -axis, we note that the effect of a small increase in the magnitude of  $\alpha$ , from  $\alpha$  to  $\alpha + \Delta\alpha$ , is to follow

the finite rotation  $R_z(\alpha)$  by the infinitesimal rotation  $R_z(\Delta\alpha)$  to give

$$R_z(\alpha + \Delta\alpha) = R_z(\Delta\alpha)R_z(\alpha) = \left[ 1 + \frac{1}{i\hbar}\Delta\alpha L_z \right] R_z(\alpha)$$

Thus

$$\frac{dR_z}{d\alpha} = \lim_{\Delta\alpha \rightarrow 0} \frac{R_z(\alpha + \Delta\alpha) - R_z(\alpha)}{\Delta\alpha} = -\frac{i}{\hbar} L_z$$

The above equation can be integrated to give

$$R_z(\alpha) = \exp \left[ -\frac{i}{\hbar} \alpha L_z \right] \quad (76)$$

where we have incorporated the boundary condition that  $R_z(0) = 1$ . It may be mentioned that the exponential of an operator has no meaning except as the infinite series given below:

$$e^{\mathcal{O}} = 1 + \mathcal{O} + \frac{1}{2!} \mathcal{O}\mathcal{O} + \frac{1}{3!} \mathcal{O}\mathcal{O}\mathcal{O} + \dots \quad (77)$$

Equations (73)–(75) can be used to obtain the differential operator representation of the components of the angular momentum operator in spherical polar coordinates [see Eqs. (20)–(22)]. For example, if we consider rotation about the  $z$ -axis through an infinitesimal angle  $\Delta\alpha$ , then the transformations of the spherical polar coordinates are given by

$$r \rightarrow r, \theta \rightarrow \theta, \phi \rightarrow \phi - \Delta\alpha$$

Therefore,

$$R_z(\Delta\alpha)\psi(r, \theta, \phi) = \psi(r, \theta, \phi - \Delta\alpha)$$

or

$$\left[ 1 - \frac{i}{\hbar} (\Delta\alpha) L_z \right] \psi(r, \theta, \phi) = \psi(r, \theta, \phi) - \Delta\alpha \frac{\partial \psi}{\partial \phi}$$

Since, the above equation is valid for arbitrary  $\psi$  one obtains the following differential operator representation of  $L_z$  [see Eq. (20)]

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$

Similarly, one can obtain the corresponding representations for  $L_x$  and  $L_y$  (see Problem 9.5).

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## 9.6. Problems

### Problem 9.1

- (a) In the simplest model of a rotating diatomic molecule<sup>5</sup>, it is assumed to be a rigid rotator, i.e. the distance between the two atoms is assumed to be fixed. Show from classical considerations, that the rotational energy of such a rigid rotator is given by

$$\frac{L^2}{2\mu r_e^2}$$

where  $\mu$  represents the reduced mass,  $r_e$  the distance between the two atoms (assumed to be fixed) and  $L$  represents the angular momentum of the molecule about the axis passing through the centre of mass. Obtain the quantized rotational energy levels.

- (b) Molecules like HCl, HF, LiH can be considered as rigid rotators and because these molecules have permanent dipole moments, transitions take place only between adjacent rotational energy levels (this is the selection rule). Show that this leads to equally spaced lines in the emission as well as in the absorption spectra.
- (c) The rotational absorption spectrum of HCl appears at wave numbers 21.18, 42.36, 63.54, 84.72 and 105.91 cm<sup>-1</sup>. Show that  $r_e \approx 1.3\text{\AA}$ ; assume  $M_{\text{Cl}} \simeq 35 M_{\text{H}}$  and  $M_{\text{H}} \simeq 1.68 \times 10^{-24}\text{g}$ . It may be mentioned that these lines correspond to the far-infrared region where frequencies can be measured with great accuracy; as such the accuracy in the determination of  $r_e$  is limited on account of the validity of the simple rigid rotator theory rather than the accuracy in the measurement of positions of the spectral lines.

**Problem 9.2**  $P_0(\mu) = 1$ ,  $P_1(\mu) = \mu$  and  $P_2(\mu) = (3\mu^2 - 1)/2$  represent one of the solutions of Eq. (36) for  $l = 0, 1$  and  $2$  respectively. Now, the second order differential equation (36) would have two independent solutions. Obtain analytical expressions for the second solution and show that it is consistent with the solution given by Eq. (43).

[Hint: Write  $F(\mu) = \phi(\mu)P_n(\mu)$  and solve the equation satisfied by  $\phi(\mu)$ .]

**Ans:** The second independent solution is given by

$$Q_0(\mu) = \frac{1}{2} \ln \frac{1 + \mu}{1 - \mu} = \tanh^{-1} \mu \quad (78)$$

$$Q_1(\mu) = \frac{\mu}{2} \ln \frac{1 + \mu}{1 - \mu} - 1 = \mu \tanh^{-1} \mu - 1 \quad (79)$$

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<sup>5</sup> A nice elementary account of diatomic molecular spectra has been given in Ref. 5.

$$Q_2(\mu) = \frac{1}{4}(3\mu^2 - 1) \ln \frac{1+\mu}{1-\mu} - \frac{3}{2}\mu \quad (80)$$

corresponding to  $l = 0, 1$  and  $2$  respectively. Notice that  $Q_n(\mu)$  diverges as  $\mu \rightarrow \pm 1$ .

### Problem 9.3

- (a) Using the recurrence relation Eq. (50) and Eq. (48), derive expressions for  $P_5(\mu)$  and  $P_6(\mu)$ .
- (b) Using Eqs (42), (43) and (47) derive  $P_5(\mu)$  and  $P_6(\mu)$  corresponding to  $\lambda = 30$  and  $\lambda = 42$  respectively.

### Problem 9.4 Derive the commutation relations

(a)

$$\begin{aligned} [L_z, x] &= i\hbar y, & [L_z, p_x] &= i\hbar p_y \\ [L_z, y] &= -i\hbar x, & [L_z, p_y] &= -i\hbar p_x \\ [L_z, z] &= 0, & [L_z, p_z] &= 0 \end{aligned}$$

(b)

$$[L_x, r^2] = [L_y, r^2] = [L_z, r^2] = 0$$

**Problem 9.5** Assuming  $R_z(\alpha) = 1 - \frac{i}{\hbar} \alpha L_z$  [see Eq. (73)] and similar relations for  $R_x$  and  $R_y$ , obtain explicit differential operator representations of  $L_x$ ,  $L_y$  and  $L_z$  in spherical polar coordinates.

### Problem 9.6 Prove that

$$L^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (81)$$

### Problem 9.7

- (a) Using Eqs (54) and (55) prove that

$$L^2 = \frac{1}{2} (L_+ L_- + L_- L_+) + L_z^2 \quad (82)$$

- (b) Substitute the differential operator representations of  $L_+$  and  $L_-$  [see Eqs (54) and (55)] to prove Eq. (25).

### Problem 9.8 Using vector methods, prove that

$$L^2 \psi = (-i\hbar \mathbf{r} \times \nabla)^2 \psi = -\hbar^2 r^2 \nabla^2 \psi + \hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) \quad (83)$$

**Problem 9.9** Using the following representation of  $p_r$

$$p_r = -i\hbar \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \quad (84)$$

prove that

$$\frac{p^2}{2m} \left( = -\frac{\hbar^2}{2m} \nabla^2 \right) = \frac{p_r^2}{2m} + \frac{L^2}{2m r^2} \quad (85)$$

Interpret the above equation physically.

**Problem 9.10** Starting from Eq. (36) prove the orthogonality condition for Legendre polynomials

$$\int_{-1}^{+1} P_l(\mu) P_{l'}(\mu) d\mu = 0 \text{ for } l \neq l'$$


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## 9.7. Solutions

### Solution 9.1

- (a) The rotational kinetic energy is  $\frac{1}{2}I\omega^2$ , where  $I$  ( $= \mu r_e^2$ ) is the moment of inertia about the axis passing through the centre of mass and  $\mu$  being the reduced mass. Further the angular momentum  $L = I\omega$ . Thus

$$\text{Rotational Kinetic Energy} = \frac{L^2}{2I} = \frac{L^2}{2\mu r_e^2} \quad (86)$$

Using Eq. (66), we get the following expression for the rotational energy levels

$$E = \frac{J(J+1)\hbar^2}{2\mu r_e^2} \quad (87)$$

where  $J$  ( $= 0, 1, 2, \dots$ ) is known as the rotational quantum number; we have written  $J(J+1)$  instead of  $l(l+1)$  so as to be consistent with the spectroscopic notation.

- (b) For emission  $J_f = J_i - 1$  ( $f$  and  $i$  refer to the final and initial states) and the wave number of the emitted radiation is given by

$$\nu (\text{cm}^{-1}) = \frac{E_i - E_f}{hc} = 2J_i B \quad (88)$$

where

$$B = \frac{h}{8\pi^2\mu r_e^2 c}$$

is known as the rotational constant. Thus the lines are equally spaced. Similarly for absorption  $J_f = J_i + 1$  and

$$\nu (\text{cm}^{-1}) = \frac{E_f - E_i}{hc} = 2(J_i + 1)B \quad (89)$$

- (c) The absorption spectra should therefore appear at  $2B, 4B, 6B, 8B, \dots$  corresponding to  $J_i = 0, 1, 2, 3, \dots$  respectively. From the data given one readily finds  $B \approx 10.59 \text{ cm}^{-1}$ . Thus

$$B = \frac{h}{8\pi^2\mu r_e^2 c} \approx 10.59 \text{ cm}^{-1}$$

Since

$$\begin{aligned} \mu &\approx \frac{M_{\text{H}} M_{\text{Cl}}}{M_{\text{H}} + M_{\text{Cl}}} \\ &\approx \frac{35}{36} M_{\text{H}} \approx \frac{35}{36} \times 1.68 \times 10^{-24} \text{ g} \end{aligned}$$

we readily get

$$r_e \approx 1.27 \text{ \AA}$$

**Solution 9.2** We consider the case  $l = 1$  and write

$$F(\mu) = \mu\phi(\mu)$$

Substituting in Eq. (36) for  $\lambda = 2$  we get

$$\frac{\phi''(\mu)}{\phi'(\mu)} = -\frac{2}{\mu} + \frac{1}{1-\mu} - \frac{1}{1+\mu}$$

Carrying out the integration, we get

$$\frac{d\phi}{d\mu} = C_1 \left[ \frac{1}{\mu^2} + \frac{1}{2} \left( \frac{1}{1+\mu} + \frac{1}{1-\mu} \right) \right]$$

or

$$\phi(\mu) = C_1 \left[ -\frac{1}{\mu} + \frac{1}{2} \ln \frac{1+\mu}{1-\mu} \right] + C_2$$

where  $C_1$  and  $C_2$  are constants of integration. Thus

$$F(\mu) = C_1 \left[ \frac{1}{2} \mu \ln \frac{1+\mu}{1-\mu} - 1 \right] + C_2 \mu \quad (90)$$

which represents the general solution of Legendre's equation for  $l = 1$ . Obviously the second term is a multiple of  $P_1(\mu)$  and the first term is  $C_1 Q_1(\mu)$ . If we expand  $Q_1(\mu)$  in a power series in  $\mu$  we would obtain the infinite series given by the first term inside the square brackets of Eq. (43).

**Solution 9.5** Let us suppose that when there is a rotation about the  $x$ -axis by an angle  $\Delta\alpha$ ,  $\theta$  becomes  $\theta + \delta\theta$  and  $\phi$  becomes  $\phi + \delta\phi$ ; obviously,  $r$  remains unchanged. Now, for rotation about the  $z$ -axis [see Eq. (72)]

$$x \rightarrow x + y\Delta\alpha, \quad y \rightarrow y - x\Delta\alpha, \quad \text{and} \quad z \rightarrow z$$

Similarly, for rotation about  $x$ -axis

$$y \rightarrow y + z\Delta\alpha, \quad z \rightarrow z - y\Delta\alpha, \quad \text{and} \quad x \rightarrow x$$

which are obtained by replacing  $z, x, y$  by  $x, y$  and  $z$  respectively.

Thus

$$\delta x = \delta(r \sin \theta \cos \phi) = 0$$

$$\delta y = \delta(r \sin \theta \sin \phi) = z\Delta\alpha$$

and

$$\delta z = \delta(r \cos \theta) = -y\Delta\alpha$$

or

$$\cos \theta (\delta\theta) \cos \phi - \sin \theta \sin \phi \delta\phi = 0,$$

$$\cos \theta (\delta\theta) \sin \phi + \sin \theta \cos \phi \delta\phi = \cos \theta \Delta\alpha$$

and

$$-\sin \theta \delta\theta = -\sin \theta \sin \phi \delta\alpha$$

which give

$$\delta\theta = \sin \phi \Delta\alpha \quad (91)$$

and

$$\delta\phi = \cot \theta \cot \phi \delta\theta = \cot \theta \cos \phi \Delta\alpha \quad (92)$$

Thus

$$\begin{aligned} R_x(\Delta\alpha)\psi(r, \theta, \phi) &= \psi(r, \theta + \delta\theta, \phi + \delta\phi) \\ &= \psi(r, \theta, \phi) + \frac{\partial \psi}{\partial \theta} \sin \phi \Delta\alpha \\ &\quad + \frac{\partial \psi}{\partial \phi} \cot \theta \cos \phi \Delta\alpha \end{aligned}$$

But

$$R_x(\Delta\alpha)\psi(r, \theta, \phi) = \left[ 1 + \frac{\Delta\alpha}{i\hbar} L_x \right] \psi$$

Therefore

$$L_x = i \hbar \left[ \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right] \quad (93)$$

Similarly

$$L_y = i \hbar \left[ -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right] \quad (94)$$

**Solution 9.7** Using Eqs (54) and (55), we get

$$\begin{aligned} L_+ L_- \psi &= (i \hbar)^2 e^{i\phi} \left[ e^{-i\phi} \frac{\partial^2 \psi}{\partial \theta^2} - i e^{-i\phi} \frac{\partial}{\partial \theta} \left( \cot \theta \frac{\partial \psi}{\partial \phi} \right) \right. \\ &\quad \left. - i \cot \theta \frac{\partial}{\partial \phi} \left( e^{-i\phi} \frac{\partial \psi}{\partial \theta} \right) + \cot^2 \theta \frac{\partial}{\partial \phi} \left( e^{-i\phi} \frac{\partial \psi}{\partial \phi} \right) \right] \\ &= -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \frac{i}{\sin^2 \theta} \frac{\partial}{\partial \phi} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} - i \cot^2 \theta \frac{\partial^2}{\partial \phi^2} \right] \end{aligned}$$

Therefore

$$L_+ L_- = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} + i \frac{\partial}{\partial \phi} \right] \quad (95)$$

Similarly

$$L_- L_+ = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} - i \frac{\partial}{\partial \phi} \right] \quad (96)$$

Since

$$L_z^2 = -\hbar^2 \frac{\partial^2}{\partial \phi^2}$$

one obtains

$$\begin{aligned} L^2 &= \frac{1}{2} (L_+ L_- + L_- L_+) + L_z^2 \\ &= -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \end{aligned}$$

**Solution 9.8**

$$\begin{aligned} L^2 \psi &= (-i \hbar \mathbf{r} \times \nabla)^2 \psi = -\hbar^2 (\mathbf{r} \times \nabla) \cdot (\mathbf{r} \times \nabla \psi) \\ &= -\hbar^2 \mathbf{r} \cdot [\nabla \times (\mathbf{r} \times \nabla \psi)] \\ &\quad (\text{by interchanging the dot and cross}) \\ &= -\hbar^2 \mathbf{r} \cdot [(\nabla \psi \cdot \nabla) \mathbf{r} - (\mathbf{r} \cdot \nabla) \nabla \psi - \nabla \psi (\nabla \cdot \mathbf{r}) + \mathbf{r} (\nabla \cdot \nabla \psi)] \end{aligned}$$

where we have used a vector identity. Thus

$$\begin{aligned}
 L^2\psi &= -\hbar^2 \left[ r \frac{\partial \psi}{\partial r} - \mathbf{r} \cdot \left( r \frac{\partial}{\partial r} \nabla \psi \right) - r \frac{\partial \psi}{\partial r} 3 + r^2 \nabla^2 \psi \right] \\
 &= -\hbar^2 \left[ -2r \frac{\partial \psi}{\partial r} - r^2 \frac{\partial^2 \psi}{\partial r^2} + r^2 \nabla^2 \psi \right] \\
 &= -\hbar^2 r^2 \left[ \nabla^2 \psi - \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) \right] \\
 &= -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right]
 \end{aligned}$$

### Solution 9.9

$$\begin{aligned}
 \frac{p_r^2}{2m}\psi &= -\frac{\hbar^2}{2m} \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \psi \\
 &= -\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \psi}{\partial r^2} - \frac{\psi}{r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \psi \right] \\
 &= -\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) \right]
 \end{aligned} \tag{97}$$

using which Eq. (85) follows immediately. Now, in classical mechanics, the kinetic energy of a particle (in spherical polar coordinates) is  $p_r^2/2m + L^2/2mr^2$  where  $p_r$  represents the radial component of the momentum and  $L^2$  the square of the angular momentum<sup>6</sup>. Thus, in quantum mechanics the radial component of the angular momentum is represented by Eq. (84).

**Solution 9.10** We rewrite Eq. (36) as

$$\frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dF}{d\mu} \right] + \lambda F(\mu) = 0 \tag{98}$$

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<sup>6</sup> Classically,

$$\mathbf{L} = (\mathbf{r} \times \mathbf{p}) = r p_\theta \hat{\theta} - r p_\phi \hat{\phi}$$

Therefore

$$L^2 = r^2 p_\theta^2 + r^2 p_\phi^2$$

and

$$p^2 = p_r^2 + p_\theta^2 + p_\phi^2 = p_r^2 + \frac{L^2}{r^2}$$

which is known as the Sturm-Liouville form (see, e.g. Chapter 12 of Reference 4). Thus

$$\frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dP_l}{d\mu} \right] + l(l+1)P_l(\mu) = 0 \quad (99)$$

and

$$\frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dP_{l'}}{d\mu} \right] + l'(l'+1)P_{l'}(\mu) = 0 \quad (100)$$

We multiply Eq. (99) by  $P_{l'}(\mu)$  and Eq. (100) by  $P_l(\mu)$  and integrate to obtain

$$\begin{aligned} & [l(l+1) - l'(l'+1)] \int_{-1}^{+1} P_l(\mu) P_{l'}(\mu) d\mu \\ &= \int_{-1}^{+1} \frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dP_l}{d\mu} \right] P_{l'}(\mu) \\ &\quad - \int_{-1}^{+1} \frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dP_{l'}}{d\mu} \right] P_l(\mu) d\mu \\ &= (1 - \mu^2) \frac{dP_l(\mu)}{d\mu} P_{l'}(\mu) \Big|_{-1}^{+1} - \int_{-1}^{+1} (1 - \mu^2) \frac{dP_l}{d\mu} \frac{dP_{l'}}{d\mu} d\mu \\ &\quad - (1 - \mu^2) \frac{dP_{l'}(\mu)}{d\mu} P_l(\mu) \Big|_{-1}^{+1} + \int_{-1}^{+1} (1 - \mu^2) \frac{dP_{l'}}{d\mu} \frac{dP_l}{d\mu} d\mu \\ &= 0 \end{aligned}$$

because at both limits, the Legendre polynomials have a finite value. Thus for  $l \neq l'$ ,  $P_l(\mu)$  and  $P_{l'}(\mu)$  are orthogonal in the domain  $-1 \leq \mu \leq +1$ .

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## 9.8. Sample questions

Q. 1 In the angular momentum problem, the  $\theta$  dependent equation for  $m = 0$  is

$$\frac{d}{d\mu} \left[ (1 - \mu^2) \frac{dF}{d\mu} \right] + \lambda F(\mu) = 0 \quad (101)$$

where  $\mu = \cos \theta$ . We assume

$$F(\mu) = \sum_{r=0}^{\infty} a_r \mu^{r+s}$$

and obtain

$$\frac{a_{r+2}}{a_r} = \frac{(r+s)(r+s+1) - \lambda}{(r+s+2)(r+s+1)} \quad (102)$$

The indicial equation gives  $s = 0$ .

- a) Why should the infinite series in Eq. (101) be terminated?
- b) For what values of  $\lambda$  will the infinite series become a polynomial?
- c) Determine the polynomial solution for  $\lambda = 12$ . What is the normalization condition? Normalize the polynomial solution corresponding to  $\lambda = 12$ .
- d) For  $\lambda = 12$ , obtain the second solution of Eq. (101) in terms of an integral.
- e) Substitute the polynomial solution

$$F(\mu) = a_0 + a_1 \mu + a_3 \mu^3 + a_5 \mu^5 \quad (103)$$

in Eq. (101) and determine the values of  $a_0, a_1, a_3, a_5$  and  $\lambda$  for which Eq. (103) is a solution of Eq. (101).

[Ans: (e) There will be 3 cases. If we assume  $a_5 \neq 0$ , then  $\lambda = 30$ , etc. If we assume  $a_5 = 0$ , then  $\lambda = 12$ , etc.]

Q. 2

$$L_{\pm} = \hbar e^{\pm i\phi} \left[ \pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right]$$

$$P_0(x) = 1; P_1(x) = x; P_2(x) = \frac{1}{2}(3x^2 - 1)$$

- a) Write  $Y_{2,0}(\theta, \phi)$  (normalized).
- b) Derive expressions for  $Y_{2,-1}(\theta, \phi)$  and  $Y_{2,-2}(\theta, \phi)$ . Are they normalized?
- c) Show that  $(Y_{1,1} - Y_{1,-1})$ ,  $(Y_{1,1} + Y_{1,-1} + \sqrt{2} Y_{1,0})$  and  $(Y_{1,1} + Y_{1,-1} - \sqrt{2} Y_{1,0})$  are eigenfunctions of  $L_x$  and  $L^2$ . What are the corresponding eigenvalues?

Q. 3 Using Ladder operators write the right-hand sides in terms of spherical harmonics

$$(a) \quad L^2 Y_{4,3}(\theta, \phi) = ; \quad (b) \quad L_z Y_{4,0}(\theta, \phi) =$$

$$(c) \quad L_y Y_{5,1}(\theta, \phi) = ; \quad (d) \quad L_- Y_{5,-5}(\theta, \phi) =$$

$$(e) \quad L_z Y_{4,3}(\theta, \phi) = ; \quad (f) \quad L^2 Y_{5,2}(\theta, \phi) =$$

$$(g) \quad L_z Y_{5,2}(\theta, \phi) = ; \quad (h) \quad L_x Y_{5,2}(\theta, \phi) =$$

$$(i) \quad L_+ Y_{5,3}(\theta, \phi) = ; \quad (j) \quad L_x Y_{4,3}(\theta, \phi) =$$

$$(k) \quad L_x Y_{1,0}(\theta, \phi) = ; \quad (l) \quad L_x Y_{2,1}(\theta, \phi) =$$

$$(m) \quad L_y Y_{5,2}(\theta, \phi) = ; \quad (n) \quad L_y Y_{4,3}(\theta, \phi) =$$

$$(o) \quad L_y Y_{1,0}(\theta, \phi) = ; \quad (p) \quad L_y Y_{2,1}(\theta, \phi) =$$

$$[\text{Ans: (c)}] \frac{\hbar}{2i} \left[ \sqrt{28} Y_{5,2}(\theta, \phi) - \sqrt{30} Y_{5,0}(\theta, \phi) \right].$$


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## 9.9. References and suggested reading

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# Chapter 10

## Spherically Symmetric Potentials Hydrogen Atom Problem, Rotation Vibration Spectra, Three-Dimensional Oscillator

Schrödinger's brilliant paper<sup>1</sup> was undoubtedly one of the most influential contributions ever made in the history of science. It deepened our understanding of atomic phenomena, served as a convenient foundation for the mathematical solution of problems in atomic physics, solid state physics, and, to some extent, also in nuclear physics, and finally opened new avenues of thought. In fact, the subsequent development of non-relativistic quantum theory was to no small extent merely an elaboration and application of Schrödinger's work.

— MAX JAMMER in *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York (1966), p. 267.

### 10.1. Introduction

In Sec. 6.7 we had shown that for a particle of mass  $\mu$  in a field described by the potential energy function  $V(\mathbf{r})$ , the solution of the time dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2\mu} \nabla^2 \Psi + V(\mathbf{r}) \Psi(\mathbf{r}, t) \quad (1)$$

is of the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar} \quad (2)$$

The wave function  $\psi(\mathbf{r})$  is the solution of the eigenvalue equation

$$H \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (3)$$

where

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r}) \quad (4)$$

<sup>1</sup> E. Schrödinger, *Quantization as an Eigenvalue Problem*, Annalen der Physik, **79**, 361 (1926). In this paper, Schrödinger had put forward his famous equation and had given the solution corresponding to the hydrogen atom problem. The paper has been reprinted in *Wave Mechanics* by G. Ludwig, Pergamon Press, Oxford (1968).

represents the Hamiltonian operator and  $E$  the energy eigenvalue. The potential energy function has been assumed to be independent of time.

In Sec. 10.2 we will show that as long as the potential is spherically symmetric (i.e. as long as the potential depends only on the magnitude of the distance from a fixed point) the angular part of the wave function is a spherical harmonic and the potential energy function enters only in the radial part of the equation. In Sec. 10.3 we will show that for a system consisting of two particles, whenever the potential energy depends only on the magnitude of the distance between the two particles, the problem can be reduced to a one particle problem along with a uniform translational motion of the centre of mass. In Sec. 10.4 we will solve the hydrogen atom problem and obtain the discrete states for the Coulomb potential and will show that the results are consistent with experimental data. In Sec. 10.5 we will discuss the vibration-rotation spectra of diatomic molecules and in Sec. 10.6 (and Problem 10.12) we will discuss the three-dimensional oscillator; the two-dimensional oscillator will be discussed in Problem 10.13.

## 10.2. Spherically symmetric potentials

One of the most important problems in quantum mechanics is that of the motion of a particle in a potential which depends only on the magnitude of the distance from a fixed point:

$$V(\mathbf{r}) = V(r) \quad (5)$$

Such a potential is referred to as a spherically symmetric potential. Now, in spherical polar coordinates

$$\begin{aligned} \nabla^2 \psi &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) \\ &\quad + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) - \frac{L^2 \psi}{\hbar^2 r^2} \end{aligned} \quad (6)$$

where we have used the fact that the operator representation of  $L^2$  is given by the following equation (see Sec. 9.2):

$$L^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (7)$$

Thus the three-dimensional Schrödinger equation

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2} [E - V(r)] \psi(r, \theta, \phi) = 0 \quad (8)$$

can be written in the form

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] \psi(r, \theta, \phi) = \frac{L^2 \psi}{\hbar^2 r^2} \quad (9)$$

In order to solve the above equation we use the method of separation of variables and write

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \quad (10)$$

Substituting in Eq. (9) we get

$$\frac{Y(\theta, \phi)}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] R(r) Y(\theta, \phi) = \frac{R(r)}{\hbar^2 r^2} L^2 Y(\theta, \phi)$$

Dividing by  $R(r) Y(\theta, \phi) / r^2$ , we obtain

$$\frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} [E - V(r)] = \frac{1}{\hbar^2} \frac{1}{Y(\theta, \phi)} L^2 Y(\theta, \phi) = \lambda \quad (11)$$

where we have set the terms equal to a constant  $\lambda$  because the left-hand side of the above equation depends only on  $r$  while the other term depends only on  $\theta$  and  $\phi$ . The above equation gives us the eigenvalue equation

$$L^2 Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi) \quad (12)$$

In Sec. 9.3 we had shown that the eigenvalues of  $L^2$  are  $l(l+1)\hbar^2$  i.e. well-behaved solutions are obtained when

$$\lambda = l(l+1); \quad l = 0, 1, 2, \dots \quad (13)$$

the corresponding eigenfunctions being the spherical harmonics

$$Y_{lm}(\theta, \phi); \quad m = -l, -l+1, \dots, l-1, l \quad (14)$$

(see Secs 9.3, 9.4 and 15.3). Thus Eq. (11) can be written in the form

*Radial part of the Schrödinger equation*

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) = 0 \quad (15)$$

which is known as the radial part of the Schrödinger equation. If we define a new radial function

$$u(r) = r R(r) \quad (16)$$

Eq. (15) becomes

$$\frac{d^2 u}{dr^2} + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] u(r) = 0 \quad (17)$$

Comparing this with Eq. (11) of Chapter 6, we may consider the radial motion to be similar to the one-dimensional motion of a particle in a potential

$$V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad (18)$$

Now, according to classical mechanics, if a particle (of mass  $\mu$ ) is rotating (with speed  $v$ ) in a circular orbit of radius  $r$  then the angular momentum associated with such a circular motion is given by

$$L = \mu v r$$

To maintain such a circular motion there must be a centripetal force given by

$$\mathbf{F} = -\frac{\mu v^2}{r} \hat{\mathbf{r}} = -\frac{L^2}{\mu r^3} \hat{\mathbf{r}} \quad (19)$$

where the negative sign implies that the force should be directed towards the origin. The corresponding potential energy is  $-L^2/2\mu r^2$  which should be supplied by  $V(r)$  and hence the effective potential is  $V(r) + L^2/2\mu r^2$  which is consistent with Eq. (17) if we replace  $L^2$  by  $l(l+1)\hbar^2$ .

### 10.3. The two body problem

We would like to solve the Schrödinger equation corresponding to the hydrogen atom which consists of two particles, viz., the electron and the proton. The interaction between the electron and the proton is described by the Coulomb potential:

*Coulomb potential*

$$V(r) = -\frac{q^2}{4\pi\epsilon_0 r} \quad (20)$$

where

$$r = |\mathbf{r}_1 - \mathbf{r}_2| \quad (21)$$

represents the magnitude of the distance between the two particles. In writing Eq. (20) we have used the MKS system of units so that

$$\begin{aligned} q &\simeq 1.6 \times 10^{-19} \text{ C} \\ \epsilon_0 &\simeq 8.854 \times 10^{-12} \text{ MKS units} \end{aligned}$$

and  $V(r)$  is measured in joules. In this book we will be almost always using the MKS system of units; however, since CGS units are used in many books, we give below the corresponding expression for  $V(r)$  in CGS units:

$$V(r) = -\frac{e^2}{r} \quad (22)$$

where  $e \simeq 4.8 \times 10^{-10}$  esu represents the electronic charge in CGS units and  $V(r)$  is measured in ergs.

We may note that the Coulomb potential described by Eq. (20) depends only on  $|\mathbf{r}_1 - \mathbf{r}_2|$ , i.e. on the magnitude of the distance between the two particles. Indeed, we will prove the general result that for a two body problem, whenever the potential energy depends only on the magnitude of the distance between the two particles, the problem can always be reduced to a one body problem along with a uniform translational motion of the centre of mass. Now, for

$$V(\mathbf{r}_1, \mathbf{r}_2) = V(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (23)$$

the Hamiltonian is given by

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\mathbf{r}_1 - \mathbf{r}_2|)$$

or

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (24)$$

where we have made use of the recipe of replacing  $\mathbf{p}$  by  $-i\hbar\nabla$ ; the subscripts 1 and 2 refer to the two particles. Further,

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}, \quad \text{etc.}$$

where  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$  represent the coordinates of the electron and the proton respectively. Now, for the Hamiltonian given by Eq. (24), the Schrödinger equation is

$$\left[ -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (25)$$

It can easily be shown that if we try to separate the variables by assuming

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_1(\mathbf{r}_1) \Psi_2(\mathbf{r}_2)$$

the variables will not separate. However, if we introduce the centre of gravity coordinates

*Centre of gravity coordinates*

$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \quad (26)$$

and the relative coordinate

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad (27)$$

of the two particles, then the Schrödinger equation becomes (see Appendix H)

$$\left[ -\frac{\hbar^2}{2(m_1 + m_2)} \left( \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(r) \right] \Psi(\mathbf{R}, \mathbf{r}) = E \Psi(\mathbf{R}, \mathbf{r}) \quad (28)$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (29)$$

is known as the reduced mass. Since the potential does not depend on  $\mathbf{R}$  at all, we write

$$\Psi(\mathbf{R}, \mathbf{r}) = \psi(\mathbf{r}) \Phi(\mathbf{R}) \quad (30)$$

and the Schrödinger equation is now separable giving the following equation for  $\Phi$ :

$$-\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) \Phi = E_R \Phi \quad (31)$$

the solution of which is

$$\Phi(\mathbf{R}) \sim \exp[i(\mathbf{P} \cdot \mathbf{R})/\hbar]; \quad E_R = \frac{\hbar^2 P^2}{2M} \quad (32)$$

where

$$M = m_1 + m_2$$

Equation (32) represents a plane wave and describes the uniform translational motion of the hydrogen atom as a whole. On the other hand,  $\psi(\mathbf{r})$  describes the internal motion of the atom and satisfies the equation

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + V(r) \psi(\mathbf{r}) = E_r \psi(\mathbf{r}) \quad (33)$$

where  $\nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$  and  $E_r$  is the relative energy, i.e. it is the difference between the total energy  $E$  and the centre of mass energy  $E_R$ :

$$E_r = E - E_R \quad (34)$$

Thus we have shown that whenever we have a two body problem with the potential energy function depending on  $|\mathbf{r}_1 - \mathbf{r}_2|$ , one need solve only one equation [Eq. (33)], which is the same as that for a single particle described by the potential energy function  $V(r)$  with the difference that the mass is replaced by the reduced mass and the coordinates are the relative coordinates.

## 10.4. The hydrogen-like atom problem

We consider a one-electron atom with a nucleus of charge  $Zq$ . The potential energy function is given by

*Potential energy function*

$$V(r) = -\frac{Zq^2}{4\pi\epsilon_0 r} \quad (35)$$

where

$Z = 1$  for the H-atom problem,

$Z = 2$  for the singly ionized He-atom problem ( $\text{He}^+$ ),

$Z = 3$  for the doubly ionized Li-atom problem ( $\text{Li}^{++}$ ),

etc. In order to solve Eq. (33), we use the same method as discussed in Sec. 10.2 and write

$$\psi(\mathbf{r}) = R(r) Y_{lm}(\theta, \phi) = \frac{u(r)}{r} Y_{lm}(\theta, \phi) \quad (36)$$

The radial part of the wave function satisfies the following equation [see Eq. (15)]:

*Radial part of Schrödinger equation*

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{2\mu}{\hbar^2} \left[ E + \frac{Zq^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) = 0 \quad (37)$$

where we have removed the subscript on  $E$  since we are interested only in the energy levels associated with the relative motion and

$$\mu = \frac{m_e M_N}{m_e + M_N} \quad (38)$$

where  $m_e$  and  $M_N$  represent the mass of the electron and that of the nucleus respectively. In order to solve Eq. (37) we introduce the dimensionless variable

$$\rho = \gamma r$$

where the parameter  $\gamma$  is to be conveniently chosen later. Equation (37) becomes

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left[ \rho^2 \frac{dR}{d\rho} \right] + \left[ \frac{2\mu E}{\hbar^2 \gamma^2} + \frac{2\mu}{\gamma \hbar^2} \frac{Zq^2}{4\pi\epsilon_0 \rho} - \frac{l(l+1)}{\rho^2} \right] R(\rho) = 0 \quad (39)$$

We choose<sup>2</sup>

$$\gamma^2 = \frac{8\mu |E|}{\hbar^2} = -\frac{8\mu E}{\hbar^2} \quad (40)$$

---

<sup>2</sup> We are looking for energy levels corresponding to bound states; therefore  $E < 0$ .

and set

$$\lambda = \frac{2\mu Z}{\hbar^2 \gamma} \left( \frac{q^2}{4\pi \epsilon_0} \right) = Z c \alpha \left( \frac{\mu}{2|E|} \right)^{1/2} \quad (41)$$

where  $c$  is the speed of light in free space and

$$\alpha \equiv \frac{q^2}{4\pi \epsilon_0 \hbar c} \simeq \frac{1}{137} \quad (42)$$

the fine structure coefficient. Thus, Eq. (39) becomes

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left[ \rho^2 \frac{dR}{d\rho} \right] + \left[ -\frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right] R(\rho) = 0 \quad (43)$$

In order to obtain an exact solution of Eq.(43) we introduce the function  $F(\rho)$  defined through the relation<sup>3</sup>

$$R(\rho) = F(\rho) e^{-\frac{1}{2}\rho} \quad (44)$$

[A direct method for obtaining solutions of Eq. (43) in terms of confluent hypergeometric functions is discussed in Sec. 10.4.2]. Now, if we substitute Eq. (44) in (43) we would obtain

$$\rho^2 \frac{d^2 F}{d\rho^2} + (2 - \rho) \rho \frac{dF}{d\rho} + [(\lambda - 1) \rho - l(l+1)] F(\rho) = 0 \quad (45)$$

We now try a series solution of the form

$$F(\rho) = \sum_{p=0,1,\dots} C_p \rho^{s+p} \quad (46)$$

Substituting this into Eq. (45) we obtain

$$\begin{aligned} & \sum_{p=0}^{\infty} C_p [(s+p)(s+p+1) - l(l+1)] \rho^p \\ & - \sum_{p=0}^{\infty} C_p [s+p - \lambda + 1] \rho^{p+1} = 0 \end{aligned}$$

or,

$$\begin{aligned} & C_0 [s(s+1) - l(l+1)] + \sum_{p=0}^{\infty} \{C_{p+1} [(s+p+1)(s+p+2) - l(l+1)] \\ & - C_p [s+p - \lambda + 1]\} \rho^{p+1} = 0 \end{aligned}$$

---

<sup>3</sup> As in the harmonic oscillator problem (see footnote 4 in Chapter 7) if we look for solutions valid for  $\rho \rightarrow +\infty$ , we find that  $R(\rho) \sim \rho^n \exp(\pm \rho/2)$  satisfies Eq. (43) for large values of  $\rho$ . This suggests that we look for a solution of the form given by Eq. (44).

We therefore obtain the indicial equation

*Indicial equation*

$$s(s+1) - l(l+1) = 0$$

Thus

$$s = l \text{ or } -l - 1 \quad (47)$$

For  $F(\rho)$  to be well-behaved<sup>4</sup> as  $\rho \rightarrow 0$  we must choose the root  $s = l$ . We also obtain the following recurrence relation

*Recurrence relation*

$$\begin{aligned} \frac{C_{p+1}}{C_p} &= \frac{s + p - \lambda + 1}{(s + p + 1)(s + p + 2) - l(l + 1)} \\ &= \frac{p + l + 1 - \lambda}{(p + 1)(p + 2l + 2)} \end{aligned} \quad (48)$$

where in the last step we have put  $s = l$ . For large values of  $p$

$$\frac{C_{p+1}}{C_p} \sim \frac{1}{p}$$

which is also the ratio of the terms in the expansion<sup>5</sup> of  $\exp(\rho)$ . Thus, if the series (46) is not terminated then  $F(\rho)$  will behave as  $\exp(\rho)$  and  $R(\rho)$  will behave as  $\exp(\frac{1}{2}\rho)$  for  $\rho \rightarrow \infty$  and will diverge; it may be noted that the infinite series given by Eq. (46) is *convergent* for all values of  $\rho$ , however, it will behave as  $\exp(\rho)$  for large values of  $\rho$ . We can terminate the series by requiring that

*Total quantum number*

$$\lambda = n = p + l + 1 \quad (49)$$

<sup>4</sup> For  $s = -l - 1$ , one of the expansion coefficients  $C_p$  becomes infinite and one has to use a special method for obtaining the second solution of Eq. (45); see, e.g., Sec. 2.3 (case 4) of Ref. 1. Alternatively, one can use a method to obtain directly the second solution (see Problems 10.6 and 10.7). In any case, this solution diverges at  $\rho = 0$  and hence is rejected.

<sup>5</sup>

$$e^\rho = 1 + \rho + \frac{\rho^2}{2!} + \dots = \sum_{p=0}^{\infty} C_p \rho^p$$

where

$$C_p = \frac{1}{p!}$$

Thus

$$\frac{C_{p+1}}{C_p} = \frac{1}{p+1} \sim \frac{1}{p} \quad \text{for large } p.$$

then  $C_{p+1} = 0$ . Since  $p$  and  $l$  can be positive integers or zero,  $n$  can have the values 1, 2, 3, . . . . The number  $n$  is called the *total quantum number*. Using Eqs (41) and (49) we obtain

$$E_n = -|E_n| = -\frac{\mu Z^2}{2n^2 \hbar^2} \left( \frac{q^2}{4\pi\epsilon_0} \right)^2 ; \quad n = 1, 2, \dots$$

Often it is more convenient to write the above equation as

*Energy eigenvalues*

$$E_n = -|E_n| = -\frac{\mu Z^2 \alpha^2 c^2}{2n^2} ; \quad n = 1, 2, \dots \quad (50)$$

where  $\alpha$  is the fine structure constant [see Eq. (42)]. Substituting in Eq. (40) we readily obtain

$$\gamma = \frac{2Z}{na_0} \quad (51)$$

with

$$a_0 = \frac{\hbar^2}{\mu(q^2/4\pi\epsilon_0)} \simeq 0.52 \times 10^{-10} \text{ m} \quad (52)$$

representing the Bohr radius. Thus

$$\rho = \frac{2Z}{na_0} r = \frac{2}{n} \xi \quad (53)$$

where we have introduced the new variable  $\xi$

$$\xi = \frac{Z}{a_0} r \quad (54)$$

which is independent of the total quantum number  $n$ .

Equation (50) gives the energy levels of the hydrogen atom (see Fig. 10.1). Before the development of quantum mechanics, it was known from experimental studies of the hydrogen atom spectrum, that the energy levels are given by

$$E_n = -E_H \cdot \frac{1}{n^2} , \quad n = 1, 2, \dots \quad (55)$$

and from observations  $E_H$  was found to be 13.6 eV. Bohr then devised a model<sup>6</sup> which gave Eq. (55) and predicted  $E_H$  should be

$$\frac{\mu}{2\hbar^2} \left( \frac{q^2}{4\pi\epsilon_0} \right)^2$$

---

<sup>6</sup> This is now known as the old quantum theory.

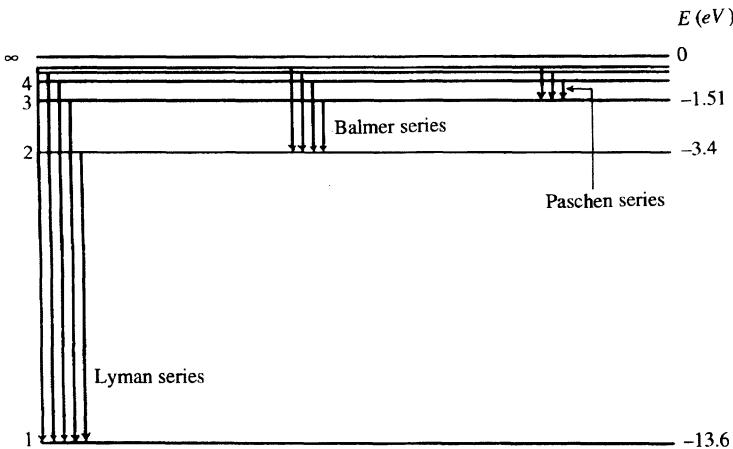


Figure 10.1. Energy levels of the hydrogen atom.

It was the first (and the most dramatic) success of Schrödinger's wave mechanics that it could reproduce this result from a basic equation of motion for the system. Now

$$\mu = \frac{m_e m_N}{m_e + m_N} \simeq m_e \left( 1 - \frac{m_e}{m_N} \right)$$

For the hydrogen atom

$$m_N = m_p \simeq 1.6726 \times 10^{-27} \text{ kg}$$

giving

$$\mu_H \simeq 9.1045 \times 10^{-31} \text{ kg}$$

where we have taken  $m_e \simeq 9.1095 \times 10^{-31} \text{ kg}$ . On the other hand, for the deuterium atom

$$m_N = m_D \simeq 3.3436 \times 10^{-27} \text{ kg}$$

giving

$$\mu_D \simeq 9.1070 \times 10^{-31} \text{ kg}$$

Now, for the  $n = n_1 \rightarrow n = n_2$  transition, the wavelength of the emitted radiation is given by

*Wavelength of emitted radiation*

$$\lambda = \frac{hc}{E_{n_1} - E_{n_2}}$$

or,

$$\lambda = \frac{2h}{\mu Z^2 \alpha^2 c^2} \left[ \frac{1}{n_2^2} - \frac{1}{n_1^2} \right]^{-1} \quad (56)$$

When  $n_2 = 1, 2$  and  $3$  we have what is known as Lyman series, the Balmer series and the Paschen series respectively (see Fig. 10.1). For the  $n = 3 \rightarrow n = 2$  transition, the wavelengths of the emitted radiation comes out to be

$$6565.2 \text{ \AA} \quad \text{and} \quad 6563.4 \text{ \AA}$$

for hydrogen and deuterium respectively. The corresponding wavelengths for the  $n = 4 \rightarrow n = 2$  transition are

$$4863.1 \text{ \AA} \quad \text{and} \quad 4861.7 \text{ \AA}$$

Such a small difference in the wavelength was first observed by Urey in 1932 which led to the discovery of deuterium. In spectroscopy the energy levels are usually written in wavenumber units which are obtained by dividing by  $hc$ :

$$T_n = \frac{E_n}{hc} = -\frac{Z^2}{n^2} R \quad (57)$$

where

$$R = \frac{2\pi^2 \mu}{ch^3} \left( \frac{q^2}{4\pi \epsilon_0} \right)^2 = \frac{\mu c \alpha^2}{2h} \quad (58)$$

is known as the Rydberg constant. Values of the Rydberg constant for different hydrogen like atoms are given below

$$\begin{aligned} R &= 109677.58 \text{ cm}^{-1} \quad (\text{for the hydrogen atom}) \\ &109707.56 \text{ cm}^{-1} \quad (\text{for the deuterium atom}) \\ &109722.40 \text{ cm}^{-1} \quad (\text{for the He}^{+}\text{-atom}) \\ &109728.90 \text{ cm}^{-1} \quad (\text{for the Li}^{++}\text{-atom}) \end{aligned}$$

The slight difference in the values is because of the difference in the values of the reduced mass  $\mu$ . The eigenfunctions are usually denoted by  $R_{nl}(r)$ . As an example, we calculate  $R_{20}(r)$  implying  $n = 2$  and  $l = 0$ . The recurrence relation [Eq. (48)] gives

$$\frac{C_{p+1}}{C_p} = \frac{p + l + 1 - \lambda}{(p + 1)(p + 2l + 2)} = \frac{p - 1}{(p + 1)(p + 2)}$$

Thus

$$C_1 = -\frac{1}{2}C_0$$

and

$$C_2 = C_3 = C_4 = \dots = 0$$

We therefore have

$$F(\rho) = C_0 \left( 1 - \frac{1}{2}\rho \right)$$

Since  $n = 2$ , we have  $\rho = \xi$  [see Eq. (53)] and therefore if we use the normalization condition

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1 \quad (59)$$

we would readily get

$$R_{20}(r) = \frac{1}{\sqrt{2}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 1 - \frac{1}{2}\xi \right) e^{-\xi/2} \quad (60)$$

where

$$\xi = \frac{Z}{a_0} r$$

Similarly, one can calculate other wave functions. We give below the first few  $R_{nl}(r)$

$$R_{10}(r) = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-\xi} \quad (61)$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{3/2} \xi e^{-\xi/2} \quad (62)$$

$$R_{30}(r) = \frac{2}{3\sqrt{3}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 1 - \frac{2}{3}\xi + \frac{2}{27}\xi^2 \right) e^{-\xi/3} \quad (63)$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}} \left( \frac{Z}{a_0} \right)^{3/2} \left( \xi - \frac{1}{6}\xi^2 \right) e^{-\xi/3} \quad (64)$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}} \left( \frac{Z}{a_0} \right)^{3/2} \xi^2 e^{-\xi/3} \quad (65)$$

All wavefunctions are normalized [see Eq.(59)]. The radial functions are usually expressed in terms of the Associated Laguerre functions (see Appendix I); however, it is more convenient to express in terms of confluent hypergeometric functions (see Sec. 10.4.2). The complete wavefunction is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad (66)$$

where  $Y_{lm}(\theta, \phi)$  are the spherical harmonics tabulated in Sec. 15.3. Looking at Eq. (50) we see that the energy depends on the total quantum number  $n$ . Since for each  $n$  we have values of  $l$  ranging from 0 to  $n - 1$  [see Eq.(49)] and for each value of  $l$ , the  $m$  values range from  $-l$  to  $+l$  [see Sec. 9.3], there are

$$\sum_{l=0}^{n-1} (2l + 1) = n^2 \quad (67)$$

states  $\psi_{nlm}$  belonging to a particular energy. The degeneracy with respect to  $m$  is due to spherical symmetry of the potential energy function. But the  $l$ -degeneracy is peculiar to the Coulomb field and is, in general, removed for non-Coulomb potentials (see e.g., Problem 10.12).

#### 10.4.1. THE PROBABILITY DISTRIBUTION FUNCTIONS

Since  $Y_{0,0} = 1/\sqrt{4\pi}$ , the ground state wave function is spherically symmetric and is given by

$$\psi_{1,0,0} = \frac{2}{\sqrt{4\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0) \quad (68)$$

If  $P(r)dr$  represents the probability of finding the electron between  $r$  and  $r + dr$ ,

$$P(r)dr = |\psi_{1,0,0}|^2 4\pi r^2 dr = 4 \left( \frac{Z}{a_0} \right)^3 r^2 \exp\left(-2\frac{Zr}{a_0}\right) dr \quad (69)$$

Thus  $P(r) = 0$  at  $r = 0$  and at  $r = \infty$  and has a maximum value at  $r = a_0/Z$ . This implies that the position of the electron is not certain but we can say for the hydrogen atom (for which  $Z = 1$ ) that most probably the electron will be found around the Bohr radius. This is consistent with the uncertainty principle [see Chapter 3]. It may be noted that

$$\int_0^\infty P(r)dr = 1 \quad (70)$$

as it indeed should be. The probability distribution functions for the first few  $l = 0$  states are given below:

$$P_{1,0,0} = \left( \frac{Z}{a_0} \right) 4\xi^2 e^{-2\xi} \quad (71)$$

$$P_{2,0,0} = \left( \frac{Z}{a_0} \right) \frac{1}{2} \left( 1 - \frac{1}{2}\xi \right)^2 4\xi^2 e^{-\xi} \quad (72)$$

$$P_{3,0,0} = \left( \frac{Z}{a_0} \right) \frac{4}{27} \left( 1 - \frac{2}{3}\xi + \frac{2}{27}\xi^2 \right)^2 \xi^2 e^{-2\xi/3} \quad (73)$$

$$P_{4,0,0} = \left( \frac{Z}{a_0} \right) \frac{1}{16} \left( 1 - \frac{3}{4}\xi + \frac{1}{8}\xi^2 - \frac{1}{192}\xi^3 \right)^2 \xi^2 e^{-\xi/2} \quad (74)$$

For higher excited states the probability distribution is maximum at a greater distance from the nucleus (see Fig. 10.2). In Fig. 10.3 we have given typical density plots of  $|\psi_{n,l,m}|^2$  on the  $y = 0$  plane.

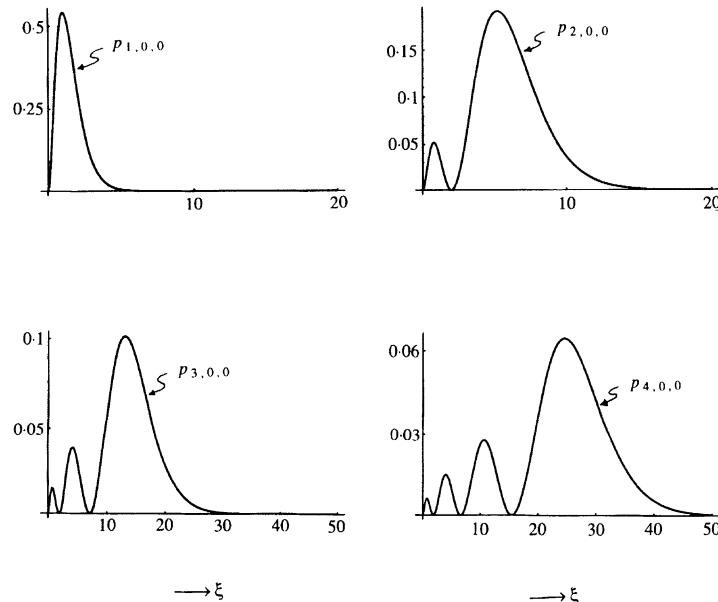


Figure 10.2. The probability distribution function  $P(r)$  for the  $(1, 0, 0)$ ,  $(2, 0, 0)$ ,  $(3, 0, 0)$  and  $(4, 0, 0)$  states.

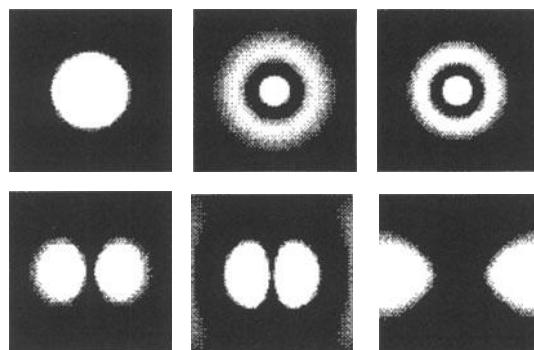


Figure 10.3. Top row: Density plots of  $|\psi_{1,0,0}|^2$ ,  $|\psi_{2,0,0}|^2$  and  $|\psi_{3,0,0}|^2$ . Bottom row: Density plots of  $|\psi_{2,1,0}|^2$ ,  $|\psi_{3,1,0}|^2$  and  $|\psi_{3,2,0}|^2$ . All density plots are on the  $y = 0$  plane.

#### 10.4.2. SOLUTION IN TERMS OF THE CONFLUENT HYPERGEOMETRIC FUNCTION

We rewrite Eq.(15) for the Coulomb potential [see Eq.(20)]

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2} \left[ E + \frac{Zq^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] u(r) = 0 \quad (75)$$

Once again we introduce the dimensionless variable

$$\rho = \gamma r$$

[where the parameter  $\gamma$  is defined by Eq.(40)] to obtain

$$\frac{d^2u}{d\rho^2} + \left[ -\frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right] u(\rho) = 0 \quad (76)$$

where  $\lambda$  is the same as given by Eq. (41). Now as  $\rho \rightarrow \infty$ , the first term inside the square bracket is the most dominating term and we may approximately write

$$\frac{d^2u}{d\rho^2} - \frac{1}{4}u(\rho) = 0$$

the solutions of which are given by  $e^{\pm\rho/2}$ . We reject the exponentially amplifying solution and write

$$u(\rho) \sim e^{-\rho/2} \quad \text{as } \rho \rightarrow \infty \quad (77)$$

Now as  $\rho \rightarrow 0$ , the third term inside the square brackets is the most dominating term and we may approximately write

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u(\rho) = 0$$

If we write

$$u(\rho) \sim \rho^g$$

then we readily obtain

$$g(g-1) = l(l+1)$$

giving

$$g = -l \text{ or } (l+1)$$

If we reject the  $g = -l$  solution [because it will diverge for  $\rho \rightarrow 0$ ], we may write

$$u(\rho) \sim \rho^{l+1} \quad \text{as } \rho \rightarrow 0 \quad (78)$$

Equations (77) and (78) suggest that we try to solve Eq. (76) by defining  $y(\rho)$  through the following equation

$$u(\rho) = \rho^{l+1}e^{-\rho/2}y(\rho) \quad (79)$$

Simple manipulations will show that  $y(\rho)$  satisfies the following equation:

$$\rho \frac{d^2y}{d\rho^2} + (c - \rho) \frac{dy}{d\rho} - ay(\rho) = 0 \quad (80)$$

where

$$\begin{aligned} a &= l + 1 - \lambda \\ c &= 2l + 2 \end{aligned} \quad (81)$$

Equation (80) is known as the confluent hypergeometric equation (see Appendix F) and using the power series method one can very easily show that one of the solutions of Eq. (80) [which is finite at the origin] is given by [see Appendix F]

$$y(\rho) = {}_1F_1(a, c, \rho) = 1 + \frac{a}{c} \frac{\rho}{1!} + \frac{a(a+1)}{c(c+1)} \frac{\rho^2}{2!} + \Lambda \quad (82)$$

which is known as the confluent hypergeometric function. Thus the complete solution of Eq.(76), which is well behaved at  $\rho = 0$ , is given by

$$u(\rho) = N \rho^{l+1} e^{-\rho/2} {}_1F_1(a, c, \rho) \quad (83)$$

where

$$N = \frac{\gamma^{3/2}}{(2l+1)!} \left\{ \frac{(n+l)!}{2n(n-l-1)!} \right\}^{1/2} \quad (84)$$

represents the normalization constant so that

$$\int_0^\infty u^2(r) dr = \int_0^\infty R^2(r) r^2 dr = 1 \quad (85)$$

We may mention the following:

- (i) The solution given by Eq.(83) is a rigorously correct solution of Eq.(76). Writing the solution in the form of Eq.(79) does *not* involve *any* approximation.
- (ii) The infinite series given by Eq. (82) is convergent for *all* values of  $\rho$  in the domain  $0 < \rho < \infty$ .
- (iii) For  $a = c$ , the infinite series given in Eq. (82) is simply  $e^\rho$ ; thus as  $\rho \rightarrow \infty$ ,  $u(\rho)$  will diverge as  $\rho^{l+1} e^{\rho/2}$ .

- (iv) Indeed

$${}_1F_1(a, c, \rho) \xrightarrow[\rho \rightarrow \infty]{} \rho^{a-c} e^\rho \quad (86)$$

(see Appendix K). Thus

$$u(\rho) \xrightarrow[\rho \rightarrow \infty]{} \rho^{l+1} \rho^{a-c} e^{\rho/2} \quad (87)$$

and will blow up as  $\rho \rightarrow \infty$  [although the infinite series given by Eq.(82) is always convergent!]. In order to avoid this we must make the infinite series a polynomial which can happen only if  $a$  is a negative integer:

$$a = -n_r; \quad n_r = 0, 1, 2, \dots \quad (88)$$

Thus

$$\lambda = l + 1 + n_r = n; \quad n = 1, 2, \dots \quad (89)$$

The quantities  $n_r$  and  $n$  are usually referred to as the radial quantum number and the total quantum number respectively.

We should mention that Eq. (83) is very convenient to use and Eq. (82) is quite easy to remember! For example, for  $n = 3, l = 2$ , we will have

$$R_{32}(\rho) = \frac{\gamma^{3/2}}{5!} \left\{ \frac{5!}{6} \right\}^{1/2} e^{-\rho/2} \rho^2 {}_1F_1(0, 6, \rho)$$

which can easily be seen to be identical to Eq. (65).

## 10.5. Vibration rotation spectra of diatomic molecules

In this section we will briefly discuss the vibration rotation spectra of diatomic molecules. In the simplest model, the potential energy function (between the two atoms of the molecule) is assumed to be represented by a Hooke's law type of interaction so that

$$V(r) = \frac{1}{2}k(r - r_e)^2 \quad (90)$$

where  $k$  is the force constant and  $r_e$  represents the equilibrium distance between the atoms (see Fig. 10.4). Since the potential is spherically symmetric, the radial part of the Schrödinger equation is given by [see Eq. (17)]

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2} \left[ E - \frac{J(J+1)}{2\mu r^2} - \frac{1}{2}k(r - r_e)^2 \right] u(r) = 0 \quad (91)$$

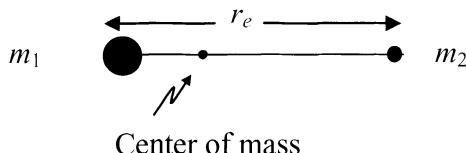


Figure 10.4. The diatomic molecule.

where  $u(r) = rR(r)$  and, to be consistent with the spectroscopic notation, we have written  $J(J + 1)$  instead of  $l(l + 1)$ ;  $J = 0, 1, 2, \dots$ . Further,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

represents the reduced mass with  $m_1$  and  $m_2$  representing the mass of the two atoms of the diatomic molecule. The boundary conditions are

$$u(r = 0) = 0 = u(r = \infty)$$

Introducing the variable

$$\rho = r - r_e$$

we get

$$\frac{d^2 u}{d\rho^2} + \frac{2\mu}{\hbar^2} \left[ E - \frac{J(J + 1)\hbar^2}{2\mu r_e^2} - \frac{1}{2}k\rho^2 \right] u(\rho) = 0 \quad (92)$$

where in the denominator we have replaced  $r_e + \rho$  by  $r_e$ ; the error involved is negligible for small vibrations (see e.g., Sec. 10.5.1). The boundary conditions become

$$u(\rho = -r_e) = 0 = u(\rho = \infty)$$

which, for small vibrations, is approximately the same as

$$u(\rho = -\infty) = 0 = u(\rho = \infty) \quad (93)$$

Equation (92) and the above boundary conditions are equivalent to the one-dimensional harmonic oscillator problem [see Sec. 7.2] so that we may write

$$E - \frac{J(J + 1)\hbar^2}{2\mu r_e^2} \approx \left( v + \frac{1}{2} \right) \hbar\omega \quad (94)$$

where

$$\omega = \left( \frac{k}{\mu} \right)^{1/2}$$

and  $v = 0, 1, 2, \dots$  represents the vibration quantum number. We rewrite Eq.(94) as

$$E = E_r + E_v \quad (95)$$

where

$$E_r = \frac{J(J + 1)\hbar^2}{2\mu r_e^2}; \quad J = 0, 1, 2, \dots \quad \left. \right\} \quad (96)$$

and

$$E_v = \left( v + \frac{1}{2} \right) \hbar\omega; \quad v = 0, 1, 2, \dots \quad \left. \right\}$$

Table 10.1. Rotational and vibrational constants of some diatomic molecules [adapted from Ref. 4].

Molecule	$r_e$ (Å)	$g = \frac{\omega}{2\pi c}$ (cm $^{-1}$ )	$\frac{\hbar^2}{2\mu r_e^2}$ (eV)
H <sub>2</sub>	0.74	4395	$7.56 \times 10^{-3}$
HD	0.74	3817	$5.69 \times 10^{-3}$
N <sub>2</sub>	1.09	2360	$2.48 \times 10^{-4}$
O <sub>2</sub>	1.21	1580	$1.78 \times 10^{-4}$
LiH	1.60	1406	$9.27 \times 10^{-4}$
HCl <sup>35</sup>	1.27	2991	$1.32 \times 10^{-3}$
NaCl <sup>35</sup>	2.51	380	$2.36 \times 10^{-5}$
KBr <sup>79</sup>	2.94	231	$9.1 \times 10^{-6}$

represent the rotational and vibrational energies respectively. In spectroscopy, the energy levels are usually written in wave number units which are obtained by dividing by  $hc$ :

$$T(\text{cm}^{-1}) = \frac{E}{hc} = \left(v + \frac{1}{2}\right)g + BJ(J+1) \quad (97)$$

where

$$g \equiv \frac{\omega}{2\pi c} \quad (98)$$

is known as the vibrational constant and

$$B = \frac{h}{8\pi^2 c(\mu r_e^2)} \quad (99)$$

is known as the rotational constant. Table 10.1 gives vibrational and rotational constants of some diatomic molecules.

The rotation-vibration states are schematically shown in Fig. 10.5. The upper state energy levels ( $v = 1$ ) are given by

$$T'(\text{cm}^{-1}) = BJ'(J'+1) + \frac{3}{2}g \quad (100)$$

and the lower state energy levels ( $v = 0$ ) are given by

$$T''(\text{cm}^{-1}) = BJ''(J''+1) + \frac{1}{2}g \quad (101)$$

The transition lines for which

$$\Delta J = J'' - J' = 1 \quad (102)$$

are referred to as the *P* branch and the lines for which

$$\Delta J = J'' - J' = 1$$

are referred to as the *R* branch. Now, for the *P* branch we have the following transitions

$$(v = 1, J = J') \leftrightarrow (v = 0, J = J' + 1); \quad J' = 0, 1, 2, 3, K$$

and the corresponding frequencies will be given by

$$\begin{aligned} \Delta T(\text{cm}^{-1}) &= g + B[J'(J' + 1) - (J' + 1)(J' + 2)] \\ &= g - 2B(J' + 1) \\ &= g - 2B, g - 4B, g - 6B, K \text{ (P branch)} \end{aligned}$$

for  $J' = 0, 1, 2, K$  respectively. On the other hand, for the *R* branch we have the following transition

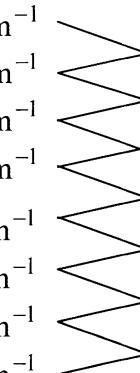
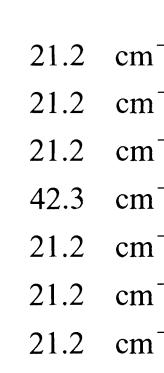
$$(v = 1, J = J') \leftrightarrow (v = 0, J = J' - 1); \quad J' = 1, 2, 3, K$$

for which

$$\begin{aligned} \Delta T(\text{cm}^{-1}) &= g + 2BJ' \\ &= g + 2B, g + 4B, g + 6B, K \text{ (R branch)} \end{aligned}$$

for  $J' = 1, 2, 3, K$  respectively.

**Example 10.1** The experimental values of the  $v = 0 \rightarrow v = 1$  absorption lines of  $\text{HCl}^{35}$  are given below<sup>7</sup>:

<i>P</i> branch	$\begin{bmatrix} 2906.3 & \text{cm}^{-1} \\ 2927.5 & \text{cm}^{-1} \\ 2948.7 & \text{cm}^{-1} \\ 2969.9 & \text{cm}^{-1} \end{bmatrix}$		$\begin{bmatrix} 21.2 & \text{cm}^{-1} \\ 21.2 & \text{cm}^{-1} \\ 21.2 & \text{cm}^{-1} \\ 42.3 & \text{cm}^{-1} \end{bmatrix}$
<i>R</i> branch	$\begin{bmatrix} 3012.2 & \text{cm}^{-1} \\ 3033.4 & \text{cm}^{-1} \\ 3054.6 & \text{cm}^{-1} \\ 3075.8 & \text{cm}^{-1} \end{bmatrix}$		$\begin{bmatrix} 21.2 & \text{cm}^{-1} \\ 21.2 & \text{cm}^{-1} \\ 21.2 & \text{cm}^{-1} \\ 21.2 & \text{cm}^{-1} \end{bmatrix}$

<sup>7</sup> Data taken from Ref. 3; this reference also gives an accurate description of infrared band analysis.

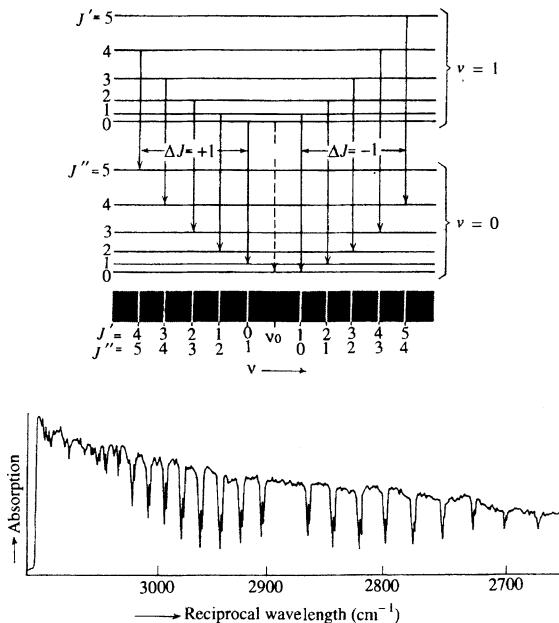


Figure 10.5. The vibration-rotation states (and the corresponding spectra) for HCl. The slightly different frequencies at each absorption line are due to the presence of the two isotopes Cl<sup>35</sup> and Cl<sup>37</sup> [adapted from Ref. 3].

Thus

$$2B \approx 21.2 \text{ cm}^{-1} \Rightarrow B \approx 10.6 \text{ cm}^{-1}$$

Now

$$\begin{aligned} \mu &\approx \frac{35}{36}m_H \approx \frac{35}{36} \times 1.67 \times 10^{-24} \text{ g} \\ &\approx 1.62 \times 10^{-24} \text{ g} \end{aligned}$$

Using Eq. (99) we get  $r_e \approx 1.27 \text{ \AA}$ . Further

$$g = \frac{\omega}{2\pi c} \approx \frac{2969.9 + 3012.2}{2} \approx 2991 \text{ cm}^{-1}$$

giving

$$\omega \approx 5.63 \times 10^{14} \text{ s}^{-1} \quad \text{and} \quad k \approx 5.14 \times 10^5 \text{ dynes/cm}$$

The absorption lines  $2948.7 \text{ cm}^{-1}$  and  $2969.9 \text{ cm}^{-1}$  correspond to  $(v = 0, J = 2) \rightarrow (v = 1, J = 1)$  and  $(v = 0, J = 1) \rightarrow (v = 1, J = 0)$  transitions in the *P* branch. Similarly, the absorption lines  $3012.2 \text{ cm}^{-1}$  and  $3033.4 \text{ cm}^{-1}$  correspond to  $(v = 0, J = 1) \rightarrow (v = 1, J = 2)$  and  $(v = 0, J = 0) \rightarrow (v = 1, J = 1)$  transitions in the *R* branch.

Figure 10.5 shows the spectra of HCl; the slightly different frequencies at each absorption line are due to the presence of two isotopes of chlorine ( $\text{HCl}^{35}$  and  $\text{HCl}^{37}$ ). Notice that the  $\Delta J = 0$  transitions are forbidden.

**Example 10.2** The experimental values of the  $v = 0 \rightarrow v = 1$  absorption lines of  $\text{C}^{12}\text{O}^{16}$  are given below<sup>8</sup>

2154.77	$\text{cm}^{-1}$		3.86	$\text{cm}^{-1}$
2158.63	$\text{cm}^{-1}$		3.86	$\text{cm}^{-1}$
2162.49	$\text{cm}^{-1}$		3.86	$\text{cm}^{-1}$
2166.35	$\text{cm}^{-1}$		3.86	$\text{cm}^{-1}$
2174.07	$\text{cm}^{-1}$		7.72	$\text{cm}^{-1}$
2177.93	$\text{cm}^{-1}$		3.86	$\text{cm}^{-1}$
2181.79	$\text{cm}^{-1}$		3.86	$\text{cm}^{-1}$
2185.65	$\text{cm}^{-1}$		3.86	$\text{cm}^{-1}$

Thus

$$B = 1.93 \text{ cm}^{-1}$$

Now

$$\mu \approx \frac{12 \times 16}{28} m_H \approx 1.145 \times 10^{-23} \text{ g}$$

Using Eq. (99) we get  $r_e \approx 1.13 \text{ \AA}$ . Further

$$g = \frac{\omega}{2\pi c} \approx 2170.21 \text{ cm}^{-1}$$

giving

$$\omega \approx 4.088 \times 10^{14} \text{ s}^{-1} \quad \text{and} \quad k \approx 1.91 \times 10^6 \text{ dynes/cm}$$

It is interesting to note that since the degeneracy of each rotational level is  $(2J+1)$ , at thermal equilibrium

$$\begin{aligned} & \frac{\text{Number of molecules in the rotational level } J''}{\text{Number of molecules in the rotational level } J'' = 0} \\ &= (2J'' + 1) \exp \left[ -\frac{E(J = J'', v) - E(J = 0, v)}{kT} \right] \\ &= (2J'' + 1) e^{-\alpha J''(J''+1)} \end{aligned} \quad (103)$$

where

$$\alpha = \frac{\hbar^2}{2\mu r_e^2} \cdot \frac{1}{kT} \quad (104)$$

---

<sup>8</sup> Data adapted from Ref. 3.

Equation (103) shows that the population increases with  $J''$  and attains its maximum value around

$$J'' \approx \frac{1}{2} \left[ \sqrt{\frac{2}{\alpha}} - 1 \right] \quad (105)$$

For HCl,

$$\frac{\hbar^2}{2\mu r_e^2} \approx 1.32 \times 10^{-3} \text{ eV}$$

and at room temperatures,

$$kT \approx \frac{1}{40} \text{ eV}$$

implying

$$J'' \approx \frac{1}{2} \left[ \sqrt{\frac{2}{\alpha}} - 1 \right] \approx 2.6$$

For  $J'' = 1, 2, 3$  and  $4$  the quantity on the RHS of Eq.(103) takes the values  $2.7, 3.6, 3.7$  and  $3.13$  respectively. Thus at room temperature, the population is maximum for the transition occurring from the level  $J'' = 3$ . Indeed, from the absorption spectra, it is possible to deduce the temperature of the gas.

#### 10.5.1. A MORE ACCURATE ANALYSIS OF THE VIBRATION ROTATION SPECTRA

In order to obtain a more accurate expression for energy eigenvalues associated with the vibration-rotation spectra, we rewrite Eq. (91) in the form

$$\frac{d^2u}{d\rho^2} + \frac{2\mu}{\hbar^2} F(\rho) u(\rho) = 0 \quad (106)$$

where

$$\begin{aligned} F(\rho) &= E - \frac{J(J+1)\hbar^2}{2\mu r_e^2} \left(1 + \frac{\rho}{r_e}\right)^{-2} - \frac{1}{2} k\rho^2 \\ &\simeq E - E_r \left(1 - \frac{2\rho}{r_e} + \frac{3\rho^2}{r_e^2}\right) - \frac{1}{2} k\rho^2 \end{aligned} \quad (107)$$

where  $E_r$  is given by Eq. (??). Thus

$$F(\rho) \simeq E - E_r - \frac{1}{2} k' [(\rho - \alpha)^2 - \alpha^2] \quad (108)$$

where

$$k' = k(1 + 3\Gamma) \quad (109)$$

$$\Gamma = \frac{E_r}{\frac{1}{2} kr_e^2} \quad (110)$$

and

$$\alpha = \left( \frac{\Gamma}{1 + 3\Gamma} \right) r_e \quad (111)$$

Thus Eq. (106) can be written in the form

$$\frac{d^2 u}{d\rho^2} + \frac{2\mu}{\hbar^2} \left[ E' - \frac{1}{2} k' \xi^2 \right] u(\xi) = 0 \quad (112)$$

where

$$\xi = \rho - \alpha \quad (113)$$

and

$$E' = E - E_r + \frac{1}{2} k' \alpha^2 \quad (114)$$

Equation (112) represents the Schrödinger equation for the linear harmonic oscillator. Assuming  $u(\xi = -\infty) = 0 = u(\xi = \infty)$  we get the following expression for the energy eigenvalues

$$E' = \left( v + \frac{1}{2} \right) \hbar \sqrt{\frac{k'}{\mu}} ; \quad v = 0, 1, 2, \dots \quad (115)$$

or,

*Energy eigenvalues*

$$E = E_r \left[ 1 - \frac{\Gamma}{1 + 3\Gamma} \right] + \left( v + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu} (1 + 3\Gamma)} \quad (116)$$

which represents a more accurate expression for the energy eigenvalues. However, the corrections are usually small because in most cases

$$\Gamma \ll 1$$

For example, for HCl<sup>35</sup>

$$\bar{v} = \frac{\omega}{2\pi c} \approx 2886 \text{ cm}^{-1}$$

$$\Rightarrow \omega \approx 5.436 \times 10^{14} \text{ s}^{-1}$$

$$\Rightarrow k = \mu \omega^2$$

$$\approx \frac{35}{36} \times 1.67 \times 10^{-24} \times (5.44 \times 10^{14})^2$$

$$\approx 4.80 \times 10^5 \text{ dynes/cm}$$

where, for consistency with books on spectroscopy, we have used CGS units. Thus

$$\begin{aligned} \frac{1}{2} k r_e^2 &\approx \frac{1}{2} \times 4.8 \times 10^5 \times (1.27 \times 10^{-8})^2 \text{ ergs} \\ &\approx 24.2 \text{ eV} \end{aligned}$$

where we have assumed  $r_e \approx 1.27 \text{ \AA}$  for the equilibrium spacing between hydrogen and chlorine atoms. Thus

$$\Gamma = \frac{J(J+1) \frac{\hbar^2}{2\mu r_e^2}}{\frac{1}{2} k r_e^2} \approx 5 \times 10^{-5} J(J+1)$$

showing that the correction terms in Eq. (116) are very small. The effect of anharmonic terms is discussed in Ref. 3.

## 10.6. The three-dimensional harmonic oscillator

In this section we will consider the three-dimensional harmonic oscillator described by the potential energy function

*Potential energy function*

$$V(x, y, z) = \frac{1}{2}\mu(\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2) \quad (117)$$

Thus in Cartesian coordinates, the three-dimensional Schrödinger equation becomes

$$\begin{aligned} & \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \\ & + \frac{2\mu}{\hbar^2} \left[ E - \frac{1}{2}\mu\omega_1^2 x^2 - \frac{1}{2}\mu\omega_2^2 y^2 - \frac{1}{2}\mu\omega_3^2 z^2 \right] \psi(x, y, z) = 0 \end{aligned} \quad (118)$$

We use the method of separation of variables to solve the above equation and write

$$\psi(x, y, z) = X(x) Y(y) Z(z) \quad (119)$$

Thus

$$\begin{aligned} & YZ \frac{d^2 X}{dx^2} + XZ \frac{d^2 Y}{dy^2} + XY \frac{d^2 Z}{dz^2} \\ & + \frac{2\mu}{\hbar^2} \left[ E - \frac{1}{2}\mu\omega_1^2 x^2 - \frac{1}{2}\mu\omega_2^2 y^2 - \frac{1}{2}\mu\omega_3^2 z^2 \right] XYZ = 0 \end{aligned}$$

or

$$\begin{aligned} & \left[ \frac{1}{X} \frac{d^2 X}{dx^2} - \frac{\mu^2 \omega_1^2}{\hbar^2} x^2 \right] + \left[ \frac{1}{Y} \frac{d^2 Y}{dy^2} - \frac{\mu^2 \omega_2^2}{\hbar^2} y^2 \right] \\ & + \left[ \frac{1}{Z} \frac{d^2 Z}{dz^2} - \frac{\mu^2 \omega_3^2}{\hbar^2} z^2 \right] = -\frac{2\mu E}{\hbar^2} \end{aligned} \quad (120)$$

The variables have indeed separated out. The first term inside the square brackets on the LHS of the above equation is a function of  $x$  alone; similarly the second and the third terms are functions of  $y$  and  $z$  and since their sum is equal to a constant, we must set each term equal to a constant

$$\frac{1}{X} \frac{d^2 X}{dx^2} - \frac{\mu^2 \omega_1^2}{\hbar^2} x^2 = -g_1 \quad (121)$$

$$\frac{1}{Y} \frac{d^2 Y}{dy^2} - \frac{\mu^2 \omega_2^2}{\hbar^2} y^2 = -g_2 \quad (122)$$

$$\frac{1}{Z} \frac{d^2 Z}{dz^2} - \frac{\mu^2 \omega_3^2}{\hbar^2} z^2 = -g_3 \quad (123)$$

where

$$g_1 + g_2 + g_3 = \frac{2\mu E}{\hbar^2} \quad (124)$$

Now, if we define

$$\xi = \gamma_1 x ; \quad \gamma_1 = \sqrt{\frac{\mu \omega_1}{\hbar}} \quad (125)$$

Eq. (121) takes the form

$$\frac{d^2 X}{d\xi^2} + (\Lambda_1 - \xi^2) X(\xi) = 0 \quad (126)$$

We had encountered the above equation in Chapter 7 while discussing the linear harmonic oscillator problem. If we apply the boundary condition that  $X(\xi) \rightarrow 0$  as  $\xi \rightarrow \pm\infty$  we would find that  $\Lambda_1$  can only take the values  $1, 3, 5, \dots$ ; i.e.

$$\Lambda_1 = (2n_1 + 1) ; \quad n_1 = 0, 1, 2, \dots \quad (127)$$

Thus

$$g_1 = (2n_1 + 1) \frac{\mu \omega_1}{\hbar} \quad (128)$$

The corresponding normalized eigenfunction would be (see Sec. 7.3):

$$X_{n_1}(x) = N_{n_1} H_{n_1}(\xi) e^{-\frac{1}{2}\xi^2} \quad (129)$$

where  $H_{n_1}(\xi)$  are the Hermite polynomials and

$$N_{n_1} = \left( \frac{\gamma_1}{2^{n_1} n_1! \sqrt{\pi}} \right)^{1/2} \quad (130)$$

Similarly

$$g_2 = (2n_2 + 1) \frac{\mu \omega_2}{\hbar}$$

and

$$g_3 = (2n_3 + 1) \frac{\mu\omega_3}{\hbar}$$

with

$$n_2, n_3 = 0, 1, 2, \dots$$

The corresponding normalized eigenfunctions would be

$$Y_{n_2}(y) = N_{n_2} H_{n_2}(\eta) e^{-\frac{1}{2}\eta^2}$$

and

$$Z_{n_3}(z) = N_{n_3} H_{n_3}(\zeta) e^{-\frac{1}{2}\zeta^2}$$

where

$$\begin{aligned} \eta &= \gamma_2 y & ; \quad \zeta &= \gamma_3 z \\ \gamma_2 &= \sqrt{\frac{\mu\omega_2}{\hbar}} & ; \quad \gamma_3 &= \sqrt{\frac{\mu\omega_3}{\hbar}} \end{aligned}$$

and

$$N_{n_2} = \left( \frac{\gamma_2}{2^{n_2} n_2! \sqrt{\pi}} \right)^{1/2}; \quad N_{n_3} = \left( \frac{\gamma_3}{2^{n_3} n_3! \sqrt{\pi}} \right)^{1/2}$$

Thus

$$\begin{aligned} \psi(x, y, z) &= \psi_{n_1, n_2, n_3}(x, y, z) \\ &= \left[ \frac{\gamma_1 \gamma_2 \gamma_3}{2^n n_1! n_2! n_3! \pi^{3/2}} \right]^{1/2} [H_{n_1}(\xi) H_{n_2}(\eta) H_{n_3}(\zeta)] \\ &\times e^{-\frac{1}{2}(\xi^2 + \eta^2 + \zeta^2)} \end{aligned} \tag{131}$$

where

$$n = n_1 + n_2 + n_3$$

The corresponding energy eigenvalues would be given by

$$E = \frac{\hbar^2}{2\mu} [g_1 + g_2 + g_3]$$

or,

*Energy eigenvalues*

$$\begin{aligned} E = E_{n_1, n_2, n_3} &= \left(n_1 + \frac{1}{2}\right) \hbar\omega_1 + \left(n_2 + \frac{1}{2}\right) \hbar\omega_2 + \left(n_3 + \frac{1}{2}\right) \hbar\omega_3; \\ n_1, n_2, n_3 &= 0, 1, 2, 3, \dots \end{aligned} \tag{132}$$

### 10.6.1. THE ISOTROPIC OSCILLATOR

For an isotropic oscillator

$$\omega_1 = \omega_2 = \omega_3 = \omega \quad (133)$$

giving

$$\begin{aligned} E &= (n_1 + n_2 + n_3 + \frac{3}{2}) \hbar\omega \\ &= (n + \frac{3}{2}) \hbar\omega ; \quad n = 0, 1, 2, \dots \end{aligned} \quad (134)$$

When  $n = 0$ , we must have

$$n_1 = n_2 = n_3 = 0$$

On the other hand, when  $n = 1$ , we could have

$$n_1 = 1, \quad n_2 = 0, \quad n_3 = 0$$

or

$$n_1 = 0, \quad n_2 = 1, \quad n_3 = 0$$

or

$$n_1 = 0, \quad n_2 = 0, \quad n_3 = 1$$

Thus we will have a three-fold degenerate state. Similarly, the energy level corresponding to  $n = 2$  will be six-fold degenerate. In general, the degree of degeneracy will be

$$1 + 2 + \cdots + n + (n + 1) = \frac{1}{2} (n + 1)(n + 2) \quad (135)$$

Now, for the isotropic oscillator, the potential energy function can be written as

*Potential function*

$$V = V(r) = \frac{1}{2} \mu\omega^2 r^2 \quad (136)$$

Since the potential is spherically symmetric, we could write the solution of the Schrödinger equation in the form

$$\psi(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi) \quad (137)$$

where  $R(r)$  satisfies the following equation

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{2\mu}{\hbar^2} \left[ E - \frac{1}{2} \mu\omega^2 r^2 - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) = 0 \quad (138)$$

One can directly solve the above equation (see Problems 10.12); however, it may be instructive to choose appropriate linear combinations<sup>9</sup> of the wave functions

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<sup>9</sup> We may recall that if  $\psi_1, \psi_2, \dots, \psi_g$  represent  $g$  linearly independent wave functions for a  $g$ -fold degenerate state then any linear combination of them (like  $c_1\psi_1 + c_2\psi_2 + \dots$ ) is also an eigenfunction corresponding to the same energy eigenvalue.

given by Eq. (131) so that they are of the form of Eq. (137). We illustrate this for the first three states:

### THE GROUND STATE

The ground state energy is given by

$$E_0 = E_{0,0,0} = \frac{3}{2} \hbar\omega$$

which corresponds to

$$n_1 = n_2 = n_3 = 0$$

The corresponding eigenfunction is given by

$$\psi_0 = \psi_{0,0,0} = \left( \frac{\gamma}{\sqrt{\pi}} \right)^{3/2} e^{-\gamma^2(x^2+y^2+z^2)/2} \quad (139)$$

where

$$\gamma = \gamma_1 = \gamma_2 = \gamma_3 = \sqrt{\frac{\mu \hbar}{\omega}} \quad (140)$$

We can also rewrite  $\psi_0$  as

$$\psi_0(r, \theta, \phi) = R_{0,0}(r) Y_{0,0} \quad (141)$$

where

$$R_{0,0}(r) = \frac{2\gamma^{3/2}}{\pi^{1/4}} e^{-\gamma^2 r^2/2} \quad (142)$$

The function  $R_{0,0}(r)$  is automatically normalized.

### THE FIRST EXCITED STATE

The energy eigenvalue corresponding to the first excited state is given by

$$E_1 = \frac{5}{2} \hbar\omega$$

which will occur when

$$n_1 = 1, \ n_2 = 0 \text{ and } n_3 = 0$$

or, when

$$n_1 = 0, \ n_2 = 1 \text{ and } n_3 = 0$$

or, when

$$n_1 = 0, \ n_2 = 0 \text{ and } n_3 = 1$$

Thus there will be three linearly independent eigenfunctions belonging to the same energy eigenvalue; hence the first excited state is said to be a three-fold degenerate state. The corresponding eigenfunctions would be

$$\psi_1 = \psi_{1,0,0} = C_1 x e^{-\gamma^2 r^2/2} = C_1 r \sin \theta \cos \phi e^{-\gamma^2 r^2/2} \quad (143)$$

$$\psi_2 = \psi_{0,1,0} = C_1 y e^{-\gamma^2 r^2/2} = C_1 r \sin \theta \sin \phi e^{-\gamma^2 r^2/2} \quad (144)$$

$$\psi_3 = \psi_{0,0,1} = C_1 z e^{-\gamma^2 r^2/2} = C_1 r \cos \theta e^{-\gamma^2 r^2/2} \quad (145)$$

where

$$C_1 = \frac{\sqrt{2}}{\pi^{3/4}} \gamma^{5/2}$$

The eigenfunctions of the form of Eq. (137) are given by

$$\phi_1 = \frac{1}{\sqrt{2}} (\psi_1 + i\psi_2) = -R_{1,1}(r) Y_{1,1}(\theta, \phi) \quad (146)$$

$$\phi_2 = \frac{1}{\sqrt{2}} (\psi_1 - i\psi_2) = R_{1,1}(r) Y_{1,-1}(\theta, \phi) \quad (147)$$

$$\phi_3 = \psi_3 = R_{1,1}(r) Y_{1,0}(\theta, \phi) \quad (148)$$

where

$$R_{1,1}(r) = \sqrt{\frac{8\pi}{3}} \cdot \frac{1}{\pi^{3/4}} \cdot \gamma^{5/2} r e^{-\gamma^2 r^2/2} \quad (149)$$

## THE SECOND EXCITED STATE

Similarly, the second excited state (with  $E_2 = \frac{7}{2}\hbar\omega$ ) is six-fold degenerate with  $n_1, n_2$  and  $n_3$  taking the following sets of values

$$(2, 0, 0); \quad (0, 2, 0); \quad (0, 0, 2);$$

$$(1, 1, 0); \quad (0, 1, 1); \quad \text{and} \quad (1, 0, 1).$$

Since  $H_2(\xi) = (4\xi^2 - 2)$ , the corresponding eigenfunctions are

$$\left. \begin{aligned} \psi_4 &= \psi_{2,0,0} = C_2 (4\gamma^2 x^2 - 2) e^{-\gamma^2 r^2/2} \\ \psi_5 &= \psi_{0,2,0} = C_2 (4\gamma^2 y^2 - 2) e^{-\gamma^2 r^2/2} \\ \psi_6 &= \psi_{0,0,2} = C_2 (4\gamma^2 z^2 - 2) e^{-\gamma^2 r^2/2} \\ \psi_7 &= \psi_{1,1,0} = \sqrt{2}C_2 (2\gamma x)(2\gamma y) e^{-\gamma^2 r^2/2} \\ \psi_8 &= \psi_{0,1,1} = \sqrt{2}C_2 (2\gamma y)(2\gamma z) e^{-\gamma^2 r^2/2} \\ \psi_9 &= \psi_{1,0,1} = \sqrt{2}C_2 (2\gamma z)(2\gamma x) e^{-\gamma^2 r^2/2} \end{aligned} \right\} \quad (150)$$

where

$$C_2 = \frac{1}{2\sqrt{2}} \left( \frac{\gamma}{\sqrt{\pi}} \right)^{3/2} \quad (151)$$

The eigenfunctions of the form of Eq. (137) are given by

$$\phi_4 = \frac{1}{\sqrt{3}} (\psi_4 + \psi_5 + \psi_6) = R_{2,0}(r) Y_{0,0}(\theta, \phi) \quad (152)$$

$$\phi_5 = \frac{1}{\sqrt{6}} (-\psi_4 - \psi_5 + 2\psi_6) = R_{2,2}(r) Y_{2,0}(\theta, \phi) \quad (153)$$

$$\phi_6 = \frac{1}{2} (\psi_4 - \psi_5 + i\sqrt{2}\psi_7) = R_{2,2}(r) Y_{2,2}(\theta, \phi) \quad (154)$$

$$\phi_7 = \frac{1}{2} (\psi_4 - \psi_5 - i\sqrt{2}\psi_7) = R_{2,2}(r) Y_{2,-2}(\theta, \phi) \quad (155)$$

$$\phi_8 = -\frac{1}{\sqrt{2}} (\psi_9 + i\psi_8) = R_{2,2}(r) Y_{2,1}(\theta, \phi) \quad (156)$$

$$\phi_9 = \frac{1}{\sqrt{2}} (\psi_9 - i\psi_8) = R_{2,2}(r) Y_{2,-1}(\theta, \phi) \quad (157)$$

where

$$R_{2,0}(r) = \sqrt{\frac{\pi}{2}} \left( \frac{\gamma}{\sqrt{\pi}} \right)^{3/2} (4\gamma^2 r^2 - 6) e^{-\gamma^2 r^2/2} \quad (158)$$

$$R_{2,2}(r) = \sqrt{\frac{\pi}{15}} \left( \frac{\gamma}{\sqrt{\pi}} \right)^{3/2} 4\gamma^2 r^2 e^{-\gamma^2 r^2/2} \quad (159)$$


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## 10.7. Problems

### Problem 10.1

- (a) Consider a spherically symmetric potential energy function of the form

$$\begin{aligned} V(r) &= 0 & 0 < r < a \\ &= \infty & r > a \end{aligned} \quad (160)$$

which represents an infinitely deep potential well of radius  $a$ . Consider the  $l = 0$  case and determine the energy eigenvalues and the normalized eigenfunctions.

- (b) In continuation of part (a), show that for a general value of  $l$  the energy eigenvalues are given by

$$E_{n,l} = \frac{\hbar^2}{2\mu} \left( \frac{g_{l,n}}{a} \right)^2; \quad l = 0, 1, 2, \dots \quad n = 1, 2, \dots \quad (161)$$

where  $g_{l,n}$  represent the zeroes of the spherical Bessel function  $j_l(x)$ ; i.e.

$$\begin{aligned} g_{01} &= \pi, & g_{02} &= 2\pi, & g_{03} &= 3\pi, \dots \\ g_{11} &= 4.4934, & g_{12} &= 7.7253, & g_{13} &= 10.9041, \dots \\ g_{21} &= 5.7635, & g_{22} &= 9.0950, & g_{23} &= 12.3229, \dots \end{aligned}$$

Show that the corresponding normalized eigenfunctions are

$$\psi(r, \theta, \phi) = N j_l \left( g_{l,n} \frac{r}{a} \right) Y_{lm}(\theta, \phi) \quad (162)$$

where

$$N = \left[ \frac{2}{a^3 [j_{l+1}(g_{l,n})]^2} \right]^{1/2} \quad (163)$$

represents the normalization constant.

**Problem 10.2** A quantum dot can be approximately described by an electron (of a certain effective mass) inside an infinitely deep spherical well as discussed in the previous problem. Assume  $a \simeq 0.4 \mu\text{m}$  and the effective mass of the electron to be  $0.065 m_e$ , calculate the frequency of radiation emitted when the electron makes a transition from the first excited state to the ground state.

[Ans: Approximately 0.91 GHz]

### Problem 10.3

- (a) We next consider the electron (of effective mass  $\mu$ ) to be confined inside an infinitely deep cylindrical well of height  $b$  and radius  $a$ . Solve the Schrödinger equation in cylindrical coordinates and show that the energy eigenvalues are given by

$$E_{m,l,n} = \frac{\hbar^2}{2\mu} \left[ \left( \frac{l\pi}{b} \right)^2 + \left( \frac{\alpha_{mn}}{a} \right)^2 \right] \quad (164)$$

where  $m = 0, 1, 2, \dots$ ;  $l = 1, 2, 3, \dots$  and  $\alpha_{mn}$  represent the zeroes of  $J_m(x)$ . Thus

$$\alpha_{01} = 2.4048, \quad \alpha_{02} = 5.5201, \quad \alpha_{03} = 8.6537, \dots$$

$$\alpha_{11} = 3.8317, \quad \alpha_{12} = 7.0156, \quad \alpha_{13} = 10.1735, \dots$$

$$\alpha_{21} = 5.1356, \quad \alpha_{22} = 8.4172, \quad \alpha_{23} = 11.6198, \dots$$

(b) Show that the corresponding normalized eigenfunctions are

$$\begin{aligned}\psi_{m,l,n}(r, z, \phi) = & \left[ \frac{\sqrt{2}}{a J_{m+1}(\alpha_{mn})} J_m\left(\alpha_{mn} \frac{r}{a}\right) \right] \\ & \times \left[ \sqrt{\frac{2}{b}} \sin\left(\frac{l\pi}{b}\right) \right] \left[ \frac{1}{\sqrt{2\pi}} e^{\pm im\phi} \right]\end{aligned}\quad (165)$$

(c) For  $a = b = 0.4 \mu\text{m}$ ,  $\mu = 0.065 m_e$  calculate the frequency of emission for transition between the first excited state and the ground state.

**Problem 10.4** The deuteron nucleus consists of a neutron and a proton. The neutron-proton interaction can be approximately described by the following spherically symmetric potential function<sup>10</sup>

$$\begin{aligned}V(r) &= \infty \quad r < b \\ &= -V_0 \quad b < r < a + b \\ &= 0 \quad r > a + b\end{aligned}\quad (166)$$

(a) Obtain the transcendental equation determining the energy eigenvalues corresponding to the  $l = 0$  state and show that if we assume  $V_0 = 40 \text{ MeV}$  and  $a \simeq 1.896 \times 10^{-15} \text{ m}$ , we obtain  $E \simeq -2.25 \text{ MeV}$  which represents the binding energy of the deuteron.

(b) Also assuming  $b \approx 0.4 \times 10^{-15} \text{ m}$  show that for the ground state

$$\langle r^2 \rangle^{1/2} \simeq 4.16 \times 10^{-15} \text{ m} \quad (167)$$

which compares well with the experimental value of  $8.4 \times 10^{-15} \text{ m}$  (data quoted from Ref. 6); the value of  $b$  is suggested from the high energy experiments, see also Ref. 5.

**Problem 10.5** Use the recurrence relation [Eq. (48)] and the normalization condition to derive Equations (61)–(65) and also the following radial functions corresponding to  $n = 4$ :

$$R_{4,0}(r) = \frac{1}{4} \left( \frac{Z}{a_0} \right)^{3/2} \left[ 1 - \frac{3}{4} \xi + \frac{1}{8} \xi^2 - \frac{1}{192} \xi^3 \right] e^{-\xi/4} \quad (168)$$

---

<sup>10</sup> The potential function described by Eq. (166) is known as the *hard core* potential according to which the two particles cannot get closer than a certain distance  $b$ . This type of potential is indeed suggested by scattering experiments. It may be mentioned that the actual potential energy function describing nuclear forces is very complicated but many low energy phenomena are rather insensitive to the form of potential energy function and are reasonably well described, by a short-range attractive force of the type given by Eq. (166). For more details see Ref. 6.

$$R_{4,1}(r) = \frac{1}{16} \sqrt{\frac{5}{3}} \left( \frac{Z}{a_0} \right)^{3/2} \left[ \xi - \frac{1}{4} \xi^2 + \frac{1}{80} \xi^3 \right] e^{-\xi/4} \quad (169)$$

$$R_{4,2}(r) = \frac{1}{64\sqrt{5}} \left( \frac{Z}{a_0} \right)^{3/2} \left[ \xi^2 - \frac{1}{12} \xi^3 \right] e^{-\xi/4} \quad (170)$$

$$R_{4,3}(r) = \frac{1}{768\sqrt{35}} \left( \frac{Z}{a_0} \right)^{3/2} \xi^3 e^{-\xi/4} \quad (171)$$

**Problem 10.6** For  $n = 1$  and  $l = 0$ , one of the solutions of Eq. (45) is a constant. Find the other solution of the equation in terms of an integral and show that it diverges for  $\rho \rightarrow 0$  as well as for  $\rho \rightarrow \infty$ .

**Problem 10.7** In continuation of the previous problem, the well-behaved solutions of Eq. (45) are

$$\begin{aligned} C_0 \left( 1 - \frac{1}{2} \rho \right) & \quad \text{for } n = 2, l = 0 \\ C_0 \rho & \quad \text{for } n = 2, l = 1 \\ C_0 \left( 1 - \rho + \frac{1}{6} \rho^2 \right) & \quad \text{for } n = 3, l = 0 \\ C_0 \left( \rho - \frac{1}{4} \rho^2 \right) & \quad \text{for } n = 3, l = 1 \\ C_0 \rho^2 & \quad \text{for } n = 3, l = 2 \end{aligned}$$

Determine the other independent solution in terms of an integral.

### Problem 10.8

(a) Consider the spherically symmetric potential well

$$V(r) = -V_0 \exp(-r/a) \quad (172)$$

For  $l = 0$ , solve the Schrödinger equation by making the following transformation

$$\xi = \exp(-r/2a) \quad (173)$$

which will transform Eq. (17) into a Bessel's equation. (Bessel functions are briefly discussed in Appendix J).

(b) Obtain the energy eigenvalue assuming  $\mu = 0.8369 \times 10^{-27}$  kg (corresponding to the deuteron problem),  $V_0 = 40$  MeV and  $a = 1.854 \times 10^{-15}$  m.

**Problem 10.9** Show that  $R_{0,0}(r)$ ,  $R_{1,1}(r)$ ,  $R_{2,0}(r)$  and  $R_{2,2}(r)$  as given by Equations (142), (149), (158) and (159) satisfy Eq. (138); determine the corresponding eigenvalues.

**Problem 10.10** (a) Using the data given in the first column of Table 10.1, verify the data given in the last column. (b) In each case calculate the value of the rotational constant  $B$ .

**Problem 10.11** For HCl<sup>35</sup> and HCl<sup>37</sup> calculate the frequencies (in cm<sup>-1</sup>) for the following transitions

$$(v = 1, J = J') \longrightarrow (v = 0, J = J' + 1); J_i = 4, 3, 2, 1, 0 \text{ (P branch)}$$

and

$$(v = 1, J = J') \longrightarrow (v = 0, J = J'' - 1); J_i = 5, 4, 3, 2, 1 \text{ (R branch)}$$

and compare with the positions shown in Fig. 10.4. Assume

$$r_e = 1.27 \text{ \AA} \text{ and } \frac{\omega}{2\pi c} = 2885.9 \text{ cm}^{-1}$$

for both the molecules.

**Problem 10.12** For the isotropic three-dimensional harmonic oscillator problem [Eq. (136)] solve the radial part of the Schrödinger equation [Eq. (138)] and show that the results are consistent with those obtained in Sec. 10.6.

[Hint: Make the transformation  $\xi = \gamma^2 r^2$  ( $\gamma = \sqrt{\mu\omega/\hbar}$ ) and remove the first derivative in the resulting equation].

**Problem 10.13** We next consider the two-dimensional isotropic oscillator for which the potential energy variation is given by

$$V(\rho) = \frac{1}{2}\mu\omega^2\rho^2 = \frac{1}{2}\mu\omega^2(x^2 + y^2) \quad (174)$$

where

$$\rho^2 = x^2 + y^2$$

(a) Using a method similar to that used in Sec. 10.6, solve the two-dimensional Schrödinger equation in Cartesian coordinates to obtain the following eigenfunctions and eigenvalues

$$\psi_{n_1, n_2}(x, y) = \left[ \frac{\gamma^2}{2^n n_1! n_2! \pi} \right]^{1/2} H_{n_1}(\gamma x) H_{n_2}(\gamma y) e^{-\frac{1}{2}\gamma^2(x^2+y^2)} \quad (175)$$

$$E = (n + 1)\hbar\omega \quad (176)$$

where  $n = n_1 + n_2; n_1, n_2 = 0, 1, 2, \dots$

- (b) Solve the two-dimensional Schrödinger equation in polar coordinates and obtain solutions in terms of the confluent hypergeometric function.

[**Hint:** Make the transformation  $\xi = \gamma^2 \rho^2$  and remove the first derivative in the resulting equation].

**Problem 10.14** Consider the spherically symmetric potential energy function

$$V(r) = \frac{A}{r^2} - \frac{B}{r} \quad (A > 0, B > 0) \quad (177)$$

Show that the radial part of the Schrödinger equation is of the same form as for the hydrogen atom problem; the corresponding discrete energy eigenvalues being given by

$$E_p = -\frac{2B^2\mu}{\hbar^2} \left[ (2p+1) + \left\{ (2l+1)^2 + \frac{8\mu A}{\hbar^2} \right\}^{1/2} \right]^{-2} \quad (178)$$

where  $p = 0, 1, 2, \dots$ . Determine the normalized eigenfunctions in terms of the confluent hypergeometric function.

**Problem 10.15** Consider the spherically symmetric potential energy function

$$V(r) = \frac{A}{r^2} + Br^2 \quad (A > 0, B > 0) \quad (179)$$

Show that the radial part of the Schrödinger equation is of the same form as that of the isotropic oscillator [Eq. (138)]; the corresponding energy eigenvalues being given by

$$E_p = \hbar \left( \frac{B}{2\mu} \right)^{1/2} \left[ 4p + 2 + \left\{ (2l+1)^2 + \frac{8\mu A}{\hbar^2} \right\}^{1/2} \right] \quad (180)$$

where  $p = 0, 1, 2, \dots$

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## 10.8. Solutions

**Solution 10.1** For  $0 < r < a$ , the radial part of the Schrödinger equation [Eq. (15)] can be written in the form

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[ 1 - \frac{l(l+1)}{\rho^2} \right] R(\rho) = 0 \quad (181)$$

where

$$\rho = kr ; \quad k = \left[ \frac{2\mu E}{\hbar^2} \right]^{1/2} \quad (182)$$

For  $l = 0$ , the transformation  $u(\rho) = \rho R(\rho)$  would give

$$\frac{d^2 u}{d\rho^2} + u(\rho) = 0 \quad (183)$$

the solutions of which are  $\sin \rho$  and  $\cos \rho$ . Thus

$$R(\rho) = A \frac{\sin \rho}{\rho} + B \frac{\cos \rho}{\rho} \quad (l = 0)$$

The second solution would blow up at  $\rho = 0$  and therefore we must have  $B = 0$ . Further,

$$R(a) = 0 \Rightarrow ka = n\pi$$

giving

$$E = E_n = \frac{n^2 \pi^2 \hbar^2}{2\mu a^2}; \quad n = 1, 2, 3, \dots \quad (184)$$

The complete wave function would be

$$\psi_{n,0,0}(r, \theta, \phi) = A \frac{\sin kr}{kr} Y_{0,0} \quad (185)$$

For  $l = 1$ , the solution ‘well-behaved’ at  $\rho = 0$  will be

$$R(\rho) = A \left( \frac{\sin \rho}{\rho^2} - \frac{\cos \rho}{\rho^2} \right) \quad (186)$$

as can be verified by direct substitution. The boundary condition  $R(a) = 0$  would give the transcendental equation

$$\tan ka = ka \quad (l = 1)$$

which determines the energy eigenvalues. In general, we have the solution

$$R(\rho) = A j_l(\rho) \quad (187)$$

where  $j_l(\rho)$  represents the spherical Bessel function (see Sec. 5.4 of Ref. 1). The energy eigenvalues are determined by solving the equation

$$j_l(ka) = 0 \quad (188)$$

**Solution 10.4** If we use the boundary conditions

$$u(r = b) = 0 = u(r = \infty) \quad (189)$$

the solution of Eq. (17) for  $l = 0$  and for  $V(r)$  given by Eq. (166) would be

$$\begin{aligned} u(r) &= A \sin k(r - b) & b < r < a + b \\ &= B e^{-\kappa r} & r > a + b \end{aligned} \quad (190)$$

where

$$k^2 = \frac{2\mu}{\hbar^2} (V_0 + E), \quad \kappa^2 = -\frac{2\mu E}{\hbar^2} \quad (191)$$

$\mu$  being the reduced mass; for bound states  $E < 0$  and therefore  $\kappa^2 > 0$ . Obviously  $|E| < V_0$ . Continuity of the wave function and its derivative at  $r = a + b$  would readily give [cf. Eq. (59) of Chapter 6]

$$-\xi \cot \xi = \sqrt{\alpha^2 - \xi^2} \quad (192)$$

where

$$\xi = ka \quad (193)$$

and<sup>11</sup>

$$\begin{aligned} \alpha &= \sqrt{\frac{2\mu V_0 a^2}{\hbar^2}} \\ &\simeq \sqrt{\frac{2 \times 0.8369 \times 10^{-27} \times 40 \times 10^6 \times 1.602 \times 10^{-19} \times (1.896 \times 10^{-15})^2}{(1.055 \times 10^{-34})^2}} \\ &\simeq 1.86 \end{aligned} \quad (194)$$

Solving Eq. (192), we get  $\xi \simeq 1.81$  giving

$$\sqrt{\frac{V_0 - |E|}{|E|}} = -\tan \xi \simeq 4.1 \quad (195)$$

$$\Rightarrow E \simeq -2.25 \text{ MeV} \quad (196)$$

which compares well with the actual value of  $-2.225$  MeV. Further

$$\begin{aligned} \langle r^2 \rangle &= \int_0^\infty r^2 |u(r)|^2 dr = A^2 \int_b^{a+b} r^2 \sin^2 k(r-b) dr \\ &\quad + B^2 \int_{a+b}^\infty r^2 \exp(-2\kappa r) dr \end{aligned} \quad (197)$$

---

<sup>11</sup> Since

$m_n \simeq 1.67543 \times 10^{-27}$  kg,  $m_p \simeq 1.6726485 \times 10^{-27}$  kg

we get

$$\mu = \frac{m_n m_p}{m_n + m_p} \simeq 0.8369 \times 10^{-27} \text{ kg}$$

with

$$A = \left[ \frac{2\kappa}{1 + \kappa a} \right]^{1/2} \quad \text{and} \quad B = A \exp [\kappa (a + b)] \sin ka \quad (198)$$

**Solution 10.6** For  $n = 1$  and  $l = 0$ , Eq. (45) can be written in the form

$$\frac{1}{dF/d\rho} \frac{d^2 F}{d\rho^2} = \left( 1 - \frac{2}{\rho} \right)$$

Thus

$$\ln \left( \frac{dF}{d\rho} \right) = \rho - 2 \ln \rho + \text{constant}$$

or,

$$\rho^2 \frac{dF}{d\rho} = K e^\rho$$

where  $K$  is a constant. Thus

$$F(\rho) = K \int \frac{e^\rho}{\rho^2} d\rho + C_0 \quad (199)$$

which represents the general solution of Eq. (45). Integrating term by term, we get

$$-\frac{1}{\rho} + \ln \rho + \frac{1}{2!} \rho + \frac{1}{2 \cdot 3!} \rho^2 + \frac{1}{3 \cdot 4!} \rho^3 + \dots \quad (200)$$

which represents the second independent solution of Eq. (45) for  $n = 1$  and  $l = 0$ .

**Solution 10.7** We have to first make the transformation

$$F(\rho) = G(\rho) \Phi(\rho)$$

where  $\Phi(\rho)$  is the known solution<sup>12</sup>. We illustrate the procedure by considering the  $n = 2, l = 1$  case for which  $\Phi(\rho) = \rho$ ; thus

$$F(\rho) = \rho G(\rho)$$

Substituting in Eq. (45) we obtain

$$\frac{1}{G'} G'' = 1 - \frac{4}{\rho}$$

Carrying out the integration we get

$$\frac{dG}{d\rho} = \frac{K}{\rho^4} e^\rho$$

---

<sup>12</sup> The same procedure was used in Problem 7.6. In the previous problem,  $\Phi(\rho)$  was a constant and therefore the transformation was not necessary.

Thus

$$G(\rho) = K \int \frac{1}{\rho^4} e^\rho d\rho + C_0$$

or,

$$F(\rho) = K \rho \int \frac{1}{\rho^4} e^\rho d\rho + C_0 \rho \quad (201)$$

which represents the general solution of Eq. (45); the second term represents the known solution  $\Phi(\rho)$ . Integrating term by term, we obtain for the second solution

$$-\frac{1}{3\rho^2} - \frac{1}{2\rho} - \frac{1}{2!} + \frac{1}{3!}\rho \ln \rho + \frac{1}{4!}\rho^2 + \frac{1}{5!2}\rho^3 + \dots$$

For  $n = 2, l = 1$  we have

$$F(\rho) = C_0 \left( \rho - \frac{1}{4}\rho^2 \right) \int \frac{1}{\rho^2} e^\rho d\rho \quad (202)$$

**Solution 10.8** The transformation  $\xi = \exp(-\frac{r}{2a})$  transforms Eq. (17) into the Bessel's equation, the solution of which (not diverging at  $\xi = 0$  or  $r = \infty$ ) is

$$u(\xi) = A J_v(g\xi) \quad (203)$$

where

$$v = \left[ -\frac{8\mu E a^2}{\hbar^2} \right]^{1/2} \quad \text{and} \quad g = \left[ \frac{8\mu V_0 a^2}{\hbar^2} \right]^{1/2} \quad (204)$$

The condition that  $u(r = 0) = 0$  gives

$$J_v(g) = 0 \quad (205)$$

which determines the energy eigenvalues. It may be mentioned that for  $g < 2.405$  (the first zero of  $J_0(x)$ ) there is no root of Eq. (205) and consequently no discrete mode exists. Now

$$\begin{aligned} g &= \left( \frac{8 \times 0.8369 \times 10^{-27} \times 40 \times 10^6 \times 1.602 \times 10^{-19} \times (1.854 \times 10^{-15})^2}{(1.055 \times 10^{-34})^2} \right)^{1/2} \\ &\simeq 3.64 \end{aligned}$$

The solution of the transcendental equation

$$J_v(3.64) = 0$$

gives  $v \simeq 0.858628$  which gives  $E \simeq -2.223$  MeV. The corresponding wave function is plotted in Fig. 17.9.

**Solution 10.11** Using Eqs. (100) and (101) we obtain for the  $(v = 1, J = J') \rightarrow (v = 0, J = J' + 1)$  transition

$$\frac{\Delta E}{hc} = \frac{\omega}{2\pi c} - 2B(J' + 1)$$

Now, assuming  $r_e = 1.27 \text{ \AA}$  we get

$$B(\text{HCl}^{35}) = 10.626 \text{ cm}^{-1}$$

and

$$B(\text{HCl}^{37}) = 10.610 \text{ cm}^{-1}$$

Thus, if we take

$$\frac{\omega}{2\pi c} = 2885.9 \text{ cm}^{-1}$$

we would get

$$\begin{aligned} \frac{\Delta E}{hc} = & (2779.8, 2779.6); (2801.0, 2800.9); \\ & (2822.2, 2822.1); (2843.5, 2843.4) \text{ and } (2864.7, 2864.6) \end{aligned}$$

for  $J' = 4, 3, 2, 1$  and  $0$  respectively. The two numbers in the parenthesis correspond to  $\text{HCl}^{37}$  and  $\text{HCl}^{35}$  respectively.

**Solution 10.12** The transformation

$$\xi = \gamma^2 r^2; \quad \gamma = \sqrt{\frac{\mu\omega}{\hbar}}$$

transforms Eq. (138) to the following form

$$\xi \frac{d^2 R}{d\xi^2} + \frac{3}{2} \frac{dR}{d\xi} + \left[ \frac{E}{2\hbar\omega} - \frac{l(l+1)}{4\xi} - \frac{\xi}{4} \right] R(\xi) = 0 \quad (206)$$

In order to remove the term involving the first derivative we write

$$R(\xi) = \xi^p u(\xi) \quad (207)$$

and obtain  $p = -3/4$ . The equation satisfied by  $u(\xi)$  is of the same form as Eq. (72) with

$$\lambda = \frac{E}{2\hbar\omega} \text{ and } \mu = \frac{l}{2} + \frac{1}{4}$$

The solution well-behaved at the origin will be [see Eq. (77)]

$$R(\xi) = N \xi^{-3/4} \left[ \xi^{l/2+3/4} e^{-\xi/2} {}_1F_1(a, c, \xi) \right] \quad (208)$$

where

$$a = \mu + \frac{1}{2} - \lambda = \frac{l}{2} + \frac{3}{4} - \frac{E}{2\hbar\omega}$$

and

$$c = 2\mu + 1 = l + \frac{3}{2}$$

Once again, for the wave function to be well behaved as  $r \rightarrow \infty$  we must have

$$a = -n_r; \quad n_r = 0, 1, 2, \dots$$

which would give us

$$E = \left( 2n_r + l + \frac{3}{2} \right) \hbar\omega \quad (209)$$

and the complete wave function would be given by

$$\psi(r, \theta, \phi) = \left[ N(\gamma r)^l e^{-\gamma^2 r^2/2} {}_1F_1 \left( -n_r, l + \frac{3}{2}, \gamma^2 r^2 \right) \right] Y_{lm}(\theta, \phi) \quad (210)$$

where the normalization constant is given by

$$\begin{aligned} N &= \gamma^{3/2} \left[ \frac{2}{\Gamma(l + \frac{3}{2})} \right]^{1/2} \quad \text{for } n_r = 0 \\ &= \gamma^{3/2} \left[ \frac{2}{\Gamma(l + \frac{3}{2}) n_r!} \left( l + \frac{3}{2} \right) \left( l + \frac{5}{2} \right) \dots \left( l + n_r + \frac{1}{2} \right) \right]^{1/2} \end{aligned} \quad (211)$$

**Solution 10.13** In polar coordinates  $(\rho, \phi)$ , the two-dimensional Schrödinger equation is given by

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial \psi}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} [E - V(\rho)] \psi(\rho, \phi) = 0 \quad (212)$$

Since the potential energy function depends on  $\rho$  only and for the wavefunction to be single valued, the solution can be written in the form [see Section 9.3]

$$\psi(\rho, \phi) = R(\rho) \left[ \frac{1}{\sqrt{2\pi}} e^{im\phi} \right]; \quad m = 0, \pm 1, \pm 2, \dots \quad (213)$$

with  $R(\rho)$  satisfying the equation

$$\frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{dR}{d\rho} \right) - \frac{m^2}{\rho^2} R(\rho) + \frac{2\mu}{\hbar^2} \left[ E - \frac{1}{2}\mu\omega^2\rho^2 \right] R(\rho) = 0 \quad (214)$$

If we make the transformation

$$\xi = \gamma^2 \rho^2; \quad \gamma = \sqrt{\frac{\mu\omega}{\hbar}}$$

we would readily obtain

$$\xi \frac{d^2 R}{d\xi^2} + \frac{dR}{d\xi} + \left[ \frac{E}{2\hbar\omega} - \frac{m^2}{4\xi} - \frac{\xi}{4} \right] R(\xi) = 0 \quad (215)$$

To remove the first derivative we make a transformation similar to that given by Eq. (207) and obtain  $p = -\frac{1}{2}$ . The equation satisfied by  $u(\xi)$  is of the same form as Eq. (72) with

$$\lambda = \frac{E}{2\hbar\omega} \text{ and } \mu = \frac{m}{2}$$

Since only  $m^2$  appears in Eq. (215) we will assume  $m > 0$  and in the final result replace  $m$  by  $|m|$ . Following an exactly similar procedure as in the previous problem we obtain

$$\begin{aligned} \psi(\rho, \phi) &= \left[ N \rho^{|m|} e^{-\gamma^2 \rho^2/2} {}_1F_1(-n, |m|+1, \gamma^2 \rho^2) \right] \\ &\times \left[ \frac{1}{\sqrt{2\pi}} e^{im\phi} \right] \end{aligned} \quad (216)$$

with

$$E = (2n + |m| + 1) \hbar\omega ; n = 0, 1, 2, \dots \quad (217)$$


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## 10.9. Sample questions

Q. 1 In the hydrogen atom problem the radial part of the Schrödinger equation can be written in the form

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR}{d\rho} \right) + \left( \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right) R(\rho) = 0 \quad (218)$$

where

$$\rho = \gamma r ; \gamma = \left( -\frac{8\mu E}{\hbar^2} \right)^{1/2} \quad (219)$$

$$\lambda = Z\alpha \left( -\frac{\mu c^2}{2E} \right)^{1/2} \quad (220)$$

and  $l = 0, 1, 2, \dots$ . If we assume a solution of the form

$$R(\rho) = e^{-\rho/2} \sum_{p=0,1,\dots}^{\infty} C_p \rho^{p+s} \quad (221)$$

then we obtain

$$\frac{C_{p+1}}{C_p} = \frac{s + p - \lambda + 1}{(s + p + 1)(s + p + 2) - l(l + 1)} \quad (222)$$

and for the solution to be well-behaved at  $\rho = 0$  we must put  $s = l$ .

- a) For what values of  $\rho$  the infinite series in Eq. (221) be a convergent series?
- b) For what values of  $\lambda$  will the infinite series in Eq. (221) become a polynomial? What will be the corresponding energy eigenvalues?
- c) Determine the eigenfunctions  $R_{nl}(r)$  for

$$(\lambda = 1, l = 0), (\lambda = 2, l = 0) (\lambda = 2, l = 1) \\ (\lambda = 3, l = 0), (\lambda = 3, l = 1) \text{ and } (\lambda = 3, l = 2)$$

In each case normalize the wave function from first principles.

- d) For  $(\lambda = 2, l = 1), (\lambda = 3, l = 2)$  determine the second solution of Eq. (218) in the form of an integral and show that it is singular at  $\rho = 0$ .
- e) Discuss the degeneracy of the level corresponding to  $\lambda = 3$ .

Q. 2 Given that the 2 independent solutions of

$$\frac{d^2\phi}{dx^2} + \left\{ -\frac{1}{4} + \frac{k}{x} + \frac{\frac{1}{4} - \mu^2}{x^2} \right\} \phi(x) = 0$$

are

$$y_1(x) = x^{\mu+\frac{1}{2}} e^{-x/2} {}_1F_1(a, c, x)$$

and

$$y_2(x) = x^{-\mu+\frac{1}{2}} e^{-x/2} {}_1F_1(a - c + 1, 2 - c, x)$$

where  $a = \mu + \frac{1}{2} - k$ ,  $c = 2\mu + 1$ . Now, the radial part of the Schrödinger equation for the hydrogen atom problem can be transformed to the form

$$\frac{d^2u}{d\rho^2} + \left[ \frac{2\mu E}{\hbar^2 \gamma^2} + \frac{2\mu Ze^2}{\hbar^2 \gamma \rho} - \frac{l(l+1)}{\rho^2} \right] u(\rho) = 0$$

where symbols have their usual meaning.

- a) Find the values of  $\gamma$ ,  $a$  and  $c$ .

- b) Derive with justification the energy eigenvalues.
- c) Derive the normalized wave function  $R_{54}(r)$  [ $n = 5, l = 4$ ].

### 10.10. References and suggested reading

1. A.K. Ghatak, I.C. Goyal and S.J. Chua, *Mathematical Physics*, Macmillan India Limited, New Delhi (1995).
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3. H.B. Dunford, *Elements of Diatomic Molecular Spectra*, Addison-Wesley Publishing Co., Reading, Massachusetts (1968).
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6. H. Enge, *Introduction to Nuclear Physics*, Addison-Wesley Publishing Co., Reading, Massachusetts (1966).

# Chapter 11

## Dirac's Bra and Ket Algebra

*Dirac to whom in my opinion we owe the most logically perfect presentation of quantum mechanics...*

— ALBERT EINSTEIN<sup>1</sup>

### 11.1. Introduction

In this chapter we will introduce Dirac's bra and ket algebra in which the states of a dynamical system will be denoted by certain vectors (which, following Dirac, will be called as bra and ket vectors) and operators representing dynamical variables (like position coordinates, components of momentum and angular momentum) by matrices.<sup>2</sup> In the following two chapters we will use the bra and ket algebra to solve the linear harmonic oscillator problem and the angular momentum problem. In both the chapters we will show the advantage of using the operator algebra in obtaining solutions of various problems.

### 11.2. The bra and ket notation

A state of a system can be represented by a certain type of vector, which we call a ket vector and represent by the symbol  $| \rangle$ . In order to distinguish the ket vectors corresponding to different states, we insert a label; thus, the ket vector (or simply the ket) corresponding to the state  $A$  is described by the symbol  $| A \rangle$ . Kets form a linear vector space implying that if we have two states described by the kets  $| A \rangle$  and  $| B \rangle$ , then the linear combination

$$c_1 | A \rangle + c_2 | B \rangle \quad (1)$$

<sup>1</sup> Quoted from N. Mukunda, *The World of Bohr and Dirac*, Wiley Eastern Limited, New Delhi (1993), p. 4.

<sup>2</sup> Portions of this chapter have been adapted from Ref. 1; this is with the kind permission of Oxford University Press.

is a vector in the same space; here  $c_1$  and  $c_2$  are arbitrary complex numbers. To quote Dirac (p. 16 of Reference 1):

*...each state of a dynamical system at a particular time corresponds to a ket vector, the correspondence being such that if a state results from the superposition of certain other states, its corresponding ket vector is expressible linearly in terms of the corresponding ket vectors of the other states, and conversely.*

Further, the ket  $| A \rangle$  and  $c | A \rangle$  (where  $c$  is an arbitrary non-zero complex number) correspond to the same state. In other words the state of the system is defined by the ‘direction’ of the vectors. In this respect the superposition principle in classical and quantum theories differ. For example, the superposition of a vibrating string on itself gives, in classical physics, a mode with twice the amplitude and four times the energy of the initial state of vibration. In contrast, in quantum mechanics, the superposition of a state on itself gives the same state.

Now, with every vector space there can be associated a dual vector space such that one can form a scalar product of the two vectors, one from each space. The vectors of the space dual to that of the ket vectors will be called bra vectors or simply ‘bras’ and will be denoted by  $\langle |$ . The scalar product of the ket  $| A \rangle$  and bra  $\langle B |$  is denoted by  $\langle B | A \rangle$  and is a complex number. The logic is very similar to the one we have in theory of matrices where with every column vector there can be associated a row vector and the scalar product of the two gives a number. We will elaborate on this point in Sec. 11.7.

A bra is said to be a null bra if the scalar product vanishes for any ket, thus

$$\langle B | = 0 \quad \text{if} \quad \langle B | A \rangle = 0 \quad \text{for any } | A \rangle \quad (2)$$

Two bras are said to be equal if their scalar product with an arbitrary ket are equal, thus

$$\langle B_1 | = \langle B_2 | \quad \text{if} \quad \langle B_1 | A \rangle = \langle B_2 | A \rangle \quad \text{for any } | A \rangle \quad (3)$$

It is further assumed that

- (i) There is a one-to-one correspondence between kets and bras in the sense that a state of a dynamical system represented by  $| A \rangle$  can be equally well represented by the corresponding bra  $\langle A |$ . Further, if

$$| P \rangle = | A \rangle + | B \rangle \quad \text{then} \quad \langle P | = \langle A | + \langle B | \quad (4)$$

and if

$$| R \rangle = c | A \rangle \quad \text{then} \quad \langle R | = \bar{c} \langle A | \quad (5)$$

where  $c$  is a complex number and  $\bar{c}$  its complex conjugate.

(ii)

$$\langle A | B \rangle = \overline{\langle B | A \rangle} \quad (6)$$

where the bar on the top implies the complex conjugate of the quantity. Putting  $|B\rangle = |A\rangle$  we get

$$\langle A | A \rangle = \overline{\langle A | A \rangle}$$

implying that the scalar product  $\langle A | A \rangle$  is a real number. We further assert that

$$\langle A | A \rangle \geq 0, \quad (7)$$

the equality sign holds only when  $|A\rangle = 0$ , i.e. where  $|A\rangle$  is a null ket.

If  $\langle A | B \rangle = 0$  then the kets  $|A\rangle$  and  $|B\rangle$  are said to be orthogonal to each other. If

$$\langle A | A \rangle = 1$$

then the ket  $|A\rangle$  is said to be normalized. Since the kets  $|A\rangle$  and  $c|A\rangle$  correspond to the same state we may always associate normalized kets to each state. It can be easily seen that a normalized ket is defined only within an arbitrary phase factor  $e^{i\gamma}$  (where  $\gamma$  is a real number).

We may mention here the relationship between the Schrödinger wave functions developed in earlier chapters to the bra and kets developed in this section. If  $|\psi\rangle$  and  $|\phi\rangle$  represent the kets corresponding to the states described by the wave functions  $\psi(\mathbf{r})$  and  $\phi(\mathbf{r})$  respectively, then

### Scalar product

$$\langle \phi | \psi \rangle = \int \phi^*(\mathbf{r}) \psi(\mathbf{r}) d\tau = \overline{\langle \psi | \phi \rangle} \quad (8)$$

where the integration is over the entire space. The integral is usually referred to as the scalar product of the two functions.

### 11.3. Linear operators

An operator  $\alpha$  converts a ket  $|A\rangle$  into another ket  $|B\rangle$

$$|B\rangle = \alpha |A\rangle \quad (9)$$

An operator is said to be *linear* if it satisfies the following equation

$$\alpha(c_1 |A_1\rangle + c_2 |A_2\rangle + \dots) = c_1 \alpha |A_1\rangle + c_2 \alpha |A_2\rangle + \dots \quad (10)$$

where  $c_1, c_2, \dots$  are arbitrary complex numbers. Henceforth, we will consider only linear operators. An operator  $\alpha$  is said to be a *null* operator if

*Null operator*

$$\alpha | A \rangle = 0 \quad \text{for any } | A \rangle \quad (11)$$

Thus a necessary and sufficient condition for an operator to be a null operator is

$$\langle A | \alpha | A \rangle = 0 \quad \text{for any } | A \rangle \quad (12)$$

An operator is said to be an *unit* operator if

*Unit operator*

$$\alpha | A \rangle = | A \rangle \quad \text{for any } | A \rangle \quad (13)$$

It can be easily seen that a number can be regarded as a linear operator.

Two operators  $\alpha$  and  $\beta$  are said to be equal if and only if

$$\langle A | \alpha | A \rangle = \langle A | \beta | A \rangle \quad \text{for any } | A \rangle \quad (14)$$

The sum (or difference) of two operators  $\alpha$  and  $\beta$  is defined through the equation

$$(\alpha \pm \beta) | A \rangle = \alpha | A \rangle \pm \beta | A \rangle \quad (15)$$

Further

*Associative Law*

$$\alpha + (\beta + \gamma) = (\alpha + \beta) + \gamma = \alpha + \beta + \gamma \quad (16)$$

and

$$(c_1 \alpha) | A \rangle = c_1 (\alpha | A \rangle) \quad (17)$$

where  $c_1$  is an arbitrary complex constant. The product of two operators  $\alpha$  and  $\beta$  is defined through the equation

$$(\beta \alpha) | A \rangle = \beta (\alpha | A \rangle) = \beta | B \rangle \quad (18)$$

where  $| B \rangle = \alpha | A \rangle$ . In general

$$\beta \alpha \neq \alpha \beta \quad (19)$$

The commutator of two operators is defined by (see Sec. 4.3)

$$[\alpha, \beta] = \alpha \beta - \beta \alpha = - [\beta, \alpha] \quad (20)$$

So far we have assumed a linear operator to act on kets; we can make a linear operator  $\alpha$  operate on bras as well; the rule is that the bra has to be put on the left of the operator like  $\langle P | \alpha$  and the operation is defined through the equation

$$\begin{aligned} \{\langle P | \alpha\} | A \rangle &= \langle P | \{\alpha | A \rangle\} \quad \text{for any } | A \rangle \\ &= \langle P | B \rangle \end{aligned}$$

where

$$|B\rangle = \alpha |A\rangle$$

(The combination  $\alpha \langle B |$  is meaningless.) Indeed because of the associative law we need not put any brackets and simply write

$$\langle P | \alpha \beta \gamma | A \rangle$$

It is interesting to note that the combination  $|B\rangle \langle A|$  can be considered as a linear operator because

$$\begin{aligned} \{|B\rangle \langle A|\} |P\rangle &= |B\rangle \{\langle A | P \rangle\} \\ &= c |B\rangle \end{aligned}$$

because  $\langle A | P \rangle (= c)$  is just a complex number.

#### *Adjoint of an operator*

The adjoint of the operator  $\alpha$  is denoted by  $\bar{\alpha}$  and is *defined* through the equation

$$\langle A | \bar{\alpha} | B \rangle = \overline{\langle B | \alpha | A \rangle} \quad (21)$$

where  $\overline{\langle B | \alpha | A \rangle}$  is the complex conjugate of the number  $\langle B | \alpha | A \rangle$ . Now

$$\begin{aligned} \langle A | \bar{\alpha} | B \rangle &= \langle A | \bar{\beta} | B \rangle \quad (\bar{\beta} \equiv \alpha) \\ &= \overline{\langle B | \beta | A \rangle} = \overline{\langle B | \bar{\alpha} | A \rangle} \\ &= \overline{\overline{\langle A | \alpha | B \rangle}} = \langle A | \alpha | B \rangle \end{aligned} \quad (22)$$

because the complex conjugate of the complex conjugate of a number is the original number itself. Since Eq. (22) holds for arbitrary  $|A\rangle$  and  $|B\rangle$  we have

$$\bar{\bar{\alpha}} = \alpha \quad (23)$$

#### *Adjoint of a product of two operators*

i.e. the adjoint of the adjoint of a linear operator is the original operator itself. Further, the adjoint of the product of the two operators  $\alpha$  and  $\beta$  is the product of the adjoint of the two operators in reverse order, i.e.

$$\bar{\alpha} \bar{\beta} = \bar{\beta} \bar{\alpha} \quad (24)$$

**Proof** The proof is simple. Let

$$\alpha |A\rangle = |P\rangle$$

then

$$\begin{aligned} \langle A | \bar{\alpha} | B \rangle &= \overline{\langle B | \alpha | A \rangle} = \overline{\langle B | P \rangle} \\ &= \langle P | B \rangle \quad [\text{using Eq. (6)}] \end{aligned}$$

Since the above equation holds for arbitrary  $|B\rangle$  we have

$$\langle P | = \langle A | \bar{\alpha} = \text{conjugate of } \alpha | A \rangle \quad (25)$$

Thus, if

$$|Q\rangle = \alpha \beta |A\rangle$$

Then

$$\langle Q | = \langle A | \overline{\alpha \beta} \quad (26)$$

But, if we write

$$|Q\rangle = \alpha \beta |A\rangle = \alpha |R\rangle$$

where  $|R\rangle = \beta |A\rangle$  (consequently  $\langle R | = \langle A | \bar{\beta}$ ), then

$$\langle Q | = \langle R | \bar{\alpha} = \langle A | \bar{\beta} \bar{\alpha} \quad (27)$$

Comparing Eqs (26) and (27) we get Eq. (24). In general

$$\overline{\alpha \beta \gamma \dots} = \dots \overline{\gamma} \overline{\beta} \overline{\alpha} \quad (28)$$

### *Self-adjoint operator*

An operator is said to be self-adjoint if

$$\overline{\alpha} = \alpha \quad (29)$$

A self-adjoint operator is also called a real operator or a Hermitian operator.

## 11.4. The eigenvalue equation

For the linear operator  $\alpha$ , consider the equation

$$\alpha |A_n\rangle = a_n |A_n\rangle \quad (30)$$

where  $a_n$  is an arbitrary complex number. Equation (30) represents an eigenvalue equation;  $|A_n\rangle$  is said to be an eigenket of the operator  $\alpha$ ,  $a_n$  being the corresponding eigenvalues. It can be easily seen that  $c |A_n\rangle$  (where  $c$  is an arbitrary complex number) is also an eigenket belonging to the same eigenvalue  $a_n$ . Now, if there is more than one ket (and they are not linearly dependent on each other<sup>3</sup>) belonging

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<sup>3</sup> A ket  $|P\rangle$  is said to be linearly dependent on the ket  $|A_1\rangle$ ,  $|A_2\rangle \dots$  and  $|A_N\rangle$  if we can write

$$|P\rangle = \sum_{n=1}^N c_n |A_n\rangle$$

to the same eigenvalue, i.e. if

### Degeneracy

$$\alpha | A_1 \rangle = a_1 | A_1 \rangle \quad (31)$$

$$\alpha | A_2 \rangle = a_1 | A_2 \rangle \quad (32)$$

then the state is said to be a degenerate state (compare discussion in Sec. 6.3). If there are  $g$  linearly independent kets belonging to the same eigenvalue then the state is said to be  $g$ -fold degenerate. For the sake of simplicity, let us consider a two-fold degenerate state described by Eqs (31) and (32). If we multiply Eq. (31) by  $c_1$  and Eq. (32) by  $c_2$  and add we would get

$$\alpha | P \rangle = a_1 | P \rangle,$$

where

$$| P \rangle = c_1 | A_1 \rangle + c_2 | A_2 \rangle$$

implying that the linear combination  $c_1 | A_1 \rangle + c_2 | A_2 \rangle$  is also an eigenket belonging to the same eigenvalue. Similarly, one can discuss for a  $g$ -fold degenerate state.

#### 11.4.1. ORTHOGONALITY OF EIGENFUNCTIONS

When  $\alpha$  is *real*, it can easily be shown that all the eigenvalues are real and for two different eigenvalues (i.e. for  $a_n \neq a_m$ ) the corresponding eigenfunctions are necessarily orthogonal, i.e.

$$\langle A_n | A_m \rangle = 0 \quad \text{for} \quad a_n \neq a_m \quad (33)$$

Further, one can always normalize the kets and choose an appropriate linear combination for the kets belonging to a degenerate state such that (see Problem 6.3)

$$\langle A_n | A_m \rangle = \delta_{nm} \quad (34)$$

The proof is very simple. Premultiplying Eq. (30) by  $\langle A_n |$  we get

$$\langle A_n | \alpha | A_n \rangle = a_n \langle A_n | A_n \rangle$$

Now  $\langle A_n | A_n \rangle$  is always real and not a null ket [otherwise Eq. (30) has no meaning]. Further, since  $\alpha$  is real

$$\langle A_n | \alpha | A_n \rangle = \langle A_n | \bar{\alpha} | A_n \rangle = \overline{\langle A_n | \alpha | A_n \rangle}$$

implying that  $\langle A_n | \alpha | A_n \rangle$  is also real and hence  $a_n$  must be real. Further, in order to prove Eq. (33) we consider

$$\alpha | A_1 \rangle = a_1 | A_1 \rangle \quad (35)$$

$$\alpha | A_2 \rangle = a_2 | A_2 \rangle \quad (36)$$

If we put  $| P \rangle = \alpha | A_2 \rangle$ , then

$$\langle P | = \langle A_2 | \bar{\alpha} = \langle A_2 | \alpha$$

Also

$$\langle P | = \overline{a_2} \langle A_2 | = a_2 \langle A_2 |$$

because  $a_2$  is real. Thus

$$\langle A_2 | \alpha = a_2 \langle A_2 | \quad (37)$$

Premultiplying Eq. (35) by  $\langle A_2 |$  and postmultiplying Eq. (37) by  $| A_1 \rangle$  gives

$$\langle A_2 | \alpha | A_1 \rangle = a_1 \langle A_2 | A_1 \rangle = a_2 \langle A_2 | A_1 \rangle$$

which immediately gives the orthogonality condition given by Eq. (33).

Since the formalism is symmetrical with respect to bras and kets we also have the eigenvalue equation

$$\langle B_n | \alpha = \langle B_n | b_n = b_n \langle B_n |$$

where  $\langle B_n |$  are the eigenbras and  $b_n$  the corresponding eigenvalues. It can be easily seen that when  $\alpha$  is a real operator and if  $| A \rangle$  is an eigenket, then  $\langle A |$  is an eigenbra belonging to the same eigenvalue. Equation (37) tells us that  $\langle A_2 |$  is an eigenbra of the operator  $\alpha$  belonging to the same eigenvalue  $a_2$ .

## 11.5. Observables

Any dynamical quantity (like the position coordinates, or components of the momentum or angular momentum, etc.) that can be measured is known as an observable. We assume that observables can be represented by linear operators and the operators corresponding to different observables need not commute. Further, the result of measurement of any observable must be an eigenvalue of the operator corresponding to the observable and since the measured value must be a real number we assume that **an observable is always represented by a real linear operator**. We denote the eigenkets of the observable  $\alpha$  by  $| \alpha_n \rangle$  which we assume to form an orthonormal set:

$$\langle \alpha_m | \alpha_n \rangle = \delta_{mn}$$

Since  $| \alpha_n \rangle$  form a complete set, an arbitrary ket  $| P \rangle$  can be expanded in terms of them

$$| P \rangle = \sum_n c_n | \alpha_n \rangle$$

If we now make a measurement of  $\alpha$ , the probability of the outcome  $\alpha_n$  is  $|c_n|^2$ ; we have assumed  $| P \rangle$  to be normalized. Further, as a result of the measurement, the

system would *collapse* to one of the states  $|\alpha_n\rangle$ . For degenerate states, one can always choose an appropriate linear combination so that they form an orthonormal set (see Sec. 6.3 and Problem 6.3).

Let us assume that a dynamical system is in a state which is an eigenket of the observable  $\alpha$  belonging to the eigenvalue  $\alpha_1$ . Now, if a measurement of the observable  $\alpha$  is made, then it is certain that the value  $\alpha_1$  will be obtained. On the other hand, if the system is in a state described by the normalized ket

$$|P\rangle = c_1 |\alpha_1\rangle + c_2 |\alpha_2\rangle$$

[ $\langle P | P \rangle = 1$ ], then a measurement of  $\alpha$  would lead either to  $\alpha_1$  or  $\alpha_2$  with probabilities  $|c_1|^2$  and  $|c_2|^2$  respectively. Since  $\langle P | P \rangle = 1$ , it immediately follows that

$$|c_1|^2 + |c_2|^2 = 1 \quad (38)$$

In general, the outcome of the measurement of an observable is one of its eigenvalues and therefore, if the system is in an arbitrary state, then a measurement of  $\alpha$  will make the dynamical system jump to one of the eigenstates of  $\alpha$ . We further assume that the possible eigenstates of  $\alpha$  to which the dynamical system may jump are such that the original state should be linearly expressible in terms of the eigenstates. Thus, any state can be expressed as a linear combination of the eigenkets of the observable and therefore, **the eigenkets of an observable must form a complete set.**

A beautiful example of the above argument is the famous Stern-Gerlach experiment where an inhomogeneous magnetic field (in the  $z$ -direction) splits the silver beam into two components, one going in the  $+z$  direction and the other going in the  $-z$  direction; the experiment tries to make a measurement of the  $z$ -component of the angular momentum (which we denote by  $J_z$ ) and the result shows that  $J_z$  has only two eigenvalues. We will have a detailed discussion of this experiment in Sec. 14.4.

## 11.6. The completeness condition

We have just stated that the eigenkets of an observable form a complete set. Let  $|n\rangle$ ,  $n = 0, 1, 2, \dots$  denote these eigenkets and let  $|P\rangle$  denote an arbitrary ket. Thus

$$|P\rangle = \sum_n c_n |n\rangle$$

where  $\sum$  denotes a sum over the discrete states and an integration over the continuum states. Since the eigenkets can be assumed to form an orthonormal set ( $\langle m | n \rangle = \delta_{mn}$ ) we have

$$\langle m | P \rangle = \sum_n c_n \langle m | n \rangle = \sum_n c_n \delta_{mn} = c_m$$

Thus

$$| P \rangle = \sum_n | n \rangle c_n = \left\{ \sum_n | n \rangle \langle n | \right\} | P \rangle \quad (39)$$

Since the above equation holds for an arbitrary ket  $| P \rangle$ , the quantity inside the curly brackets must be a unit operator

$$\sum_n | n \rangle \langle n | = 1 \quad (40)$$

which is usually referred to as the *completeness condition*. The above equation may be compared with the completeness condition of the Schrödinger wave functions [see Eq. (41) of Chapter 7].

### 11.7. Examples from matrix algebra

The various axiomatic rules discussed so far can be readily understood if we consider some simple examples from the theory of matrices. Let us consider a  $3 \times 3$  Hermitian matrix  $\alpha$  given by

$$\alpha = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

We have assumed  $\alpha$  to be a  $3 \times 3$  matrix; we could have assumed it to be of an arbitrary order.

Let

$$| A \rangle = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \quad \text{and} \quad | B \rangle = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix}$$

denote two arbitrary column vectors in the same field (i.e. having 3 rows). Now corresponding to every ket vector there is a bra vector which, in this case, is nothing but a row vector. Thus

$$\langle A | = (\overline{a_1}, \overline{a_2}, \overline{a_3})$$

and

$$\langle B | = (\overline{b_1}, \overline{b_2}, \overline{b_3})$$

where  $\overline{a_1}, \overline{a_2}, \dots$  are the complex conjugates of  $a_1, a_2, \dots$ . The scalar product is given by

$$\begin{aligned} \langle A | B \rangle &= (\overline{a_1} \ \overline{a_2} \ \overline{a_3}) \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} \\ &= \overline{a_1} b_1 + \overline{a_2} b_2 + \overline{a_3} b_3 \end{aligned}$$

which is a complex number. Obviously

$$\langle A | B \rangle = \overline{\langle B | A \rangle}$$

Further

$$\langle A | A \rangle = |a_1|^2 + |a_2|^2 + |a_3|^2 \geq 0$$

The scalar product  $\langle A | A \rangle = 0$  if and only if

$$a_1 = a_2 = a_3 = 0$$

which corresponds to a “null vector”. Since

$$\alpha \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

implying that a linear operator operating on a null vector will always give a null vector. Further

$$| A \rangle = | B \rangle$$

if and only if

$$a_1 = b_1, a_2 = b_2 \text{ and } a_3 = b_3$$

Now, it can be easily shown that the eigenvalues of the operator  $\alpha$  are  $+1, -1$  and  $+2$ . The corresponding normalized eigenvectors are

$$| 1 \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

$$| 2 \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}$$

and

$$| 3 \rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

One can easily see that

#### *Orthonormality condition*

$$\langle i | j \rangle = \delta_{ij}; \quad i, j = 1, 2, 3$$

which represents the orthonormality condition. Further, they form a complete set of functions in the sense that an arbitrary vector (in the three-dimensional space) can be expressed as a linear combination of  $| 1 \rangle, | 2 \rangle$  and  $| 3 \rangle$ . Thus

$$| A \rangle = \frac{a_1 + a_2}{\sqrt{2}} | 1 \rangle + \frac{a_1 - a_2}{\sqrt{2}} | 2 \rangle + a_3 | 3 \rangle$$

Further

*Completeness condition*

$$\begin{aligned}\sum_i |i\rangle\langle i| &= |1\rangle\langle 1| + |2\rangle\langle 2| + |3\rangle\langle 3| \\ &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\end{aligned}$$

which represents the completeness condition [see Eq. (40)].

## 11.8. Simultaneous eigenkets of commuting observables

In this section we will show that if two observables commute then one can have a complete set of simultaneous eigenkets of the two observables.

Let  $\alpha$  and  $\beta$  represent the operators corresponding to two observables. We assume that the two operators commute, i.e.

$$\alpha\beta = \beta\alpha \quad (41)$$

Let  $|\alpha_1\rangle$  be an eigenket of  $\alpha$  belonging to the eigenvalue  $\alpha_1$ :

$$\alpha|\alpha_1\rangle = \alpha_1|\alpha_1\rangle \quad (42)$$

then

$$\begin{aligned}\alpha\{\beta|\alpha_1\rangle\} &= \beta\alpha|\alpha\rangle \\ &= \beta\alpha_1|\alpha_1\rangle \quad [\text{using Eq. (42)}]\end{aligned}$$

or

$$\alpha\{\beta|\alpha_1\rangle\} = \alpha_1\{\beta|\alpha_1\rangle\} \quad (43)$$

where the last step follows from the fact that  $\alpha_1$  is a number. Equation (43) tells us that  $\beta|\alpha_1\rangle$  is also an eigenket of  $\alpha$  belonging to the *same* eigenvalue  $\alpha_1$ . If  $|\alpha_1\rangle$  corresponds to a non-degenerate state, then Eq. (43) tells us that

$$\beta|\alpha_1\rangle \quad \text{must be a multiple of } |\alpha_1\rangle$$

implying

$$\beta|\alpha_1\rangle = \beta_1|\alpha_1\rangle \quad (44)$$

where  $\beta_1$  is a number. Thus  $|\alpha_1\rangle$  must be an eigenket of  $\beta$ . Hence, all eigenkets of  $\alpha$  which correspond to nondegenerate states, must also be eigenkets of  $\beta$  and hence these will be simultaneous eigenkets.

We next consider the case when the eigenvalue  $\alpha_1$  corresponds to a degenerate state. To keep the analysis simple let the state be two-fold degenerate and let the eigenkets be  $|\alpha_1\rangle$  and  $|\alpha_2\rangle$ ; i.e.

$$\alpha |\alpha_1\rangle = \alpha_1 |\alpha_1\rangle \quad (45)$$

$$\alpha |\alpha_2\rangle = \alpha_1 |\alpha_2\rangle \quad (46)$$

The kets  $|\alpha_1\rangle$  and  $|\alpha_2\rangle$  are assumed to be orthogonal to each other. Now, since  $\beta |\alpha_1\rangle$  and  $\beta |\alpha_2\rangle$  are eigenkets of  $\beta$  belonging to the same eigenvalue  $\alpha_1$  [see Eq. (43)], they must be expressible as a linear combination of  $|\alpha_1\rangle$  and  $|\alpha_2\rangle$ :

$$\beta |\alpha_1\rangle = c_{11} |\alpha_1\rangle + c_{12} |\alpha_2\rangle \quad (47)$$

and

$$\beta |\alpha_2\rangle = c_{21} |\alpha_1\rangle + c_{22} |\alpha_2\rangle \quad (48)$$

The kets  $|\alpha_1\rangle$  and  $|\alpha_2\rangle$  need not be eigenkets of  $\beta$ ; however, we may always choose appropriate linear combinations so that they are eigenkets of  $\beta$  (and hence simultaneous eigenkets of  $\alpha$  and  $\beta$ ). Let the required linear combination be

$$d_1 |\alpha_1\rangle + d_2 |\alpha_2\rangle$$

Then

$$\beta [d_1 |\alpha_1\rangle + d_2 |\alpha_2\rangle] = \beta' [d_1 |\alpha_1\rangle + d_2 |\alpha_2\rangle]$$

If we now use Eqs (47) and (48), we would obtain

$$d_1 [c_{11} |\alpha_1\rangle + c_{12} |\alpha_2\rangle] + d_2 [c_{21} |\alpha_1\rangle + c_{22} |\alpha_2\rangle] = \beta' d_1 |\alpha_1\rangle + \beta' d_2 |\alpha_2\rangle$$

Since  $|\alpha_1\rangle$  and  $|\alpha_2\rangle$  are orthogonal to each other, we get

$$d_1 (c_{11} - \beta') + d_2 c_{21} = 0$$

and

$$d_1 c_{12} + d_2 (c_{22} - \beta') = 0$$

For non-trivial solutions, we must have

$$\begin{vmatrix} c_{11} - \beta' & c_{21} \\ c_{12} & c_{22} - \beta' \end{vmatrix} = 0 \quad (49)$$

the roots of which will give the two allowed values of  $\beta'$ . Once  $\beta'$  is known, we can obtain the ratio  $d_1/d_2$  which will give the simultaneous eigenket. As an example we consider the two matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad \alpha = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

which commute with each other, i.e.

$$\sigma_x \alpha = \alpha \sigma_x$$

Now, the eigenvalues of  $\sigma_x$  are  $+1$  and  $-1$  and are non-degenerate; hence both the eigenvectors are also eigenvectors of  $\alpha$ . Thus

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

(which are eigenvectors of  $\sigma_x$ ) represent a complete set of simultaneous eigenvectors of  $\sigma_x$  and  $\alpha$ . They form a complete set in the sense that an arbitrary vector can be represented as a linear combination of  $|1\rangle$  and  $|2\rangle$

$$\begin{pmatrix} a \\ b \end{pmatrix} = \frac{(a+b)}{\sqrt{2}} \left[ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \right] + \frac{(a-b)}{\sqrt{2}} \left[ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \right]$$

It may be seen that

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

are eigenvectors of  $\alpha$  but *not* eigenvectors of  $\sigma_x$ . However,  $|1\rangle$  and  $|2\rangle$  can be expressed as a linear combination of the above vectors.

We next consider the two matrices

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad \alpha = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Once again

$$\sigma_z \alpha = \alpha \sigma_z$$

and the eigenvectors

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

form a complete set of simultaneous eigenvectors of  $\sigma_z$  and  $\alpha$ . Similarly

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad \text{and} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

form a complete set of simultaneous eigenvectors of

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \alpha = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Notice that although  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$  do not commute with each other, they commute independently with  $\alpha$ ; and one can form simultaneous eigenkets of either  $\sigma_x$  and  $\alpha$  or of  $\sigma_y$  and  $\alpha$  or of  $\sigma_z$  and  $\alpha$ .

### 11.9. Problems

**Problem 11.1** Determine the orthonormal set of the eigenvectors of the matrix

$$\begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

Prove the completeness condition.

**Problem 11.2** Repeat the above problem for the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

**Problem 11.3** Prove that

$$| P \rangle \langle Q | = | Q \rangle \langle P |$$

**Problem 11.4** Consider the linear operator  $\sigma$  defined by the equation

$$\sigma^2 = 0$$

Write the eigenvalue equation for  $\sigma$  and show that eigenvalues of  $\sigma$  are  $\pm 1$ . Also show that  $(1 \pm \sigma) | P \rangle$  (where  $| P \rangle$  is an arbitrary ket) are eigenkets of  $\sigma$  belonging to the eigenvalues  $\pm 1$ . Notice that an arbitrary ket can always be written as

$$| P \rangle = \frac{1}{2} (1 + \sigma) | P \rangle + \frac{1}{2} (1 - \sigma) | P \rangle$$

which shows that eigenkets of  $\sigma$  form a complete set.

**Problem 11.5** Consider the matrices

$$\alpha_1 = \frac{1}{2} \begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix}$$

$$\alpha_2 = \frac{1}{2} \begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix}$$

$$\alpha_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

and

$$\beta = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Show that  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  commute independently with  $\beta$  but not with each other. Construct simultaneous set of eigenvectors of  $\alpha_1$  and  $\beta$ . Repeat the analysis for  $\alpha_2$  and  $\beta$  and for  $\alpha_3$  and  $\beta$ .

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## 11.10. Solutions

**Solution 11.1** The normalized eigenvectors are

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}; |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}; |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

**Solution 11.3** Let  $\alpha = |P\rangle\langle Q|$  and let

$$|B\rangle = \alpha|A\rangle = [(\langle Q|A\rangle)|P\rangle]$$

Thus

$$\begin{aligned} \langle B | &= \overline{(\langle Q | A \rangle)} \langle P | \\ &= \langle A | Q \rangle \langle P | \end{aligned}$$

But  $\langle B | = \langle A | \bar{\alpha} \rangle$ . Therefore

$$\bar{\alpha} = |Q\rangle\langle P|$$

**Solution 11.5** Simultaneous eigenvectors of  $\alpha_1$  and  $\beta$  are

$$\frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \text{ and } \frac{1}{\sqrt{5}} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}$$

Simultaneous eigenvectors of  $\alpha_2$  and  $\beta$  are

$$\frac{1}{2} \begin{pmatrix} 1 \\ i\sqrt{2} \\ -1 \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \text{ and } \frac{1}{2} \begin{pmatrix} 1 \\ -i\sqrt{2} \\ -1 \end{pmatrix}$$

Simultaneous eigenvectors of  $\alpha_3$  and  $\beta$  are

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

### 11.11. References and suggested reading

1. P.A.M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press, Oxford (1958).
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3. H.S. Green, *Matrix Methods in Quantum Mechanics*, Barnes and Noble, New York (1968).
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## Chapter 12

# Linear Harmonic Oscillator II Solutions Using Bra and Ket Algebra

HEISENBERG banished the picture of electron orbits with definite radii and periods of rotation, because these quantities are not observable; he demanded that the theory should be built up by means of quadratic arrays .... Instead of describing the motion by giving a coordinate as a function of time  $x(t)$ , one ought to determine an array of transition probabilities  $x_{mn}$ . By consideration of known examples discovered by guesswork he found the rule for determining the array of the square  $(x^2)_{mn}$  and applied it with success to simple examples such as the harmonic and anharmonic oscillator. This was in the summer of 1925. HEISENBERG, suffering from a severe attack of hay fever, took leave of absence for a course of treatment at the seaside and handed over his paper to me for publication ...

The significance of the idea was immediately clear to me, and I sent the manuscript to the *Zeitschrift für Physik*. HEISENBERG'S rule of multiplication left me no peace, and after a week of intensive thought and trial, I suddenly remembered an algebraic theory that I had learned from my teacher, ROSANES, in Breslau. Such quadratic arrays are quite familiar to mathematicians and are called matrices, in association with a definite rule of multiplication. I applied this rule to HEISENBERG'S quantum condition and found that it agreed for the diagonal elements. It was easy to guess what the remaining elements must be, namely, null; and immediately there stood before me the strange formula

$$pq - qp = h/2\pi i$$

This meant that coordinates  $q$  and momenta  $p$  are not to be represented by the values of numbers but by symbols whose product depends on the order of multiplication—which do not ‘commute’, as we say.

My excitement over this result was like that of the mariner who, after long voyaging, sees the desired land from afar, and my only regret was that HEISENBERG was not with me. I was convinced from the first that we had stumbled on the truth. Yet again a large part was only guesswork, in particular the vanishing of the nondiagonal elements in the foregoing expression. For this problem I secured the collaboration of my pupil PASCUAL JORDAN, and in a few days we succeeded in showing that I had guessed correctly. The joint paper by JORDAN and myself contains the most important principles of quantum mechanics, including its extension to electrodynamics.

— MAX BORN in *Physics in my Generation*,  
Springer Verlag, New York (1969).

## 12.1. Introduction

In Chapter 7 we had solved the Schrödinger equation for the linear harmonic oscillator problem. In this chapter we will use Dirac's bra and ket algebra to solve the same problem. Although the final results are the same, the analysis using bra and ket algebra is extremely elegant; it allows us to determine the various expectation values and also explicit expressions for the wave functions with considerable ease. The time evolution of the coherent state can also be studied in a very straightforward manner. For all this, we feel that the use of the operator algebra in solving the harmonic oscillator problem should be understood right in the beginning of the quantum mechanics course.

## 12.2. The solution of the eigenvalue problem

For the linear harmonic oscillator problem, the Hamiltonian is given by

*Hamiltonian*

$$H = \frac{p^2}{2\mu} + \frac{1}{2} \mu\omega^2 x^2 \quad (1)$$

where the symbols have been defined in Sec. 7.2. Since  $H$ ,  $p$ , and  $x$  are observables

$$\bar{H} = H, \quad \bar{p} = p, \quad \bar{x} = x \quad (2)$$

Further, the operators  $x$  and  $p$  will be assumed to satisfy the commutation relation (see Sec. 4.3)

$$[x, p] = xp - px = i\hbar \quad (3)$$

Our objective is to solve the eigenvalue equation

$$H | H' \rangle = H' | H' \rangle \quad (4)$$

where  $| H' \rangle$  is the eigenket of the operator  $H$  belonging to the eigenvalue  $H'$ . It may be noted that in the above equation  $H$  is an operator and  $H'$  is simply a number.

*Definitions of  $a$  and  $\bar{a}$*

It is convenient to introduce the dimensionless complex operator

$$a = \frac{1}{(2\mu\hbar\omega)^{1/2}} (\mu\omega x + ip) \quad (5)$$

Since  $\bar{x} = x$  and  $\bar{p} = p$ , the adjoint of  $a$  would be given by

$$\bar{a} = \frac{1}{(2\mu\hbar\omega)^{1/2}} (\mu\omega x - ip) \quad (6)$$

In terms of the above operators

$$\begin{aligned}\hbar\omega a\bar{a} &= \frac{1}{2\mu} (\mu\omega x + ip)(\mu\omega x - ip) \\ &= \frac{1}{2\mu} [\mu^2\omega x^2 + p^2 - i\omega\mu(xp - px)] \\ &= H + \frac{1}{2}\hbar\omega\end{aligned}\quad (7)$$

where we have used Eqs (1) and (3). Similarly

$$\hbar\omega\bar{a}a = H - \frac{1}{2}\hbar\omega \quad (8)$$

Thus

$$H = \frac{1}{2}\hbar\omega(\bar{a}a + a\bar{a}) \quad (9)$$

and

*Commutation relation*

$$a\bar{a} - \bar{a}a = [a, \bar{a}] = 1 \quad (10)$$

From Eq. (7)

$$\hbar\omega a\bar{a}a = Ha + \frac{1}{2}\hbar\omega a \quad (11)$$

and from Eq. (8)

$$\hbar\omega a\bar{a}a = aH - \frac{1}{2}\hbar\omega a \quad (12)$$

Thus

$$aH - Ha = [a, H] = \hbar\omega a \quad (13)$$

Similarly

$$\bar{a}H - H\bar{a} = [\bar{a}, H] = -\hbar\omega\bar{a} \quad (14)$$

The above equation can also be obtained by taking the adjoint of Eq. (13). Now, let

$$| P \rangle = a | H' \rangle$$

where  $| H' \rangle$  is an eigenket of  $H$  belonging to the eigenvalue  $H'$  [see Eq. (4)].

Then

$$\langle P | = \langle H' | \bar{a}$$

and

$$\begin{aligned}\hbar\omega \langle P | P \rangle &= \hbar\omega \langle H' | \bar{a}a | H' \rangle \\ &= \langle H' | H - \frac{1}{2}\hbar\omega | H' \rangle \quad [\text{using Eq. (8)}] \\ &= (H' - \frac{1}{2}\hbar\omega) \langle H' | H' \rangle \quad [\text{using Eq. (4)}]\end{aligned}$$

where  $(H' - \frac{1}{2}\hbar\omega)$  has been taken outside as it is just a number. But  $\langle P | P \rangle$  and  $\langle H' | H' \rangle$  are positive numbers (see Sec. 11.2) and therefore

$$H' \geq \frac{1}{2}\hbar\omega \quad (15)$$

and

$$H' = \frac{1}{2}\hbar\omega$$

if and only if

$$|P\rangle = a |H'\rangle = 0 \quad (16)$$

Conversely,

$$a |H'\rangle = 0 \text{ only when } H' = \frac{1}{2}\hbar\omega \quad (17)$$

That  $H'$  should be positive follows from the fact that the expectation values of  $x^2$  and  $p^2$  should be positive or zero for *any* state of the system. This can be seen from the following:

$$\langle Q | H | Q \rangle = \frac{1}{2\mu} \langle Q | p^2 | Q \rangle + \frac{1}{2} \mu\omega^2 \langle Q | x^2 | Q \rangle$$

where  $|Q\rangle$  represents an arbitrary state of the system. Let

$$|R\rangle = p |Q\rangle$$

then

$$\langle R | = \langle Q | \bar{p} = \langle Q | p$$

because  $p$  is a Hermitian operator. Thus

$$\langle R | R \rangle = \langle Q | p^2 | Q \rangle \geq 0$$

the equality sign if and only if  $|R\rangle$  is a null ket. Similarly

$$\langle Q | x^2 | Q \rangle \geq 0$$

Thus

$$\langle Q | H | Q \rangle \geq 0$$

proving that the expectation value of the energy of the oscillator should be positive for *any* state of the system.

Next, let us consider the operator  $Ha$  operating on  $|H'\rangle$ :

$$\begin{aligned} Ha |H'\rangle &= (aH - \hbar\omega a) |H'\rangle \quad [\text{using Eq. (13)}] \\ &= (aH' - \hbar\omega a) |H'\rangle \\ &= (H' - \hbar\omega) a |H'\rangle \end{aligned} \quad (18)$$

Thus

if  $| H' \rangle$  is an eigenket of  $H$

then

$a | H' \rangle$  is also an eigenket of  $H$

belonging to the eigenvalue  $H' - \hbar\omega$  provided

$$H' \neq \frac{1}{2} \hbar\omega$$

because if  $H' = \frac{1}{2} \hbar\omega$ ,  $a | H' \rangle$  is a null ket. Thus, if

$$H' \neq \frac{1}{2} \hbar\omega$$

then

$H' - \hbar\omega$  is also an eigenvalue of  $H$ .

Similarly, if

$$H' - \hbar\omega \neq \frac{1}{2} \hbar\omega$$

then

$H' - 2\hbar\omega$  is also an eigenvalue of  $H$ .

Therefore,

$$H' - \hbar\omega, H' - 2\hbar\omega, H' - 3\hbar\omega, \dots$$

are all eigenvalues of  $H$ . This, however, cannot go on indefinitely because it will then contradict Eq. (15). Further, it can only terminate at  $H' = \frac{1}{2} \hbar\omega$ , because then

$$a | \frac{1}{2} \hbar\omega \rangle = 0$$

Thus the possible eigenvalues can be

$$\frac{1}{2} \hbar\omega, \frac{3}{2} \hbar\omega, \frac{5}{2} \hbar\omega, \dots$$

We *cannot* have any other eigenvalue. In order to prove this let us assume that  $H' = \frac{7}{3} \hbar\omega$  is an eigenvalue. Then from Eq. (18),  $\frac{4}{3} \hbar\omega, \frac{1}{3} \hbar\omega, -\frac{2}{3} \hbar\omega, \dots$  will be eigenvalues because  $a | H' \rangle$  cannot be a null ket. Obviously, this will contradict Eq. (15).

We next show that we will have an infinite number of eigenvalues. Now, using Eq. (14)

$$\begin{aligned} H\bar{a} | H' \rangle &= (\bar{a}H + \hbar\omega\bar{a}) | H' \rangle \\ &= (\bar{a}H' + \hbar\omega\bar{a}) | H' \rangle \\ &= (H' + \hbar\omega)\bar{a} | H' \rangle \end{aligned} \quad (19)$$

implying that  $(H' + \hbar\omega)$  is another eigenvalue of  $H$ , with  $\bar{a} | H' \rangle$  as the eigenket belonging to it, unless  $\bar{a} | H' \rangle = 0$ . However,  $\bar{a} | H' \rangle$  can never be a null ket, since it would lead to

$$\begin{aligned} 0 &= \hbar\omega a\bar{a} | H' \rangle = \left(H + \frac{1}{2}\hbar\omega\right) | H' \rangle \quad [\text{using Eq. (7)}] \\ &= \left(H' + \frac{1}{2}\hbar\omega\right) | H' \rangle \end{aligned}$$

giving  $H' + \frac{1}{2}\hbar\omega = 0$ , which contradicts Eq. (15). Thus if  $H'$  is an eigenvalue, then  $H' + \hbar\omega$  is always another eigenvalue of  $H$ , and so are

$$H' + 2\hbar\omega, \quad H' + 3\hbar\omega, \dots$$

and so on. Hence the eigenvalues of the Hamiltonian for the linear harmonic oscillator problem are

*Eigenvalues*

$$\frac{1}{2}\hbar\omega, \quad \frac{3}{2}\hbar\omega, \quad \frac{5}{2}\hbar\omega, \quad \frac{7}{2}\hbar\omega, \dots \quad (20)$$

extending to infinity, which is the same as obtained in Sec. 7.2.

We now relabel the eigenfunctions with the index  $n$ ; thus  $| n \rangle$  denotes the eigenfunction corresponding to the eigenvalue  $(n + \frac{1}{2})\hbar\omega$ :

$$H | n \rangle = \left(n + \frac{1}{2}\right)\hbar\omega | n \rangle ; \quad n = 0, 1, 2, \dots \quad (21)$$

Since  $| n \rangle$  are eigenkets of the Hermitian operator  $H$ , they must be orthogonal to each other; we further assume that the states  $| n \rangle$  are normalized, so that

$$\langle m | n \rangle = \delta_{mn} \quad (22)$$

Further, since  $| 0 \rangle$  corresponds to  $H' = \frac{1}{2}\hbar\omega$ , we must have

$$a | 0 \rangle = 0 \quad (23)$$

Now, for  $n = 1, 2, 3, \dots$   $a | n \rangle$  is an eigenket of  $H$  belonging to the eigenvalue  $(n - \frac{1}{2})\hbar\omega$  [see Eq. (18)]; therefore  $a | n \rangle$  must be a multiple of  $| n - 1 \rangle$ :

$$a | n \rangle = \alpha_n | n - 1 \rangle$$

In order to determine  $\alpha_n$ , we calculate the square of the length of  $a | n \rangle$ :

$$\langle n | \bar{a}a | n \rangle = |\alpha_n|^2 \langle n-1 | n-1 \rangle = |\alpha_n|^2$$

But

$$\begin{aligned}\hbar\omega \langle n | \bar{a}a | n \rangle &= \langle n | (H - \frac{1}{2}\hbar\omega) | n \rangle \\ &= \langle n | (n + \frac{1}{2})\hbar\omega - \frac{1}{2}\hbar\omega | n \rangle \\ &= n\hbar\omega \langle n | n \rangle = n\hbar\omega\end{aligned}$$

Thus

$$|\alpha_n|^2 = n$$

and therefore we may write

$$a | n \rangle = \sqrt{n} | n-1 \rangle \quad (24)$$

Similarly

$$\bar{a} | n \rangle = \sqrt{(n+1)} | n+1 \rangle \quad (25)$$

Thus, if  $|0\rangle$  denotes the ground-state eigenket, then

$$|1\rangle = \frac{\bar{a}}{\sqrt{1}} |0\rangle, \quad |2\rangle = \frac{\bar{a}}{\sqrt{1}} \frac{\bar{a}}{\sqrt{2}} |0\rangle = \frac{(\bar{a})^2}{\sqrt{2!}} |0\rangle, \quad |3\rangle = \frac{(\bar{a})^3}{\sqrt{3!}} |0\rangle, \dots$$

and, in general,

$$|n\rangle = \frac{(\bar{a})^n}{\sqrt{n!}} |0\rangle \quad (26)$$

We can think of an excited state  $|n\rangle$  of the oscillator as containing  $n$  quanta of energy  $\hbar\omega$ , in addition to the zero-point energy of  $\frac{1}{2}\hbar\omega$ . The operator  $\bar{a}$ , according to Eq. (25), creates a quantum of energy; and, therefore,  $\bar{a}$  is called the *creation* operator. Similarly, the operator  $a$ , according to Eq. (24), annihilates a quantum of energy; and, therefore,  $a$  is called the *annihilation* or *destruction* operator.

The eigenkets of  $H$  form a complete set of orthogonal kets; thus (see Sec. 11.6)

$$\sum_{n=0,1,2,\dots} |n\rangle \langle n| = 1$$

#### *Solution of the linear harmonic oscillator problem*

Thus the solution of the linear harmonic oscillator problem can be summarized through the following equations:

$$\left. \begin{aligned} H | n \rangle &= \left(n + \frac{1}{2}\right) \hbar\omega | n \rangle; \quad n = 0, 1, 2, \dots \\ \langle m | n \rangle &= \delta_{mn} \\ \sum_{n=0,1,2,\dots} |n\rangle \langle n| &= 1 \end{aligned} \right\} \quad (27)$$

Further,

$$\begin{aligned} a | n \rangle &= \sqrt{n} | n - 1 \rangle \\ a | 0 \rangle &= 0 \\ \bar{a} | n \rangle &= \sqrt{n+1} | n + 1 \rangle \end{aligned}$$

We may pause here for a moment and appreciate the beauty of the operator algebra which has enabled us to solve the eigenvalue equation; the only assumption has been the commutation relation along with the basic axioms of quantum mechanics.

### 12.3. The uncertainty product

In this section we will calculate the uncertainty product  $\Delta x \Delta p$  for the harmonic oscillator states. The uncertainties  $\Delta x$  and  $\Delta p$  are given by (see Sec. 4.6)

$$\Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{1/2} \quad (28)$$

and

$$\Delta p = [\langle p^2 \rangle - \langle p \rangle^2]^{1/2} \quad (29)$$

where

$$\begin{aligned} \langle x \rangle &= \langle n | x | n \rangle, & \langle x^2 \rangle &= \langle n | x^2 | n \rangle \\ \langle p \rangle &= \langle n | p | n \rangle, & \langle p^2 \rangle &= \langle n | p^2 | n \rangle \end{aligned}$$

represent the expectation values of the operators in the  $n^{th}$  eigenstate of the oscillator. Now, using Eqs. (5) and (6)

$$x = \left( \frac{\hbar}{2\mu\omega} \right)^{1/2} (\bar{a} + a) \quad (30)$$

$$p = i \left( \frac{\mu \hbar \omega}{2} \right)^{1/2} (\bar{a} - a) \quad (31)$$

Thus

$$\begin{aligned} \langle x \rangle &= \langle n | x | n \rangle = \left( \frac{\hbar}{2\mu\omega} \right)^{1/2} \langle n | \bar{a} + a | n \rangle \\ &= \left( \frac{\hbar}{2\mu\omega} \right)^{1/2} \left[ \sqrt{n+1} \langle n | n+1 \rangle + \sqrt{n} \langle n | n-1 \rangle \right] \\ &\quad [\text{using Eqs (24) and (25)}] \\ &= 0 \end{aligned}$$

and

$$\begin{aligned}
 \langle x^2 \rangle &= \langle n | x^2 | n \rangle = \frac{\hbar}{2\mu\omega} [\langle n | \bar{a} \bar{a} | n \rangle + \langle n | \bar{a} a | n \rangle \\
 &\quad + \langle n | a \bar{a} | n \rangle + \langle n | aa | n \rangle] \\
 &= \frac{\hbar}{2\mu\omega} [0 + n + (n + 1) + 0] \\
 &= \frac{\hbar}{2\mu\omega} (n + \frac{1}{2})
 \end{aligned} \tag{32}$$

Similarly

$$\langle p \rangle = \langle n | p | n \rangle = 0 \text{ and } \langle p^2 \rangle = \mu\omega\hbar(n + \frac{1}{2}) \tag{33}$$

giving

$$\Delta x \Delta p = (n + \frac{1}{2})\hbar \tag{34}$$

the minimum value ( $= \frac{1}{2}\hbar$ ) occurring for the ground state. Once again, we may see the ease with which we can use the operator algebra to calculate the various expectation values. We may recall that if we were to use the solutions obtained in Sec. 7.3, then

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} \psi_n^*(x) x^2 \psi_n(x) dx \tag{35}$$

and

$$\langle p^2 \rangle = \int_{-\infty}^{+\infty} \psi_n^*(x) \left[ -\hbar^2 \frac{d^2}{dx^2} \right] \psi_n(x) dx \tag{36}$$

where  $\psi_n(x)$  are the Hermite-Gauss functions [see Eq. (35) of Chapter 7] representing the normalized eigenfunction of the harmonic oscillator problem. Although the final results are the same, the explicit evaluation of the integrals in Eqs (35) and (36) is fairly tedious.

## 12.4. Harmonic oscillator wave functions

In Sec. 12.2 we had shown that

$$a | 0 \rangle = 0 \tag{37}$$

where  $| 0 \rangle$  represents the eigenket corresponding to the ground state. Now, if  $\psi_0(x)$  represents the Schrödinger wave function corresponding to the ground state,

the above equation would imply

$$\frac{1}{\sqrt{2\mu\hbar\omega}} (\mu\omega x + ip) \psi_0(x) = 0 \quad (38)$$

where we have used Eq. (5) which defines the operator  $a$ . Replacing  $p$  by  $-i\hbar d/dx$ , we get

$$\left( \mu\omega x + \hbar \frac{d}{dx} \right) \psi_0(x) = 0$$

or,

$$\frac{d\psi_0}{dx} = -\frac{\mu\omega}{\hbar} x \psi_0(x)$$

or

$$\frac{1}{\psi_0} \frac{d\psi_0(x)}{dx} = -\frac{\mu\omega}{\hbar} x$$

Carrying out the straightforward integration we get

$$\ln \psi_0(x) = -\frac{\mu\omega}{2\hbar} x^2 + \text{const}$$

or

$$\psi_0(x) = N e^{-\frac{1}{2}\gamma^2 x^2}$$

where

$$\gamma = \sqrt{\frac{\mu\omega}{\hbar}}$$

If we use the normalization condition

$$\int_{-\infty}^{+\infty} |\psi_0(x)|^2 dx = 1$$

we would readily get

*Normalized ground state wave function*

$$\psi_0(x) = \left[ \frac{\gamma}{\sqrt{\pi}} \right]^{1/2} e^{-\frac{1}{2}\gamma^2 x^2} \quad (39)$$

which represents the normalized ground state wave function [see Eq. (33) of Chapter 7]. Since

$$\bar{a} |n\rangle = \sqrt{n+1} |n+1\rangle$$

we may write

$$|n+1\rangle = \frac{1}{\sqrt{n+1}} \bar{a} |n\rangle$$

or

$$\psi_{n+1}(x) = \frac{1}{\sqrt{n+1}} \frac{\mu\omega x - ip}{\sqrt{2\mu\hbar\omega}} \psi_n(x) \quad (40)$$

or

$$\begin{aligned} \psi_{n+1}(x) &= \frac{1}{[2(n+1)]^{1/2}} \left[ \sqrt{\frac{\mu\omega}{\hbar}} x - \sqrt{\frac{\hbar}{\mu\omega}} \frac{d}{dx} \right] \psi_n(x) \\ &= \frac{1}{[2(n+1)]^{1/2}} \left[ \xi - \frac{d}{d\xi} \right] \psi_n(x) \end{aligned} \quad (41)$$

where

$$\xi = \gamma x = \sqrt{\frac{\mu\omega}{\hbar}} x$$

Thus

$$\begin{aligned} \psi_1(x) &= \frac{1}{\sqrt{2}} \left[ \xi - \frac{d}{d\xi} \right] \left[ \frac{\gamma}{\sqrt{\pi}} \right]^{1/2} e^{-\frac{1}{2}\xi^2} \\ &= \left[ \frac{\gamma}{2\sqrt{\pi}} \right]^{1/2} 2\xi e^{-\frac{1}{2}\xi^2} \end{aligned} \quad (42)$$

which is automatically normalized! Further,

$$\begin{aligned} \psi_2(x) &= \frac{1}{\sqrt{2}\sqrt{2}} \left[ \frac{\gamma}{2\sqrt{\pi}} \right]^{1/2} \left[ \xi - \frac{d}{d\xi} \right] (2\xi e^{-\frac{1}{2}\xi^2}) \\ &= \left[ \frac{\gamma}{2^2 2\sqrt{\pi}} \right]^{1/2} (4\xi^2 - 2) e^{-\frac{1}{2}\xi^2} \end{aligned} \quad (43)$$

and

$$\begin{aligned} \psi_3(x) &= \frac{1}{\sqrt{2}\sqrt{3}} \left[ \frac{\gamma}{2^2 2\sqrt{\pi}} \right]^{1/2} \left( \xi - \frac{d}{d\xi} \right) (4\xi^2 - 2) e^{-\frac{1}{2}\xi^2} \\ &= \left[ \frac{\gamma}{2^3 3!\sqrt{\pi}} \right]^{1/2} (8\xi^3 - 12\xi) e^{-\frac{1}{2}\xi^2} \end{aligned} \quad (44)$$

In general,

*Wave function of the  $n^{\text{th}}$  state*

$$\psi_n(x) = \left[ \frac{\gamma}{2^n n! \sqrt{\pi}} \right]^{1/2} H_n(\xi) e^{-\frac{1}{2}\xi^2} \quad (45)$$

which can be proved by induction (see Problem 12.7). Equations (42), (43) and (44) are identical to the expressions derived in Sec. 7.3.

## 12.5. The coherent state

In this section we will obtain the eigenvalues and eigenfunctions of the annihilation operator  $a$ , i.e. we will solve the eigenvalue equation

*Eigenvalue equation of  $a$*

$$a |\alpha\rangle = \alpha |\alpha\rangle \quad (46)$$

The eigenkets  $|\alpha\rangle$  describe what are known as coherent states which represent the quantum mechanical analogs of the “classical oscillator” (see also Sec. 7.4). Since the eigenkets of an observable form a complete set, we expand  $|\alpha\rangle$  in terms of the kets  $|n\rangle$ :

$$|\alpha\rangle = \sum_{n=0,1,2,\dots}^{\infty} c_n |n\rangle \quad (47)$$

Now

$$a |\alpha\rangle = \sum_{n=0,1,2,\dots}^{\infty} c_n a |n\rangle = \sum_{n=1,2,\dots}^{\infty} c_n \sqrt{n} |n-1\rangle$$

Also

$$a |\alpha\rangle = \alpha |\alpha\rangle = \alpha \sum_{n=0,1,2,\dots}^{\infty} c_n |n\rangle$$

Thus

$$c_1 |0\rangle + c_2 \sqrt{2} |1\rangle + c_3 \sqrt{3} |2\rangle + \dots = \alpha (c_0 |0\rangle + c_1 |1\rangle + c_2 |2\rangle + \dots)$$

or

$$\begin{aligned} c_1 &= \alpha c_0, \\ c_2 &= \frac{\alpha c_1}{\sqrt{2}} = \frac{\alpha^2}{\sqrt{2}} c_0, \\ c_3 &= \alpha \frac{c_2}{\sqrt{3}} = \frac{\alpha^3}{\sqrt{3!}} c_0, \dots \end{aligned}$$

In general,

$$c_n = \frac{\alpha^n}{\sqrt{n!}} c_0$$

Thus

$$|\alpha\rangle = c_0 \sum_{n=0,1,2,\dots}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$

If we normalize  $|\alpha\rangle$ , we would get

$$\begin{aligned} 1 &= \langle\alpha|\alpha\rangle = |c_0|^2 \sum_n \sum_m \frac{\alpha^n \alpha^{*m}}{\sqrt{n!}\sqrt{m!}} \delta_{nm} \\ &= |c_0|^2 \sum_{n=0,1,2,\dots}^{\infty} \frac{(|\alpha|^2)^n}{n!} = |c_0|^2 e^{|\alpha|^2} \end{aligned}$$

or

$$c_0 = e^{-\frac{1}{2}|\alpha|^2}$$

within an arbitrary phase factor. Thus

$$c_n = \frac{\alpha^n}{\sqrt{n!}} e^{-\frac{1}{2}|\alpha|^2} \quad (48)$$

and

$$|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0,1,2,\dots}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle \quad (49)$$

which represents the (normalized) coherent state.

Notice that there is no restriction on the value of  $\alpha$ , i.e.  $\alpha$  can take *any* complex value.

## 12.6. Time evolution of the coherent state

The time dependent Schrödinger equation for the linear harmonic oscillator problem is given by

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\Psi\rangle &= H |\Psi\rangle \\ &= \left( \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2 x^2 \right) |\Psi\rangle \end{aligned} \quad (50)$$

In order to solve the above equation, we use the method of separation of variables (cf. Sec. 7.2)

$$|\Psi\rangle = e^{-iEt/\hbar} |\psi\rangle \quad (51)$$

where  $|\psi\rangle$  are the eigenkets of the Hamiltonian  $H$ :

$$H |\psi\rangle = E |\psi\rangle \quad (52)$$

In Sec. 12.2 we have solved the above eigenvalue equation and have shown that  $E$  can take the following discrete values:

$$E = E_n = \left( n + \frac{1}{2} \right) \hbar\omega$$

with  $| n \rangle$  representing the corresponding (normalized) eigenkets. Thus the most general solution of Eq. (50) is given by

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{n=0,1,2,\dots}^{\infty} c_n \exp\left[-\frac{iE_n t}{\hbar}\right] |n\rangle \\ &= \sum_{n=0,1,2,\dots}^{\infty} c_n e^{-i(n+\frac{1}{2})\omega t} |n\rangle \end{aligned} \quad (53)$$

where the coefficients  $c_n$  are to be determined from the following equation (cf. Sec. 7.3):

$$|\Psi(0)\rangle = \sum_{n=0,1,2,\dots}^{\infty} c_n |n\rangle \quad (54)$$

If  $|\Psi(0)\rangle$  is normalized, i.e. if

$$\langle \Psi(0) | \Psi(0) \rangle = 1 \quad (55)$$

then

$$\begin{aligned} 1 &= \sum_{m=0,1,2,\dots}^{\infty} c_m^* \langle m | \sum_{n=0,1,2,\dots}^{\infty} c_n |n\rangle \\ &= \sum_{m=0,1,2,\dots}^{\infty} \sum_{n=0,1,2,\dots}^{\infty} c_m^* c_n \langle m | n \rangle \\ &= \sum_{m=0,1,2,\dots}^{\infty} \sum_{n=0,1,2,\dots}^{\infty} c_m^* c_n \delta_{mn} \end{aligned}$$

Thus

$$\sum_{n=0,1,2,\dots}^{\infty} |c_n|^2 = 1 \quad (56)$$

and we may interpret  $|c_n|^2$  to represent the probability of finding the oscillator in the  $n^{th}$  state (which would not change with time). Furthermore, using Eq. (53)

$$\begin{aligned}\langle \Psi(t) | \Psi(t) \rangle &= \sum_{n=0,1,2,\dots}^{\infty} \sum_{m=0,1,2,\dots}^{\infty} c_m^* c_n e^{i(m-n)\omega t} \langle m | n \rangle \\ &= \sum_{n=0,1,2,\dots}^{\infty} \sum_{m=0,1,2,\dots}^{\infty} c_m^* c_n e^{i(m-n)\omega t} \delta_{mn} \\ &= \sum_{n=0,1,2,\dots}^{\infty} |c_n|^2 = 1\end{aligned}$$

Thus if  $|\Psi(0)\rangle$  is normalized, then  $|\Psi(t)\rangle$  is also normalized for all values of time.

Let us assume that at  $t = 0$ , the oscillator is in a coherent state, i.e.

$$|\Psi(t=0)\rangle = |\alpha\rangle$$

For the coherent state,  $c_n$  is given by Eq. (48) and therefore,

*Time evolution of the coherent state*

$$\begin{aligned}|\Psi(t)\rangle &= \sum_{n=0,1,2,\dots}^{\infty} c_n e^{-iE_nt/\hbar} |n\rangle \\ &= e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0,1,2,\dots}^{\infty} \left[ \frac{\alpha^n}{\sqrt{n!}} \right] e^{-i(n+\frac{1}{2})\omega t} |n\rangle\end{aligned}\quad (57)$$

The above equation describes the time evolution of the coherent state. We would next like to calculate the corresponding time variations of  $\langle x \rangle$  and  $\langle p \rangle$  which represent the expectation values of  $x$  and  $p$ :

$$\begin{aligned}\langle x \rangle &= \langle \Psi(t) | x | \Psi(t) \rangle \\ \langle p \rangle &= \langle \Psi(t) | p | \Psi(t) \rangle\end{aligned}$$

Since

$$x = \sqrt{\frac{\hbar}{2\mu\omega}} (a + \bar{a}) \quad (58)$$

and

$$p = \frac{1}{i} \sqrt{\frac{\mu\hbar\omega}{2}} (a - \bar{a}) \quad (59)$$

We must first calculate  $\langle a \rangle$  and  $\langle \bar{a} \rangle$ . Now

$$\begin{aligned}\bar{a} | \Psi(t) \rangle &= e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0,1,2,\dots}^{\infty} \frac{\alpha^n}{\sqrt{n!}} e^{-i(n+\frac{1}{2})\omega t} \bar{a} | n \rangle \\ &= e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0,1,2,\dots}^{\infty} \frac{\alpha^n}{\sqrt{n!}} e^{-i(n+\frac{1}{2})\omega t} \sqrt{n+1} | n+1 \rangle\end{aligned}\quad (60)$$

Since

$$\langle \Psi(t) | = e^{-\frac{1}{2}|\alpha|^2} \sum_{m=0,1,2,\dots}^{\infty} \frac{\alpha^{*m}}{\sqrt{m!}} e^{+i(m+\frac{1}{2})\omega t} \langle m | \quad (61)$$

we get

$$\begin{aligned}\langle \bar{a} \rangle &= \langle \Psi(t) | \bar{a} | \Psi(t) \rangle \\ &= e^{-|\alpha|^2} \sum_m \sum_n \frac{\alpha^{*m} \alpha^n}{\sqrt{m!n!}} e^{i(m-n)\omega t} \sqrt{n+1} \langle m | n+1 \rangle \\ &= e^{-|\alpha|^2} \sum_{n=0,1,2,\dots}^{\infty} \frac{\alpha^* (\alpha \alpha^*)^n}{n!} e^{i\omega t} \\ &= e^{-|\alpha|^2} \alpha^* e^{i\omega t} e^{|\alpha|^2}\end{aligned}$$

or

$$\langle \Psi(t) | \bar{a} | \Psi(t) \rangle = \alpha^* e^{i\omega t} \quad (62)$$

Similarly<sup>1</sup>

$$\langle \Psi(t) | a | \Psi(t) \rangle = \alpha e^{-i\omega t} \quad (63)$$

Thus

*Expectation value of x*

$$\begin{aligned}\langle x \rangle &= \langle \Psi(t) | x | \Psi(t) \rangle \\ &= \sqrt{\frac{\hbar}{2\mu\omega}} \langle \Psi(t) | a + \bar{a} | \Psi(t) \rangle \\ &= \sqrt{\frac{\hbar}{2\mu\omega}} [\alpha e^{-i\omega t} + \alpha^* e^{i\omega t}] \\ &= \sqrt{\frac{2\hbar}{\mu\omega}} |\alpha| \cos(\omega t - \phi)\end{aligned}$$

---

<sup>1</sup> Alternatively, if we take the complex conjugate of Eq. (62), we would obtain Eq. (63).

where we have written

$$\alpha = |\alpha| e^{+i\phi}$$

Thus we may write

$$\langle x \rangle = x_0 \cos(\omega t - \phi) \quad (64)$$

where

$$x_0 = \sqrt{\frac{2\hbar}{\mu\omega}} |\alpha| \quad (65)$$

Similarly,

*Expectation value of p*

$$\begin{aligned} \langle p \rangle &= \sqrt{\frac{\mu\hbar\omega}{2}} \frac{1}{i} \Psi(t) |a - \bar{a}| \Psi(t) \\ &= \sqrt{2\mu\hbar\omega} \frac{1}{2i} [\alpha e^{-i\omega t} - \alpha^* e^{i\omega t}] \\ &= -\mu\omega x_0 \sin(\omega t - \phi) \end{aligned} \quad (66)$$

From Eqs (64) and (66) we may write

$$\langle p \rangle = \mu \frac{d\langle x \rangle}{dt} \quad (67)$$

which is nothing but the equation of motion for a classical particle (see Sec. 4.5). Once again, it is much more convenient to use the bra and ket algebra to evaluate the various expectation values.

## 12.7. The number operator

Consider the operator

$$N_{op} = \bar{a}a \quad (68)$$

Using Eq. (8) we may write

$$H = \left( N_{op} + \frac{1}{2} \right) \hbar\omega \quad (69)$$

Since

$$H |n\rangle = \left( n + \frac{1}{2} \right) \hbar\omega |n\rangle$$

we have

$$N_{op} |n\rangle = n |n\rangle \quad (70)$$

Thus  $|n\rangle$  are also the eigenkets of  $N_{op}$ , the corresponding eigenvalues being  $n$  and since  $n$  takes the values  $0, 1, 2, \dots$ , the operator  $N_{op}$  is called the number operator. For this reason,  $|n\rangle$  are often referred to as number states. Obviously

$$\langle m | N_{op} | n \rangle = n \delta_{mn} \quad (71)$$

## 12.8. The unitary transformation

Let  $|\Psi_i\rangle$  represent a set of orthonormal kets, i.e.

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$$

We consider a transformation

$$|\Phi_i\rangle = \sum_j U_{ij} |\Psi_j\rangle \quad (72)$$

If the kets  $|\Phi_i\rangle$  also form a set of orthonormal kets, i.e. if  $\langle \Phi_i | \Phi_j \rangle = \delta_{ij}$  then the transformation is said to be unitary and  $U_{ij}$  is said to be a unitary matrix. Now

$$\begin{aligned} \delta_{ij} &= \langle \Phi_i | \Phi_j \rangle = \sum_m \sum_n \overline{U}_{im} U_{jn} \langle \Psi_m | \Psi_n \rangle \\ &= \sum_m \sum_n \overline{U}_{im} U_{jn} \delta_{mn} \\ &= \sum_n \overline{U}_{in} U_{jn} \end{aligned}$$

or

$$\overline{U} U = 1 \quad (73)$$

where  $\overline{U}$  represents the hermitian adjoint of  $U$ . Thus if  $U$  describes an arbitrary transformation then

$$\overline{U} = U^{-1}$$

## 12.9. The Schrödinger and Heisenberg pictures

While solving the linear harmonic oscillator problem in Sec. 12.2, we had assumed the observables  $x$ ,  $p$  and  $H$  to be real operators and independent of time. This is the so-called Schrödinger picture and the time development of the ket describing the

quantum mechanical system is obtained by solving the time dependent Schrödinger equation:

$$i \hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle \quad (74)$$

If the Hamiltonian is independent of time, we can *integrate* the above equation to obtain

$$|\Psi(t)\rangle = e^{-iHt/\hbar} |\Psi(0)\rangle \quad (75)$$

where the exponential of an operator is defined through the power series

$$e^{\mathcal{O}} = 1 + \mathcal{O} + \frac{1}{2!} \mathcal{O} \cdot \mathcal{O} + \frac{1}{3!} \mathcal{O} \cdot \mathcal{O} \cdot \mathcal{O} \dots \quad (76)$$

That Eq. (75) is the solution of Eq. (74) can be immediately seen by direct substitution. Next, let  $|n\rangle$  represent the eigenkets of  $H$ :

$$H|n\rangle = E_n|n\rangle$$

then by inserting the unit operator [see Eq. (27)] in Eq. (75) we obtain

$$\begin{aligned} |\Psi(t)\rangle &= e^{-iHt/\hbar} \left\{ \sum_n |n\rangle \langle n| \right\} |\Psi(0)\rangle \\ &= \sum_n e^{-iE_n t/\hbar} |n\rangle [\langle n| \Psi(0)\rangle] \end{aligned} \quad (77)$$

The above equation may be used to study the time development of states. Now, the expectation value of an observable characterised by the operator  $\mathcal{O}$  is given by

$$\langle \mathcal{O} \rangle = \langle \Psi(t) | \mathcal{O} | \Psi(t) \rangle \quad (78)$$

If we substitute for  $|\Psi(t)\rangle$  from Eq. (75), we would get

$$\begin{aligned} \langle \mathcal{O} \rangle &= \langle \Psi(0) | e^{iHt/\hbar} \mathcal{O} e^{-iHt/\hbar} | \Psi(0) \rangle \\ &= \langle \Psi(0) | \mathcal{O}_H(t) | \Psi(0) \rangle \end{aligned} \quad (79)$$

where the operator  $\mathcal{O}_H(t)$  is defined by the following equation:

$$\mathcal{O}_H(t) = e^{iHt/\hbar} \mathcal{O} e^{-iHt/\hbar} \quad (80)$$

Eqs (78) and (79) tell us that the expectation values remain the same if we endow the operators  $\mathcal{O}_H(t)$  with the entire time dependence but assume that the kets are time dependent. This is known as the Heisenberg picture (and hence the subscript  $H$ ) in which operators representing the observable change with time but the ket describing the system is time independent. On the other hand, in the Schrödinger picture [see Eqs (77) and (78)], we may visualize the basis vectors (here  $|n\rangle$ ) as a fixed set of vectors and  $|\Psi(t)\rangle$  (describing the system) as moving.

From Eq. (80), we have,

$$\frac{d}{dt}\mathcal{O}_H(t) = e^{iHt/\hbar} \frac{\partial \mathcal{O}}{\partial t} e^{-iHt/\hbar} + \frac{i}{\hbar} e^{iHt/\hbar} [H\mathcal{O} - \mathcal{O}H] e^{-iHt/\hbar}$$

where  $\frac{\partial \mathcal{O}}{\partial t}$  is introduced to allow for any explicit time dependence of the operator. If there is no such explicit time dependence, we may write

$$\begin{aligned} i\hbar \frac{d}{dt}\mathcal{O}_H(t) &= [e^{iHt/\hbar} \mathcal{O} e^{-iHt/\hbar}] H \\ &\quad - H [e^{iHt/\hbar} \mathcal{O} e^{-iHt/\hbar}] \\ &= \mathcal{O}_H(t)H - H\mathcal{O}_H(t) \end{aligned} \quad (81)$$

or

*Heisenberg equation of motion*

$$i\hbar \frac{d}{dt}\mathcal{O}_H(t) = [\mathcal{O}_H(t), H] \quad (82)$$

Equation (82) gives the time dependence of an operator in the Heisenberg picture and is called the *Heisenberg equation of motion*.

If the Hamiltonian is assumed to be independent of time in the Schrödinger representation, then it is also independent of time in the Heisenberg representation:

$$H_H(t) = e^{-iHt/\hbar} H e^{iHt/\hbar} = e^{-iHt/\hbar} e^{iHt/\hbar} H = H \quad (83)$$

It should be mentioned that if  $H$  had an explicit time dependence, the analysis would have been much more involved (see, e.g. Chapter 5 of Ref.2).

We next consider the operators  $\alpha$  and  $\beta$  which, in the Schrödinger representation, satisfy the commutation relation

$$[\alpha, \beta] = i\gamma \quad (84)$$

or

$$\alpha\beta - \beta\alpha = i\gamma \quad (85)$$

If we multiply on the left by  $e^{iHt/\hbar}$  and on the right by  $e^{-iHt/\hbar}$ , we obtain

$$\begin{aligned} &e^{iHt/\hbar} \alpha \ e^{-iHt/\hbar} e^{-iHt/\hbar} \beta e^{-iHt/\hbar} \\ &\quad - e^{iHt/\hbar} \beta e^{-iHt/\hbar} e^{iHt/\hbar} \alpha e^{-iHt/\hbar} \\ &= i e^{iHt/\hbar} \gamma e^{-iHt/\hbar} \end{aligned} \quad (86)$$

where we have inserted  $e^{-iHt/\hbar} e^{iHt/\hbar}$  ( $= 1$ ) between  $\alpha$  and  $\beta$ . Using Eq. (80), we get

$$[\alpha_H(t), \beta_H(t)] = i\gamma_H(t) \quad (87)$$

which shows the physical equivalence of Heisenberg and Schrödinger pictures.

As an illustration we consider the harmonic oscillator problem. However, before we do so, we note that

$$[x, p^n] = i \hbar n p^{n-1} = i \hbar \frac{\partial}{\partial p} p^n \quad (88)$$

and

$$[p, x^n] = -i \hbar n x^{n-1} = -i \hbar \frac{\partial}{\partial x} x^n \quad (89)$$

Thus if  $P(p)$  and  $X(x)$  can be expanded in a power series in  $p$  and  $x$  respectively we will have

$$[X, P(p)] = i \hbar \frac{\partial P}{\partial p} \quad (90)$$

and

$$[p, X(x)] = -i \hbar \frac{\partial X}{\partial x} \quad (91)$$

#### *Harmonic oscillator problem*

Now for the harmonic oscillator problem

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 = H_H = \frac{p_H^2(t)}{2m} + \frac{1}{2} m \omega^2 x_H^2(t) \quad (92)$$

where we have used Eq. (83). Thus, using Eq. (83)

$$\frac{d}{dt} x_H(t) = \frac{1}{i \hbar} [x_H, H_H] = \frac{\partial H_H}{\partial p} = \frac{p_H(t)}{m} \quad (93)$$

and

$$\frac{d}{dt} p_H(t) = \frac{1}{i \hbar} [p_H(t), H_H] = -\frac{\partial H_H}{\partial x} = -m \omega^2 x_H(t) \quad (94)$$

These are the Hamilton's equations of motion (see e.g. Ref.3). The solution of the above equations are

$$x_H(t) = x \cos \omega t + \frac{p}{m \omega} \sin \omega t \quad (95)$$

$$p_H(t) = -m \omega x \sin \omega t + p \cos \omega t \quad (96)$$

where  $x = x_H(t = 0)$  and  $p = p_H(t = 0)$  represent the operators in the Schrödinger representation. Further,

$$\begin{aligned} a_H(t) &= \frac{1}{(2m \hbar \omega)^{1/2}} (m \omega x_H(t) + i p_H(t)) \\ &= a e^{-i \omega t} \end{aligned} \quad (97)$$

where  $a = a_H(t = 0)$ . Similarly

$$\bar{a}_H(t) = \bar{a} e^{i\omega t} \quad (98)$$

These relations will be used in Chapter 27.

## 12.10. The density operator

Let the kets  $|0\rangle, |1\rangle, |2\rangle, \dots |n\rangle, \dots$  form a complete set of orthonormal kets; i.e.

$$\sum_n |n\rangle \langle n| = 1 \quad (99)$$

and

$$\langle m|n\rangle = \delta_{mn} \quad (100)$$

An arbitrary ket  $|P\rangle$  can be expanded in terms of the ket  $|n\rangle$

$$|P\rangle = \sum_n c_n |n\rangle; \quad c_n = \langle n|P\rangle \quad (101)$$

A state can be characterised by the density operator  $\rho$  defined by the following equation

$$\rho = |P\rangle \langle P| \quad (102)$$

### *Trace of an operator*

The trace<sup>2</sup> of an operator is defined to be equal to the sum of the diagonal matrix elements for any complete set of states; thus

$$Tr O = \sum_n \langle n|O|n\rangle \quad (103)$$

Hence

$$\begin{aligned} Tr(|P\rangle \langle Q|) &= \sum_n \langle n|P\rangle \langle Q|n\rangle \\ &= \langle Q| \left\{ \sum_n |n\rangle \langle n| \right\} |P\rangle \end{aligned}$$

or

$$Tr(|P\rangle \langle Q|) = \langle Q|P\rangle \quad (104)$$

where in the last step we have used Eq. (27). Thus

$$Tr \rho = Tr|P\rangle \langle P| = \langle P|P\rangle = 1 \quad (105)$$

---

<sup>2</sup> Abbreviated as *Tr*.

where we have assumed  $|P\rangle$  to be normalized. Also

$$\rho_{nn} = \langle n | P \rangle \langle P | n \rangle = |c_n|^2$$

implying that the diagonal matrix elements of the density operator represent the probabilities of the system in the base states.

### *Expectation value*

Now, the expectation value of the operator  $O$  is given by

$$\begin{aligned} \langle O \rangle &= \langle P | O | P \rangle = \sum_n \langle P | O | n \rangle \langle n | P \rangle \\ &= \sum_n \langle n | P \rangle \langle P | O | n \rangle \\ &= \sum_n \langle n | \rho O | n \rangle \\ &= \text{Tr}(\rho O) \end{aligned} \quad (106)$$

Perhaps the most important application of the density operator is in the field of statistical mechanics where we consider an ensemble of a large number of identical systems; each system may be in a different quantum state (see, e.g. Ref. 4).

If  $W_\Psi$  represents the probability of finding the system in the state characterized by  $|\Psi\rangle$ , then the corresponding density operator is given by

$$\rho = \sum_\Psi W_\Psi |\Psi\rangle \langle \Psi| \quad (107)$$

where the summation is carried over all possible states of the system; the density operator contains all the information about the ensemble. Obviously, since

$$\sum_\Psi W_\Psi = 1 \quad (108)$$

we have

$$\begin{aligned} \text{Tr } \rho &= \sum_\Psi W_\Psi \text{Tr} |\Psi\rangle \langle \Psi| \\ &= \sum_\Psi W_\Psi \langle \Psi | \Psi \rangle \\ &= \sum_\Psi W_\Psi = 1 \end{aligned} \quad (109)$$

### *Radiation field inside a cavity*

As an example, we consider the radiation field at thermal equilibrium (at temperature  $T$ ) inside a cavity. We will show in Chapter 27 that the radiation field can

be visualized as consisting of an infinite number of simple harmonic oscillators. The energy of each oscillator can decrease or increase by integral multiples of  $\hbar\omega_\lambda$ ; if we consider  $\hbar\omega_\lambda$  as the energy of a photon, then each oscillator can have energy corresponding to  $n_\lambda$  photons. Restricting ourselves to a particular mode (i.e. to a particular frequency which we will denote by  $\omega$ ), the probability of finding  $n$  photons (i.e. the probability of finding the system in the  $n^{\text{th}}$  excited state) is proportional to

$$\exp\left(-\frac{E_n}{kT}\right) = \exp\left[-\frac{(n + \frac{1}{2})\hbar\omega}{kT}\right]$$

Thus

$$\begin{aligned} W_n &= \frac{\exp\left[-\frac{(n + \frac{1}{2})\hbar\omega}{kT}\right]}{\sum_{n=0,1,\dots} \exp\left[-\frac{(n + \frac{1}{2})\hbar\omega}{kT}\right]} = \frac{\exp[-n\xi]}{1 + e^{-\xi} + e^{-2\xi} + \dots} \\ &= \frac{e^{-n\xi}}{1/(1 - e^{-\xi})} = e^{-n\xi} (1 - e^{-\xi}) \end{aligned} \quad (110)$$

where  $\xi = \hbar\omega/kT$ . Thus

$$\begin{aligned} \rho &= [1 - e^{-\xi}] \sum_n e^{-n\xi} |n\rangle\langle n| \\ &= [1 - e^{-\xi}] \sum_n e^{-\xi\bar{a}a} |n\rangle\langle n| \\ &\quad (\text{because } \bar{a}a \text{ is the number operator, see Sec. 12.7}) \\ &= [1 - e^{-\xi}] e^{-\xi\bar{a}a} \sum_n |n\rangle\langle n| \end{aligned}$$

or

$$\rho = [1 - e^{-\xi}] e^{-\xi\bar{a}a} \quad (111)$$

The above equation can be put in the form

$$\rho = \frac{e^{-\beta H}}{\text{Tr}(e^{-\beta H})}, \quad \beta = \frac{1}{kT} \quad (112)$$

where  $H$  represents the Hamiltonian of the system.

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## 12.11. Problems

**Problem 12.1** Show that

$$\langle n | \frac{1}{2}\mu\omega^2x^2 | n \rangle = \langle n | \frac{p^2}{2\mu} | n \rangle$$

implying that the expectation values of the potential and kinetic energies are equal.

**Problem 12.2** Using Eqs (25) and (26) evaluate the matrix elements

$$\langle m | a | n \rangle \quad \text{and} \quad \langle m | \bar{a} | n \rangle$$

Write the matrices representing  $a$  and  $\bar{a}$  and show that they are not Hermitian.

**Problem 12.3** Using Eqs (30) and (31) and the results of the previous problem show that

$$\langle m | x | n \rangle = \begin{cases} \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} \sqrt{n+1} & \text{for } m = n + 1 \\ \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} \sqrt{n} & \text{for } m = n - 1 \\ 0 & \text{otherwise} \end{cases}$$

and

$$\langle m | p | n \rangle = \begin{cases} i \left(\frac{\mu\hbar\omega}{2}\right)^{1/2} \sqrt{n+1} & \text{for } m = n + 1 \\ -i \left(\frac{\mu\hbar\omega}{2}\right)^{1/2} \sqrt{n} & \text{for } m = n - 1 \\ 0 & \text{otherwise} \end{cases}$$

Write the matrices representing  $x$  and  $p$  and show that they are both Hermitian.

**Problem 12.4 (a)** Show that

$$\langle m | x^2 | n \rangle = \begin{cases} \frac{\hbar}{2\mu\omega} \sqrt{(n+1)(n+2)} & \text{for } m = n + 2 \\ \frac{\hbar}{2\mu\omega} (2n+1) & \text{for } m = n \\ \frac{\hbar}{2\mu\omega} \sqrt{n(n-1)} & \text{for } m = n - 2 \\ 0 & \text{otherwise} \end{cases}$$

**(b)** Similarly evaluate  $\langle m | p^2 | n \rangle$  and show that

$$\langle m | \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2x^2 | n \rangle = \left(n + \frac{1}{2}\right)\hbar\omega\delta_{mn}$$

(The above result follows directly from the fact that  $|n\rangle$  are the orthonormal eigenkets of  $H$ ; thus the matrix representing  $H$  would be diagonal with diagonal elements representing the energy eigenvalues).

**Problem 12.5** Show that

$$\langle n | x^4 | n \rangle = \frac{3}{2} \left( \frac{\hbar}{\mu\omega} \right)^2 \left( n^2 + n + \frac{1}{2} \right)$$

**Problem 12.6** Show that the operator  $\bar{a}$  cannot have any eigenkets and similarly the operator  $a$  cannot have any eigenbras.

**[Hint:** Write the eigenvalue equation and express the eigenket as a linear combination of  $|n\rangle$ ; similarly, express the eigenbra as a linear combination of  $\langle n|$ ].

**Problem 12.7 (a)** Let

$$\langle n \rangle = \langle \alpha | N_{op} | \alpha \rangle \quad (113)$$

represent the expectation value of the number operator  $N_{op}$  ( $= \bar{a}a$ ) corresponding to the coherent state. Show that

$$\langle n \rangle = |\alpha|^2 \quad (114)$$

and

$$|\alpha\rangle = e^{-\langle n \rangle / 2} \sum_{n=0,1,2,\dots}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle \quad (115)$$

**(b)** If we write

$$\xi_0 = \sqrt{2}\alpha \quad (116)$$

show that the above equations are the same as given by Eqs (56), (57) and (113) of Chapter 7.

**Problem 12.8** Using Eqs (58) and (59) and assuming  $\alpha$  to be real, prove

$$\langle \Psi(t) | x^2 | \Psi(t) \rangle = x_0^2 \cos^2 \omega t + \frac{1}{2\gamma^2} \quad (117)$$

$$\langle \Psi(t) | p^2 | \Psi(t) \rangle = p_0^2 \sin^2 \omega t + \frac{1}{2} \gamma^2 \hbar^2 \quad (118)$$

$$\langle \Psi(t) | H | \Psi(t) \rangle = \frac{1}{2} \xi_0^2 + \frac{1}{2} \hbar \omega \quad (119)$$

$$\langle \Psi(t) | N_{op} | \Psi(t) \rangle = \frac{1}{2} \xi_0^2 \quad (120)$$

$$\langle \Psi(t) | N_{op}^2 | \Psi(t) \rangle = \left( \frac{1}{2} \xi_0^2 \right)^2 + \frac{1}{2} \xi_0^2 \quad (121)$$

$$\begin{aligned} \Delta n &= [\langle N_{op}^2 \rangle - \langle N_{op} \rangle^2]^{1/2} \\ &= \frac{1}{\sqrt{2}} \xi_0 = \sqrt{\langle n \rangle} \end{aligned} \quad (122)$$

where

$$\xi_0 \left( = \sqrt{2} \alpha \right) = \gamma x_0 \quad (123)$$

Show that the above equations are the same as derived in Sec. 7.5.

**Problem 12.9** Prove Eq. (45) by induction.

**Problem 12.10** For a two-dimensional isotropic oscillator

$$H = \frac{1}{2\mu} (p_x^2 + p_y^2) + \frac{1}{2} \mu \omega^2 (x^2 + y^2) \quad (124)$$

Show that

$$H = (a_1 \bar{a}_1 + a_2 \bar{a}_2 + 1) \hbar \omega \quad (125)$$

where

$$a_1 = \frac{1}{\sqrt{2\mu \hbar \omega}} (\mu \omega x + i p_x) \quad (126)$$

and

$$a_2 = \frac{1}{\sqrt{2\mu \hbar \omega}} (\mu \omega y + i p_y) \quad (127)$$

Show that the eigenvalues would be  $\hbar \omega, 2 \hbar \omega, \dots$  and will be  $n$ -fold degenerate.

**Problem 12.11** If  $|\alpha\rangle$  and  $|\beta\rangle$  are eigenkets of the operator  $a$  belonging to the eigenvalues  $\alpha$  and  $\beta$  respectively, then show that

$$|\langle \alpha | \beta \rangle|^2 = e^{-|\alpha - \beta|} \quad (128)$$

The above equation shows that the eigenkets are not orthogonal.

**Problem 12.12**

(a) Show that

$$|\alpha\rangle = e^{-\alpha^2/2} e^{\alpha \bar{a}} |0\rangle$$

(b) If

$$|\Psi(t=0)\rangle = |\alpha\rangle$$

then show that

$$|\Psi(t)\rangle = e^{-i\omega_0 t/2} e^{-\alpha^2/2} e^{\alpha e^{i\omega_0 t} \bar{a}} |0\rangle$$

[Hint:  $|\Psi(t)\rangle = e^{-iHt/\hbar} |\Psi(0)\rangle$  and use Eq. (8) for  $H$ ].

## 12.12. Solutions

### Solution 12.2

$$\langle m | a | n \rangle = \sqrt{n} \langle m | n - 1 \rangle = \sqrt{n} \delta_{m, n-1} \quad (129)$$

and

$$\langle m | \bar{a} | n \rangle = \sqrt{n+1} \langle m | n + 1 \rangle = \sqrt{n+1} \delta_{m, n+1} \quad (130)$$

Thus the matrices which represent  $a$  and  $\bar{a}$  are

$$a = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & 0 & 0 & \sqrt{3} & 0 & \dots \\ 0 & 0 & 0 & 0 & \sqrt{4} & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \dots \end{pmatrix} \quad (131)$$

and

$$\bar{a} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \dots \end{pmatrix} \quad (132)$$

which are non-Hermitian matrices.

**Solution 12.8** We will evaluate  $\langle \Psi(t) | p^2 | \Psi(t) \rangle$ ; other expectation values can be evaluated in a similar manner. Using Eq. (59)

$$\begin{aligned} \langle \Psi(t) | p^2 | \Psi(t) \rangle &= -\frac{\mu \hbar \omega}{2} \langle \Psi(t) | (a - \bar{a})(a - \bar{a}) | \Psi(t) \rangle \\ &= -\frac{\mu \hbar \omega}{2} [\langle \Psi(t) | a a | \Psi(t) \rangle \\ &\quad - \langle \Psi(t) | a \bar{a} | \Psi(t) \rangle \\ &\quad - \langle \Psi(t) | \bar{a} a | \Psi(t) \rangle \\ &\quad + \langle \Psi(t) | \bar{a} \bar{a} | \Psi(t) \rangle] \end{aligned} \quad (133)$$

Now using Eqs (57) and (61)

$$\begin{aligned}
 & \langle \Psi(t) | a a | \Psi(t) \rangle \\
 &= e^{-\alpha^2} \sum_{m=0,1,2,\dots}^{\infty} \sum_{n=0,1,2,\dots}^{\infty} \frac{\alpha^{m+n}}{\sqrt{m!n!}} e^{i(m-n)\omega t} \langle m | a a | n \rangle \\
 &= e^{-\alpha^2} \sum_{m=0,1,\dots}^{\infty} \sum_{n=2,3,\dots}^{\infty} \frac{\alpha^{m+n}}{\sqrt{m!n!}} e^{i(m-n)\omega t} \sqrt{n(n-1)} \delta_{m,n-2} \\
 &= e^{-\alpha^2} \sum_{m=0,1,2,\dots}^{\infty} \frac{\alpha^{2m+2}}{m!} e^{-2i\omega t} \\
 &= \alpha^2 e^{-2i\omega t}
 \end{aligned} \tag{134}$$

If we take the complex conjugate of the above equation, we would get

$$\langle \Psi(t) | \bar{a} \bar{a} | \Psi(t) \rangle = \alpha^2 e^{2i\omega t} \tag{135}$$

Similarly

$$\langle \Psi(t) | a \bar{a} | \Psi(t) \rangle = 1 + \alpha^2 \tag{136}$$

and

$$\langle \Psi(t) | \bar{a} a | \Psi(t) \rangle = \alpha^2 \tag{137}$$

Thus

$$\begin{aligned}
 \langle \Psi(t) | p^2 | \Psi(t) \rangle &= -\frac{\mu \hbar \omega}{2} [2\alpha^2 \cos 2\omega t - 1 - 2\alpha^2] \\
 &= 2\mu \hbar \omega \alpha^2 \sin^2 \omega t + \frac{\mu \hbar \omega}{2} \\
 &= p_0^2 \sin^2 \omega t + \frac{1}{2} \gamma^2 \hbar^2
 \end{aligned} \tag{138}$$

where

$$p_0 = \sqrt{2\mu \hbar \omega} \alpha \tag{139}$$

consistent with Eq. (66).

**Solution 12.9** We assume Eq. (45) to be valid so that

$$\begin{aligned}
 \psi_{n+1}(x) &= \frac{1}{[2(n+1)]^{1/2}} \left[ \frac{\gamma}{2^n n! \sqrt{\pi}} \right]^{1/2} \left( \xi - \frac{d}{d\xi} \right) \left[ H_n(\xi) e^{-\xi^2/2} \right] \\
 &= \left[ \frac{\gamma}{2^{n+1} (n+1)! \sqrt{\pi}} \right]^{1/2} [2\xi H_n(\xi) - H_n'(\xi)] e^{-\xi^2/2}
 \end{aligned} \tag{140}$$

Now, if we use the well-known recurrence relations

$$2\xi H_n(\xi) = 2n H_{n-1}(\xi) + H_{n+1}(\xi) \tag{141}$$

and

$$H_n'(\xi) = 2n H_{n-1}(\xi) \quad (142)$$

we readily get

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - H_n'(\xi) \quad (143)$$

Equation (140) therefore becomes

$$\psi_{n+1}(x) = \left[ \frac{\gamma}{2^{n+1} (n+1)! \sqrt{\pi}} \right]^{1/2} H_{n+1}(\xi) e^{-\xi^2/2} \quad (144)$$

Thus if Eq. (45) is valid then Eq. (144) must also be valid. Since Eq. (45) is valid for  $n = 0, 1$  and  $2$  [see Eqs (42)–(44)], it must be valid for all integer values of  $n$ .

Thus, we have been able to derive the normalized Hermite-Gauss functions in a very straightforward manner.

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### 12.13. Sample questions

Q. 1 In the linear harmonic oscillator problem, let  $|n\rangle$  represent the set of orthonormal eigenkets of  $H$ .

a) Evaluate

$$\langle 4 | x^2 | 6 \rangle, \quad \langle 5 | p^2 | 6 \rangle$$

b) Are  $|0\rangle$ ,  $|1\rangle$  and  $|2\rangle$  eigenkets of  $a$ ?

c) Evaluate (i)  $H[\bar{a} \bar{a} |n\rangle]$ , (ii)  $H[aa |n\rangle]$

d) If

$$|\Psi(t=0)\rangle = \frac{1}{\sqrt{2}}[|1\rangle + i|3\rangle]$$

then what would be  $|\Psi(t)\rangle$ ?

[Ans: (b) Only  $|0\rangle$  is an eigenket of  $a$ .

(c) (ii)  $\sqrt{n(n-1)}(n-\frac{5}{2})\hbar\omega|n\rangle$ .]

Q. 2 At  $t = 0$ , the linear harmonic oscillator is in the coherent state given by

$$|\Psi(t=0)\rangle = |\alpha\rangle = \sum c_n |n\rangle$$

a)

$$c_n = \frac{\alpha^n}{\sqrt{n!}} c_0$$

- b) Normalize  $|\alpha\rangle$  and determine  $c_0$ .  
 c) What would be  $|\Psi(t)\rangle$ ?  
 d) Assume  $\alpha$  to be real and calculate

$$\langle \Psi(t) | p | \Psi(t) \rangle$$

$$\langle \Psi(t) | x | \Psi(t) \rangle$$

$$\langle \Psi(t) | a | \Psi(t) \rangle$$

and

$$\langle \Psi(t) | \bar{a} | \Psi(t) \rangle$$


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## 12.14. References and suggested reading

1. P.A.M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press, Oxford (1958).
2. G. Baym, *Lectures on Quantum Mechanics*, W.A. Benjamin, New York (1969).
3. H. Goldstein, *Classical Mechanics*, Addison-Wesley Publishing Co., Reading, Massachusetts (1950).
4. W.H. Louisell, *Quantum Statistical Properties of Radiation*, John Wiley, New York (1973).

# Chapter 13

## Angular Momentum II Using Bra and Ket Algebra

*In a one-page letter to the Editor of Naturwissenschaften dated 17 October 1925, Samuel A. Goudsmit and I proposed the idea that each electron rotates with an angular momentum  $\hbar/2$  and carries, besides its charge  $e$ , a magnetic moment equal to one Bohr magneton<sup>1</sup>,  $e\hbar/2mc\dots$*

— GEORGE E. UHLENBECK in *Fifty Years of Spin: Personal Reminiscences*, Physics Today, p. 43, June 1976.

### 13.1. Introduction

In Chapter 9 we had introduced the quantum mechanical angular momentum operator  $\mathbf{L}$  and had shown that its components satisfy the following commutation relations:

$$\begin{aligned} [L_x, L_y] &= i\hbar L_z \\ [L_y, L_z] &= i\hbar L_x \\ [L_z, L_x] &= i\hbar L_y \end{aligned} \quad (1)$$

We had also shown that the square of the angular momentum operator  $L^2 (\equiv L_x^2 + L_y^2 + L_z^2)$  commutes with  $L_x$ ,  $L_y$  and  $L_z$ ; i.e.

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0 \quad (2)$$

In this chapter we will use just these commutation relations (and basic axioms of quantum mechanics) to show that if one makes a measurement of a Cartesian component of the angular momentum operator then it will always be an integral or a half integral multiple of  $\hbar$ , a result which is one of the remarkable features of quantum mechanics. It may be mentioned that in Chapter 9 we had shown that  $L_z$  (and similarly  $L_x$  and  $L_y$ ) can only have eigenvalues  $0, \hbar, 2\hbar, \dots$

<sup>1</sup> Using CGS units, the value of one Bohr magneton is  $e\hbar/2mc$ ; in MKS units, the value is  $e\hbar/2m$ . See also Sec. 14.5.

In Sec. 13.2 we will obtain the eigenvalues of a Cartesian component of the angular momentum operator and of the square of the angular momentum operator. In Sec. 13.3 we will consider the representation of the angular momentum operator in terms of matrices and discuss their significance. In Secs. 13.4 and 13.5 we will derive the angular momentum matrices for  $j = \frac{1}{2}$  and  $j = 1$ . In the next chapter we will discuss the famous Stern-Gerlach experiment which demonstrated the quantization of angular momentum.

### 13.2. Eigenvalues

In this section we will use the commutation relations [see Eqs (1) and (2)] to determine the eigenvalues of a particular component of the angular momentum operator. For reasons to be discussed later, we will denote the angular momentum operator by  $\mathbf{J}$  and use a system of units in which  $\hbar = 1$ . Thus, Eqs (1) and (2) become

$$[J_x, J_y] = i J_z \quad (3)$$

$$[J^2, J_z] = 0 \quad (4)$$

and other equations can be written in cyclic order.

It is convenient to use the Dirac notation introduced in Chapter 11. Since  $J^2$  and  $J_z$  commute, we can construct a complete set of orthonormal eigenkets which are simultaneous eigenkets of the operators  $J^2$  and  $J_z$  belonging to the eigenvalues  $\lambda$  and  $m$  respectively (see Sec. 11.8). Thus,

$$J^2 |\lambda, m\rangle = \lambda |\lambda, m\rangle \quad (5)$$

$$J_z |\lambda, m\rangle = m |\lambda, m\rangle \quad (6)$$

*Ladder operators*

We define the *ladder operators*

$$J_+ = J_x + i J_y \quad (7)$$

and

$$J_- = J_x - i J_y \quad (8)$$

Now

$$\begin{aligned} [J_z, J_+] &= [J_z, J_x] + i [J_z, J_y] \\ &= i J_y + J_x = J_+ \end{aligned}$$

Thus

$$[J_z, J_+] = J_+ \quad (9)$$

Similarly

$$[J_z, J_-] = -J_- \quad (10)$$

We also have

$$J_+ J_- = J_x^2 + J_y^2 - i [J_x, J_y]$$

or

$$J_+ J_- = J^2 - J_z^2 + J_z \quad (11)$$

Similarly

$$J_- J_+ = J^2 - J_z^2 - J_z \quad (12)$$

Further

$$\overline{J_+} = J_- \quad (13)$$

and

$$\overline{J_-} = J_+ \quad (14)$$

i.e.  $J_-$  and  $J_+$  are adjoints of  $J_+$  and  $J_-$  respectively. In writing Eqs (13) and (14) we have used the fact that since  $J_x$ ,  $J_y$  and  $J_z$  are observables, they are represented by real operators:

$$\overline{J_x} = J_x, \quad \overline{J_y} = J_y, \quad \overline{J_z} = J_z$$

We first show that  $\lambda \geq m^2$ . Now

$$\begin{aligned} \langle P | J^2 - J_z^2 | P \rangle &= \langle P | J_x^2 + J_y^2 | P \rangle \\ &= \langle P | J_x J_x | P \rangle + \langle P | J_y J_y | P \rangle \\ &= \langle Q | Q \rangle + \langle R | R \rangle \geq 0 \end{aligned} \quad (15)$$

where

$$|Q\rangle = J_x |P\rangle, \quad |R\rangle = J_y |P\rangle$$

and since  $J_x$  and  $J_y$  are real operators

$$\langle Q | = \langle P | \overline{J_x} = \langle P | J_x \quad \text{and} \quad \langle R | = \langle P | \overline{J_y} = \langle P | J_y$$

In the last step of Eq. (15) we have used Eq. (25) of Chapter 11. If we choose  $|P\rangle = |\lambda, m\rangle$ , then

$$0 \leq \langle \lambda, m | J^2 - J_z^2 | \lambda, m \rangle = (\lambda - m^2) \langle \lambda, m | \lambda, m \rangle$$

Thus

$$\lambda \geq m^2 \quad (16)$$

We next consider the effect of the ladder operator on the ket  $|\lambda, m\rangle$ . Using Eq. (9) we get

$$J_z J_+ |\lambda, m\rangle = (J_+ + J_z J_z) |\lambda, m\rangle$$

or

$$J_z [J_+ | \lambda, m \rangle] = (m + 1) [J_+ | \lambda, m \rangle] \quad (17)$$

Further, since  $J^2$  commutes with  $J_x$  and  $J_y$  we will have

$$[J^2, J_{\pm}] = 0$$

or

$$J^2 J_{\pm} | \lambda, m \rangle = J_{\pm} J^2 | \lambda, m \rangle$$

or

$$J^2 [J_{\pm} | \lambda, m \rangle] = \lambda [J_{\pm} | \lambda, m \rangle] \quad (18)$$

Equations (17) and (18) tell us that  $J_+ | \lambda, m \rangle$  is a simultaneous eigenket of the operators  $J^2$  and  $J_z$  belonging to the eigenvalues  $\lambda$  and  $(m + 1)$ , provided  $J_+ | \lambda, m \rangle$  is not a null ket. Similarly, using Eq. (10) one can show

$$J_z [J_- | \lambda, m \rangle] = (m - 1) [J_- | \lambda, m \rangle] \quad (19)$$

implying that  $J_- | \lambda, m \rangle$  is a simultaneous eigenket of  $J^2$  and  $J_z$  belonging to the eigenvalues  $\lambda$  and  $(m - 1)$  respectively provided  $J_- | \lambda, m \rangle$  is not a null ket. We may, therefore, write

$$J_+ | \lambda, m \rangle = C_+ | \lambda, m + 1 \rangle \quad (20)$$

and

$$J_- | \lambda, m \rangle = C_- | \lambda, m - 1 \rangle \quad (21)$$

These equations show why  $J_{\pm}$  are called *ladder* operators;  $J_+$  is an operator that *raises* the eigenket to the next higher value of  $m$  and  $J_-$  is an operator that *lowers* the eigenket to the next lower value of  $m$ . In a similar manner we may argue that  $J_+ | \lambda, m + 1 \rangle$  and  $J_- | \lambda, m - 1 \rangle$  are proportional to  $| \lambda, m + 2 \rangle$  and  $| \lambda, m - 2 \rangle$  respectively. This, however, cannot go on indefinitely; otherwise we will violate the condition  $\lambda \geq m^2$ . Consequently, there must exist a particular value of  $m$ , say  $m = j$ , for which

$$J_+ | \lambda, j \rangle = 0 \quad (22)$$

Operating on the left by  $J_-$ , we obtain [using Eq. (12)]

$$(J^2 - J_z^2 - J_z) | \lambda, j \rangle = 0$$

or

$$(\lambda - j^2 - j) | \lambda, j \rangle = 0 \quad (23)$$

Since  $| \lambda, j \rangle \neq 0$ , the number  $\lambda - j^2 - j = 0$ ; and hence,<sup>2</sup>

$$\lambda = j(j + 1) \quad (24)$$

<sup>2</sup> The reader not yet attuned to operator algebra may pause here and reflect on Eqs (22) and (23) to see how we treat them differently. In Eq. (22) neither the operator  $J_+$  nor the ket  $| \lambda, j \rangle$  need be zero in order to produce a null ket. For example,  $\frac{d^2(x)}{dx^2} = 0$  does not permit us to identify either  $\frac{d^2}{dx^2}$  or  $x$  with a null quantity. But in Eq. (23), a ket is multiplied by a number and one of them must vanish.

We can determine the lowest value of  $m$ , say  $j'$ , by requiring

$$J_- |\lambda, j' \rangle = 0$$

Operating on the left by  $J_+$  and using Eq. (11) we obtain

$$(\lambda - j'^2 + j') = 0$$

or

$$\lambda = j'(j' - 1) \quad (25)$$

Using Eqs (24) and (25) we obtain

$$j'(j' - 1) = j(j + 1)$$

Thus either  $j' = j + 1$  (which we reject since  $j'$  is supposed to be less than  $j$ ), or

$$j' = -j \quad (26)$$

Thus, we have a family of kets which correspond to the same eigenvalue  $\lambda [= j(j + 1)]$  of  $J^2$  but different eigenvalues of  $J_z$ . These we denote by

$$|\lambda, j\rangle, |\lambda, j-1\rangle, \dots, |\lambda, -j\rangle \quad (27)$$

Successive application of the ladder operator  $J_-$  on  $|\lambda, j\rangle$  should ultimately lead to  $|\lambda, -j\rangle$ . (Also, successive application of  $J_+$  on  $|\lambda, -j\rangle$  should lead to  $|\lambda, j\rangle$ .) This will happen only if  $2j$  is an integer, so that the allowed values of  $j$  are

*Allowed values of  $j$*

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \quad (28)$$

and for each value of  $j$  the  $m$  values go from  $-j$  to  $j$  in steps of unity. Thus there are  $(2j + 1)$  eigenkets of  $J^2$ , each having the same eigenvalue  $j(j + 1)$ . We label the eigenkets as

$$|j, m\rangle ; m = -j, -j + 1, \dots, j - 1, j$$

with  $j = 0, 1/2, 1, 3/2, \dots$  The kets are assumed to satisfy the orthonormality condition

$$\langle j', m' | j, m \rangle = \delta_{jj'} \delta_{mm'} \quad (29)$$

Thus we obtain the important result that the Cartesian components of the angular momentum operator (say  $J_z$ ) can have half integral values. On the other hand, components of orbital angular momenta, defined as  $\mathbf{r} \times \mathbf{p}$ , can have only eigenvalues  $0, \hbar, 2\hbar, \dots$  etc. (see Sec. 9.3). The question arises whether nature provides

systems which do have values  $\frac{1}{2}\hbar$  for angular momenta. It is remarkable that the most elementary system known, the electron, is an example of this. Obviously we cannot write this spin angular momentum as an operator operating on the coordinates of the electron. Spin has no classical analogue and is introduced in non-relativistic theory in an ad hoc manner; the relativistic Dirac theory provides a natural explanation of this. The suggestion about spin came from a study of Zeeman patterns from which it appeared that the  $(2l + 1)$  multiplicity of levels often turned out to be even. We may mention here that an attempt was made to attribute spin to the rotation of the electron about its axis but this exercise proved abortive.

### 13.3. The constants $C_+$ and $C_-$

We now determine the normalization constants  $C_+$  and  $C_-$ . First, we note that if we define

$$| P \rangle = J_+ | j, m \rangle = C_+ | j, m + 1 \rangle$$

then

$$\langle P | = \langle j, m | J_- = C_+^* \langle j, m + 1 | \quad (\text{since } \overline{J_+} = J_-)$$

Thus

$$\langle P | P \rangle = \langle j, m | J_- J_+ | j, m \rangle = |C_+|^2 \langle j, m + 1 | j, m + 1 \rangle$$

But

$$\begin{aligned} \langle j, m | J_- J_+ | j, m \rangle &= \langle j, m | J^2 - J_z^2 - J_z | j, m \rangle \\ &= j(j+1) - m^2 - m = (j-m)(j+m+1) \end{aligned}$$

Hence

$$C_+ = [(j-m)(j+m+1)]^{\frac{1}{2}}$$

or

$$J_+ | j, m \rangle = [(j-m)(j+m+1)]^{\frac{1}{2}} | j, m + 1 \rangle \quad (30)$$

Similarly

$$J_- | j, m \rangle = [(j+m)(j-m+1)]^{\frac{1}{2}} | j, m - 1 \rangle \quad (31)$$

Notice that the coefficients in front of  $| j, m + 1 \rangle$  and  $| j, m - 1 \rangle$  are zero for  $m = +j$  and  $m = -j$  respectively. Thus

$$J_+ | j, j \rangle = 0 \quad (32)$$

and

$$J_- | j, -j \rangle = 0 \quad (33)$$

### 13.4. Angular momentum matrices corresponding to $j = \frac{1}{2}$ and the Pauli spin matrices

We will consider the matrix representation of the components of the angular momentum operator (corresponding to  $j = \frac{1}{2}$ ) in a system in which  $J^2$  and  $J_z$  are diagonal, i.e. we will choose as basis vectors the simultaneous eigenfunctions of  $J^2$  and  $J_z$ . Now, corresponding to  $j = \frac{1}{2}$  we have  $m = \frac{1}{2}$  and  $-\frac{1}{2}$ ; thus we have two base states which we denote by  $| 1 \rangle$  and  $| 2 \rangle$ :

*Base states*

$$| 1 \rangle = | \frac{1}{2}, \frac{1}{2} \rangle = | j = \frac{1}{2}, m = \frac{1}{2} \rangle \quad (34)$$

and

$$| 2 \rangle = | \frac{1}{2}, -\frac{1}{2} \rangle = | j = \frac{1}{2}, m = -\frac{1}{2} \rangle \quad (35)$$

Obviously

$$\left. \begin{aligned} J_z | 1 \rangle &= \frac{1}{2} \hbar | 1 \rangle, & J_z | 2 \rangle &= -\frac{1}{2} \hbar | 2 \rangle \\ J^2 | 1 \rangle &= \frac{3}{4} \hbar^2 | 1 \rangle, & J^2 | 2 \rangle &= \frac{3}{4} \hbar^2 | 2 \rangle \end{aligned} \right\} \quad (36)$$

The  $(i, j)^{th}$  matrix element of an operator  $\mathcal{O}$  is defined by

$$\mathcal{O}_{ij} = \langle i | \mathcal{O} | j \rangle$$

Consequently

$$(J_z)_{12} = \langle 1 | J_z | 2 \rangle = 0 = \langle 2 | J_z | 1 \rangle = (J_z)_{21}$$

$$(J_z)_{11} = \langle 1 | J_z | 1 \rangle = \frac{1}{2} \hbar, \quad (J_z)_{22} = \langle 2 | J_z | 2 \rangle = -\frac{1}{2} \hbar$$

Similarly

$$(J^2)_{12} = (J^2)_{21} = 0$$

and

$$(J^2)_{11} = (J^2)_{22} = \frac{3}{4} \hbar^2$$

Now

$$\begin{aligned} \langle j, m | J_x | j, m \rangle &= \langle j, m | \frac{1}{2} [J_+ + J_-] | j, m \rangle \\ &= \frac{1}{2} [(j+m+1)(j-m)]^{\frac{1}{2}} \hbar \langle j, m' | j, m+1 \rangle \\ &\quad + \frac{1}{2} [(j+m)(j-m+1)]^{\frac{1}{2}} \hbar \langle j, m' | j, m-1 \rangle \\ &= \frac{1}{2} [(j+m+1)(j-m)]^{\frac{1}{2}} \hbar \delta_{m',m+1} \\ &\quad + \frac{1}{2} [(j+m)(j-m+1)]^{\frac{1}{2}} \hbar \delta_{m',m-1} \end{aligned}$$

i.e. the matrix element is zero unless  $m' = m + 1$  or  $m' = m - 1$ . Thus

$$(J_x)_{11} = \langle 1 | J_x | 1 \rangle = \left\langle \frac{1}{2}, \frac{1}{2} | J_x | \frac{1}{2}, \frac{1}{2} \right\rangle = 0$$

and similarly  $(J_x)_{22} = 0$ . However,

$$\begin{aligned} (J_x)_{12} &= \langle 1 | J_x | 2 \rangle = \left\langle \frac{1}{2}, \frac{1}{2} | J_x | \frac{1}{2}, -\frac{1}{2} \right\rangle \\ &= \frac{1}{2} \left[ \left( \frac{1}{2} - \frac{1}{2} + 1 \right) \left( \frac{1}{2} + \frac{1}{2} \right) \right]^{\frac{1}{2}} \hbar = \frac{1}{2} \hbar = (J_x)_{21} \end{aligned}$$

Similarly

$$(J_y)_{11} = (J_y)_{22} = 0$$

$$(J_y)_{12} = -\frac{i}{2} \hbar \quad \text{and} \quad (J_y)_{21} = \frac{i}{2} \hbar$$

### *Pauli spin matrices*

Thus the angular momentum matrices for  $j = \frac{1}{2}$  are

$$\left. \begin{aligned} J_x &= \frac{1}{2} \hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, & J_y &= \frac{1}{2} \hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ J_z &= \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, & J^2 &= \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned} \right\} \quad (37)$$

We can also write

$$\mathbf{J} = \frac{1}{2} \hbar \boldsymbol{\sigma} \quad (38)$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (39)$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (40)$$

and

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (41)$$

are known as Pauli spin matrices. Further  $\sigma_x^2$ ,  $\sigma_y^2$ , and  $\sigma_z^2$  are all unit matrices. It may be noted that the Pauli spin matrices as well as  $J_x$ ,  $J_y$ ,  $J_z$  and  $J^2$  are all Hermitian. Further, the eigenvalues of  $J_x$ ,  $J_y$  and  $J_z$  are  $\pm \frac{1}{2} \hbar$  and  $-\frac{1}{2} \hbar$ . Thus, if we make a measurement of  $J_x$  (or  $J_y$  or  $J_z$ ) we will either get  $\pm \frac{1}{2} \hbar$  or  $-\frac{1}{2} \hbar$ .

*Spin up and spin down states*

Now, the simultaneous eigenfunctions of  $J^2$  and  $J_z$  are

$$| 1 \rangle = | \frac{1}{2}, \frac{1}{2} \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (42)$$

and

$$| 2 \rangle = | \frac{1}{2}, -\frac{1}{2} \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (43)$$

which are known as the spin up ( $| \uparrow \rangle$ ) and spin down ( $| \downarrow \rangle$ ) states. They are also denoted by  $| \hat{\mathbf{z}} \uparrow \rangle$  and  $| \hat{\mathbf{z}} \downarrow \rangle$  states implying that if the electron is in the state (say)  $| \hat{\mathbf{z}} \downarrow \rangle$  and if the  $z$ -component of the spin angular momentum is measured then the measurement will yield  $-\frac{1}{2}\hbar$ .

From the matrices representing  $J_x$  and  $J_y$ , one can calculate the corresponding eigenvalues and eigenvectors and one can immediately see that

$$| \hat{\mathbf{x}} \uparrow \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} | \hat{\mathbf{z}} \uparrow \rangle + \frac{1}{\sqrt{2}} | \hat{\mathbf{z}} \downarrow \rangle \quad (44)$$

$$| \hat{\mathbf{x}} \downarrow \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} | \hat{\mathbf{z}} \uparrow \rangle - \frac{1}{\sqrt{2}} | \hat{\mathbf{z}} \downarrow \rangle \quad (45)$$

We also have

$$| \hat{\mathbf{z}} \uparrow \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} | \hat{\mathbf{x}} \uparrow \rangle + \frac{1}{\sqrt{2}} | \hat{\mathbf{x}} \downarrow \rangle \quad (46)$$

and

$$| \hat{\mathbf{z}} \downarrow \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} | \hat{\mathbf{x}} \uparrow \rangle - \frac{1}{\sqrt{2}} | \hat{\mathbf{x}} \downarrow \rangle \quad (47)$$

Thus if a system is in the  $| \hat{\mathbf{z}} \uparrow \rangle$  state and if one makes a measurement of  $J_x$ , then the probability of obtaining the value  $+\frac{1}{2}\hbar$  is  $\frac{1}{2}$  and the value  $-\frac{1}{2}\hbar$  is also  $\frac{1}{2}$ . This will become more explicit when we discuss the Stern-Gerlach experiment in the next chapter.

Similarly one can write down for the  $| \hat{\mathbf{y}} \uparrow \rangle$  and  $| \hat{\mathbf{y}} \downarrow \rangle$  states in terms of  $| \hat{\mathbf{x}} \uparrow \rangle$  &  $| \hat{\mathbf{x}} \downarrow \rangle$  and  $| \hat{\mathbf{z}} \uparrow \rangle$  &  $| \hat{\mathbf{z}} \downarrow \rangle$  states.

### 13.5. Angular momentum matrices for $j = 1$

In this section we will derive the angular momentum matrices corresponding to  $j = 1$ ; the procedure will be similar to that in the previous section. Now, for  $j = 1$

we have  $m = 1, 0$  and  $-1$ ; thus we have three base states which we denote by  $| 1 \rangle$ ,  $| 2 \rangle$  and  $| 3 \rangle$ :

$$\begin{aligned} | 1 \rangle &= | j = 1, m = 1 \rangle = | 1, 1 \rangle \\ | 2 \rangle &= | j = 1, m = 0 \rangle = | 1, 0 \rangle \\ | 3 \rangle &= | j = 1, m = -1 \rangle = | 1, -1 \rangle \end{aligned}$$

Obviously

$$\begin{aligned} J_z | 1 \rangle &= \hbar | 1 \rangle \\ J_z | 2 \rangle &= 0 \\ J_z | 3 \rangle &= -\hbar | 1 \rangle \end{aligned}$$

and

$$\begin{aligned} J_z^2 | 1 \rangle &= 2\hbar^2 | 1 \rangle \\ J_z^2 | 2 \rangle &= 2\hbar^2 | 2 \rangle \\ J_z^2 | 3 \rangle &= 2\hbar^2 | 3 \rangle \end{aligned}$$

Thus when the base kets are  $| 1 \rangle$ ,  $| 2 \rangle$  and  $| 3 \rangle$ , the matrices representing  $J^2$  and  $J_z$  are diagonal and are given by

*Matrix representing  $J_z$*

$$J_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (48)$$

and

*Matrix representing  $J^2$*

$$J^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (49)$$

Further

$$J_+ | 1 \rangle = 0 \quad (50)$$

$$J_+ | 2 \rangle = \sqrt{2}\hbar | 1 \rangle \quad (51)$$

$$J_+ | 3 \rangle = \sqrt{2}\hbar | 2 \rangle \quad (52)$$

and

$$J_- | 1 \rangle = \sqrt{2}\hbar | 2 \rangle \quad (53)$$

$$J_- | 2 \rangle = \sqrt{2}\hbar | 3 \rangle \quad (54)$$

$$J_- | 3 \rangle = 0 \quad (55)$$

Thus, for example,

$$\begin{aligned}\langle 1 | J_x | 2 \rangle &= \frac{1}{2} \langle 1 | J_+ + J_- | 2 \rangle \\ &= \frac{1}{\sqrt{2}} \hbar\end{aligned}$$

Similarly other matrix elements can be calculated. The final result is

*Matrix representing  $J_x$*

$$J_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad (56)$$

Similarly,

*Matrix representing  $J_y$*

$$J_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad (57)$$

Finally,

$$| 1 \rangle = | 1, 1 \rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (58)$$

$$| 2 \rangle = | 1, 0 \rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad (59)$$

and

$$| 3 \rangle = | 1, -1 \rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (60)$$

### 13.6. The Pauli wavefunction and the Pauli equation

The electron is endowed with two internal degrees of freedom corresponding to values of  $\pm \frac{1}{2} \hbar$  for the component of its intrinsic angular momentum along a specified axis (say the  $z$ -axis). Accordingly, we need two wave functions to describe the state of an electron at each point in space. Writing them in matrix form, we have

$$\psi_P = \begin{pmatrix} \psi_+(x, y, z) \\ \psi_-(x, y, z) \end{pmatrix} \quad (61)$$

Such single column matrices are known as spinors<sup>3</sup> and the wave function is known as the Pauli wave function (hence the subscript  $P$  on  $\psi$ ). Writing

$$\psi_P = \psi_+ \chi_+ + \psi_- \chi_- = \psi_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (62)$$

we say that any spinor can be written as a linear combination of the basic spinors

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\hat{\mathbf{z}}\uparrow\rangle \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\hat{\mathbf{z}}\downarrow\rangle \quad (63)$$

Thus

$$\int |\psi_+|^2 d\tau \quad \text{and} \quad \int |\psi_-|^2 d\tau$$

would represent the probabilities of obtaining the  $|\hat{\mathbf{z}}\uparrow\rangle$  and  $|\hat{\mathbf{z}}\downarrow\rangle$  states respectively and we must have

$$\int |\psi_+|^2 d\tau + \int |\psi_-|^2 d\tau = 1 \quad (64)$$

Since the electron requires information regarding its spin as well as position coordinates, the Pauli wave function satisfies the equation

*Pauli equation*

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = H \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} \quad (65)$$

where  $H$  represents the Hamiltonian. For the hydrogen atom, in the absence of any interaction other than the Coulomb interaction,  $H$ , will be of the form

$$H \psi_P = \left[ -\frac{\hbar^2}{2m} \nabla^2 \cdot \mathbf{I} + V(\mathbf{r}) \cdot \mathbf{I} \right] \psi_P \quad (66)$$

where  $\mathbf{I}$  is the  $2 \times 2$  unit matrix. Thus  $\psi_+$  and  $\psi_-$  satisfy the same equation and the spin up and spin down states have the same energy. On the other hand, if we take into account the spin-orbit interaction,  $H$  will be of the form

$$H \psi_P = \left[ -\frac{\hbar^2}{2m} \nabla^2 \cdot \mathbf{I} + V(\mathbf{r}) \cdot \mathbf{I} + H' \right] \psi_P \quad (67)$$

---

<sup>3</sup> Spinors are characterized by special properties under rotations. We do not wish to leave the impression that they are just single column matrices.

where (see Sec. 20.5)

$$\begin{aligned}
 H' &= \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{s} \\
 &= \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \frac{1}{2} \hbar [L_x \sigma_x + L_y \sigma_y + L_z \sigma_z] \\
 &= \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \frac{1}{2} \hbar \begin{pmatrix} L_z & L_x - iL_y \\ L_x + iL_y & -L_z \end{pmatrix}
 \end{aligned} \tag{68}$$

which is known as the Pauli operator for  $H'$ . Obviously, now the equations for  $\psi_+$  and  $\psi_-$  will be coupled and one has to use perturbation theory to consider the effect of  $H'$ . This will be discussed in Problem 19.12.

### 13.7. Some historical remarks

In Sec. 13.2 we had shown that Cartesian components of the angular momentum operator can have values which are half integral multiples of  $\hbar$ . Indeed, it was in 1925 that G.E. Uhlenbeck and S. Goudsmit introduced the idea that an electron has a spin angular momentum of  $\pm \frac{1}{2} \hbar$ . May be it would be of interest to give a brief historical perspective of the development of the subject.

To quote Uhlenbeck,

*... He (Sam Goudsmit) had told me about Pauli's proposal to ascribe four quantum numbers to each electron. He now continued with the discussion of the famous paper of January 1925 in which Pauli formulated the exclusion principle; no two electrons could have the same **four** quantum numbers. . . . Sam himself had simplified the argument by introducing the quantum numbers,  $n$ ,  $l$ ,  $m_l$  and  $m_s$  instead of those used by Pauli, and he noticed that then  $m_s$  was always  $\pm 1/2$ .*

*I was impressed, but since the whole argument was purely formal, it seemed like abracadabra to me. There was no picture that at least qualitatively connected Pauli's formalism with the old Bohr atomic model. It was then that it occurred to me that, since (as I had learned) each quantum number corresponds to a degree of freedom of the electron, the fourth quantum number must mean that the electron had an additional degree of freedom—in other words, the electron must be rotating! Sam has written that he did not know at that time what a degree of freedom was. This may be so, as Sam had not done his exam in mechanics yet; in fact, he never passed this exam, and as a result he did not have the right to teach mechanics in the Dutch high schools even after he got his Ph.D. However, this did not prevent him later from teaching the graduate course in mechanics at the University of Michigan.*

gan, which he did regularly because he liked the subject so much; furthermore, it was much appreciated by the students.

In spite of this he appreciated right away that if the angular momentum of the electron was  $\hbar/2$ , one had a picture of the alkali doublets as the two ways the electron could rotate with respect to its orbital motion. In fact, if one assumed that the gyromagnetic ratio for the rotation was twice the classical value, so that the magnetic moment was

$$2 \frac{e}{2mc} \frac{\hbar}{2} = \text{one Bohr magneton}$$

then the properties formerly attributed to the core were now properties of the electron....

I remember that when this became clear to us, we had a feeling of euphoria, but we also both agreed that one could not possibly publish such stuff. Since it had not been mentioned by any of the authorities (we did not know about Kronig, of course) it must for some reason be nonsense. But, of course, we told Ehrenfest, who was immediately interested. I am not sure precisely what happened next. Sam is wrong when he writes that he was satisfied and did not think any more about how our model could be justified. I remember that he wrote me a postcard from Amsterdam very soon afterward, in which he asked whether I was sure that the gyromagnetic ratio had to be  $e/2mc$  classically—perhaps it was different for the rotation of an extended charged body. I showed this postcard to Ehrenfest, who then recalled a paper by Max Abraham about the magnetic properties of rotating electrons. I studied this paper very hard and found there to my great satisfaction that if the electron has only surface charge the gyromagnetic ratio was  $2e/2mc$ , just as we had postulated! I think that when I showed this to Ehrenfest he thought (as he told us later) that our idea was either very important or nonsense, but that it should be published. The Abraham calculations were nonrelativistic and based on the old-fashioned rigid electron, so that they were at best only suggestive. Anyway, Ehrenfest told us to write a short, modest Letter to Naturwissenschaften and to give it to him. “**Und dann werden wir Herrn Lorentz fragen.**” (“And then we will ask Mr. Lorentz.”) A letter of 16 October to H.A. Lorentz in which he mentions this (among other things) was found and shown to me by Martin Klein.

Lorentz, who was of course the great old man of Dutch physics, was retired and lived in Haarlem but gave a lecture in Leiden every Monday at 11:00 am, in which he discussed the recent developments in physics. Everybody who could possibly make it came. So when school started in the middle of October (remember, we had long vacations) I had the opportunity to tell Lorentz about our ideas. Sam was not present because he had to resume his duties at the Zeeman laboratory. Lorentz was very kind and interested, although I also got the impression that he was rather skeptical. He said that he would think about it and that we should talk again the next Monday.

*In fact, when we met that day he showed me a stack of papers full of calculations written in his beautiful handwriting, which he tried to explain to me. They were above my head but I understood enough to realize that there were serious difficulties. If the radius of the electron was*

$$r_0 = e^2 / mc^2$$

*and if it rotated with an angular momentum  $\hbar/2$ , then the surface velocity would be about ten times the light velocity! If the electron had a magnetic moment  $e\hbar/2mc$ , its magnetic energy would have to be so big that, to keep the mass  $m$ , its radius would have to be at least ten times  $r_0$ .*

*It seemed to me that if one extended the Abraham calculations properly as Lorentz had apparently done (and published in revised form), then our picture of a quantized rotation of the electron could not possibly be reconciled with classical electrodynamics. I told this to Ehrenfest, of course, and said that his second alternative had turned out to be the right one. The whole thing was nonsense, and it would be better that our Letter not be published. Then, to my surprise, Ehrenfest answered that he had already sent the Letter off quite a while ago, and that it would appear pretty soon. He added: “Sie sind beide jung genug um sich eine Dummheit leisten zu können!” (“You are both young enough to be able to afford a stupidity!”)*

*This is not yet the end of the story. Our letter appeared in the middle of November, and soon afterwards (21 November) Goudsmit received a letter from Heisenberg, whom he knew quite well. In this letter Heisenberg expressed his appreciation for Sam’s courageous idea and agreed that it would remove all of the difficulties of the Pauli theory.*

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### 13.8. Problems

**Problem 13.1** For an eigenstate of  $J^2$  and  $J_z$ , show that

$$\langle J_x \rangle = \langle J_y \rangle = 0 \quad (69)$$

and

$$\langle J_x^2 \rangle = \langle J_y^2 \rangle = \frac{1}{2} \hbar^2 [j(j+1) - m^2] \quad (70)$$

From the above results develop a classical model for angular momentum.

**Problem 13.2** In Sec. 13.3 we had derived the angular momentum matrices in a representation in which  $J^2$  and  $J_z$  are diagonal. Carry out a similar analysis in a representation in which  $J^2$  and  $J_x$  are diagonal; assume  $j = \frac{1}{2}$ .

**Problem 13.3** Show that the Pauli spin matrices satisfy the following relation

$$\sigma_i \sigma_j = \delta_{ij} + i \epsilon_{ijk} \sigma_k \quad (71)$$

where  $\epsilon_{ijk}$ , which is known as the totally antisymmetric unit tensor, is defined by

$$\begin{aligned}\epsilon_{123} &= \epsilon_{231} = \epsilon_{312} = 1 && \text{(cyclic indices)} \\ \epsilon_{321} &= \epsilon_{213} = \epsilon_{132} = -1 && \text{(anticyclic indices)}\end{aligned}$$

with all other components equal to zero.

**Problem 13.4** Using Eq. (71) show

$$(\boldsymbol{\sigma} \cdot \mathbf{A}) (\boldsymbol{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) \quad (72)$$

where  $\mathbf{A}$  and  $\mathbf{B}$  are arbitrary vectors. Thus

$$(\boldsymbol{\sigma} \cdot \hat{\mathbf{n}})^2 = 1 \quad (73)$$

where  $\hat{\mathbf{n}}$  is an arbitrary unit vector.

**Problem 13.5** For  $j = \frac{1}{2}$ , obtain the eigenvectors of  $s_y$  and express them as a linear combination of  $|\hat{\mathbf{z}}\uparrow\rangle$  and  $|\hat{\mathbf{z}}\downarrow\rangle$  states.

**Problem 13.6 (a)** Using (37) write the matrices for  $J_+$  and  $J_-$  (for  $j = \frac{1}{2}$ ) and derive

$$\begin{aligned}J_+ |1\rangle &= 0 \\ J_+ |2\rangle &= \hbar |1\rangle \\ J_- |1\rangle &= \hbar |2\rangle \\ J_- |2\rangle &= 0\end{aligned}$$

where  $|1\rangle$  and  $|2\rangle$  are given by Eqs (42) and (43).

**(b)** Similarly, using Eqs (56) and (57) write the matrices for  $J_+$  and  $J_-$  (for  $j = 1$ ) and derive Eqs (50)–(55).

**Problem 13.7** In Sec. 13.4 and 13.5 we had derived the angular momentum matrices corresponding to  $j = \frac{1}{2}$  and  $j = 1$  in a representation in which  $J^2$  and  $J_z$  are diagonal. Carry out a similar analysis for  $j = 3/2$ .

---

### 13.9. Solutions

#### Solution 13.1

$$\begin{aligned}
 & \langle j, m | J_x | j, m \rangle \\
 &= \frac{1}{2} (\langle j, m | J_+ | j, m \rangle + \langle j, m | J_- | j, m \rangle) = 0 \\
 &\quad [\text{using Eqs (30 - 31)}] \\
 & \langle j, m | J_x^2 | j, m \rangle \\
 &= \frac{1}{2} [\langle j, m | J_+ J_+ | j, m \rangle + \langle j, m | J_+ J_- | j, m \rangle \\
 &\quad + \langle j, m | J_- J_+ | j, m \rangle + \langle j, m | J_- J_- | j, m \rangle] \\
 &= \frac{1}{2} [0 + \{(j+m)(j-m+1)\}^{\frac{1}{2}} \langle j, m | J_+ | j, m-1 \rangle \\
 &\quad + \{(j-m)(j+m+1)\}^{\frac{1}{2}} \langle j, m | J_- | j, m+1 \rangle + 0] \\
 &= \frac{1}{2} \hbar^2 [j(j+1) - m^2] \tag{74}
 \end{aligned}$$

etc. Obviously

$$\langle j, m | J_z^2 | j, m \rangle = m^2 \hbar^2 \tag{75}$$

and

$$\langle j, m | J^2 | j, m \rangle = j(j+1) \hbar^2 \tag{76}$$

From the above equations we can develop a classical model for angular momentum. The total angular momentum vector **OP** (whose length is assumed to be  $\sqrt{j(j+1)} \hbar$ ) is assumed to precess about the  $z$ -axis (see Fig. 13.1). As it precesses, the  $z$ -component of **OP** ( $= OQ$ ) remains constant, which we assume to be equal to  $m \hbar$ . The  $x$ - and  $y$ -components of **OP** change with time and their average value is zero. Now

$$PQ^2 = j(j+1) \hbar^2 - m^2 \hbar^2 \tag{77}$$

represents  $\langle J_x^2 \rangle + \langle J_y^2 \rangle$  consistent with Eq. (74). Thus for the state  $| j, m \rangle$  we may assume the total angular momentum vector precessing about the  $z$ -axis.

#### Solution 13.2

$$J_x = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad J_y = \frac{1}{2} \hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad J_z = \frac{1}{2} \hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

**Solution 13.3** The following properties of the Pauli matrices are easily established

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \tag{78}$$

$$\sigma_x \sigma_y = i \sigma_z, \quad \text{etc.} \tag{79}$$

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0, \quad \text{etc.} \tag{80}$$

from which Eq. (71) immediately follows.

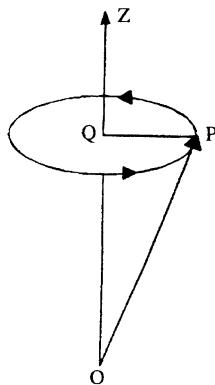


Figure 13.1. A classical model for the angular momentum vector.

### Solution 13.4

$$(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = \sum_{i,j} \sigma_i A_i \sigma_j B_j = (\mathbf{A} \cdot \mathbf{B}) + i \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) \quad (81)$$

as can be verified by expanding the RHS and using Eqs (78)–(80).

### Solution 13.7

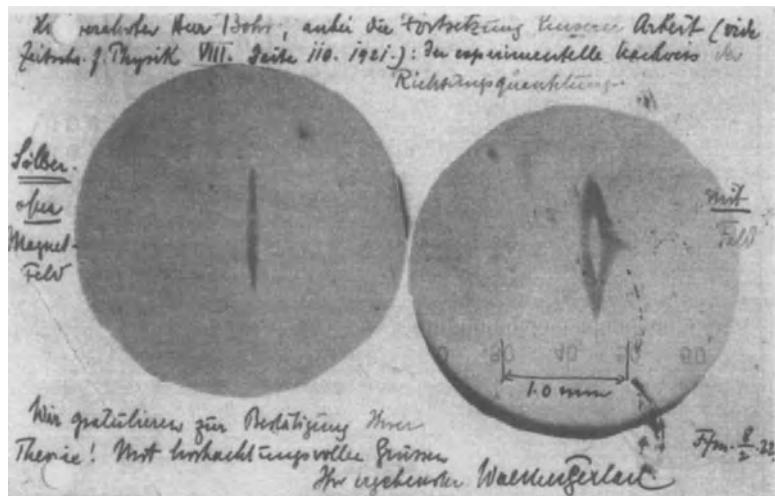
$$J_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$J_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i\sqrt{3} & 0 & 0 \\ i\sqrt{3} & 0 & -2i & 0 \\ 0 & 2i & 0 & -i\sqrt{3} \\ 0 & 0 & i\sqrt{3} & 0 \end{pmatrix}$$

$$J_z = \hbar \begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix}$$

$$J^2 = \frac{15}{4}\hbar^2 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

## Experiments with Spin Half Particles The Stern-Gerlach Experiment, Larmor Precession and Magnetic Resonance



A replica of the postcard sent by Walther Gerlach to Niels Bohr on February 8, 1922. The left-hand image of the beam profile without the magnetic field shows the effect of the finite width of the collimating slit. The right-hand image shows the beam profile with the magnetic field. Only in the centre of the apparatus is the magnitude of the magnetic field gradient sufficiently strong to cause splitting. The pattern is smeared because of the range of speeds of the atoms coming from the oven. Translation of the message: “My esteemed Herr Bohr, attached is the continuation of our work [vide *Zeitschr. f. Phys.* 8, 110 (1921)]: the experimental proof of directional quantization. We congratulate you on the confirmation of your theory! With respectful greetings. Your most humble Walther Gerlach.”

— Adapted from J.S. TOWNSEND, *A Modern Approach to Quantum Mechanics*, McGraw-Hill, New York (1992). The photograph was kindly provided by the Niels Bohr Archives in Copenhagen.

## 14.1. Introduction

The analysis of the *spin half* problem is of great significance because it is not only of tremendous practical importance but it also allows us to understand some of the fundamental postulates of quantum mechanics.

We will first discuss the magnetic moment associated with the orbital angular momentum of a charged particle, this will be followed by the magnetic moment associated with the spin angular momentum of the electron. We will then discuss the famous Stern-Gerlach experiment which had led to the concept of *space quantization*. We will then obtain solutions of the time dependent Schrödinger equation corresponding to the spin half particle in a uniform magnetic field thereby giving a quantum mechanical description of the *Larmor precession*. We will conclude this chapter with an analysis of magnetic resonance experiments and in the process we will obtain rigorous solutions of the Schrödinger equation for a time dependent Hamiltonian.

## 14.2. Orbital angular momentum and magnetic moment

Consider a particle (of mass  $m$  and charge  $Q$ ) rotating in a circular orbit of radius  $r$  (see Fig. 14.1). As shown in the figure, the angular momentum vector  $\mathbf{L}$  is perpendicular to the plane of the circular orbit and its magnitude is given by

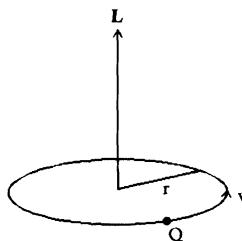


Figure 14.1. A particle (of mass  $m$  and charge  $Q$ ) rotating in a circular orbit of radius  $r$ .

$$L = mvr \quad (1)$$

The rotating charge constitutes a current  $I$  which is given by

$$\begin{aligned} I &= Q \times (\text{Number of rotations in a unit time}) \\ &= Q \frac{v}{2\pi r} \end{aligned} \quad (2)$$

Now, at large distances from the loop, the magnetic field produced by the circulating current loop is the same as that by a magnet of dipole moment  $\mu$  given by

$$\mu = I \times \text{Area of the loop}$$

Thus

$$\mu = Q \frac{v}{2\pi r} \pi r^2$$

or

*Magnetic moment due to orbital motion*

$$\boldsymbol{\mu}_l = \frac{Q}{2m} \mathbf{L} \quad (3)$$

where the subscript  $l$  implies that we are considering the magnetic moment due to the orbital motion. Equation (3) is a classical result; however, quantum mechanics also gives the same result. Equation (3) tells us that if  $Q$  is positive then  $\boldsymbol{\mu}$  and  $\mathbf{L}$  are in the same direction and if  $Q$  is negative,  $\boldsymbol{\mu}$  and  $\mathbf{L}$  are in opposite directions.

### 14.3. Spin angular momentum and magnetic moment

As mentioned in Sec. 13.6, Uhlenbeck and Goudsmit (in 1925) had introduced the idea that an electron has a spin angular momentum of  $\pm \frac{1}{2} \hbar$ ; associated with this spin angular momentum, the electron has a magnetic moment which is given by

*Spin magnetic moment*

$$\boldsymbol{\mu} = -g \frac{q}{2m} \mathbf{s} \quad (4)$$

where  $q$  ( $\simeq 1.6 \times 10^{-19}$  C) represents the magnitude of the electronic charge,  $m$  ( $\simeq 9.1 \times 10^{-31}$  kg) represents the electron mass and  $g$  ( $\simeq 2.0023$ ) is known as the *Landé g factor*;  $\mathbf{s}$  represents the spin angular momentum operator. In Sec. 13.4 we had shown that the cartesian components of the  $j = \frac{1}{2}$  angular momentum operator can be represented by  $2 \times 2$  matrices; these are given by

$$s_x = \frac{1}{2} \hbar \sigma_x, \quad s_y = \frac{1}{2} \hbar \sigma_y, \quad s_z = \frac{1}{2} \hbar \sigma_z \quad (5)$$

where  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$  are Pauli spin matrices and are given by

*Pauli spin matrices*

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (6)$$

We may mention here that the magnetic moment of the proton is given by

$$\boldsymbol{\mu}_p = g_p \frac{q}{2M_p} \mathbf{s} \quad (7)$$

where  $q$  ( $\simeq 1.6 \times 10^{-19}$  C) represents the proton charge,  $M_p$  ( $\simeq 1.673 \times 10^{-27}$  kg) represents the proton mass and  $g_p \simeq 5.56$ . Even the neutron (which has no charge) has a spin magnetic moment given by

$$\boldsymbol{\mu}_n = -g_n \frac{q}{2M_n} \mathbf{s} \quad (8)$$

where  $q$  ( $\simeq 1.6 \times 10^{-19}$  C) represents the magnitude of the electron charge,  $M_n$  ( $\simeq 1.675 \times 10^{-27}$  kg) represents the neutron mass and  $g_n \simeq 3.83$ . The magnetic moment of the neutron is attributed to its internal charge distribution.

#### 14.4. The Stern-Gerlach experiment

Let us consider the operator corresponding to  $s_z$ :

$$s_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (9)$$

The eigenvalues of  $s_z$  are  $+\frac{1}{2}\hbar$  and  $-\frac{1}{2}\hbar$ ; the corresponding (normalized) eigenvectors are

$$|\hat{\mathbf{z}}\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } |\hat{\mathbf{z}}\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (10)$$

which are usually referred to as *spin up* and *spin down* states. They are also referred as *z up* and *z down* states. Now, if we try to make a measurement of  $s_z$  then it will be one of its eigenvalues, i.e. either  $+\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$ . Indeed this is what happens in the Stern-Gerlach experiment where one passes neutral Ag atoms through an inhomogeneous magnetic field in the  $z$ -direction. For a silver atom in its ground state, the angular momentum is just the spin angular momentum of the electron<sup>1</sup> and therefore the magnetic moment of the silver atom is simply that of the electron<sup>2</sup>. The atoms behaving like magnets of moment  $\boldsymbol{\mu}$ , will be acted upon by a force given by

$$\mathbf{F} = -\nabla U = \nabla(\boldsymbol{\mu} \cdot \mathbf{B}) \quad (11)$$

where  $U$  ( $= -\boldsymbol{\mu} \cdot \mathbf{B}$ ) represents the interaction energy. We assume the magnetic field to be predominantly in the  $z$ -direction and therefore<sup>3</sup>

$$\mathbf{F} = \mu_z \nabla B_z \approx \mu_z \frac{\partial B_z}{\partial z} \hat{\mathbf{z}} \quad (12)$$

<sup>1</sup> The silver atom has 47 electrons; 46 electrons form a state with  $L = 0$  and  $S = 0$ , i.e. the total angular momentum of the silver atom (in its ground state) is just that due to the last electron.

<sup>2</sup> The Stern-Gerlach experiment cannot be performed with electrons; this is because of the fact that since the electron has a charge, it will experience a Lorentz force. On the other hand, although the neutral Ag atom possesses the magnetic moment of the electron, it does not have any charge and therefore does not experience any Lorentz force.

<sup>3</sup> In Example 14.2 we will discuss the Larmor precession where we will show that the components of  $\mathbf{s}$  perpendicular to  $\mathbf{B}$  will vary with time and will average out to zero. On the other hand,

where  $\mu_z$  represents the  $z$ -component of the magnetic moment. Now, travelling a distance  $l$  through the region of the magnetic field, the beam will experience a deflection  $\Delta z$  given by

### Deflection of the beam

$$\Delta z = \frac{1}{2} \left( \frac{F_z}{M} \right) t^2 = \frac{1}{2M} \mu_z \frac{\partial B}{\partial z} \left( \frac{l}{v} \right)^2 \quad (13)$$

where  $M$  is the mass and  $v$  the velocity of the atoms.

The atomic velocities, although not unique, will range around a mean value  $v$  determined by the temperature of the oven. In the absence of the magnetic field, the beam, defined by the slits, forms a narrow line.

Now, according to the classical theory

$$\mu_z = \mu \cos \theta \quad (14)$$

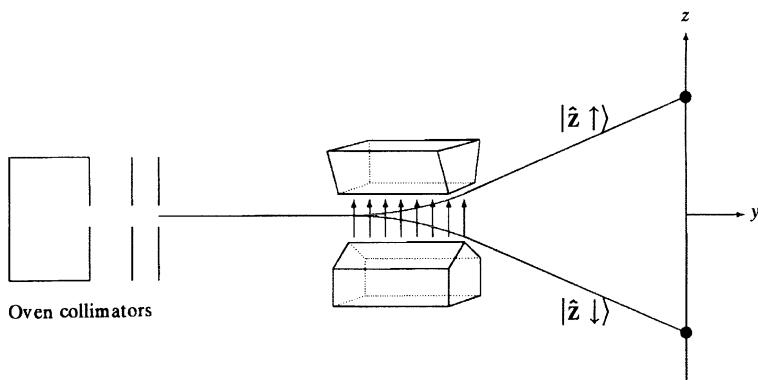
where  $\theta$  is the angle that the direction of the magnetic moment makes with the direction of the magnetic field. Thus, as the atoms come out of the oven, their magnetic moment would point in every possible direction and we should expect all values of  $\theta$  (between 0 and  $\pi$ ) to be possible. Consequently, when the field is turned on, the line ought to widen continuously in the  $z$ -direction, the deflection depending on the value of  $\theta$ . Thus, classically, the largest deflections will occur for atoms whose magnetic moments are aligned along or opposite the  $z$ -direction (i.e. for  $\cos \theta = \pm 1$ ); and for atoms for which  $\cos \theta = 0$ , the deflection should be zero. However, when the experiment was performed (see Fig. 14.2), the detector recorded a two line pattern showing that the silver beam had split into two components on passing through the inhomogeneous magnetic field. Since the displacement is proportional to  $\mu_z$ , the result of the above experiment implies that *an attempt to measure  $\mu_z$  would lead to one of the two eigenvalues  $+\mu_0$  and  $-\mu_0$ .* The quantization of the  $z$ -component of the magnetic moment suggests that the atomic magnets would be oriented in a quantized manner in space; this is often referred to as *space quantization*. In Fig. 14.2, the two beams emerging from the magnet would correspond to the  $|\hat{\mathbf{z}} \uparrow\rangle$  and  $|\hat{\mathbf{z}} \downarrow\rangle$  states respectively.

Now, the eigenvalues of  $s_x$  (and also of  $s_y$ ) are  $\pm \frac{1}{2} \hbar$ . Thus, there is nothing sacred about the  $z$ -direction; if the inhomogeneous magnetic field was applied in the  $x$ -direction, we would have again obtained only two beams but this time they will correspond to the  $|\hat{\mathbf{x}} \uparrow\rangle$  and  $|\hat{\mathbf{x}} \downarrow\rangle$  states.

Referring back to Fig. 14.2, let us suppose that we block the  $|\hat{\mathbf{z}} \downarrow\rangle$  beam and allow only the  $|\hat{\mathbf{z}} \uparrow\rangle$  beam to pass through. If we allow this beam to pass through

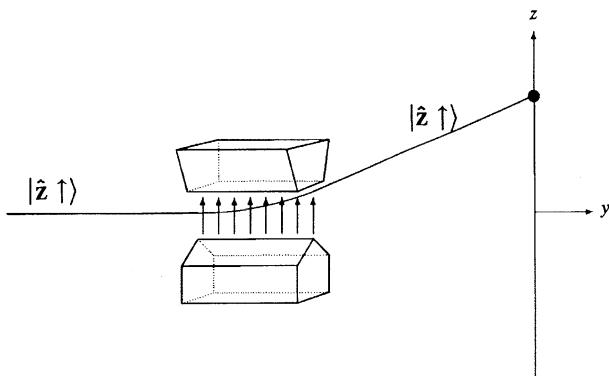
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the component parallel to  $\mathbf{B}$  will remain constant. Thus, although  $\left| \frac{\partial B_y}{\partial y} \right| \approx \left| \frac{\partial B_z}{\partial z} \right|$  because of the Maxwell equation ( $\nabla \cdot \mathbf{B} = 0$ ), since  $\mathbf{B}$  is predominantly in the  $z$ -direction, we may neglect the terms proportional to  $\mu_x$  and  $\mu_y$  in Eq. (12) because they will average out to zero.



*Figure 14.2.* In the Stern-Gerlach experiment the beam of silver atoms (coming out of the oven) is first collimated and then passed through an inhomogeneous magnetic field in the  $z$ -direction.

an inhomogeneous magnetic field in the  $z$ -direction, then since it is already in the  $|\hat{z} \uparrow\rangle$  state, we will get only one spot on the screen as shown in Fig. 14.3



*Figure 14.3.* If we block the  $|\hat{z} \downarrow\rangle$  beam (in Fig. 14.2) and allow the  $|\hat{z} \uparrow\rangle$  beam to pass through an inhomogeneous magnetic field in the  $z$ -direction, we would get only one spot on the screen.

What would happen if we allow the  $|\hat{z} \uparrow\rangle$  beam to pass through an inhomogeneous magnetic field in the  $x$ -direction as shown in Fig. 14.4? Obviously we are now trying to measure  $s_x$  and therefore we must expand the  $|\hat{z} \uparrow\rangle$  state in terms of the eigenfunctions of  $s_x$ . Simple matrix algebra gives us the following (normalized) eigenfunctions of  $s_x$ :

$$|\hat{x} \uparrow\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

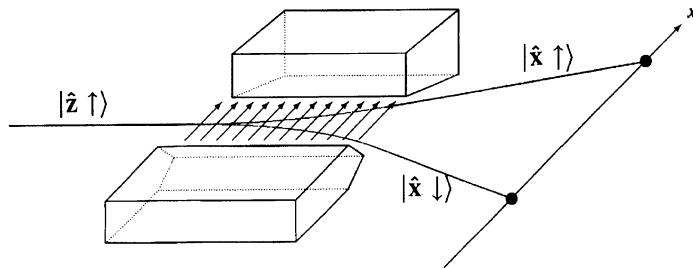


Figure 14.4. If we allow the  $|\hat{z} \uparrow\rangle$  beam to pass through an inhomogeneous magnetic field in the  $x$ -direction, we would get two spots on the screen corresponding to  $|\hat{x} \uparrow\rangle$  and  $|\hat{x} \downarrow\rangle$  states.

and

$$|\hat{x} \downarrow\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Now,

$$|\hat{z} \uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} |\hat{x} \uparrow\rangle + \frac{1}{\sqrt{2}} |\hat{x} \downarrow\rangle$$

Thus if the system is in the  $|\hat{z} \uparrow\rangle$  state and if we try to measure  $s_x$  then we would get one of the two eigenvalues ( $+\frac{1}{2}\hbar$  and  $-\frac{1}{2}\hbar$ ) with equal probabilities ( $= \frac{1}{2}$ ). In a particular measurement, one can never say for sure whether the Ag-atom will be found in the  $|\hat{x} \uparrow\rangle$  state or in the  $|\hat{x} \downarrow\rangle$  state — one can only predict the probabilities of such an event so that if the experiment is carried out with a large number of Ag atoms then (approximately) half of them will be found in the  $|\hat{x} \uparrow\rangle$  state and half of them in the  $|\hat{x} \downarrow\rangle$  state. What should we have expected classically? Well, since the magnet was initially pointing in the  $z$ -direction, the magnetic moment vector would make an angle of  $\pi/2$  with the  $x$ -axis resulting in a zero force acting on the magnet. Thus, classically, we should not have expected any deflection at all!

We end this section by mentioning that in 1927 Phipps and Taylor carried out the Stern-Gerlach experiment using a beam of hydrogen atoms. This experiment conclusively showed that the observed magnetic moment is due to the electron.

## 14.5. The Larmor precession

The magnetic moment of the neutral Ag atom is the same as that of an electron and is given by

$$\mu = -\frac{gq}{2m} \mathbf{s} \simeq -\frac{q}{m} \mathbf{s} \quad (15)$$

where the symbols have been defined earlier. If such a particle is placed in a static magnetic field given by

$$\mathbf{B} = B_0 \hat{\mathbf{z}} \quad (16)$$

then the potential energy associated with the magnetic field would be given by

$$H_0 = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{1}{2} \hbar \omega_0 \sigma_z \quad (17)$$

where

$$\omega_0 \equiv \frac{q B_0}{m} = \frac{2\mu_B B_0}{\hbar} \quad (18)$$

and

*Bohr magnetron*

$$\mu_B = \frac{|q| \hbar}{2m} \simeq 9.274 \times 10^{-24} \text{ J/T} \quad (19)$$

represents the Bohr magneton. Since the eigenvalues of  $\sigma_z$  are +1 and -1, this is essentially a two-state problem and the solution of the eigenvalue equation

$$H_0 |n\rangle = E_n |n\rangle ; \quad n = 1, 2 \quad (20)$$

would be given by

$$E_1 = \frac{1}{2} \hbar \omega_0 \Leftrightarrow |1\rangle = |\hat{\mathbf{z}} \uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (21)$$

$$E_2 = -\frac{1}{2} \hbar \omega_0 \Leftrightarrow |2\rangle = |\hat{\mathbf{z}} \downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (22)$$

Therefore, the most general solution of the time dependent Schrödinger equation

$$i \hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H_0 |\Psi(t)\rangle \quad (23)$$

would be

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{n=1}^2 C_n e^{-i E_n t / \hbar} |n\rangle \\ &= C_1 e^{-i \omega_0 t / 2} |1\rangle + C_2 e^{i \omega_0 t / 2} |2\rangle \end{aligned} \quad (24)$$

where the coefficients  $C_1$  and  $C_2$  are to be determined from the knowledge of  $|\Psi(t=0)\rangle$ :

$$C_1 = \langle 1 | \Psi(0) \rangle$$

and

$$C_2 = \langle 2 | \Psi(0) \rangle$$

Of course, if the system is initially in the  $|\hat{\mathbf{z}} \uparrow\rangle$  or  $|\hat{\mathbf{z}} \downarrow\rangle$  state, then it will remain in that state for all time to come; these are the *stationary states* of the problem.

**Example 14.1** As an example, we assume that at  $t = 0$ , the atom is in the  $|\widehat{\mathbf{x}} \uparrow\rangle$  state. Since

$$|\widehat{\mathbf{x}} \uparrow\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

we readily get

$$C_1 = \langle \widehat{\mathbf{z}} \uparrow | \widehat{\mathbf{x}} \uparrow \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}$$

Similarly  $C_2 = 1/\sqrt{2}$ . Thus

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}} e^{-i\theta} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}} e^{i\theta} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

or

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta} \\ e^{i\theta} \end{pmatrix} \quad (25)$$

where

$$\theta \equiv \frac{1}{2}\omega_0 t \quad (26)$$

Equation (25) describes the time evolution of the state. For example, if we wish to determine  $\langle s_x \rangle$ , then

$$\begin{aligned} \langle s_x \rangle &= \frac{1}{2} \hbar \langle \Psi(t) | \sigma_x | \Psi(t) \rangle \\ &= \frac{1}{4} \hbar \begin{pmatrix} e^{i\theta} & e^{-i\theta} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} e^{-i\theta} \\ e^{+i\theta} \end{pmatrix} \end{aligned}$$

or

$$\langle s_x \rangle = \frac{1}{2} \hbar \cos \omega_0 t \quad (27)$$

Similarly

$$\langle s_y \rangle = \frac{1}{2} \hbar \sin \omega_0 t \quad (28)$$

and

$$\langle s_z \rangle = 0 \quad (29)$$

The above equations physically imply that the direction of the spin angular momentum vector rotates about the  $z$ -axis with angular velocity  $\omega_0$ . We should point out that the above equations represent average values of  $s_x$ ,  $s_y$  and  $s_z$ ; however, if we carry out a measurement of  $s_z$ , then we would obtain either  $+\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$  (i.e. one of the eigenvalues) but since they will occur with equal probabilities the average value of  $s_z$  would be zero. On the other hand, the probabilities of obtaining the  $|\widehat{\mathbf{x}} \uparrow\rangle$  and  $|\widehat{\mathbf{x}} \downarrow\rangle$  states are

$$| \langle \widehat{\mathbf{x}} \uparrow | \Psi(t) \rangle |^2 \quad \text{and} \quad | \langle \widehat{\mathbf{x}} \downarrow | \Psi(t) \rangle |^2$$

which can readily be evaluated to give

$$\cos^2\left(\frac{1}{2}\omega_0 t\right) \text{ and } \sin^2\left(\frac{1}{2}\omega_0 t\right)$$

respectively. Thus if one carries out a measurement of  $s_x$  then one would get either  $+\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$  with probabilities

$$\cos^2\left(\frac{1}{2}\omega_0 t\right) \text{ and } \sin^2\left(\frac{1}{2}\omega_0 t\right)$$

and therefore the average value of  $s_x$  would be

$$\begin{aligned} \langle s_x \rangle &= \left(\frac{1}{2}\hbar\right) \cos^2\left(\frac{1}{2}\omega_0 t\right) + \left(-\frac{1}{2}\hbar\right) \sin^2\left(\frac{1}{2}\omega_0 t\right) \\ &= \frac{1}{2}\hbar \cos\omega_0 t \end{aligned} \quad (30)$$

consistent with Eq. (27). One can carry out a similar analysis for evaluating  $\langle s_y \rangle$ .

**Example 14.2** We next consider the more general case when

$$|\Psi(0)\rangle = \cos \frac{\phi}{2} |\hat{\mathbf{z}}\uparrow\rangle + \sin \frac{\phi}{2} |\hat{\mathbf{z}}\downarrow\rangle \quad (31)$$

[when  $\phi = \pi/2$ , we obtain the results of the previous example]. Obviously

$$C_1 = \cos \frac{\phi}{2} \quad \text{and} \quad C_2 = \sin \frac{\phi}{2}$$

so that

$$\begin{aligned} |\Psi(t)\rangle &= \cos \frac{\phi}{2} e^{-i\theta} |\hat{\mathbf{z}}\uparrow\rangle + \sin \frac{\phi}{2} e^{i\theta} |\hat{\mathbf{z}}\downarrow\rangle \\ &= \begin{pmatrix} \cos \frac{\phi}{2} e^{-i\theta} \\ \sin \frac{\phi}{2} e^{i\theta} \end{pmatrix} \end{aligned}$$

Thus

$$\langle s_x \rangle = \frac{1}{2}\hbar \langle \Psi(t) | \sigma_x | \Psi(t) \rangle$$

or

$$\langle s_x \rangle = \frac{1}{2}\hbar \sin \phi \cos \omega_0 t \quad (32)$$

Similarly

$$\langle s_y \rangle = \frac{1}{2}\hbar \sin \phi \sin \omega_0 t \quad (33)$$

and

$$\langle s_z \rangle = \frac{1}{2} \hbar \cos \phi \quad (34)$$

From the above equations we can develop a classical model for the precession of the spin angular momentum vector about the  $z$ -axis (see Fig. 14.5).

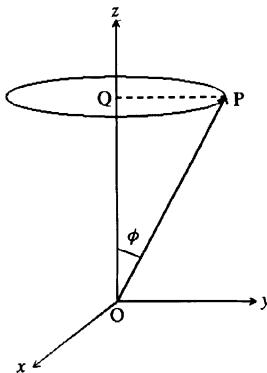


Figure 14.5. The Larmor precession.

From Eqs (29), (30) and (31) it readily follows that if at  $t = 0$ ,  $\mathbf{s}$  is assumed to lie in the  $x$ - $z$  plane then  $\mathbf{s}$  will lie in the  $y$ - $z$  plane at  $t = \pi/2\omega_0, 3\pi/2\omega_0, \dots$  Thus the spin angular momentum vector (represented by the vector  $\mathbf{OP}$ ) can be assumed to precess about the  $z$ -axis with angular velocity  $\omega_0$ ; this is known as *Larmor precession*. Further, the  $z$ -component of the spin angular momentum vector (represented by  $OQ$ ) remains constant with time [see Eq. (34)]. Of course, if one measures any cartesian component of  $\mathbf{s}$  one would only get  $+\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$ .

#### *Classical treatment*

We may mention here that the same expression for the Larmor frequency is obtained from classical considerations. This can be seen as follows:<sup>4</sup>: If an atomic magnet (of dipole moment  $\mu$ ) is suspended freely in a magnetic field  $\mathbf{B}$ , it will experience a torque  $\tau$  given by

$$\tau = \mu \times \mathbf{B} \quad (35)$$

which tries to align the magnet along the direction of  $\mathbf{B}$ . Since the atomic magnet has an angular momentum (say  $\mathbf{J}$ ) then classical mechanics tells us that (see also Problems 14.4 and 14.7)

$$\frac{d\mathbf{J}}{dt} = \tau = \mu \times \mathbf{B} \quad (36)$$

or

$$\Delta\mathbf{J} = (\mu B_0 \sin \phi) \Delta t \quad (37)$$

---

<sup>4</sup> For more details, the reader is referred to *The Feynman Lectures on Physics*, Vol. II, Chapter 34.

where  $\phi$  is the angle that  $\mu$  makes with  $\mathbf{B}$  and  $B_0$  represents the magnitude of  $\mathbf{B}$ . Since  $\mu$  has the same direction as  $\mathbf{J}$ ,  $\Delta\mathbf{J}$  will be at right angles to  $\mathbf{J}$  and the angular momentum vector will precess about the direction of  $\mathbf{B}$ .

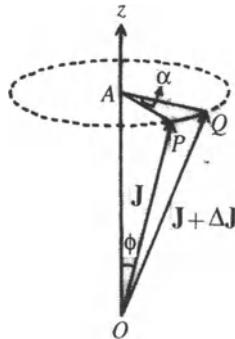


Figure 14.6. Larmor precession using classical mechanics. The magnetic field is in the  $z$ -direction.

Referring to Fig. 14.6, if we assume that at  $t = 0$ ,  $\mathbf{J}$  is along  $\mathbf{OP}$  and at  $t = \Delta t$ , it is along  $\mathbf{OQ}$ , then

$$AP = J \sin \phi$$

and

$$\begin{aligned} \Delta J &= AP \times \alpha \\ &= (J_0 \sin \phi) \times (\omega_0 \Delta t) \end{aligned} \quad (38)$$

where  $\omega_0$  represents the angular velocity associated with the precession. Comparing Eqs (37) and (38) we get

$$\omega_0 = \frac{\mu B_0}{J} = g \frac{q B_0}{2m} \simeq \frac{q B_0}{m} \quad (39)$$

## 14.6. Principle of the magnetic resonance experiment

In the examples discussed in the previous section, we have considered an electron in a uniform magnetic field (of magnitude  $B_0$ ) in the  $z$ -direction. The energy eigenvalues were

$$+\frac{1}{2}\hbar\omega_0 \quad \text{and} \quad -\frac{1}{2}\hbar\omega_0 \quad \left( \omega_0 = \frac{gqB_0}{2m} \simeq \frac{qB_0}{m} \right)$$

*Electron in a uniform and a rotating r.f. field*

The corresponding eigenkets were the *spin up* and *spin down* states respectively (denoted by  $|\hat{\mathbf{z}}\uparrow\rangle$  and  $|\hat{\mathbf{z}}\downarrow\rangle$ ). In this section we will show that in addition to

the uniform magnetic field (in the  $z$ -direction), if we apply a rotating r.f. (radio frequency) field in the  $x$ - $y$  plane given by

$$B_x = B_1 \cos \omega t, \quad B_y = B_1 \sin \omega t, \quad B_z = 0 \quad (40)$$

then this r.f. field would cause transitions between the *spin up* and *spin down* states.

Now, in the presence of the r.f. field, the Hamiltonian is given by

$$H = H_0 + H' \quad (41)$$

where

$$H_0 = \frac{1}{2} \hbar \omega_0 \sigma_z \quad (42)$$

and

$$\begin{aligned} H' &= -\mu \cdot \mathbf{B} \\ &= \frac{g q}{2m} \cdot \frac{1}{2} \hbar \boldsymbol{\sigma} \cdot [B_1 \cos \omega t \hat{\mathbf{x}} + B_1 \sin \omega t \hat{\mathbf{y}}] \end{aligned}$$

or

$$H' = \mu_B B_1 [\sigma_x \cos \omega t + \sigma_y \sin \omega t] \quad (43)$$

where  $\mu_B$  is defined through Eq. (19). If we substitute for  $\sigma_x$  and  $\sigma_y$  from Eq. (6) we would get

$$H' = \mu_B B_1 \begin{pmatrix} 0 & e^{-i\omega t} \\ e^{i\omega t} & 0 \end{pmatrix} \quad (44)$$

Our objective is to solve the Schrödinger equation

$$i \hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (H_0 + H') |\Psi(t)\rangle \quad (45)$$

We write

$$|\Psi(t)\rangle = \sum_{n=1}^2 C_n(t) e^{-iE_n t/\hbar} |n\rangle \quad (46)$$

The physical significance of the above equation is obvious: At each instant of time, we are expanding the wave function as a linear combination of the eigenfunctions of  $H_0$  which form a complete set. Thus the expansion given by Eq. (46) is

rigorously correct. Substituting Eq. (46) in Eq. (45) we get

$$\begin{aligned}
 i\hbar \sum_{n=1}^2 \frac{dC_n}{dt} e^{-iE_nt/\hbar} |n\rangle + \sum_{n=1}^2 C_n(t) E_n e^{-iE_nt/\hbar} |n\rangle \\
 = H_0 \sum_{n=1}^2 C_n(t) e^{-iE_nt/\hbar} |n\rangle \\
 + H' \sum_{n=1}^2 C_n(t) e^{-iE_nt/\hbar} |n\rangle \\
 = \sum_{n=1}^2 C_n(t) e^{-iE_nt/\hbar} E_n |n\rangle \\
 + \sum_{n=1}^2 C_n(t) e^{-iE_nt/\hbar} H' |n\rangle
 \end{aligned}$$

where we have used Eq. (20). The second term on the LHS cancels with the first term on the RHS and we obtain

$$\begin{aligned}
 i\hbar \frac{dC_1}{dt} e^{-iE_1t/\hbar} |1\rangle + i\hbar \frac{dC_2}{dt} e^{-iE_2t/\hbar} |2\rangle \\
 = C_1(t) e^{-iE_1t/\hbar} H' |1\rangle + C_2(t) e^{-iE_2t/\hbar} H' |2\rangle
 \end{aligned} \tag{47}$$

If we premultiply by  $\langle 1|$ , we would get

$$i\hbar \frac{dC_1}{dt} = C_2(t) e^{i(E_1-E_2)t/\hbar} [\mu_B B_1 e^{-i\omega t}] \tag{48}$$

where we have used the following relations

$$\begin{aligned}
 \langle 1 | 1 \rangle &= 1, \quad \langle 1 | 2 \rangle = 0 \\
 \langle 1 | H' | 1 \rangle &= \mu_B B_1 (1 \ 0) \begin{pmatrix} 0 & e^{-i\omega t} \\ e^{i\omega t} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\
 &= 0
 \end{aligned}$$

and

$$\begin{aligned}
 \langle 1 | H' | 2 \rangle &= \mu_B B_1 (1 \ 0) \begin{pmatrix} 0 & e^{-i\omega t} \\ e^{i\omega t} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\
 &= \mu_B B_1 e^{-i\omega t}
 \end{aligned}$$

We define

$$\omega_1 \equiv \frac{\mu_B B_1}{\hbar} = \frac{qB_1}{2m} \tag{49}$$

using which Eq. (48) can be written in the following form

$$i \frac{dC_1}{dt} = \omega_1 C_2(t) e^{i(\omega_0 - \omega)t} \quad (50)$$

where we have used Eqs (21) and (22). Similarly, if we premultiply Eq. (47) by (2) we would get

$$i \frac{dC_2}{dt} = \omega_1 C_1(t) e^{i(\omega - \omega_0)t} \quad (51)$$

If we differentiate the above equation and substitute for  $dC_1/dt$  and  $C_1(t)$  from Eqs (50) and (51) we would readily get

$$\frac{d^2C_2}{dt^2} - 2i\Delta \frac{dC_2}{dt} + \omega_1^2 C_2(t) = 0 \quad (52)$$

where

$$\Delta \equiv \frac{\omega - \omega_0}{2} \quad (53)$$

Assuming a solution of the form

$$C_2(t) \sim e^{i\alpha t} \quad (54)$$

we readily get

$$\alpha = \Delta \pm \Gamma \quad (55)$$

where

$$\Gamma \equiv \sqrt{\Delta^2 + \omega_1^2} \quad (56)$$

Thus the general solution of Eq. (52) is given by

$$C_2(t) = A_1 e^{i[\Delta + \Gamma]t} + A_2 e^{i[\Delta - \Gamma]t} \quad (57)$$

We assume that at  $t = 0$ , the atomic magnet is in the  $|\hat{\mathbf{z}} \uparrow\rangle$  state. Thus

$$C_1(0) = 1 \text{ and } C_2(0) = 0 \quad (58)$$

and Eq. (57) can be written in the form

$$C_2(t) = A e^{i\Delta t} \sin \Gamma t \quad (59)$$

We now use Eq. (51) to determine  $C_1(t)$ :

$$\begin{aligned} C_1(t) &= \frac{i}{\omega_1} \frac{dC_2}{dt} e^{-2i\Delta t} \\ &= \frac{iA\Gamma}{\omega_1} \left[ \cos \Gamma t + \frac{i\Delta}{\Gamma} \sin \Gamma t \right] e^{-i\Delta t} \end{aligned}$$

The condition  $C_1(0) = 1$  gives us

$$A = \frac{\omega_1}{i\Gamma}$$

Thus, we obtain

$$C_1(t) = \left[ \cos \Gamma t + \frac{i\Delta}{\Gamma} \sin \Gamma t \right] e^{-i\Delta t} \quad (60)$$

and

$$C_2(t) = \frac{\omega_1}{i\Gamma} \sin \Gamma t e^{i\Delta t} \quad (61)$$

and  $|\Psi(t)\rangle$  is completely determined [see Eq. (46)]. Further,

$$|C_1(t)|^2 = \cos^2 \Gamma t + \frac{\Delta^2}{\Gamma^2} \sin^2 \Gamma t \quad (62)$$

and

$$|C_2(t)|^2 = \frac{\omega_1^2}{\Gamma^2} \sin^2 \Gamma t \quad (63)$$

giving the obvious result that

$$|C_1(t)|^2 + |C_2(t)|^2 = 1 \quad (64)$$

### *Spin-flip probability*

The quantity  $|C_2(t)|^2$  represents the probability of *spin-flip*; it oscillates between 0 and  $\omega_1^2/\Gamma^2$ , the maximum value occurring at

$$t = \frac{\pi}{2\Gamma}, \frac{3\pi}{2\Gamma}, \dots \quad (65)$$

Equation (63) can be rewritten in the form

$$P_{\text{spin-flip}} = |C_2(t)|^2 = \frac{\omega_1^2}{\omega_1^2 + \frac{1}{4}(\omega - \omega_0)^2} \sin^2 \Gamma t \quad (66)$$

### *Resonance*

For  $(\omega - \omega_0)/\omega_1 \gg 1$ , the *spin-flip* probability is small. The condition  $\omega = \omega_0$  is known as the *resonance condition* and at resonance, the *spin-flips for certainty* at  $t = \pi/2\Gamma, 3\pi/2\Gamma, \dots$ . The resonance condition is achieved either by varying the frequency of the r.f. field ( $\omega$ ) or by varying the strength of the dc magnetic field  $B_0$  (and hence  $\omega_0$ ). Notice that the resonance becomes sharper as the value of  $B_1$  is made smaller—see Fig. 14.7.

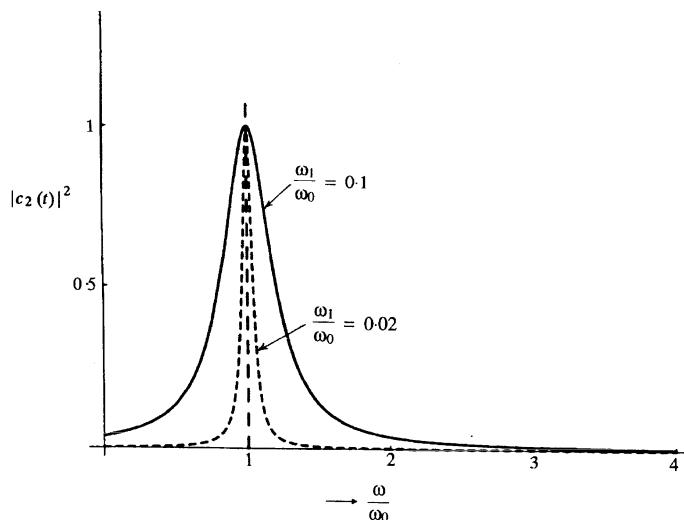


Figure 14.7. The resonance condition corresponds to  $\omega = \omega_0$ , where the spin flips for certainty. The solid and the dashed curves correspond to  $\omega_1/\omega_0 (= B_1/B_0) = 0.1$ , and 0.02 respectively. The resonance becomes sharper for smaller values of B.

#### *Principle of ESR and NSR experiments*

Now, at a particular temperature, the number of particles in the  $|\hat{\mathbf{z}}\uparrow\rangle$  state (which has higher energy) will be less in comparison to the number of particles in the  $|\hat{\mathbf{z}}\downarrow\rangle$  state. Further, when a transition occurs from the  $|\hat{\mathbf{z}}\downarrow\rangle$  state to the  $|\hat{\mathbf{z}}\uparrow\rangle$  state, energy is supplied by the r.f. field. At resonance, the probability of spin-flip will be maximum and hence the power supplied by the r.f. field will be maximum. This is the basic principle behind the electron spin resonance (ESR) and nuclear magnetic resonance (NMR) experiments which primarily involve obtaining the resonance condition  $\omega = \omega_0$ . This condition can be used either to accurately measure static magnetic fields (assuming the value of the electron magnetic moment or the proton magnetic moment) or to determine the magnetic moment of the atomic system.

#### 14.7. The EPR paradox

Theories derive their authority from observations and experiments. What one can infer from experiments is crucial in deciding the validity of a theory. One of the most important activities of experiments is to make measurements on a system which is used to infer its properties. Nevertheless, in classical physics no particular emphasis is made on the process of measurements since it is assumed that in principle measurement of a property can be made with as high a degree of precision as necessary without interfering with system measured. This is fundamentally impossible in quantum physics in a direct measurement; for example, if we wish

to determine the position of an electron, at least one photon must be exchanged between the electron and the observing apparatus and that does disturb the system. Indeed the elementary discussion of the uncertainty principle was based on these ideas (see Chapter 3).

But it is not always necessary to rely on directly interfering with a system to measure a property. For example in particle physics one often deduces the properties of a particle from the known properties of others produced in a ‘collision’. The necessary ingredients for such inferences are well established conservation laws governing the process (such as angular momentum). We are able to draw such inferences because the system studied had been a part of a bigger system from which it separated and yet retains ‘memory’ of its lineage. Thus even when parts are well separated subsequently, a measurement on one part of the system will give information on the other part.

All this is not unusual in that they are a feature of measurements in classical physics. This is to caution us from unwarranted surprise at results of Quantum Mechanics (we will abbreviate this by QM). However, there are peculiar features in QM which lead to predictions that we do not encounter in classical physics. Perhaps the most spectacular is the one that goes by the name of the ‘EPR paradox’ named after the authors of a famous paper describing a gedanken (i.e, thought) experiment<sup>5</sup>. EPR showed that in a quantum process long distance correlations do seem to violate common sense when applied to simultaneous measurements of the so called incommensurate observables that do not commute (such as position of a particle, say the x-coordinate and the x-component of its momentum). We shall present a reconstructed version, due to David Bohm<sup>6</sup> using spin measurements.

Consider a molecule composed of two atoms A and B each of which has a spin  $\frac{1}{2}$  (i.e, angular momentum  $\frac{1}{2}\hbar$ ). Assume that the spin of the molecule itself is 0. Suppose at time  $t = 0$ , the molecule dissociates and the component atoms A and B, go off in opposite directions. Soon they will be far apart so that we can think of them as isolated from each other so that we would expect that measurements on A do not disturb B and vice-versa.

Now in Classical as well as in Quantum Mechanics, angular momenta of isolated systems stay constant. This means that each of the components of spin of the system will be conserved (i.e, will be unchanged). Let us denote the components of spin of A as  $s_x(A)$ ,  $s_y(A)$  and  $s_z(A)$  and similarly the components of B. In QM, there is then the additional feature that each of these components can only take the values  $+\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$ . It will be more convenient to talk of the integer quantities  $\sigma_x = 2s_x/\hbar$  etc., whose values can be +1 or -1. For simplicity, we shall refer to these components of  $\sigma$  as ‘spin’.

<sup>5</sup> A. Einstein, B. Podolsky and N. Rosen, Physical Review **47**, 777 (1935).

<sup>6</sup> *Quantum Theory*, D. Bohm, Prentice Hall, N.J. (1951).

Now the spin components of the molecule are all zero—since its total spin is zero and conservation of angular momentum demands:

$$\left. \begin{array}{l} \sigma_x(A) + \sigma_x(B) = 0 \\ \sigma_y(A) + \sigma_y(B) = 0 \\ \sigma_z(A) + \sigma_z(B) = 0 \end{array} \right\} \quad (67)$$

Thus, measurement of a component of spin of either atom determines the value of the same component of the other atom. For example, if we measure and obtain  $\sigma_x(A) = +1$ , then we would have inferred that  $\sigma_x(B) = -1$ . This is a typical example of indirect measurement that we have talked about and is not at all a peculiarity of QM. The spin components of A and B are correlated—a result of the conservation laws applicable to classical systems as well. But QM does impose two restrictions. The first, as we have already mentioned, is that the only possible results that we can obtain by measuring any spin component are  $\pm \frac{1}{2}\hbar$  (or, in terms of the Pauli variables  $\sigma, \pm 1$ ). The second is that only one component of spin of each atom can have definite values. For example, we cannot talk of atom A being simultaneously in the spin states specified by  $\sigma_x(A) = +1$  and  $\sigma_y(A) = -1$ . This statement still requires elaboration.

In classical mechanics, when we make a measurement and obtain a value, we can think of the system being in a state as specified by the value obtained—unless it is a very bad measurement. In principle, a good measurement implies that if we can prepare a system to be in the same condition several times, then each time we shall obtain the same value on measurement. This permits us to indulge in such language as “the system has an angular momentum of 15 units”. A more picturesque way of stating this is that *there is an element of reality* in the quantity measured. In QM too, occasionally such a statement is valid but in general it is not. Thus, when we measure the spin component  $\sigma_x(A)$  and obtain a value +1, we ought not, in general, assume that the atom A is precisely in the state specified by that value. This does not mean that the measurement made by us is necessarily a bad one—a careless one; it is merely a normal manifestation of a quantum system that a measurement of  $\sigma_x(A)$  has a probability of giving as answer +1 or -1 and we happen to have obtained one of those values. This particular property of ‘probability’ is not peculiar to QM; after all, the probability of a head in a toss of a coin is  $\frac{1}{2}$  but a specific result can be a head and we cannot conclude anything about the behaviour of the coin under the ‘same’ conditions in subsequent tosses. Now it would seem quite reasonable to assume that when the atoms A and B are far apart, they cease to interact; if now, we measure the  $x$  component of spins of both A and B simultaneously there is no reason to suspect that a measurement of one influences the other. Nevertheless, there need be no surprise if we always find that the two results are correlated in the sense that if we obtain +1 for  $\sigma_x(A)$  we always obtain -1 for  $\sigma_x(B)$  or vice-versa. This correlation, in fact, is what one will obtain

in such a measurement of the above quantum system; a classical system will also exhibit such a perfect correlation.

Now in the case of a classical system, this perfect correlation will have an easy explanation, namely that the angular momentum component carried by A will have to be opposite that carried by B. Indeed it makes sense to say that A and B have those angular momenta. In the quantum system, we already have a little problem. Although it need not occasion any surprise that we obtain a value  $\sigma_x(A) = +1$ , it may seem a little odd that we simultaneously obtain a correlated value  $\sigma_x(B) = -1$  always. However, this is a relatively minor difficulty as we shall see. We can invent a simple model to reproduce such a correlation for a quantum system.

On the other hand such a definite correlation does seem to suggest that we may, in some sense, assume that there is an element of reality in these quantities  $\sigma_x(A)$  and  $\sigma_x(B)$ . Indeed, if we only measured  $\sigma_x(A)$ , we can now be confident of predicting the value of  $\sigma_x(B)$ . Now suppose we measure simultaneously the  $x$  component of the spin of A and the  $y$  component of the spin of B and obtain (as is possible)  $\sigma_x(A) = +1$  and  $\sigma_y(B) = -1$ . Now the first two relations in Eq. (67) permit us to infer, with certainty, that  $\sigma_x(B) = -1$  and  $\sigma_y(A) = +1$ . We would conclude that there indeed is an element of reality in all these four quantities. In fact, the argument is easily extended to conclude that all the six components of angular momenta have elements of reality. In a classical system, that statement is indeed true; alas, it violates one of the fundamental results of QM, that we cannot assign simultaneously values for more than one spin component of each atom.

An explanation for this seeming violation of QM that suggests itself is that somehow, the measurement of a spin component of A has influenced—disturbed—the state of B so that our conclusions about the elements of reality pertaining to B are not valid any more. In fact, the statement that two components of spin of the same atom, say  $\sigma_x(A)$  and  $\sigma_y(A)$ , cannot both be assigned definite values simultaneously is sometimes explained by saying that the measurement of one does physically influence the other. On the other hand, it is extremely difficult to think of such a physical influence of the well separated atoms A and B. In principle, the measurements can be completed before any physical influence can travel from one to the other. Current advances of technology do permit such experiment.

In one sense, the term EPR Paradox is a misnomer. What is strange here is that the prediction of QM does not accord with what may seem to be just common sense. This point was made succinctly by Einstein: “The following idea characterizes the relative independence of objects far apart in space: External influence on one has no direct influence on the other.”

To repeat: the EPR discussion and predictions are within the framework of QM. There is no particular confusion about how to calculate the various probabilities since the rules of QM are quite precise. For example, the joint probability of, say  $\sigma_x(A) = +1$  and  $\sigma_x(B) = +1$  is zero and the joint probability of  $\sigma_x(A) = +1$  and  $\sigma_y(B) = +1$  is  $\frac{1}{2}$ ; these are results that an experiment will bear out and there

will be no violation of QM. Thus there are no specific contradictions within the framework of QM. The problem is really a conceptual one – reconciling ourselves to an injury to common sense.

#### 14.7.1. A TOY MODEL FOR SPIN

One of the odd things in QM is that no matter in which direction we choose to measure a component of spin (angular momentum) of a spin  $\frac{1}{2}$  particle such as our atoms in the EPR example, we are bound to get an answer of either  $+\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$ , (i.e., +1 or -1 for the  $\sigma$  values). Text books on QM display the mathematical apparatus that reproduces this result. Now in classical mechanics, angular momentum can take on a continuous range of values. Nevertheless, discreteness by itself is not to be thought of as a strange result that arises fundamentally from quantum mechanical behaviour. Take for example, our (overused!) example of tossing a coin. Despite the large variety of conditions during the toss, all the conditions somehow conspire to produce just one of two discreet possibilities—head or tail. Thus if it is only discreteness that we want to reproduce in the quantum version of spin measurement, we should be able to invent a classical model to do the trick. The following is one such:

Suppose, as in a classical system, the axis of the spin angular momentum is along a direction specified by the unit vector  $\hat{\mathbf{p}}$ . We now postulate that if we measure the spin component along any direction  $\hat{\mathbf{a}}$  such that  $\hat{\mathbf{a}} \cdot \hat{\mathbf{p}}$  is positive, then the result of measurement will be +1; otherwise, it will be -1. To picture this, think of the direction  $\hat{\mathbf{p}}$  (the direction of polarization) as the one from the center of a sphere (of unit radius) to the north pole. Then, if the measurement of angular momentum is along the direction  $\hat{\mathbf{a}}$  directed from the center to a point on the upper hemisphere, the result will be +1 and if it is to point on the lower hemisphere, the result will be -1.

It turns out that this model is much too crude to reproduce the QM results of probabilities for obtaining the results +1 or -1; but it entirely demystifies the perfect correlation of the values of  $\sigma_x(A)$  and  $\sigma_x(B)$ , in the EPR example. When the molecule splits, in that example, conservation of angular momentum demands that the spin axes of the atoms A and B must be exactly in the opposite directions. It is therefore inevitable that if one of them points to the upper hemisphere, the other points to the lower hemisphere and the result of measurement, the perfect correlation, is not surprising. The problem posed by the EPR paradox, however, is not quite this trivial, as we shall see.

Let us now look at the probabilities that we expect from the crude model above and compare them with the predictions of QM. As stated above, the directions of spin of A and B, in our toy model, are opposite each other. Thus, if the polarization of A is along  $\hat{\mathbf{p}}$ , that of B is along  $-\hat{\mathbf{p}}$ . Now suppose we choose to measure the spin

components of A and B along directions not quite opposite each other, but along directions that make an angle  $\pi - \varphi$  with each other.

What will be the probability for obtaining various pairs of results? (There are, obviously, four possibilities.) To obtain +1 for one atom and -1 for the other, the two directions of measurement must point to opposite hemispheres (recall that the polar direction of our sphere is the direction  $\hat{\mathbf{p}}$  of polarization of A). A little thought will convince us that the probability for this to happen is  $1 - \varphi/\pi$ ; i.e, to obtain +1 for A and -1 for B is half this probability, the other half will be for obtaining -1 for A and +1 for B. The other probabilities can be similarly worked out. The table below gives the results. The last column gives the value of the product  $\sigma_\varphi(A) \cdot \sigma_z(B)$ .

$\sigma_\varphi(A)$	$\sigma_z(B)$	Probability	$\sigma_\varphi(A) \cdot \sigma_z(B)$
+	-	$\frac{1}{2}(1 - \varphi/\pi)$	-1
-	+	$\frac{1}{2}(1 - \varphi/\pi)$	-1
+	+	$\varphi/2\pi$	+1
-	-	$\varphi/2\pi$	+1

The average value  $\langle \sigma_\varphi(A) \cdot \sigma_z(B) \rangle$  is the sum of the products of the third and fourth columns and is  $-1 + 2\varphi/\pi$ .

Let us now look at the probabilities according to QM. This requires a bit of elementary QM. Assume that we measure the spin of A along a direction  $\hat{\mathbf{n}}$  in the  $x$ - $z$  plane at an angle  $\varphi$  to the  $z$ -axis. Then the relevant spin component for A is the operator:

$$\boldsymbol{\sigma} \cdot \hat{\mathbf{n}} = \sigma_x \sin \varphi + \sigma_z \cos \varphi = \begin{pmatrix} \cos \varphi & \sin \varphi \\ \sin \varphi & -\cos \varphi \end{pmatrix}$$

Denote the ‘up’ spin eigenvector (along  $\hat{\mathbf{n}}$ ) by the spinor:  $\begin{pmatrix} a \\ b \end{pmatrix}$ . Then,

$$\boldsymbol{\sigma} \cdot \hat{\mathbf{n}} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \quad (\text{since the eigenvalue is } +1)$$

This gives  $b/a = \tan(\varphi/2)$ , and the normalized ‘up’ state is:

$$A_{\hat{\mathbf{n}}} (+) = \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \cos \frac{\varphi}{2} \\ \sin \frac{\varphi}{2} \end{pmatrix}$$

Similarly the ‘down’ state (eigenvalue: -1) can be shown to be:

$$A_{\hat{\mathbf{n}}} (-) = \begin{pmatrix} -\sin \frac{\varphi}{2} \\ \cos \frac{\varphi}{2} \end{pmatrix}$$

(We have chosen irrelevant phase factors suitably.) These results are well known from elementary QM.

Now suppose we know that the spin state of the atom B is  $B_z(-)$ , i.e, it is in a definite state of spin, along the  $-z$ -direction. Then, A must be in the spin state denoted by  $A_z(+)$ . We can write:

$$A_z(+) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \cos \varphi / 2 A_{\hat{n}}(+) + \sin \varphi / 2 A_{\hat{n}}(-)$$

so that the probability of obtaining  $+1$  for the spin of A in the  $\hat{n}$  direction is  $\cos^2(\varphi/2)$  and, for obtaining  $-1$  is  $\sin^2(\varphi/2)$ .

We can now construct a table of probabilities for the various alternatives exactly as we did for the crude model. (We denote the state of the two atoms in the first column; the notation is self evident.)

State	Probability	$\sigma_\varphi(A) \cdot \sigma_z(B)$
$A_{\hat{n}}(+)B_z(-)$	$\frac{1}{2}(\cos^2(\varphi/2))$	$-1$
$A_{\hat{n}}(-)B_z(+)$	$\frac{1}{2}(\cos^2(\varphi/2))$	$-1$
$A_{\hat{n}}(+)B_z(+)$	$\frac{1}{2}(\sin^2(\varphi/2))$	$+1$
$A_{\hat{n}}(-)B_z(-)$	$\frac{1}{2}(\sin^2(\varphi/2))$	$+1$

Calculating as before, we obtain  $\langle \sigma_\varphi(A) \cdot \sigma_z(B) \rangle = -\cos \varphi$ . It is easily checked that the total probability adds to 1. Neither the probabilities nor the mean value  $\langle \sigma_\varphi(A) \cdot \sigma_z(B) \rangle$  agrees with the toy model. Remarkably, the probabilities do agree for the specific values of  $\varphi = 0, \pi/2$  and  $\pi$ . J. S. Bell commented ruefully, on this fortuitous agreement: “indeed the discussion for long entirely concentrated in the points (specified by these three angles)”. Bell’s attention was now devoted to the correlations at other angles too and he produced some remarkable inequalities which could test whether QM can be replaced by more sophisticated versions of our toy model.

#### 14.7.2. BELL’S INEQUALITIES

We have seen that our toy model was unable to reproduce all the features of QM. Is it possible that a more sophisticated model can? Now it may seem that the trouble with QM is that the state of a system is not completely specified by the wave function of a system. (It is one of the tenets of QM that the wave function does contain all the information that can be known about the system.) For example, state specified as  $A_z(+)$  for the spin wave function implies that the atom is definitely polarized in the  $z$ -direction. If we measure the spin component in any other direction, we do not get the same answer each time. Instead, we obtain the values  $+1$  and  $-1$  with certain probabilities. Could it not be that this indeterminate behaviour of

A (in regard to its  $x$  and  $y$  components) is only because we are unaware of other parameters pertaining to the system A, whose values (if we knew them) would completely specify the spin state of A? In other words, if we knew the values of these hidden variables, we can predict in each measurement, whether we shall get +1 or -1 for the  $x$  or  $y$  spin components (assuming that its  $z$  component is known to be +1). The theory then, will no longer be a statistical one and we will not have to reckon with fluctuations in the results of measurements. Such states which are *completely specified* will be called **dispersion free states**.

Let us assume that in the EPR example, the spin state of each of the two atoms will be completely specified by a hidden variable  $\Lambda$  (this can even represent more than one hidden variable, although we shall think of it as just one in the discussion below). Now the essential requirement for a predictable result of each measurement is not that there should be a one to one correspondence of  $\Lambda$  and spin but rather that if you know  $\Lambda$  you can predict the spin (for example, in our toy model, measurement of a spin component in a direction pointing to anywhere on an entire hemisphere would give the same result). Specifically, we assume that for a range of values of  $\Lambda$ , we shall obtain +1 and for another, -1.

Assume now that each splitting of a molecule is characterized by a specific value of  $\Lambda$  within a range  $d\Lambda$ . The probability for a particular value of  $\Lambda$  within an interval  $d\Lambda$  is denoted by  $p(\Lambda)d\Lambda$  so that:

$$\int p(\Lambda)d\Lambda = 1 \quad (68)$$

Now the values of  $\sigma_\varphi(A)$  and  $\sigma_z(B)$  are automatically assumed to be determined by the value of the parameter  $\Lambda$ . We therefore denote these values by  $\sigma_\varphi(A, \Lambda)$  and  $\sigma_z(B, \Lambda)$ . We must remember however, that these quantities can really be only +1 or -1. Now the expectation value of the spin product  $\langle \sigma_\varphi(A, \Lambda) \cdot \sigma_z(B, \Lambda) \rangle$  is:

$$C(\varphi) = \int d\Lambda \cdot p(\Lambda) \sigma_\varphi(A, \Lambda) \cdot \sigma_z(B, \Lambda) \quad (69)$$

For another value  $\theta$  (representing the direction of the spin component of A measured) we may write:

$$C(\theta) = \int d\Lambda \cdot p(\Lambda) \sigma_\theta(A, \Lambda) \cdot \sigma_z(B, \Lambda) \quad (70)$$

The difference is:

$$\begin{aligned} C(\varphi) - C(\theta) &= \int d\Lambda \cdot p(\Lambda) \sigma_z(B, \Lambda) [\sigma_\varphi(A, \Lambda) - \sigma_\theta(A, \Lambda)] \\ &= \int d\Lambda \cdot p(\Lambda) \sigma_z(B, \Lambda) \sigma_\varphi(A, \Lambda) [1 - \sigma_\varphi(A, \Lambda) \cdot \sigma_\theta(A, \Lambda)] \end{aligned}$$

where we have used the result that  $\sigma_\varphi^2$  is always +1. The modulus of the above is:

$$|C(\varphi) - C(\theta)| \leq \int d\Lambda \cdot p(\Lambda) \sigma_z(B, \Lambda) \sigma_\varphi(A, \Lambda) [1 - \sigma_\varphi(A, \Lambda) \cdot \sigma_\theta(A, \Lambda)] \quad (71)$$

In this integrand, the probability  $p(\Lambda)$  should always be non-negative (assuming that we stick to conventional ideas of probability). Further, the term within the square brackets is always non-negative, so that we can rewrite the inequality as:

$$|C(\varphi) - C(\theta)| \leq \int d\Lambda \cdot p(\Lambda) |\sigma_z(B, \Lambda) \sigma_\varphi(A, \Lambda)| [1 - \sigma_\varphi(A, \Lambda) \cdot \sigma_\theta(A, \Lambda)] \quad (72)$$

Since  $|\sigma_z(B, \Lambda) \sigma_\varphi(A, \Lambda)| = 1$ , we have:

$$\begin{aligned} |C(\varphi) - C(\theta)| &\leq \int d\Lambda \cdot p(\Lambda) [1 - \sigma_\varphi(A, \Lambda) \cdot \sigma_\theta(A, \Lambda)] \\ &= 1 - \int d\Lambda p(\Lambda) \sigma_\varphi(A, \Lambda) \cdot \sigma_\theta(A, \Lambda) \end{aligned} \quad (73)$$

Now  $\sigma_\varphi(A, \Lambda)$  measures the spin component of A in the ' $\varphi$ ' direction for a fixed  $\Lambda$ . Perfect correlation in the EPR example implies that this must give the result:  $\sigma_\varphi(A, \Lambda) = -\sigma_\varphi(B, \Lambda)$ , so that we have:

$$|C(\varphi) - C(\theta)| \leq 1 + \int d\Lambda p(\Lambda) \sigma_\varphi(B, \Lambda) \cdot \sigma_\theta(A, \Lambda) \quad (74)$$

The integral in the above expression signifies the expectation value of a simultaneous measurement of B in the ' $\varphi$ ' direction and of A in the ' $\theta$ ' direction. We now specialize to the case when these three directions all lie in the same plane. We then expect that this correlation can only be a function of the difference  $\theta - \varphi$ , so that:

$$\int d\Lambda p(\Lambda) \sigma_\varphi(B, \Lambda) \cdot \sigma_\theta(A, \Lambda) = C(\theta - \varphi) \quad (75)$$

Thus we have the result:

$$|C(\varphi) - C(\theta)| - C(\theta - \varphi) \leq 1 \quad (76)$$

This is one version of the Bell inequalities.

Let us now check if QM obeys this inequality. Now the QM results, it may be recalled, is that  $C(\varphi) = -\cos \varphi$ . If we specifically choose  $\theta = 2\varphi$ , we obtain:

$$|-\cos \varphi + \cos 2\varphi| + \cos \varphi \leq 1$$

a result that is easily shown to be violated for  $\varphi = \pi/6$ , for example. The inequality would read:

$$\left| \frac{1 - \sqrt{3}}{2} \right| + \frac{\sqrt{3}}{2} \leq 1$$

Since the left hand side is  $\approx 1.23$ , it is obvious that QM in general violated Bell's inequality, derived ostensibly from very general arguments of what we expect from a deterministic theory. The question, however, is what do experiments say? The experiments clearly favour QM. Bell's great contribution was to take the debate of the conceptual status of QM from a purely philosophical debate to the laboratory. So far, the results all seem to be consistent with QM—in other words, they violate the Bell inequalities.

It is important to take stock of what all this means in a very general sense. It is not just that the hidden variable models are consistent with determinism. They have the pleasing feature that they do not demand mysterious long distance correlations between the spin components of two (non-interacting?) systems such as the atoms A and B in the EPR example. Rather, correlations that we do observe are, in these models, those that were there to begin with, persist. There is a continuity which is missing (it would seem) in QM. The QM version demands a correlation that seems to appear (mysteriously) rather suddenly, on measurement, between A and B. If we think of such a correlation appearing as a result of a physical communication between A and B, then that communication is almost instantaneous—at least, it would have to travel faster than light. It is this non-locality implicit in the correlations that is the mystery of QM. Thus experimental tests on QM have specifically addressed themselves to this question, apart from just testing the Bell inequalities. This spooky action-at-a-distance verification is quite difficult; experiments have become possible only because of the spectacular technical advance that have come in recent years. This is a case, often repeated in history, of seemingly free philosophical debates coming under the scrutiny of experimental tests.

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## 14.8. Problems

**Problem 14.1** In the Stern-Gerlach experiment using Ag atoms, assume the oven temperature to be 1000 K, with

$$l \approx 25 \text{ cm}$$

and

$$\frac{\partial B_z}{\partial z} \approx 10^3 \text{ Tesla/m } (= 10^4 \text{ Gauss/cm})$$

Calculate the separation of the two components.

**Problem 14.2** In Example 14.1 we had assumed the magnetic field in the  $z$ -direction. If the static magnetic field is assumed in the  $x$ -direction we will have

$$H_0 = \frac{1}{2} \hbar \omega_0 \sigma_x$$

What would be the eigenvalues and eigenkets of  $H_0$ ? Assume

$$|\Psi(0)\rangle = \cos \frac{\phi}{2} |\hat{\mathbf{z}}\uparrow\rangle + \sin \frac{\phi}{2} |\hat{\mathbf{z}}\downarrow\rangle$$

Evaluate  $|\Psi(t)\rangle$ .

**Problem 14.3** For a uniform magnetic field  $B_0$  along the  $y$ -direction the Hamiltonian is given by

$$H_0 = \frac{1}{2} \hbar \omega_0 \sigma_y$$

- (a) What are the eigenvalues and normalized eigenkets of  $H_0$ ?
- (b) What is the general solution of the time dependent Schrödinger equation?
- (c) Assume  $|\Psi(0)\rangle = |\hat{\mathbf{z}}\uparrow\rangle$ . Evaluate  $|\Psi(t)\rangle$  and  $\langle s_z \rangle$ .

**Problem 14.4** Using Eqs (32), (33) and (34), prove

$$\begin{aligned} \frac{d}{dt} \langle s_x \rangle &= \langle \mu_y \rangle B_z - \langle \mu_z \rangle B_y \\ &= -\frac{q}{m} [\langle s_y \rangle B_z - \langle s_z \rangle B_y] \end{aligned} \quad (77)$$

Similarly

$$\frac{d}{dt} \langle s_y \rangle = -\frac{q}{m} [\langle s_z \rangle B_x - \langle s_x \rangle B_z] \quad (78)$$

and

$$\frac{d}{dt} \langle s_z \rangle = -\frac{q}{m} [\langle s_x \rangle B_y - \langle s_y \rangle B_x] \quad (79)$$

Thus we may write

$$\frac{d}{dt} \langle \mathbf{s} \rangle = \langle \boldsymbol{\tau} \rangle = \langle \boldsymbol{\mu} \rangle \times \mathbf{B} \quad (80)$$

**Problem 14.5** In the magnetic resonance experiment discussed in Sec. 14.6, the time evolution of the wave function can be written in the form [see Eq. (46)]:

$$|\Psi(t)\rangle = C_1(t) e^{-i\omega_0 t/2} |1\rangle + C_2(t) e^{i\omega_0 t/2} |2\rangle \quad (81)$$

Using the expressions for  $C_1(t)$  and  $C_2(t)$  at resonance ( $\Rightarrow \Delta = 0$ ), show that

$$\langle s_x \rangle = \frac{1}{2} \hbar \sin(2\omega_1 t) \sin \omega_0 t \quad (82)$$

$$\langle s_y \rangle = -\frac{1}{2} \hbar \sin(2\omega_1 t) \cos \omega_0 t \quad (83)$$

and

$$\langle s_z \rangle = \frac{1}{2} \hbar \cos(2\omega_1 t) \quad (84)$$

**Problem 14.6** Using the results of the previous problem, verify Eqs (77), (78) and (79).

**Problem 14.7** Using Eqs (46), (60) and (61), show that

$$\begin{aligned} \langle s_x \rangle &= \frac{\hbar\omega_1}{2\Gamma} \left[ \sin 2\Gamma t \sin \omega t - \frac{\Delta}{\Gamma} \cos \omega t \right. \\ &\quad \left. + \frac{\Delta}{\Gamma} \cos 2\Gamma t \cos \omega t \right] \end{aligned} \quad (85)$$

$$\begin{aligned} \langle s_y \rangle &= \frac{\hbar\omega_1}{2\Gamma} \left[ -\sin 2\Gamma t \cos \omega t + \frac{\Delta}{\Gamma} \sin \omega t \right. \\ &\quad \left. - \frac{\Delta}{\Gamma} \cos 2\Gamma t \sin \omega t \right] \end{aligned} \quad (86)$$

and

$$\langle s_z \rangle = \hbar\omega_1 \left[ \cos^2 \Gamma t + \frac{\Delta^2 - \omega_1^2}{\Gamma^2} \sin^2 \Gamma t \right] \quad (87)$$

Hence prove

$$\begin{aligned} \frac{d}{dt} \langle s_x \rangle &= -\frac{q}{m} [\langle s_y \rangle B_z - \langle s_z \rangle B_y] \\ &= -\omega_0 \langle s_y \rangle + 2\omega_1 \langle s_z \rangle \sin \omega t \end{aligned} \quad (88)$$

and similar relations for

$$\frac{d}{dt} \langle s_y \rangle \quad \text{and} \quad \frac{d}{dt} \langle s_z \rangle$$


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## 14.9. Solutions

**Solution 14.1** Because of collimation, the atoms entering the inhomogeneous magnetic field have their velocities in the  $y$ -direction; thus

$$\frac{3}{2}kT = \frac{1}{2}Mv^2 \approx \frac{1}{2}Mv_y^2$$

where  $T$  is the temperature of the oven. Thus

$$v_y \approx \sqrt{\frac{3kT}{M}}$$

Thus Eq. (13) becomes

$$\Delta z \approx \frac{l^2}{6kT} \mu_z \frac{\partial B_z}{\partial z}$$

Now

$$\mu_z = \pm \frac{q \hbar}{2m} \approx \pm 9.27 \times 10^{-24} \text{ J/T}$$

Thus

$$\begin{aligned} \Delta z &\approx \pm \frac{(0.25)^2}{6 \times 1.38 \times 10^{-23} \times 10^3} \times 9.27 \times 10^{-24} \times 10^3 \text{ m} \\ &\approx \pm 0.7 \text{ cm} \end{aligned}$$

The separation is about 1.4 cm.

**Solution 14.2** The eigenkets of  $H_0$  are now given by

$$|1\rangle = |\hat{\mathbf{x}} \uparrow\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

and

$$|2\rangle = |\hat{\mathbf{x}} \downarrow\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Thus the general solution of the time dependent Schrödinger equation is given by Eq. (24) with  $|1\rangle$  and  $|2\rangle$  given by the above equations. Now

$$\begin{aligned} |\Psi(0)\rangle &= \cos \frac{\phi}{2} |\hat{\mathbf{z}} \uparrow\rangle + \sin \frac{\phi}{2} |\hat{\mathbf{z}} \downarrow\rangle \\ &= \cos \frac{\phi}{2} \left[ \frac{1}{\sqrt{2}} |\hat{\mathbf{x}} \uparrow\rangle + \frac{1}{\sqrt{2}} |\hat{\mathbf{x}} \downarrow\rangle \right] \\ &\quad + \sin \frac{\phi}{2} \left[ \frac{1}{\sqrt{2}} |\hat{\mathbf{x}} \uparrow\rangle - \frac{1}{\sqrt{2}} |\hat{\mathbf{x}} \downarrow\rangle \right] \\ &= \frac{1}{\sqrt{2}} \left( \cos \frac{\phi}{2} + \sin \frac{\phi}{2} \right) |\hat{\mathbf{x}} \uparrow\rangle + \frac{1}{\sqrt{2}} \left( \cos \frac{\phi}{2} - \sin \frac{\phi}{2} \right) |\hat{\mathbf{x}} \downarrow\rangle \end{aligned}$$

Thus

$$\begin{aligned} |\Psi(t)\rangle &= \frac{1}{\sqrt{2}} \left( \cos \frac{\phi}{2} + \sin \frac{\phi}{2} \right) e^{-iE_1 t/\hbar} |\hat{\mathbf{x}} \uparrow\rangle \\ &\quad + \frac{1}{\sqrt{2}} \left( \cos \frac{\phi}{2} - \sin \frac{\phi}{2} \right) e^{-iE_2 t/\hbar} |\hat{\mathbf{x}} \downarrow\rangle \\ &= \frac{1}{2} \begin{pmatrix} \left( \cos \frac{\phi}{2} + \sin \frac{\phi}{2} \right) e^{-i\theta} + \left( \cos \frac{\phi}{2} - \sin \frac{\phi}{2} \right) e^{i\theta} \\ \left( \cos \frac{\phi}{2} + \sin \frac{\phi}{2} \right) e^{-i\theta} + \left( \cos \frac{\phi}{2} - \sin \frac{\phi}{2} \right) e^{i\theta} \end{pmatrix} \end{aligned}$$

where  $\theta = \omega_0 t / 2$ .

**Solution 14.3 (b)**

$$\begin{aligned} |\Psi(0)\rangle &= C_1 e^{-i\theta} |\hat{\mathbf{y}} \uparrow\rangle + C_2 e^{i\theta} |\hat{\mathbf{y}} \downarrow\rangle \\ &= \frac{1}{\sqrt{2}} C_1 e^{-i\theta} \begin{pmatrix} 1 \\ i \end{pmatrix} + \frac{1}{\sqrt{2}} C_2 e^{i\theta} \begin{pmatrix} 1 \\ -i \end{pmatrix} \end{aligned}$$

where  $\theta = \omega_0 t / 2$ .

(c)

$$C_1 = \frac{1}{\sqrt{2}}, \quad C_2 = -\frac{1}{\sqrt{2}}$$

Thus

$$|\Psi(t)\rangle = \begin{pmatrix} \cos \omega_0 t / 2 \\ \sin \omega_0 t / 2 \end{pmatrix}$$

**Solution 14.4** Using Eq. (32), we get

$$\frac{d}{dt} \langle s_x \rangle = -\frac{1}{2} \hbar \omega_0 \sin \phi \sin \omega_0 t$$

Since  $B_x = 0 = B_y$  and  $B_z = B_0$

$$\begin{aligned} -\frac{q}{m} [\langle s_y \rangle B_z - \langle s_z \rangle B_y] &= -\frac{qB_0}{m} \left[ \frac{1}{2} \hbar \sin \phi \sin \omega_0 t \right] \\ &= -\frac{1}{2} \hbar \omega_0 \sin \phi \sin \omega_0 t \end{aligned}$$

**Solution 14.5** At resonance

$$\omega = \omega_0 (\Rightarrow \Delta = 0 \text{ and } \Gamma = \omega_1)$$

and Eqs (60) and (61) simplify to

$$C_1(t) = \cos \omega_1 t \quad (89)$$

and

$$C_2(t) = -i \sin \omega_1 t \quad (90)$$

Now

$$|\Psi(t)\rangle = C_1(t) e^{-i\omega_0 t / 2} |1\rangle + C_2(t) e^{i\omega_0 t / 2} |2\rangle \quad (91)$$

and

$$\langle \Psi(t) | = \langle 1| C_1^*(t) e^{i\omega_0 t / 2} + \langle 2| C_2^*(t) e^{-i\omega_0 t / 2} \quad (92)$$

Thus

$$\begin{aligned}\langle s_x \rangle &= \langle \Psi(t) | s_x | \Psi(t) \rangle \\ &= \frac{1}{2} \hbar \langle \Psi(t) | \sigma_x | \Psi(t) \rangle \\ &= C_1^*(t) C_2(t) e^{i\omega_0 t} + C_2^*(t) C_1(t) e^{-i\omega_0 t}\end{aligned}$$

where we have used the relations

$$\langle 1 | \sigma_x | 1 \rangle = 0 = \langle 2 | \sigma_x | 2 \rangle$$

and

$$\langle 1 | \sigma_x | 2 \rangle = 1 = \langle 2 | \sigma_x | 1 \rangle$$

Substituting for  $C_1(t)$  and  $C_2(t)$  we readily obtain

$$\langle s_x \rangle = \frac{1}{2} \hbar \sin(2\omega_1 t) \sin \omega_0 t \quad (93)$$

Similarly

$$\langle s_y \rangle = -\frac{1}{2} \hbar \sin(2\omega_1 t) \cos \omega_0 t \quad (94)$$

and

$$\langle s_z \rangle = \frac{1}{2} \hbar \cos(2\omega_1 t) \quad (95)$$

The last equation shows the *spin-flip* at

$$t = \frac{\pi}{2\omega_1}, \frac{3\pi}{2\omega_1}, \frac{5\pi}{2\omega_1}, \dots$$

**Solution 14.6** From Eq. (77) we readily have

$$\frac{d}{dt} \langle s_x \rangle = -\frac{qB_0}{m} \langle s_y \rangle + \frac{qB_1 \sin \omega t}{m} \langle s_z \rangle$$

where we have used Eq. (40). Now,

$$\begin{aligned}\frac{d}{dt} \langle s_x \rangle &= \frac{1}{2} \hbar \omega_0 \sin(2\omega_1 t) \cos \omega_0 t \\ &\quad + \hbar \omega_1 \cos(2\omega_1 t) \sin \omega_0 t\end{aligned}$$

and

$$\begin{aligned}-\frac{qB_0}{m} \langle s_y \rangle + \frac{qB_1 \sin \omega t}{m} \langle s_z \rangle &= \frac{1}{2} \hbar \omega_0 \sin(2\omega_1 t) \cos \omega_0 t \\ &\quad + \hbar \omega_1 \cos(2\omega_1 t) \sin \omega_0 t\end{aligned}$$

Similarly one can prove other equations.

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#### 14.10. References and suggested reading

1. G. Baym, *Lectures on Quantum Mechanics*, W.A. Benjamin, Inc., New York (1969).
2. R.P. Feynman, R.B. Leighton and M. Sands, *The Feynman Lectures on Physics*, Vol III, Addison-Wesley, Reading, Massachusetts (1965).
3. C.P. Slichter, *Principles of Magnetic Resonance*, Harper and Row, New York (1963).
4. J.S. Townsend, *A Modern Approach to Quantum Mechanics*, McGraw-Hill, New York (1992).

# Chapter 15

## Angular momentum III Eigenfunctions Using Operator Algebra

*It seems that if one is working from the point of view of getting beauty in one's equations, and if one has a really sound insight, one is on a sure line of progress.*

— P.A.M. DIRAC in *The Evolution of the Physicist's Picture of Nature*, Scientific American, May 1963.

### 15.1. Introduction

In Chapter 13 we had shown that we can have a set of simultaneous eigenkets of the operators  $J^2$  and  $J_z$ :

$$J^2 |j, m\rangle = j(j+1)\hbar^2 |j, m\rangle \quad (1)$$

$$J_z |j, m\rangle = m\hbar |j, m\rangle \quad (2)$$

where

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots \quad (3)$$

and

$$m = -j, -j+1, \dots, j \quad (4)$$

Further, we had defined the ladder operators through the equations

$$J_+ = J_x + i J_y \quad (5)$$

and

$$J_- = \overline{J_+} = J_x - i J_y \quad (6)$$

which were shown to have the following properties:

$$J_+ |j, m\rangle = [(j-m)(j+m+1)]^{\frac{1}{2}} \hbar |j, m+1\rangle \quad (7)$$

$$J_- |j, m\rangle = [(j+m)(j-m+1)]^{\frac{1}{2}} \hbar |j, m-1\rangle \quad (8)$$

Thus,

$$J_+ |j, j\rangle = 0 \quad (9)$$

and

$$J_- |j, -j\rangle = 0 \quad (10)$$

In this chapter, we will use the above equations and the operator representations of the angular momentum operators to derive explicit expressions for the eigenfunctions of  $L^2$  and  $L_z$ . It will be seen that the procedure discussed in this chapter is extremely straightforward in determining the explicit expressions for the spherical harmonics.

## 15.2. The spherical harmonics

### *Operator representations*

In Sec. 9.2 we had shown the following operator representations of the components of the angular momentum operator

$$L_x = i\hbar \left[ \sin\phi \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right] \quad (11)$$

$$L_y = i\hbar \left[ -\cos\phi \frac{\partial}{\partial\theta} + \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right] \quad (12)$$

$$L_z = -i\hbar \frac{\partial}{\partial\phi} \quad (13)$$

Thus

$$\begin{aligned} L_+ &= L_x + iL_y \\ &= \hbar e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi} \right] \end{aligned} \quad (14)$$

and

$$\begin{aligned} L_- &= L_x - iL_y \\ &= \hbar e^{-i\phi} \left[ -\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi} \right] \end{aligned} \quad (15)$$

### *Simultaneous eigenfunction of $L^2$ and $L_z$*

Let  $Y_{lm}(\theta, \phi)$  represent the simultaneous eigenfunction of  $L^2$  and  $L_z$  [cf. Eqs (1) and (2)]:

$$L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \quad (16)$$

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \quad (17)$$

where

$$m = -l, -l+1, \dots, l-1, l \quad (18)$$

Using Eq. (13), Eq. (17) becomes

$$-i \hbar \frac{\partial Y}{\partial \phi} = m \hbar Y(\theta, \phi) \quad (19)$$

If we use the method of separation of variables

$$Y(\theta, \phi) = F(\theta) \Phi(\phi) \quad (20)$$

we would obtain

$$\frac{d\Phi}{d\phi} = im \Phi(\phi)$$

the solution of which is given by

$$\Phi(\phi) = \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (21)$$

For  $\Phi(\phi)$  to be single-valued

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (22)$$

we must have

$$e^{im2\pi} = 1$$

implying

$$m = 0, \pm 1, \pm 2, \dots \quad (23)$$

The factor  $1/\sqrt{2\pi}$  makes  $\Phi_m(\phi)$  normalized:

*Normalization condition*

$$\int_0^{2\pi} |\Phi_m(\phi)|^2 d\phi = 1 \quad (24)$$

Furthermore

*Orthonormality condition*

$$\int_0^{2\pi} \Phi_{m'}^*(\phi) \Phi_m(\phi) d\phi = \delta_{mm'} \quad (25)$$

Now, using Eq. (10) we obtain

$$L_- Y_{l,-l}(\theta, \phi) = 0 \quad (26)$$

or, using Eq. (15)

$$\hbar e^{-i\phi} \left[ -\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] Y_{l,-l}(\theta, \phi) = 0$$

or

$$\left[ -\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] (F(\theta) e^{-il\phi}) = 0$$

or

$$-\frac{dF}{d\theta} + l \cot\theta F(\theta) = 0$$

or

$$\frac{1}{F(\theta)} \frac{dF}{d\theta} = l \cot\theta$$

Integrating, we get

$$\ln F(\theta) = l \ln(\sin\theta) + \text{constant}$$

or,

$$\ln \left[ \frac{F(\theta)}{(\sin\theta)^l} \right] = \text{constant}$$

or,

$$F(\theta) = C_- \sin^l \theta \quad (27)$$

The normalization condition

$$\int_0^\pi |F(\theta)|^2 \sin\theta \, d\theta = 1 \quad (28)$$

gives us

$$|C_-|^2 \int_{-1}^{+1} (1 - \mu^2)^l \, d\mu = 1 \quad (29)$$

where

$$\mu = \cos\theta$$

For a particular value of  $l$ , the integral in Eq. (29) can be readily evaluated by making an expansion of the integrand and integrating term by term; the evaluation for an arbitrary value of  $l$  is a bit tedious—the final result is:

$$C_- = \frac{1}{2^l l!} \left[ \frac{(2l+1)!}{2} \right]^{\frac{1}{2}} \quad (30)$$

within an arbitrary phase factor. Thus

$$F(\theta) = \frac{1}{2^l l!} \left[ \frac{(2l+1)!}{2} \right]^{\frac{1}{2}} \sin^l \theta \quad (31)$$

and using Eq. (21) we would get

$$Y_{l,-l}(\theta, \phi) = \frac{1}{2^l l!} \left[ \frac{(2l+1)!}{4\pi} \right]^{\frac{1}{2}} \sin^l \theta e^{-il\phi} \quad (32)$$

In order to determine  $Y_{l,-l+1}$ ;  $Y_{l,-l+2}$  etc., we use Eq. (7) to write

$$L_+ Y_{lm}(\theta, \phi) = [(l-m)(l+m+1)]^{\frac{1}{2}} \hbar Y_{l,m+1}(\theta, \phi) \quad (33)$$

Thus

$$\begin{aligned} Y_{l,m+1} &= \frac{1}{\hbar} [(l-m)(l+m+1)]^{-\frac{1}{2}} L_+ Y_{l,m} \\ &= [(l-m)(l+m+1)]^{-\frac{1}{2}} e^{i\phi} \left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] Y_{l,m} \end{aligned} \quad (34)$$

Starting with  $m = -l$  and by repeated use of the above formula, one can readily obtain the (normalized) expressions for all values of  $m$ . We show this through two examples.

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**Example 15.1** For  $l = 1$ , we have

$$\begin{aligned} Y_{1,-1}(\theta, \phi) &= \frac{1}{2} \sqrt{\frac{6}{4\pi}} \sin \theta e^{-i\phi} \\ &= \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \end{aligned}$$

Using Eq. (34) we get

$$\begin{aligned} Y_{1,0}(\theta, \phi) &= \frac{1}{\hbar \sqrt{2}} L_+ Y_{1,-1}(\theta, \phi) \\ &= \frac{1}{\sqrt{2}} e^{i\phi} \left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] \sqrt{\frac{3}{8\pi}} [\sin \theta e^{-i\phi}] \\ &= \sqrt{\frac{3}{16\pi}} e^{i\phi} [\cos \theta + \cos \theta] e^{-i\phi} \\ &= \sqrt{\frac{3}{4\pi}} \cos \theta \end{aligned}$$

Similarly

$$\begin{aligned} Y_{1,+1}(\theta, \phi) &= \frac{1}{\hbar\sqrt{2}} L_+ Y_{1,0}(\theta, \phi) \\ &= \frac{1}{\sqrt{2}} e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \sqrt{\frac{3}{4\pi}} \cos\theta \\ &= -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} \end{aligned}$$

**Example 15.2** For  $l = 2$ , we have

$$\begin{aligned} Y_{2,-2}(\theta, \phi) &= \left( \frac{1}{8} \sqrt{\frac{5!}{4\pi}} \right) \sin^2\theta e^{-2i\phi} \\ &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{-2i\phi} \end{aligned}$$

Using Eq. (34) with  $l = 2$ ,  $m = -2$ , we get

$$\begin{aligned} Y_{2,-1}(\theta, \phi) &= \frac{1}{\sqrt{4}\hbar} L_+ Y_{2,-2}(\theta, \phi) \\ &= \frac{1}{2} e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \sqrt{\frac{15}{32\pi}} [\sin^2\theta e^{-2i\phi}] \\ &= \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{-i\phi} \end{aligned}$$

Similarly

$$\begin{aligned} Y_{2,0} &= \frac{1}{\sqrt{6}\hbar} L_+ Y_{2,-1}(\theta, \phi) \\ &= \frac{1}{\sqrt{6}} e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \sqrt{\frac{15}{8\pi}} [\sin\theta \cos\theta e^{-i\phi}] \\ &= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1) \end{aligned}$$

Further,

$$\begin{aligned} Y_{2,1} &= \frac{1}{\sqrt{6}\hbar} L_+ Y_{2,0}(\theta, \phi) \\ &= -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{i\phi} \\ Y_{2,2} &= \frac{1}{\hbar\sqrt{4}} L_+ Y_{2,1} \\ &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\phi} \end{aligned}$$

Similarly, for the  $l = 3$  case, we have

$$\begin{aligned} Y_{3,-3}(\theta, \phi) &= \frac{1}{2^3 3!} \left[ \frac{7!}{4\pi} \right]^{\frac{1}{2}} \sin^3 \theta e^{-3i\phi} \\ &= \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{-3i\phi} \end{aligned}$$

Therefore

$$\begin{aligned} Y_{3,-2}(\theta, \phi) &= \frac{1}{\hbar\sqrt{6}} L_+ Y_{3,-3}(\theta, \phi) \\ &= \frac{1}{\sqrt{6}} e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \sqrt{\frac{35}{64\pi}} [\sin^3 \theta e^{-3i\phi}] \\ &= \sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos\theta e^{-2i\phi} \end{aligned}$$

We can repeat the process to obtain  $Y_{3,-1}(\theta, \phi)$ ,  $Y_{3,0}(\theta, \phi)$ , etc. The final results are summarized in the next section.

We should point out that, as in the case of the harmonic oscillator problem, if the wave function with which we start is properly normalized, then all subsequent wave functions obtained by applying the ladder operator are automatically normalized.

### 15.3. Expressions for spherical harmonics

$$l = 0; \quad 2l + 1 = 1; \quad m = 0$$

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \quad (35)$$

$$l = 1; \quad 2l + 1 = 3; \quad m = -1, 0, +1$$

$$Y_{1,-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi} = -Y_{1,1}^* \quad (36)$$

$$Y_{1,0}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta \quad (37)$$

$$Y_{1,1}(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} = -Y_{1,-1}^* \quad (38)$$

$$l = 2; \quad 2l + 1 = 5; \quad m = -2, -1, 0, 1, 2$$

$$Y_{2,-2}(\theta, \phi) = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\phi} = Y_{2,2}^* \quad (39)$$

$$Y_{2,-1}(\theta, \phi) = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\phi} = -Y_{2,1}^* \quad (40)$$

$$Y_{2,0}(\theta, \phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \quad (41)$$

$$Y_{2,1}(\theta, \phi) = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi} = -Y_{2,-1}^* \quad (42)$$

$$Y_{2,2}(\theta, \phi) = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi} = Y_{2,-2}^* \quad (43)$$

$$l = 3; \quad 2l + 1 = 7; \quad m = -3, -2, -1, 0, 1, 2, 3$$

$$Y_{3,-3}(\theta, \phi) = \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{-3i\phi} = -Y_{3,3}^* \quad (44)$$

$$Y_{3,-2}(\theta, \phi) = \sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos \theta e^{-2i\phi} = Y_{3,2}^* \quad (45)$$

$$Y_{3,-1}(\theta, \phi) = \sqrt{\frac{21}{64\pi}} (5 \cos^2 \theta - 1) \sin \theta e^{-i\theta} = -Y_{3,1}^* \quad (46)$$

$$Y_{3,0}(\theta, \phi) = \sqrt{\frac{7}{4\pi}} \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta) \quad (47)$$

The above equations are consistent with those derived in Sec. 9.3.

#### 15.4. The $l = \frac{1}{2}$ case

In the entire analysis presented in this chapter we have assumed  $l$  to be a positive integer (including the value zero) and therefore  $m$  takes positive and negative integer values. What happens if we push our luck and try to obtain the wave functions for  $l = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ ? We will see that the procedure leads to ill-behaved and inconsistent wave functions.

Let us assume  $l = \frac{1}{2}$ ; then

$$m = -\frac{1}{2} \quad \text{or} \quad +\frac{1}{2}$$

Thus [see Eq. (21)]

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i\phi/2} \quad (48)$$

Of course, such a wave function is not single-valued; however,  $|\Phi(\phi)|^2$  is single valued and one may argue that the wave function described by the above equation may be acceptable. We consider the case  $m = -\frac{1}{2}$  so that Eq. (32) becomes

$$Y_{\frac{1}{2}, -\frac{1}{2}}(\theta, \phi) = C \sqrt{\sin \theta} e^{-i\phi/2} \quad (49)$$

where  $C$  is a constant. Using Eq. (34) for  $l = \frac{1}{2}$ ,  $m = -\frac{1}{2}$  we obtain

$$\begin{aligned} Y_{\frac{1}{2}, \frac{1}{2}}(\theta, \phi) &= \frac{1}{\hbar\sqrt{1}} L_+ Y_{\frac{1}{2}, -\frac{1}{2}} \\ &= C e^{i\phi} \left[ \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right] \left[ \sqrt{\sin\theta} e^{-i\phi/2} \right] \\ &= C \frac{\cos\theta}{\sqrt{\sin\theta}} e^{-i\phi/2} \end{aligned}$$

which is incorrect because we should have had (see Problem 15.8):

$$Y_{\frac{1}{2}, \frac{1}{2}} = (\text{const}) \sqrt{\sin\theta} e^{-i\phi/2} \quad (50)$$

Thus we *must* restrict the  $l$  values to  $0, 1, 2, 3, \dots$  with  $m$  going from  $-l$  to  $+l$ .

---

## 15.5. Problems

**Problem 15.1** Show by explicit differentiation that

$$\begin{aligned} L_+ Y_{1,1} &= 0 \\ L_+ Y_{2,2} &= 0 \end{aligned}$$

and

$$L_+ Y_{3,3} = 0$$

where the  $L_+$  operator is given by Eq. (14) and  $Y_{1,1}$ ,  $Y_{2,2}$  and  $Y_{3,3}$  are given by Eqs (38), (43) and (44) respectively.

**Problem 15.2** With  $l = 4$ , use Eq. (26) to show that

$$Y_{4,-4} = \sqrt{\frac{315}{512\pi}} \sin^4\theta e^{-4i\phi} \quad (51)$$

Using Eq. (34) derive  $Y_{4,-3}$ ,  $Y_{4,-2}$ ,  $Y_{4,-1}$ ,  $Y_{4,0}$ ,  $Y_{4,1}$ ,  $Y_{4,2}$ ,  $Y_{4,3}$  and  $Y_{4,4}$ .

**Problem 15.3** Show that  $Y_{0,0}$  is a simultaneous eigenfunction of  $L^2$ ,  $L_x$ ,  $L_y$  and  $L_z$ . What are the corresponding eigenvalues?

**Problem 15.4** Use

$$L_x = \frac{1}{2} (L_+ + L_-)$$

to show

$$L_x Y_{1,1} = \frac{1}{\sqrt{2}} \hbar Y_{1,0} \quad (52)$$

$$L_x Y_{1,0} = \frac{1}{\sqrt{2}} \hbar (Y_{1,1} + Y_{1,-1}) \quad (53)$$

$$L_x Y_{1,-1} = \frac{1}{\sqrt{2}} \hbar Y_{1,0} \quad (54)$$

Verify the above equations by using the operator representation of  $L_x$  [see Eq. (11)].

**Problem 15.5** The functions  $Y_{1,1}$ ,  $Y_{1,0}$  and  $Y_{1,-1}$  are simultaneous eigenfunctions of  $L^2$  and  $L_z$  (and *not* of  $L_x$  and  $L_y$ ). Using the results of the previous problem show that

$$L_x \psi_1 = \hbar\psi_1 \quad (55)$$

$$L_x \psi_2 = 0 \quad (56)$$

$$L_x \psi_3 = -\hbar\psi_3 \quad (57)$$

where

$$\psi_1 = \frac{1}{2} \left[ Y_{1,1} + Y_{1,-1} + \sqrt{2} Y_{1,0} \right] \quad (58)$$

$$\psi_2 = \frac{1}{\sqrt{2}} \left[ Y_{1,1} - Y_{1,-1} \right] \quad (59)$$

$$\psi_3 = \frac{1}{2} \left[ Y_{1,1} + Y_{1,-1} - \sqrt{2} Y_{1,0} \right] \quad (60)$$

Thus  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  are simultaneous eigenfunctions of  $L^2$  and  $L_x$ .

**Problem 15.6** Using Eqs (7) and (8), show that

$$L_y Y_{1,1} = \frac{i}{\sqrt{2}} \hbar Y_{1,0} \quad (61)$$

$$L_y Y_{1,0} = -\frac{i}{\sqrt{2}} \hbar [Y_{1,1} - Y_{1,-1}] \quad (62)$$

$$L_y Y_{1,-1} = -\frac{i}{\sqrt{2}} \hbar Y_{1,1} \quad (63)$$

Also verify the above equations by using the operator representation of  $L_y$  [see Eq. (12)]. Using the above equations determine the eigenfunctions of  $L_y$ ; these will be simultaneous eigenfunctions of  $L^2$  and  $L_y$ .

**Problem 15.7** The angular part of the wave function is described by the following equation:

$$\psi(\theta, \phi) = \frac{1}{2} \left[ -2i \sqrt{\frac{3}{8\pi}} \sin\theta \sin\phi + \sqrt{\frac{3}{2\pi}} \cos\theta \right]$$

- (a) If we make a measurement of  $L_z$ , what values will we obtain and with what probabilities? Evaluate  $\langle L_z \rangle$ .
- (b) If we make a measurement of  $L_x$ , what values will we obtain and with what probabilities? Evaluate  $\langle L_x \rangle$ .

**Problem 15.8** Using the condition

$$L_+ Y_{l,l} = 0 \quad (64)$$

show that

$$Y_{l,l} = (\text{const}) \sin^l \theta e^{i l \phi} \quad (65)$$

**Problem 15.9** For  $m = 0$ , we have

$$Y_{l,0}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta) \quad (66)$$

Thus

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

Use ladder operators to show that  $Y_{1,-1}$  and  $Y_{1,+1}$  are given by Eq. (36) and Eq. (38). Similarly,

$$Y_{2,0} = \sqrt{\frac{5}{4\pi}} \frac{1}{2} (3 \cos^2 \theta - 1)$$

Use ladder operators to determine  $Y_{2,2}$ ,  $Y_{2,1}$ ,  $Y_{2,-1}$ , and  $Y_{2,-2}$ .

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## 15.6. Solutions

**Solution 15.5** Let

$$\psi(\theta, \phi) = \alpha Y_{1,1} + \beta Y_{1,0} + \gamma Y_{1,-1}$$

represent the required linear combination which is an eigenfunction of  $L_x$ . Thus

$$\begin{aligned} L_x [\alpha Y_{1,1} + \beta Y_{1,0} + \gamma Y_{1,-1}] \\ = \lambda [\alpha Y_{1,1} + \beta Y_{1,0} + \gamma Y_{1,-1}] \end{aligned}$$

where  $\lambda$  represents the eigenvalue which can be  $+\hbar$ ,  $0$  or  $-\hbar$ . Using Eqs (51)–(53), the above equation becomes

$$\begin{aligned} \frac{\alpha + \gamma}{\sqrt{2}} \hbar Y_{1,0} + \frac{\beta}{\sqrt{2}} \hbar (Y_{1,1} + Y_{1,-1}) \\ = \lambda [\alpha Y_{1,1} + \beta Y_{1,0} + \gamma Y_{1,-1}] \end{aligned}$$

Thus

$$\begin{aligned} \frac{\alpha + \gamma}{\sqrt{2}} \hbar &= \lambda \beta \\ \frac{\beta}{\sqrt{2}} \hbar &= \lambda \alpha = \lambda \gamma \end{aligned}$$

Hence

$$\begin{aligned}\lambda = \hbar &\Rightarrow \alpha = \gamma = \frac{1}{\sqrt{2}} \beta \\ \lambda = 0 &\Rightarrow \alpha = -\gamma; \quad \beta = 0 \\ \lambda = -\hbar &\Rightarrow \alpha = \gamma = -\frac{1}{\sqrt{2}} \beta\end{aligned}$$

The three eigenfunctions are therefore given by Eqs (58)–(60).

### Solution 15.7

$$\begin{aligned}\psi(\theta, \phi) &= \frac{1}{2} \left[ -\sqrt{\frac{3}{8\pi}} \sin \theta (e^{i\phi} - e^{-i\phi}) + \sqrt{\frac{3}{2\pi}} \cos \theta \right] \\ &= \frac{1}{2} \left[ Y_{1,1} + Y_{1,-1} + \sqrt{2} Y_{1,0} \right]\end{aligned}$$

If we make a measurement of  $L_z$  we would get the values  $+\hbar$ ,  $0$  or  $-\hbar$  with probabilities  $\frac{1}{4}$ ,  $\frac{1}{2}$  and  $\frac{1}{4}$  respectively. Further

$$\begin{aligned}\langle L_z \rangle &= \iint \psi^*(\theta, \phi) L_z \psi(\theta, \phi) \sin \theta d\theta d\phi \\ &= \frac{1}{4} \hbar - \frac{1}{4} \hbar + 0 = 0\end{aligned}$$

On the other hand, if we make a measurement of  $L_x$ , we should express  $\psi(\theta, \phi)$  as a linear combination of  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  which represent the eigenfunctions of  $L_x$  [see Eqs (55)–(57)]. We find

$$\psi(\theta, \phi) = \psi_1$$

and therefore if we make a measurement  $L_x$ , we will for certain obtain the value  $+\hbar$ . Obviously,

$$\langle L_x \rangle = +\hbar$$

# Chapter 16

## The Double Well Potential and the Krönig-Penney Model

*I look upon quantum mechanics with admiration and suspicion.*

— ALBERT EINSTEIN in a letter<sup>1</sup> to his intimate friend Paul Ehrenfest, dated August 28, 1926.

### 16.1. Introduction

In this chapter we will first discuss the solutions of the Schrödinger equation for the double well problem which will be followed by a discussion of the ammonia molecule as a two state system. We will also discuss the Krönig-Penney model leading to the formation of energy bands in a solid.

### 16.2. Two isolated wells

Before we consider a double well structure, we consider two isolated wells as shown in Fig. 16.1. The potential energy variation corresponding to the well on the left is given by

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < a \\ V_0 & x > a \end{cases} \quad (1)$$

The Schrödinger equation in regions  $0 < x < a$  and  $x > a$  would be given by

$$\frac{d^2\psi}{dx^2} + k^2 \psi(x) = 0 \quad \text{for } 0 < x < a \quad (2)$$

---

<sup>1</sup> Actually the original letter was in German and it read *Der Quanten-Mechanik stehe ich bewundernd-misstrauisch gegenüber....* [Quoted from M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill Book Co., New York (1966)].

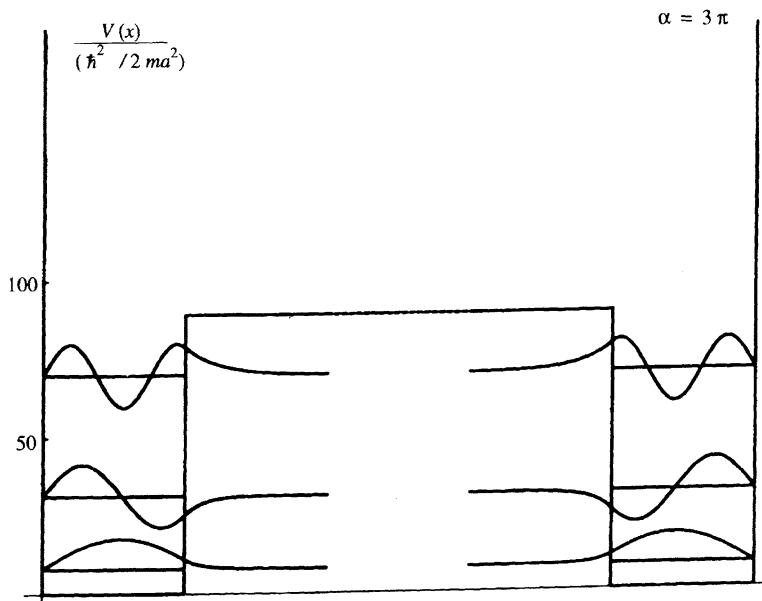


Figure 16.1. The first three eigenvalues and eigenfunctions of two isolated wells for  $\alpha = 3\pi$ .

and

$$\frac{d^2\psi}{dx^2} - \kappa^2 \psi(x) = 0 \quad \text{for } x > a \quad (3)$$

where

$$k^2 = \frac{2mE}{\hbar^2} \quad (4)$$

and

$$\kappa^2 = \frac{2m}{\hbar^2} (V_0 - E) \quad (5)$$

We are assuming  $E < V_0$ . As discussed in Sec. 6.2, the wave function should vanish at  $x = 0$  so that

$$\psi(x) = A \sin kx \quad \text{for } 0 < x < a \quad (6)$$

and

$$\psi(x) = C e^{-\kappa(x-a)} \quad \text{for } x > a \quad (7)$$

where we have rejected the exponentially amplifying solution in the region  $x > a$ . Continuity of  $\psi(x)$  and  $d\psi/dx$  at  $x = a$  gives us

*Transcendental equation*

$$-\xi \cot \xi = \sqrt{\alpha^2 - \xi^2} \quad (8)$$

where

$$\xi = ka = \sqrt{\frac{2mEa^2}{\hbar^2}} \quad (9)$$

and

$$\alpha = \sqrt{\frac{2mV_0a^2}{\hbar^2}} \quad (10)$$

### Numerical example

Let us assume  $\alpha = 3\pi$ . Thus

$$V_0 = 9\pi^2 (\hbar^2/2ma^2)$$

(see Fig. 16.1 where the vertical axis represents the energy in units of  $\hbar^2/2ma^2$ .) The solution of the transcendental equation [Eq. (8)] gives us three bound states for which

$$\xi = 2.83595, 5.64146 \text{ and } 8.33877 \quad (11)$$

We define the normalized energy eigenvalue

$$\mathcal{E} = \frac{E}{\hbar^2/2ma^2} = \xi^2 \quad (12)$$

Thus the corresponding discrete values of  $\mathcal{E}$  are given by

$$\mathcal{E} = 8.0426, 31.8261 \text{ and } 69.5351 \quad (13)$$

The energy eigenvalues (represented by horizontal lines) and the corresponding eigenfunctions are shown in Fig. 16.1. Obviously, the particle would belong to one of the wells and there will not be any tunnelling from one well to the other.

### 16.3. The double well potential

We next consider the solution of the one-dimensional Schrödinger equation (see Eq. (11) of Chapter 6) for a double well potential characterized by the following potential energy distribution

*Potential energy*

$$V(x) = \begin{cases} V_0 & \text{for } 0 < |x| < b \\ 0 & \text{for } b < |x| < a + b \\ \infty & \text{for } |x| > a + b \end{cases} \quad (14)$$

(see Fig. 16.2.) The analysis of such a structure is one of the most beautiful prob-

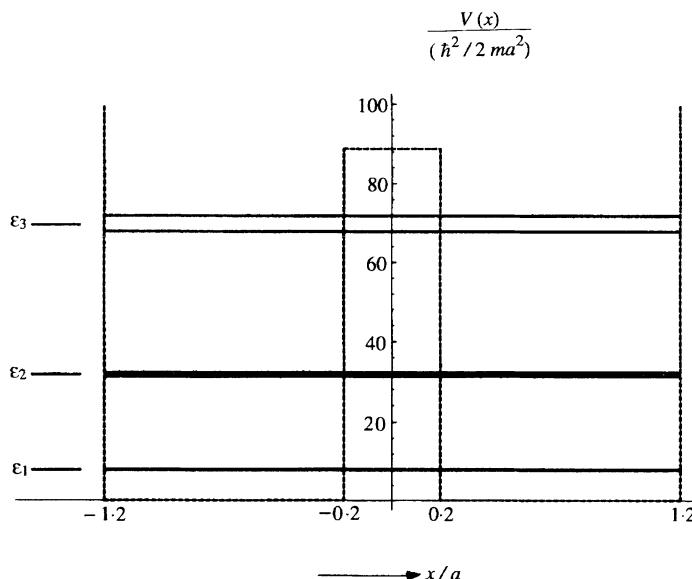


Figure 16.2. The double well potential and the corresponding energy eigenstates for  $\alpha = 3\pi$  and  $b/a = 0.2$ . The short horizontal lines on the extreme left represent the degenerate energy eigenvalues corresponding to two isolated wells [see Fig. 16.1]; each of the levels get split because of the coupling between the two wells.

lems in quantum mechanics. It not only allows us to understand the formation of energy bands in a solid; it also allows us to understand quantitatively how an electron confined in the first well (at  $t = 0$ ) would tunnel to the second well and then return to the first well.

Since  $V(-x) = V(x)$ , the solutions will be either symmetric or antisymmetric functions of  $x$ . We assume  $E < V_0$ . Thus the Schrödinger equation can be written in the form

$$\frac{d^2\psi}{dx^2} - \kappa^2 \psi(x) = 0 \quad \text{for } |x| < b \quad (15)$$

and

$$\frac{d^2\psi}{dx^2} + k^2 \psi(x) = 0 \quad \text{for } b < |x| < a + b \quad (16)$$

where  $k^2$  and  $\kappa^2$  have been defined earlier [see Eqs (4) and (5)]. The solution symmetric in  $x$  would be given by

*Symmetric solution*

$$\psi_s(x) = \begin{cases} A_s \cosh \kappa x & \text{for } |x| < b \\ A_s \frac{\cosh \kappa b}{\sin \kappa a} \sin [\kappa (a + b - |x|)] & \text{for } b < |x| < a + b \end{cases} \quad (17)$$

where we have assumed the continuity of  $\psi(x)$  at  $x = b$ . Further, since  $V(x)$  becomes infinite at  $x = a + b$ , the wave function has to vanish at  $x = a + b$  which has been incorporated in the solution given by Eq. (17). Continuity of  $d\psi/dx$  at  $x = b$  readily gives us

$$\tan ka = -\frac{k}{\kappa} \coth(\kappa b) \quad (18)$$

which represents the transcendental equation determining the energy eigenvalues corresponding to symmetric states. Similarly, the antisymmetric solution would be given by

#### *Antisymmetric solution*

$$\psi_s(x) = \begin{cases} A_a \sinh \kappa x & \text{for } |x| < b \\ A_a \frac{\sinh \kappa b}{\sinh \kappa a} \sin[k(a+b-x)] & \text{for } b < x < a+b \\ -A_a \frac{\sinh \kappa b}{\sinh \kappa a} \sin[k(a+b+x)] & \text{for } -(a+b) < x < -b \end{cases} \quad (19)$$

where, once again, we have assumed  $\psi(x)$  to be continuous at  $x = \pm b$ . Continuity of  $d\psi/dx$  at  $x = +b$  (or at  $x = -b$ ) would give us

$$\tan ka = -\frac{k}{\kappa} \tanh(\kappa b) \quad (20)$$

which represents the transcendental equation determining the energy eigenvalues corresponding to antisymmetric states. Eqs (18) and (20) can be rewritten in the following form

#### *Transcendental equations*

$$-\xi \cot \xi = \sqrt{\alpha^2 - \xi^2} \tanh \left[ \sqrt{\alpha^2 - \xi^2} \left( \frac{b}{a} \right) \right] \quad (\text{symmetric states}) \quad (21)$$

and

$$-\xi \cot \xi = \sqrt{\alpha^2 - \xi^2} \coth \left[ \sqrt{\alpha^2 - \xi^2} \left( \frac{b}{a} \right) \right] \quad (\text{antisymmetric states}) \quad (22)$$

where  $\xi$  and  $\alpha$  have been defined through Eqs (9) and (10) respectively. For  $b/a \rightarrow \infty$ , Eqs (21) and (22) reduce to Eq. (8) and we have degenerate states (see Fig. 16.1).

#### *Numerical example*

As a numerical example, we assume

$$\alpha = 3\pi \quad \text{and} \quad \frac{b}{a} = 0.2$$

The  $\xi$  values [as obtained by solving Eqs (21) and (20)] are given by

$$\xi = \begin{cases} 2.82154 (s), & 5.60021 (s), & 8.23678 (s) \\ 2.84990 (a), & 5.68284 (a), & 8.47649 (a) \end{cases} \quad (23)$$

where  $s$  and  $a$  refer to symmetric and antisymmetric states. These are shown as horizontal lines in Fig. 16.2. The normalized energy eigenvalues

*Normalized energy eigenvalues*

$$\mathcal{E} = \frac{E}{\hbar^2/2ma^2} = \xi^2 \quad (24)$$

would be given by

$$\mathcal{E} = \begin{cases} 7.96109 (s), & 31.3624 (s), & 67.8445 (s) \\ 8.12193 (a), & 32.2947 (a), & 71.8509 (a) \end{cases} \quad (25)$$

so that

$$\Delta\mathcal{E} \simeq 0.16084, 0.9323, 4.0064 \quad (26)$$

Comparing Fig. 16.2 with Fig. 16.1 we find that there is a coupling between the wells and each level splits into two levels<sup>2</sup>; the splitting becoming more for higher energy states [see Eq. (26)].

Figures 16.3 and 16.4 give the spatial variation of the first four wave functions. In Fig. 16.3, the solid and dashed curves correspond to the first energy eigenstate ( $\mathcal{E} = 7.96109$ ) and the second energy eigenstate ( $\mathcal{E} = 8.12193$ ) respectively. Similarly, in Fig. 16.4, the solid and the dashed curves correspond to the third and the fourth eigenstates respectively ( $\mathcal{E} = 31.3624$  and  $32.2947$ ). Notice that they are alternately symmetric and antisymmetric functions of  $x$ . Let us suppose that at  $t = 0$ , a particle is described by the wave function

$$\Psi(x, t=0) = \frac{1}{\sqrt{2}} [\psi_s^{(1)}(x) + \psi_a^{(1)}(x)] \quad (27)$$

where  $\psi_s^{(1)}(x)$  and  $\psi_a^{(1)}(x)$  represent respectively the lowest symmetric and the lowest antisymmetric wave functions shown in Fig. 16.3; and the factor of  $1/\sqrt{2}$  makes it normalized. How will the wave function evolve with time? Well, as in earlier chapters, we just have to multiply  $\psi_s^{(1)}(x)$  and  $\psi_a^{(1)}(x)$  by appropriate time dependent phase factors to obtain

$$\Psi(x, t) = \frac{1}{\sqrt{2}} \left[ \psi_s^{(1)}(x) \exp\left(-\frac{iE_s^{(1)}t}{\hbar}\right) + \psi_a^{(1)}(x) \exp\left(-\frac{iE_a^{(1)}t}{\hbar}\right) \right] \quad (28)$$

<sup>2</sup> If there are three wells then each level will split into three levels. In general, if there are  $N$  such wells (see Fig. 8.9) each level will form a band comprising of  $N$  levels; these are the energy bands in a solid; see also Sec. 23.3.

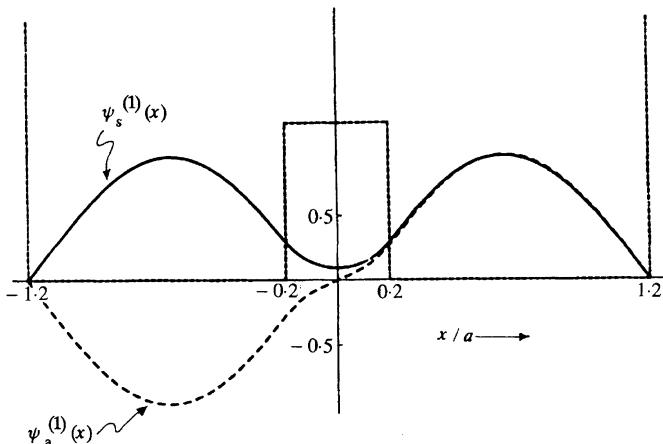


Figure 16.3. The solid and dashed curves correspond to the first energy eigenstate ( $\mathcal{E} = 7.96109$ ) and the second eigenstate ( $\mathcal{E} = 8.12193$ ) respectively.

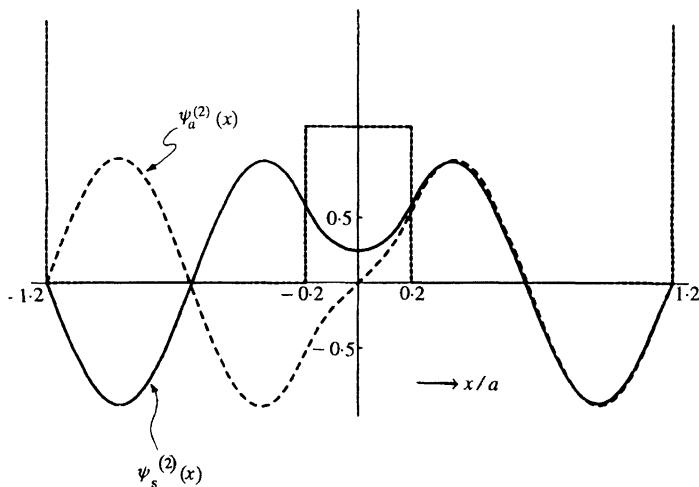


Figure 16.4. The solid and the dashed curves correspond to the third and the fourth eigenstates respectively ( $\mathcal{E} = 31.3624$  and  $32.2947$ ).

which represents a rigorously correct solution of the time dependent Schrödinger equation corresponding to the double well potential. The above equation can be rewritten in the form

$$\Psi(x, t) = \frac{1}{\sqrt{2}} e^{-i E_s^{(1)} t / \hbar} [\psi_s^{(1)}(x) + \psi_a^{(1)}(x) e^{-i \pi t / T}] \quad (29)$$

where

$$T = \frac{\pi \hbar}{\Delta E^{(1)}} = \left( \frac{2\pi m a^2}{\hbar} \right) \frac{1}{\Delta \mathcal{E}} \quad (30)$$

and

$$\Delta E^{(1)} = E_a^{(1)} - E_s^{(1)} = \frac{\hbar^2}{2ma^2} \Delta \mathcal{E}^{(1)} \quad (31)$$

From Eq. (29) it immediately follows that at  $t = 0, 2T, 4T, \dots$

$$|\Psi(x, t)|^2 = \frac{1}{2} [\psi_s^{(1)}(x) + \psi_a^{(1)}(x)]^2 \quad (32)$$

and the particle is most likely to be found in the first well. On the other hand, at  $t = T, 3T, 5T, \dots$

$$|\Psi(x, t)|^2 = \frac{1}{2} [\psi_s^{(1)}(x) - \psi_a^{(1)}(x)]^2 \quad (33)$$

and the particle is most likely to be found in the second well. Thus the particle tunnels through the barrier in a time  $\sim T$ . Figure 16.5 gives the time evolution of

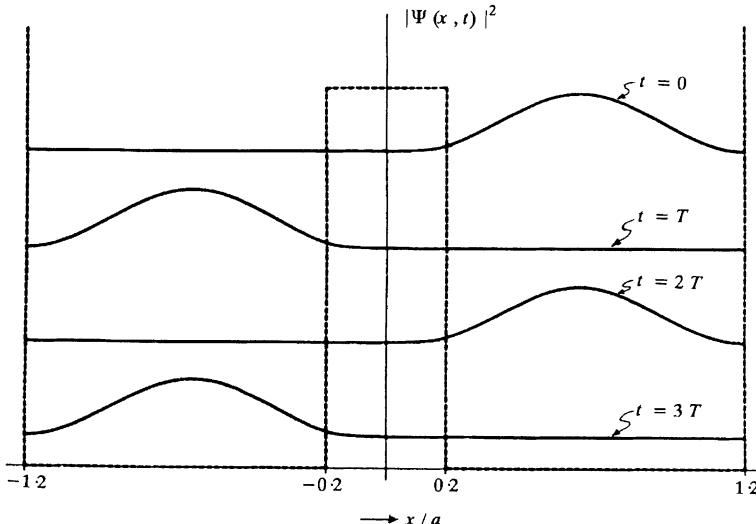


Figure 16.5. Time evolution of  $|\Psi(x, t)|^2$  [as given by Eq. (29)] for  $t = 0, T, 2T$  and  $3T$ .

$|\Psi(x, t)|^2$  for  $t = 0, T, 2T$  and  $3T$ . It may be seen that the particle which has a very high probability of being found in the first well at  $t = 0$  tunnels to the second well at  $t = T$  and then tunnels back to the initial state at  $t = 2T$ . At  $t = T/2$ , the probability of finding the particle in either of the wells would be approximately equal.

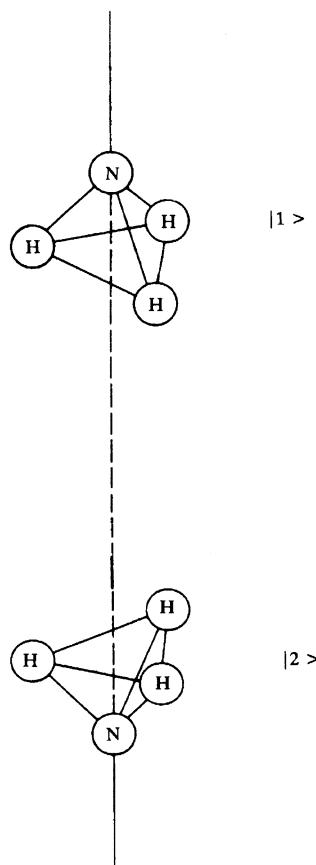


Figure 16.6. The two states of the ammonia molecule.

#### 16.4. The ammonia molecule as a two-state system

The ammonia molecule has a nitrogen atom and three hydrogen atoms forming a pyramid (see Fig. 16.6). The potential energy function associated with the ammonia molecule can be, to a first approximation, described by a double well potential (similar to the ones shown in Figs 16.2 and 17.9) and with  $x$  representing the distance between the nitrogen atom and the plane containing the hydrogen atoms. We assume that only two states are needed for the dynamical description of the ammonia molecule; these two states of the molecule are:

1. the state with the nitrogen atom above the plane of the hydrogen atoms (see the top figure in Fig. 16.6), and
2. the state with the nitrogen atom below this plane (see bottom figure in Fig. 16.6).

We denote these states by  $|1\rangle$  and  $|2\rangle$  respectively. The state<sup>3</sup> of the ammonia molecule can be assumed to be described by

$$|\Psi(t)\rangle = C_1(t)|1\rangle + C_2(t)|2\rangle \quad (34)$$

This is referred to as the two state approximation. The time evolution is described by the equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle \quad (35)$$

or,

$$i\hbar\left[\frac{dC_1}{dt}|1\rangle + \frac{dC_2}{dt}|2\rangle\right] = C_1(t)H|1\rangle + C_2(t)H|2\rangle \quad (36)$$

If we premultiply the above equation by  $\langle 1|$  we would obtain

$$i\hbar\frac{dC_1}{dt} = H_{11}C_1(t) + H_{12}C_2(t) \quad (37)$$

Similarly,

$$i\hbar\frac{dC_2}{dt} = H_{21}C_1(t) + H_{22}C_2(t) \quad (38)$$

where

$$H_{11} = \langle 1 | H | 1 \rangle$$

$$H_{12} = \langle 1 | H | 2 \rangle$$

etc. We really do not know the precise values for  $H_{11}$ ,  $H_{12}$ , etc., However, from the symmetry of the problem we may write<sup>4</sup>

$$H_{11} = H_{22} = E_0 \quad (39)$$

<sup>3</sup> We must point out that  $|1\rangle$  and  $|2\rangle$  are *not* the eigenstates of the Hamiltonian. In order to understand this point, we refer to the case of two isolated wells shown in Fig. 16.1. If we consider only the lowest state then  $\psi_1$  and  $\psi_2$  are the eigenfunctions of the isolated wells; the eigenfunctions of the double well are approximately given by

$$\psi_s^{(1)}(x) \approx \frac{1}{\sqrt{2}} [\psi_1(x) + \psi_2(x)]$$

and

$$\psi_a^{(1)}(x) \approx \frac{1}{\sqrt{2}} [\psi_1(x) - \psi_2(x)]$$

(see Figs 16.1 and 16.3).

<sup>4</sup> The notation and the analysis are essentially based on the Feynman lectures (see Chapter 19 of Ref. 1); see also Ref. 2. To quote Feynman *In the discussion up to this point, we have assumed values of  $E_0$  and  $A$  without knowing how to calculate them. According to the correct physical theory, it should be possible to calculate these constants in terms of the positions and motions of all the nuclei and electrons. But nobody has ever done it. Such a system involves ten electrons and four nuclei and that's just too complicated a problem. As a matter of fact, there is no one who knows much more about this molecule than we do.*

and

$$H_{12} = H_{21} = -A \quad (40)$$

Thus

$$i \hbar \frac{dC_1}{dt} = E_0 C_1(t) - A C_2(t) \quad (41)$$

and

$$i \hbar \frac{dC_2}{dt} = -A C_1(t) + E_0 C_2(t) \quad (42)$$

The solution of the above equations is very straightforward. We assume

$$C_1(t) = c_1 e^{-iEt/\hbar}$$

and

$$C_2(t) = c_2 e^{-iEt/\hbar}$$

to obtain

$$(E - E_0) c_1 + A c_2 = 0$$

and

$$A c_1 + (E - E_0) c_2 = 0$$

Thus

$$\begin{pmatrix} E - E_0 & A \\ A & E - E_0 \end{pmatrix} = 0$$

or,

$$(E - E_0)^2 = A^2$$

or,

$$E = E_0 \pm A \quad (43)$$

The levels split (similar to the splitting shown in Fig. 16.2). Further,

$$c_1 = +c_2 \quad \text{for } E = E_0 - A \quad (44)$$

and

$$c_1 = -c_2 \quad \text{for } E = E_0 + A \quad (45)$$

Thus the eigenstates are

*Approximate eigenstates*

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) \quad \text{for } E = E_0 - A \quad (46)$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) \quad \text{for } E = E_0 + A \quad (47)$$

In the two state approximation, these are the eigenfunctions of the total Hamiltonian (see, e.g. Figs 16.1 and 16.3). If

$$C_1(0) = \pm C_2(0)$$

the system will be in an eigenstate of the system. However, if

$$C_1(0) = 1$$

and

$$C_2(0) = 0$$

we would obtain

$$C_1(t) = \cos\left(\frac{At}{\hbar}\right) e^{-iE_0 t/\hbar} \quad (48)$$

and

$$C_2(t) = i \sin\left(\frac{At}{\hbar}\right) e^{iE_0 t/\hbar} \quad (49)$$

giving

$$|C_1(t)|^2 = \cos^2\left(\frac{At}{\hbar}\right) \quad (50)$$

and

$$|C_2(t)|^2 = \sin^2\left(\frac{At}{\hbar}\right) \quad (51)$$

We may compare this with the evolution of the wave packet discussed in Example 14.1.

In above, what we have essentially implied is that if we assume  $|1\rangle$  and  $|2\rangle$  as base kets, then the representation of the Hamiltonian is given by

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} E_0 & -A \\ A & E_0 \end{pmatrix} \quad (52)$$

and the eigenvalues of the above matrix are

$$E_0 \pm A \quad (53)$$

Now, the two states  $|1\rangle$  and  $|2\rangle$  of the ammonia molecule (see Fig. 16.6) have equal and opposite dipole moments. Thus in the presence of an electric field  $\mathcal{E}$  we may write

$$\left. \begin{array}{l} H_{11} = E_0 + \mu \mathcal{E} \\ H_{22} = E_0 - \mu \mathcal{E} \\ H_{12} = H_{21} = -A \end{array} \right\} \quad (54)$$

where  $\mu$  represents the electric dipole moment<sup>5</sup>. Thus instead of Eq. (52) the Hamiltonian matrix is

*Hamiltonian matrix*

$$\begin{pmatrix} E_0 + \mu \epsilon & -A \\ -A & E_0 - \mu \epsilon \end{pmatrix} \quad (55)$$

The corresponding eigenvalues would be

*Eigenvalues*

$$\begin{aligned} E &= E_0 \pm [A^2 + \mu^2 \epsilon^2]^{1/2} \\ &\simeq E_0 \pm \left[ A + \frac{1}{2A} \mu^2 \epsilon^2 \right] \end{aligned} \quad (56)$$

where the last expression is valid for  $\mu \epsilon \ll A$ .

Now, if a collimated beam of ammonia molecules is passed through an inhomogeneous electric field whose gradient is in a direction perpendicular to the beam then the force acting on the molecules in the lower state will be opposite in direction to the force acting on the molecules which are in the upper state. Thus the two molecular states can be separated by passing the molecules through an inhomogeneous electric field. The molecules in the upper state are then passed through a resonant cavity whose resonance frequency  $\omega_0$  equals  $2A/\hbar$ , then for particular lengths of the cavity all the ammonia molecules (as they pass through the cavity) will make a transition to the lower state, thereby emitting electromagnetic waves at the resonant frequency. It should be mentioned that if the two states were not separated, then the molecules in the lower state would have taken the energy from the cavity and made a transition to the upper state. This is nothing but the condition for *population inversion* which is necessary for the operation of laser or maser. For more details about the working of the maser, the reader is referred to Ref. 1 and also to the Nobel lecture of Townes (Ref. 3).

---

<sup>5</sup> To quote Feynman again, *All anyone can say is that when there is an electric field, the energy of the two states is different, the difference being proportional to the electric field. We have called the coefficient of proportionality  $2\mu$ , but its value must be determined experimentally. We can also say that the molecule has the amplitude  $A$  to flip over, but this will have to be measured experimentally. Nobody can give us accurate theoretical values of  $\mu$  and  $A$ , because the calculations are too complicated to do in detail.*

## 16.5. The Krönig-Penney model

In this section we will discuss solutions of the one-dimensional Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (57)$$

for a periodic potential<sup>6</sup> given by

*Periodic potential*

$$V(x+L) = V(x) \quad (58)$$

Now, according to Bloch's theorem (see e.g. Ref. 5), for a periodic potential given by Eq. (58), the solution of the one-dimensional Schrödinger equation is of the form

$$\psi(x) = e^{ikx} u(x) \quad (59)$$

where  $u(x)$  has the periodicity of the lattice, i.e.

$$u(x+L) = u(x) \quad (60)$$

Thus

$$\begin{aligned} \psi(x+L) &= e^{ik(x+L)} u((x+L)) \\ &= e^{ikL} e^{ikx} u(x) \end{aligned}$$

or,

$$\psi(x+L) = e^{ikL} \psi(x) \quad (61)$$

Now

$$\frac{d\psi}{dx} = ik e^{ikx} u(x) + e^{ikx} \frac{du}{dx}$$

Thus

$$\begin{aligned} \left. \frac{d\psi}{dx} \right|_{x+L} &= ik e^{ik(x+L)} u(x) + e^{ik(x+L)} \frac{du}{dx} \\ &= e^{ikL} \left. \frac{d\psi}{dx} \right|_x \end{aligned}$$

or,

$$\left. \frac{d\psi}{dx} \right|_x = e^{-ikL} \left. \frac{d\psi}{dx} \right|_{x+L}$$

or,

$$\left. \frac{d\psi}{dx} \right|_{x=-\epsilon} = e^{-ikL} \left. \frac{d\psi}{dx} \right|_{L-\epsilon} \quad (62)$$

---

<sup>6</sup> We may recall that in Problem 8.4 we had used a matrix method to solve the Schrödinger equation. We will use here a method discussed by Wolfe in Ref. 4.

We assume the periodic potential to be given by

$$V(x) = A \sum_{n=-\infty}^{+\infty} \delta(x - nL) \quad (63)$$

which represents a series of delta functions (see Fig. 16.7). If we refer to Eq. (69)

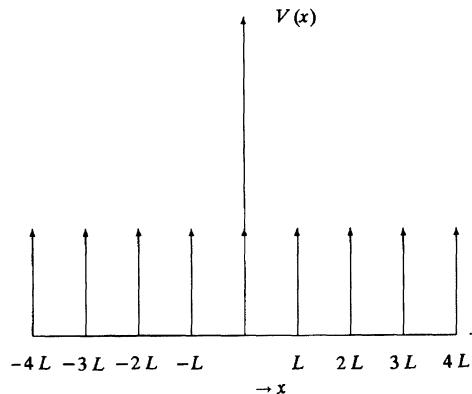


Figure 16.7. A periodic potential described by a series of delta functions.

of Chapter 8 (which is shown in Fig. 8.9) and make  $a \rightarrow 0$  and  $V_0 \rightarrow \infty$  such that the product

$$V_0 a \rightarrow A \quad (64)$$

we will obtain a series of delta functions as shown in Fig. 16.7.

We first calculate the discontinuity of  $d\psi/dx$  at a point where  $V(x)$  is a delta function (compare Problems 6.9 and 6.10). Now,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (65)$$

If we integrate the above equation from  $x = -\epsilon$  to  $x = +\epsilon$  we would obtain

$$\int_{-\epsilon}^{+\epsilon} \frac{d^2\psi}{dx^2} dx = -\frac{2mE}{\hbar^2} \int_{-\epsilon}^{\epsilon} \psi(x) dx + \frac{2mA}{\hbar^2} \int_{-\epsilon}^{\epsilon} \delta(x) \psi(x) dx$$

or

$$\left. \frac{d\psi}{dx} \right|_{x=\epsilon} - \left. \frac{d\psi}{dx} \right|_{x=-\epsilon} = +\frac{2mA}{\hbar^2} \psi(0) \quad (66)$$

which is consistent with the results of Problem 6.9. Thus

$$\left. \frac{d\psi}{dx} \right|_{x=-\epsilon} = \left. \frac{d\psi}{dx} \right|_{x=\epsilon} - \frac{2mA}{\hbar^2} \psi(0)$$

If we now use Eq. (62) we would get

$$e^{-ikL} \frac{d\psi}{dx} \Big|_{L-\epsilon} = \frac{d\psi}{dx} \Big|_{x=\epsilon} - \frac{2mA}{\hbar^2} \psi(0) \quad (67)$$

Let us consider the solution of the Schrödinger equation in the region (see Fig. 16.7)

$$\epsilon < x < L - \epsilon \quad (\epsilon \rightarrow 0)$$

where  $V(x) = 0$ . Thus we may write the solution as

$$\psi(x) = D e^{i\alpha x} + B e^{-i\alpha x}; \quad \epsilon < x < L - \epsilon \quad (68)$$

where

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad (69)$$

Using the condition given by Eq. (61) we get

$$e^{-ikL} \psi(L) = \psi(0)$$

or,

$$e^{-ikL} [D e^{i\alpha L} + B e^{-i\alpha L}] = D + B$$

or,

$$D [1 - e^{i\beta}] + B [1 - e^{-i\gamma}] = 0 \quad (70)$$

where

$$\beta = (\alpha - k)L$$

and

$$\gamma = (\alpha + k)L$$

Now,

$$\frac{d\psi}{dx} = i\alpha [D e^{i\alpha x} - B e^{-i\alpha x}]$$

Since [see Eq. (67)]

$$\frac{d\psi}{dx} \Big|_{x=\epsilon} - \frac{2mA}{\hbar^2} \psi(0) = e^{-ikL} \frac{d\psi}{dx} \Big|_{L-\epsilon}$$

we get (in the limit of  $\epsilon \rightarrow 0$ )

$$\begin{aligned} & i\alpha(D - B) - \frac{2mA}{\hbar^2}(D + B) \\ &= e^{-ikL} i\alpha(D e^{i\alpha L} - B e^{-i\alpha L}) \\ &= i\alpha(D e^{i\beta} - B e^{-i\gamma}) \end{aligned}$$

or,

$$\left[1 - e^{i\beta} + \frac{2iP}{L\alpha}\right] D + \left[1 - e^{-i\gamma} - \frac{2iP}{L\alpha}\right] B = 0 \quad (71)$$

where

$$P = \frac{mAL}{\hbar^2} \quad (72)$$

We rewrite Eq. (70)

$$\left[1 - e^{i\beta}\right] D + \left[1 - e^{-i\gamma}\right] B = 0 \quad (73)$$

From Eqs (71) and (73) we readily get

$$\left(1 - e^{i\beta} + \frac{2iP}{L\alpha}\right) (1 - e^{-i\gamma}) + (1 - e^{i\beta}) \left(1 - e^{-i\gamma} - \frac{2iP}{L\alpha}\right) = 0$$

or

$$\begin{aligned} 2(1 - e^{i\beta})(1 - e^{-i\gamma}) &= \frac{2iP}{L\alpha} [1 - e^{i\beta} - 1 + e^{-i\gamma}] \\ &= -\frac{2iP}{L\alpha} [e^{i(\alpha-k)L} - e^{-i(\alpha+k)L}] \\ &= \frac{4P}{L\alpha} e^{-ikL} \sin \alpha L \end{aligned}$$

On the other hand, the left-hand side is given by

$$\begin{aligned} &= 2[1 - e^{i\beta} - e^{-i\gamma} + e^{i(\beta-\gamma)}] \\ &= 2[1 - e^{-ikL}(e^{ikL} + e^{-i\alpha L}) + e^{-2ikL}] \\ &= 2e^{-ikL}[e^{ikL} - 2 \cos \alpha L + e^{-ikL}] \\ &= 4e^{-ikL}[\cos kL - \cos \alpha L] \end{aligned}$$

Thus we get

$$P \frac{\sin \alpha L}{\alpha L} + \cos \alpha L = \cos kL \quad (74)$$

We rewrite the above equation as

$$f(\xi) = \cos kL \quad (75)$$

where

$$f(\xi) = P \frac{\sin \xi}{\xi} + \cos \xi \quad (76)$$

and

$$\xi = \alpha L \quad (77)$$

From Eq. (74) it readily follows that we must have

$$-1 \leq f(\xi) \leq +1 \quad (78)$$

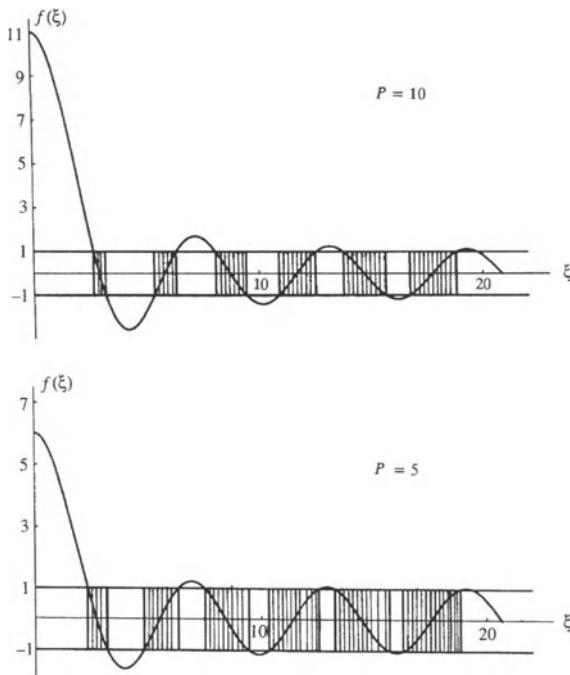


Figure 16.8.  $f(\xi)$  as a function of  $\xi$  for  $P = 10$  (top figure) and for  $P = 5$  (bottom figure).

In Fig. 16.8 we have plotted  $f(\xi)$  as a function of  $\xi$  for  $P = 10$  (top figure) and for  $P = 5$  (bottom figure). In Fig. 16.9 we have made corresponding plots of  $f(\xi)$  as a function of

$$\mathcal{E} = \xi^2 = \frac{E}{(\hbar^2/2mL^2)} \quad (79)$$

The shaded regions in Fig. 16.8 correspond to  $|f(\xi)| \leq 1$  and therefore represent allowed values of energy. Notice the formation of allowed and forbidden energy bands. Obviously,

$$P \rightarrow 0$$

corresponds to a free particle with all values of  $E$  possible. On the other hand, for

$$P \rightarrow \infty$$

we must have

$$\xi = n\pi \quad (80)$$

implying

$$E = E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad (81)$$

which represent the energy levels of a particle in an infinitely deep potential well (see Sec. 6.6.1).

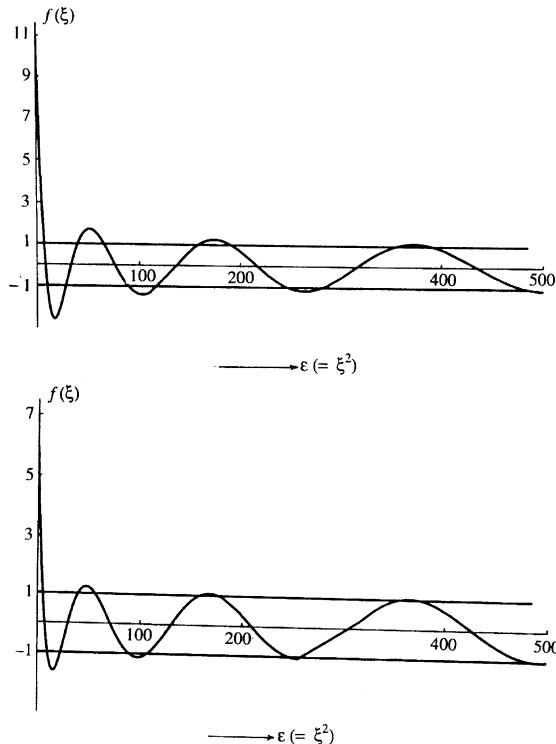


Figure 16.9. Variation of  $f(\xi)$  with  $\epsilon (= \xi^2)$  for  $P = 10$  (top figure) and for  $P = 5$  (bottom figure).

In Tables 16.1 and 16.2 we have tabulated the values of  $\xi$  where  $f(\xi) = +1$  or  $-1$ . From the corresponding values of  $\xi^2$  we can readily calculate the energy gap between successive bands from the following relation

*Energy gap*

$$\begin{aligned}\Delta E &= \frac{\hbar^2}{2mL^2} \Delta(\xi^2) \\ &= 0.152 \Delta(\xi^2) \text{ eV}\end{aligned}\quad (82)$$

where we have used  $m = 9.1095 \times 10^{-31}$  kg,  $\hbar = 1.0546 \times 10^{-34}$  J.s and  $L = 5\text{\AA} = 5 \times 10^{-10}$  m. It may be seen that the band gap increases with  $P$ .

## 16.6. Problems

**Problem 16.1** In the numerical example discussed in Sec. 16.3 calculate the value of the tunnelling time  $T$  (in seconds) for  $a = 2\text{\AA}$  and  $a = 5\text{\AA}$ .

Table 16.1. Energy gap of an electron at various wave numbers

$P = 5;$		$A = 7.62 \text{ eV } \text{\AA};$		$L = 5 \times 10^{-10} \text{ m}$	
$\xi$	$k(\text{\AA})^{-1}$	$f(\xi)$	$\xi^2$	$\Delta(\xi^2)$	$\Delta E (\text{eV})$
0		6	0		
				5.22	0.80
2.28445	0	+1	5.21871		
$\pi$	0.628	-1	$\pi^2$		
				12.8	1.9
4.76129	0.628	-1	22.6699		
$2\pi$	1.2566	+1	$4\pi^2$		
				16.23	2.47
7.46368	1.2566	+1	55.7065		
$3\pi$	1.88496	-1	$9\pi^2$		
				17.81	2.71
10.3266	1.88496	-1	106.639		
$4\pi$	2.51327	+1	$16\pi^2$		
				18.61	2.84
13.2862	2.51327	+1	176.524		
$5\pi$	3.14159	-1	$25\pi^2$		
				19.05	2.90
16.3031	3.14159	-1	265.792		

**Problem 16.2** Numerically solve Eqs (21) and (22) for  $\alpha = 3\pi$  and  $b/a = 0.5$  and show that the splitting of the energy levels become smaller.

**Problem 16.3** For the Krönig-Penney model discussed in Sec. 16.5, calculate the band gap energies (in electron volts) for  $P = 2$  and  $P = 20$ .

[Ans: For  $P = 2$ , the band gap energies are approximately 0.46 eV, 1.02 eV, 1.16 eV, 1.20 eV.]

**Problem 16.4** For  $x \gg 1$

$$\coth x \simeq 1 + 2e^{-2x}$$

and

$$\tanh x \simeq 1 - 2e^{-2x}$$

Using the above expressions, show that Eqs (21) and (22) can be written in the following approximate forms

$$\tan ka \approx -\frac{k}{\kappa} \mp \frac{2k}{\kappa} e^{-2\kappa b}$$

Table 16.2. Energy gap of an electron at various wave numbers

$P = 10;$		$A = 15.24 \text{ eV Å};$		$L = 5 \times 10^{-10} \text{ m}$	
$\xi$	$k(\text{Å})^{-1}$	$f(\xi)$	$\xi^2$	$\Delta(\xi^2)$	$\Delta E (\text{eV})$
0		11	0	6.90	1.05
2.6265	0	+1	6.90		
$\pi$	0.63	-1	$\pi^2$	18.30	2.79
5.30732	0.63	-1	28.17		
$2\pi$	1.26	+1	$4\pi^2$	25.60	3.90
8.06714	1.26	+1	65.08		
$3\pi$	1.88	-1	$9\pi^2$	30.17	4.60
10.9087	1.88	-1	119.0		
$4\pi$	2.51	+1	$16\pi^2$	33.66	5.04
13.8192	2.51	+1	191.0		
$5\pi$	3.14	-1	$25\pi^2$	34.92	5.32
16.7827	3.14	-1	281.7		

where the upper and lower signs correspond to the symmetric and antisymmetric states.

For  $k/\kappa \ll 1$  we obtain

$$ka \approx k^{(0)}a \approx n\pi$$

giving

$$E_n^{(0)} \approx \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Write  $k = k^{(0)} + k^{(1)}$  and assuming  $k^{(1)}a \ll 1$  show that

$$E_n \approx E_n^{(0)} - \frac{2E_n^{(0)}}{\kappa_n^{(0)}a} \mp \frac{4E_n^{(0)}}{\kappa_n^{(0)}a} e^{-2\kappa_n^{(0)}b}$$

which shows the splitting of the energy levels. In the above equation

$$\kappa_n^{(0)}a = \sqrt{\frac{2m}{\hbar^2} \left( V_0 - E_n^{(0)} \right) a^2}$$

### 16.7. References and suggested reading

1. R.P. Feynman, R.B. Leighton and M. Sands, *The Feynman Lectures on Physics*, Vol. 3, Addison-Wesley Publishing Co., Reading, Massachusetts (1965).
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# Chapter 17

## The JWKB Approximation

*God is a mathematician of very high order and He used very advanced mathematics in constructing the universe.*

— P.A.M. DIRAC<sup>1</sup>

### 17.1. Introduction

The exact solution of the Schrödinger equation can be obtained only for a few potential energy variations. In this chapter we will develop a widely used approximate method which gives a direct solution of the one-dimensional Schrödinger equation

$$\frac{d^2\psi}{dx^2} + k^2(x) \psi(x) = 0 \quad (1)$$

where

$$k^2(x) = \frac{2\mu}{\hbar^2} [E - V(x)] \quad (2)$$

*Validity*

and other symbols have their usual meaning. The method, which is usually abbreviated as the JWKB (after Jeffreys, Wentzel, Kramers and Brillouin) method, is applicable to potentials which are slowly varying such that

$$\left| \frac{1}{k(x)} \frac{dk}{dx} \right| \ll k(x) \quad (3)$$

We may mention here that Eq. (1) is also encountered in many other areas of physics and engineering (see, e.g. Ref. 1–3). For example, in electromagnetic theory, if a plane electromagnetic wave propagating in the  $x$ -direction is incident normally on an inhomogeneous medium characterized by the refractive index variation

<sup>1</sup> Quoted from *The Quantum Physicists* by W.H. Cropper, Oxford University Press, New York (1970), p. 5.

$n(x)$ , then the electric field satisfies Eq. (1) with

$$k^2(x) = \frac{\omega^2}{c^2} n^2(x) = \frac{4\pi^2}{\lambda_0^2} n^2(x) \quad (4)$$

where

$$\lambda_0 = \frac{2\pi c}{\omega} \quad (5)$$

represents the free space wavelength,  $c$  the speed of light in free space and  $\omega (= 2\pi\nu)$  is the angular frequency of the wave. For such a plane wave, the wave function  $\psi$  is either  $E_y$  or  $E_z$ ;  $E_x$  is taken to be zero (see, e.g. Ref. 1). Since

$$k(x) = \frac{\omega}{c} n(x) \quad (6)$$

Eq. (3) can be written in the form

$$\left| \frac{1}{n(x)} \frac{dn}{dx} \right| \ll \frac{2\pi}{\lambda} \quad (7)$$

where

$$\lambda(x) = \frac{2\pi}{k(x)} = \frac{\lambda_0}{n(x)} \quad (8)$$

represents the local wavelength. We rewrite Eq. (7) as

$$\left| \frac{dn}{dx} \lambda \right| \ll n \quad (9)$$

where we have omitted the factor of  $2\pi$ . The quantity on the left-hand side approximately represents the change in the refractive index in a distance of one wavelength; thus Eq. (9) implies *that the refractive index should change very little over a distance  $\lambda$* . This is the condition for the validity of the JWKB approximation.<sup>2</sup>

We may mention here that a second-order differential equation of the type

$$p(x) \frac{d^2y}{dx^2} + q(x) \frac{dy}{dx} + r(x) y(x) = 0 \quad (10)$$

can always be transformed to Eq. (1) (see Problem 17.4); thus the JWKB method can be applied to obtain direct solutions of Eq. (10). In Sec. 17.2 we will derive the JWKB solutions and will show that they are not valid near the turning points where  $k^2(x) = 0$ . In Sec. 17.3 we will give the *connection formulae* which connect the

---

<sup>2</sup> As  $\lambda \rightarrow 0$ , the JWKB approximation should become more and more accurate. This is also the geometrical optics limit. In quantum mechanics this would imply the approach towards classical mechanics. It is because of this reason that the JWKB formalism is often referred to as the *semi-classical theory*.

JWKB solutions from the left of the turning point to the right of the turning point (and vice versa); a heuristic derivation of the connection formulae will be given at the end of this chapter (Sec. 17.8).

In Sec. 17.4 we will use the JWKB solutions to derive an equation which would give the energy eigenvalues of the one-dimensional Schrödinger equation. In Sec. 17.5 we will use the JWKB solutions to study the tunnelling problem in quantum mechanics. In Sec. 17.6 we will discuss the JWKB solutions of the radial part of the Schrödinger equation for spherically symmetric potentials corresponding to  $l = 0$ . In Sec. 17.7 we will discuss the tunnelling of alpha particles from the nucleus.

## 17.2. The JWKB solutions

We first note that if  $k^2(x)$  is a constant, the solution of Eq. (1) would be given by

$$\psi(x) = e^{\pm i k x} \quad (11)$$

where we have omitted the arbitrary multiplicative constant. This suggests that we may try out a solution of the form

$$\psi(x) = e^{i u(x)} \quad (12)$$

where  $u(x)$  is to be determined. Substituting Eq. (12) in Eq. (1), we get

$$i \frac{d^2 u}{dx^2} - \left( \frac{du}{dx} \right)^2 + k^2(x) = 0 \quad (13)$$

The solution given by Eq. (12) is exact, provided  $u(x)$  is a solution of Eq. (13). Now, if  $k^2(x)$  was independent of  $x$  then  $d^2 u / dx^2 = 0$ ; thus when  $k^2(x)$  is slowly-varying, we may neglect the term proportional to  $d^2 u / dx^2$  to obtain

$$\left( \frac{du}{dx} \right)^2 = k^2(x) \quad (14)$$

implying

$$u(x) = \pm \int^x k(x) \, dx \quad (15)$$

Thus, in this approximation, we obtain

*Zeroeth-order JWKB solution*

$$\psi(x) \approx \psi_0(x) = \exp \left[ \pm i \int^x k(x) \, dx \right] \quad (16)$$

which is usually referred to as the zeroeth-order JWKB solution. The physical interpretation of Eq. (16) is as follows: For a slowly-varying refractive index, there is a change in phase only which is given by the integral

$$\Delta\phi = \int^x k(x) dx$$

It is for this reason that the JWKB method is often referred to as the phase-integral method (see, e.g. Ref. 4).

In order to obtain the condition for the validity of the solution given by Eq. (16), we differentiate  $\psi_0(x)$  twice to obtain

$$\frac{d^2\psi_0}{dx^2} + \left[ k^2(x) \mp i \frac{dk}{dx} \right] \psi_0(x) = 0 \quad (17)$$

Thus  $\psi_0(x)$  [as defined by Eq. (16)] rigorously satisfies Eq. (17). If we compare Eq. (17) with Eq. (1) we find that the two equations are the same provided we can neglect the term proportional to  $dk/dx$  in comparison with  $k^2(x)$ , i.e. provided

$$\left| \frac{dk}{dx} \right| \ll k^2(x) \quad (18)$$

or

$$\left| \frac{1}{k} \frac{dk}{dx} \right| \ll k(x) \quad (19)$$

which represents the condition for the validity of the JWKB solution. Points for which  $k^2(x) = 0$  are known as *turning points*<sup>3</sup> and obviously the JWKB solutions are not valid near the turning points.

In order to obtain a more accurate solution, we write

$$\psi(x) = F(x) \psi_0(x) = F(x) \exp \left[ \pm i \int^x k(x) dx \right] \quad (20)$$

where  $F(x)$  is yet to be determined. We substitute Eq. (20) in Eq. (1) to obtain

$$\frac{d^2F}{dx^2} \pm 2ik \frac{dF}{dx} \pm i \frac{dk}{dx} F(x) = 0 \quad (21)$$

Once again Eq. (20) represents a rigorous solution of Eq. (1) provided  $F(x)$  is the solution of Eq. (21). Since  $F(x)$  is expected to be slowly-varying, we neglect

---

<sup>3</sup> Why are they called turning points? For example, for the harmonic oscillator problem for which  $V(x) = \frac{1}{2}\mu\omega^2x^2$  [see Example 17.1], classical mechanics tells us that the particle will *turn back* at  $x = \pm\sqrt{2E/\mu\omega^2}$  which are the *turning points* [see Eq. (46)]. Similarly, if a particle is thrown up in earth's gravitational field [see Example 17.2] it will *turn back* at  $x = E/\gamma; \gamma = \mu g$ .

$d^2 F/dx^2$  to obtain

$$\frac{1}{F} \frac{dF}{dx} + \frac{1}{2k(x)} \frac{dk}{dx} = 0$$

or

$$\frac{d}{dx} \left[ \ln F(x) \sqrt{k(x)} \right] = 0$$

or

$$F(x) = \frac{\text{const}}{\sqrt{k(x)}} \quad (22)$$

The solutions

*JWKB solutions*

$$\psi(x) = \frac{\text{const}}{\sqrt{k(x)}} e^{\pm i \int^x k(x) dx} \quad (23)$$

are known as the JWKB solutions. The condition for the validity of the above solution is given in Problem 17.3.

### 17.2.1. THE GENERAL JWKB SOLUTIONS

The general JWKB solution is the linear combination

$$\psi(x) = \frac{C_1}{\sqrt{k(x)}} \exp \left[ i \int^x k(x) dx \right] + \frac{C_2}{\sqrt{k(x)}} \exp \left[ -i \int^x k(x) dx \right] \quad (24)$$

We could also have used the sine and cosine solutions:

$$\psi(x) = \frac{C_1}{\sqrt{k(x)}} \sin \left( \int^x k(x) dx \right) + \frac{C_2}{\sqrt{k(x)}} \cos \left( \int^x k(x) dx \right) \quad (25)$$

Till now we have assumed  $k^2(x)$  to be positive. For  $k^2(x) < 0$ , we write Eq. (1) as

$$\frac{d^2 \psi}{dx^2} - \kappa^2(x) \psi(x) = 0 \quad (26)$$

where

$$\kappa^2(x) = -k^2(x) \quad (27)$$

Using a method similar to that used in the preceding section, we obtain the following general JWKB solution

$$\psi(x) = \frac{D_1}{\sqrt{\kappa(x)}} \exp \left[ \int^x \kappa(x) dx \right] + \frac{D_2}{\sqrt{\kappa(x)}} \exp \left[ - \int^x \kappa(x) dx \right] \quad (28)$$

The solutions given by Eqs (24), (25) and (28) are valid when  $k^2(x)$  and  $\kappa^2(x)$  are slowly-varying, i.e. when

$$\left| \frac{1}{k(x)} \frac{dk}{dx} \right| \ll k(x) \quad \text{and} \quad \left| \frac{1}{\kappa(x)} \frac{d\kappa}{dx} \right| \ll \kappa(x) \quad (29)$$

A more precise condition is given in Problem 17.3.

### 17.3. The connection formulae

We next consider a typical variation of  $k^2(x)$  (see Fig. 17.1). The point  $x = a$

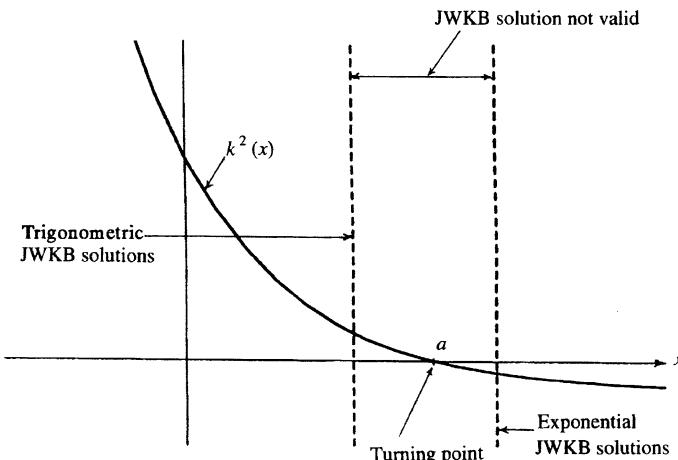


Figure 17.1. A typical variation of  $k^2(x)$  where the oscillatory trigonometric solutions are to the left of the turning point at  $x = a$  and exponential solutions are to the right of the turning point.

represents the turning point where  $k^2(x) = 0$ . Obviously, the JWKB solutions (as given in the preceding section) are valid far to the left of the turning point and also far to the right of the turning point. The question now arises that if we know the JWKB solutions to the left of the turning point, then how can we determine the JWKB solutions to the right of the turning point and conversely. This is done through what are known as the *connection formulae* which are given by (see Sec. 17.8)

$$\frac{2}{\sqrt{k(x)}} \sin \left[ \int_x^a k(x) dx + \frac{\pi}{4} \right] \leftrightarrow \frac{1}{\sqrt{\kappa(x)}} \exp \left[ - \int_a^x \kappa(x) dx \right] \quad (30)$$

and

$$\frac{1}{\sqrt{k(x)}} \cos \left[ \int_x^a k(x) dx + \frac{\pi}{4} \right] \leftrightarrow \frac{1}{\sqrt{\kappa(x)}} \exp \left[ + \int_a^x \kappa(x) dx \right] \quad (31)$$

Thus, the JWKB solution given by

$$\frac{2}{\sqrt{k(x)}} \sin \left[ \int_x^a k(x) dx + \frac{\pi}{4} \right]$$

in the region  $x < a$  goes over to an exponentially decaying solution in the region  $x > a$ , and the solution

$$\frac{1}{\sqrt{k(x)}} \cos \left[ \int_x^a k(x) dx + \frac{\pi}{4} \right]$$

in the region  $x < a$  goes over to an exponentially amplifying solution in the region  $x > a$ .

Similarly, if the variation of  $k^2(x)$  is similar to that shown in Fig. 17.2, the

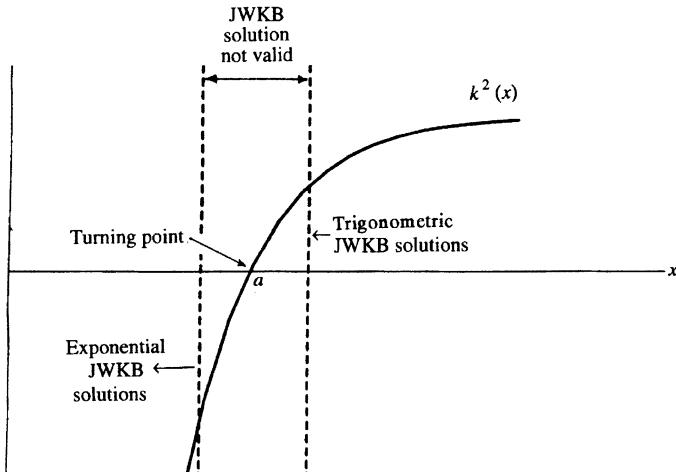


Figure 17.2. A typical variation of  $k^2(x)$  where the oscillatory trigonometric solutions are to the right of the turning point at  $x = a$ .

connection formulae would be given by

$$\frac{1}{\sqrt{\kappa(x)}} \exp \left[ - \int_x^a \kappa(x) dx \right] \leftrightarrow \frac{2}{\sqrt{k(x)}} \sin \left[ \int_a^x k(x) dx + \frac{\pi}{4} \right] \quad (32)$$

$$\frac{1}{\sqrt{\kappa(x)}} \exp \left[ + \int_x^a \kappa(x) dx \right] \leftrightarrow \frac{1}{\sqrt{k(x)}} \cos \left[ \int_a^x k(x) dx + \frac{\pi}{4} \right] \quad (33)$$

### 17.4. Application of the JWKB solutions to eigenvalue problems

One of the very important applications of the JWKB method is in the solution of the eigenvalue equations encountered in many areas like quantum mechanics, waveguide theory, etc. One usually comes across the equation

$$\frac{d^2\psi}{dx^2} + k^2(x) \psi(x) = 0 \quad (34)$$

with  $k^2(x)$  becoming negative for  $x \rightarrow +\infty$  and also for  $x \rightarrow -\infty$  (see, e.g. Fig. 17.3). The general approach is as follows: We start with an exponentially decaying solution in the region where  $x$  is large and positive, and use connection formulae to obtain the solution in the region where  $x$  is negative and large. We then derive the condition so that there is only an exponentially decaying solution in the region  $x \rightarrow -\infty$ . This condition leads to eigenvalues of the problem which are contained in  $k^2(x)$ .

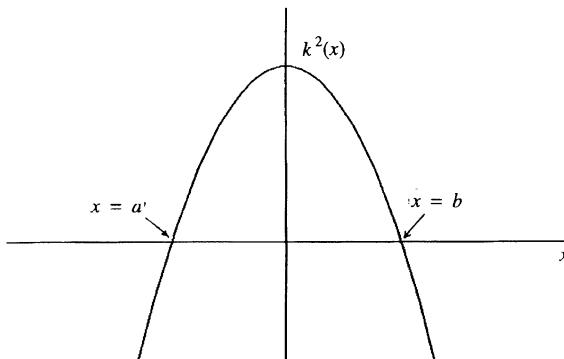


Figure 17.3. A typical variation of  $k^2(x)$  corresponding to the eigenvalue problem. The points  $x = a$  and  $x = b$  represent the turning points.

In most problems we have two turning points<sup>4</sup> which we denote by

*Turning points*

$$x = a \quad \text{and} \quad x = b \quad (35)$$

---

<sup>4</sup> Figure 17.3 corresponds to the situation where we have two turning points. We can have more than two turning points (see Problems 17.5 and 17.6); however, for bound state problems,  $k^2(x)$  must become negative for  $x \rightarrow \infty$  and also for  $x \rightarrow -\infty$ .

We first look for the JWKB solution for  $x > b$  (Region III) where  $k^2(x)$  is negative. If we use the boundary condition that  $\psi(x)$  must tend to 0 as  $x \rightarrow \infty$ , we must choose the exponentially decaying solution in Region III; thus

$$\psi_{\text{III}}(x) = \frac{A}{\sqrt{k(x)}} \exp \left[ - \int_b^x \kappa(x) dx \right] \quad (36)$$

where

$$\kappa^2(x) = -k^2(x) \quad (37)$$

Using the connection formula given by Eq. (30) we obtain the following JWKB solution in Region II ( $a < x < b$ ):

$$\psi_{\text{II}}(x) = \frac{2A}{\sqrt{k(x)}} \sin \left[ \int_x^b k(x) dx + \frac{\pi}{4} \right] \quad (38)$$

Now in order to use the connection formulae given by Eqs (32) and (33) (to obtain the JWKB solution in Region I) the argument of the sine or cosine function should be

$$\left( \int_a^x k(x) dx + \frac{\pi}{4} \right)$$

Thus, we write

$$\int_x^b k(x) dx + \frac{\pi}{4} = \left( \int_a^b k(x) dx + \frac{\pi}{2} \right) - \left( \int_a^x k(x) dx + \frac{\pi}{4} \right) \quad (39)$$

using which, we obtain

$$\psi_{\text{II}}(x) = \frac{2A}{\sqrt{k(x)}} \cos \left[ \theta - \left( \int_a^x k(x) dx + \frac{\pi}{4} \right) \right] \quad (40)$$

where

$$\theta = \int_a^b k(x) dx \quad (41)$$

Thus

$$\begin{aligned} \psi_{\text{II}}(x) &= (2A \cos \theta) \frac{1}{\sqrt{k(x)}} \cos \left[ \int_a^x k(x) dx + \frac{\pi}{4} \right] \\ &\quad + (2A \sin \theta) \frac{1}{\sqrt{k(x)}} \sin \left[ \int_a^x k(x) dx + \frac{\pi}{4} \right] \end{aligned} \quad (42)$$

Using the connection formulae given by Eqs (32) and (33), we obtain (in Region I)

$$\begin{aligned}\psi_1(x) &= 2A \cos \theta \frac{1}{\sqrt{\kappa(x)}} \exp \left[ + \int_x^a \kappa(x) dx \right] \\ &\quad + A \sin \theta \frac{1}{\sqrt{\kappa(x)}} \exp \left[ - \int_x^a \kappa(x) dx \right]\end{aligned}\quad (43)$$

The first term on the term right-hand side of this equation represents an exponentially growing solution<sup>5</sup> that should not be present; we therefore require

$$\cos \theta = 0 \Rightarrow \theta = \left( n + \frac{1}{2} \right) \pi$$

or

*JWKB quantization condition*

$$\theta = \int_a^b k(x) dx = \left( n + \frac{1}{2} \right) \pi \quad (44)$$

The above eigenvalue equation is a general relation and holds good for an arbitrary  $k^2(x)$  as long as it becomes negative<sup>6</sup> for  $x \rightarrow +\infty$  and  $x \rightarrow -\infty$ .

**Example 17.1** For the linear harmonic oscillator problem

*Harmonic oscillator problem*

$$V(x) = \frac{1}{2} \mu \omega^2 x^2$$

Thus

$$k^2(x) = \frac{2\mu}{\hbar^2} \left[ E - \frac{1}{2} \mu \omega^2 x^2 \right] \quad (45)$$

<sup>5</sup> This can be seen by noting that if  $\kappa(x)$  were equal to a constant ( $= \kappa$ ) then

$$\exp \left[ \int_x^a \kappa dx \right] = e^{\kappa a} e^{-\kappa x}$$

For  $x \rightarrow -\infty$ , the above solution would blow up exponentially.

<sup>6</sup> If  $k^2(x)$  becomes positive when  $x$  tends either to  $+\infty$  or  $-\infty$ , we have what is known as a scattering problem; the quantization condition does not exist and a continuum of energy values is possible (see also Sec. 17.5).

and the turning points are given by

$$a = -\sqrt{\frac{2E}{\mu \omega^2}} \quad \text{and} \quad b = +\sqrt{\frac{2E}{\mu \omega^2}} \quad (46)$$

Thus the JWKB quantization condition becomes

*JWKB quantization condition*

$$\begin{aligned} \left(n + \frac{1}{2}\right)\pi &= \int_a^b k(x) \, dx \\ &= \frac{\mu\omega}{\hbar} \int_a^b \left[ \frac{2E}{\mu\omega^2} - x^2 \right]^{1/2} \, dx \\ &= \int_{-\sqrt{\lambda}}^{+\sqrt{\lambda}} [\lambda - \xi^2]^{1/2} \, d\xi \end{aligned} \quad (47)$$

where

$$\xi = \gamma x; \quad \gamma = \sqrt{\frac{\mu\omega}{\hbar}}$$

and

$$\lambda = \frac{2E}{\hbar\omega} \quad (48)$$

If we make the substitution

$$\xi = \sqrt{\lambda} \sin \theta$$

we will readily get

$$\lambda \left[ \frac{\theta}{2} + \frac{1}{4} \sin 2\theta \right]_{-\pi/2}^{+\pi/2} = \left(n + \frac{1}{2}\right)\pi$$

or

$$\lambda = (2n + 1); \quad n = 0, 1, 2, \dots \quad (49)$$

giving

*Energy eigenvalues*

$$E = \left(n + \frac{1}{2}\right)\hbar\omega \quad (50)$$

Comparing with Eq. (28) of Chapter 7 we find that, for the linear harmonic oscillator problem, the JWKB quantization condition happens to give the exact result!

Having determined the allowed values of  $\lambda$ , the JWKB solutions are completely known and are given by

*JWKB solutions*

$$\psi(x) = \frac{(-1)^n A}{\sqrt{\kappa(x)}} \exp \left[ - \int_x^a \kappa(x) dx \right], \quad x < a \quad (51a)$$

$$= \frac{(-1)^n 2A}{\sqrt{k(x)}} \sin \left[ \int_a^x k(x) dx + \frac{\pi}{4} \right], \quad a < x < b \quad (51b)$$

$$= \frac{2A}{\sqrt{k(x)}} \sin \left[ \int_x^b k(x) dx + \frac{\pi}{4} \right], \quad a < x < b \quad (51c)$$

$$= \frac{A}{\sqrt{\kappa(x)}} \exp \left[ - \int_b^x \kappa(x) dx \right], \quad x > b \quad (51d)$$

Indeed the above solution is valid for an arbitrary variation of  $k^2(x)$  as long as there are two turning points and  $k^2(x)$  remains negative for  $x < a$  and  $x > b$ . For the linear harmonic oscillator problem the integrals are easy to evaluate:

$$\begin{aligned} \int_x^b k(x) dx &= \int_{\xi}^{\sqrt{\lambda}} \sqrt{\lambda - \xi^2} d\xi \\ &= \lambda \left[ \frac{1}{2} \sin^{-1} \frac{\xi}{\sqrt{\lambda}} + \frac{\xi}{2\lambda} \sqrt{\lambda - \xi^2} \right]_{\xi}^{\sqrt{\lambda}} \\ &= \lambda \left[ \frac{\pi}{4} - \frac{1}{2} \sin^{-1} \frac{\xi}{\sqrt{\lambda}} - \frac{1}{2} \xi \sqrt{\lambda - \xi^2} \right] \end{aligned} \quad (52)$$

Also

$$\frac{1}{\sqrt{k(x)}} = \frac{1}{\sqrt{\gamma}} \frac{1}{(\lambda - \xi^2)^{1/4}}$$

For example, for  $n = 1$  ( $\lambda = 3$ ), the JWKB wave function (in the region  $-\sqrt{\lambda} < x < \sqrt{\lambda}$ ) would be given by [using Eq. (51c)]:

$$\begin{aligned} \psi(\xi) &= \frac{2A}{(3 - \xi^2)^{1/4}} \sin \left[ \pi - \frac{3}{2} \sin^{-1} \frac{\xi}{\sqrt{3}} - \frac{\xi}{2} \sqrt{3 - \xi^2} \right] \\ &= \frac{2A}{(3 - \xi^2)^{1/4}} \sin \left[ \frac{3}{2} \sin^{-1} \frac{\xi}{\sqrt{3}} + \frac{\xi}{2} \sqrt{3 - \xi^2} \right] \end{aligned}$$

The same result would be obtained by using Eq. (51b):

$$\begin{aligned}\psi(\xi) &= -\frac{2A}{(3-\xi^2)^{1/4}} \sin \left[ \pi + \frac{3}{2} \sin^{-1} \frac{\xi}{\sqrt{3}} + \frac{\xi}{2} \sqrt{3-\xi^2} \right] \\ &= \frac{2A}{(3-\xi^2)^{1/4}} \sin \left[ \frac{3}{2} \sin^{-1} \frac{\xi}{\sqrt{3}} + \frac{\xi}{2} \sqrt{3-\xi^2} \right]\end{aligned}$$

which is an antisymmetric function of  $\xi$ . Similarly,

$$\begin{aligned}\int_{\lambda}^x \kappa(x) dx &= \int_{\sqrt{\lambda}}^{\xi} \sqrt{\xi^2 - \lambda} d\xi \\ &= \frac{1}{2} \xi \sqrt{\xi^2 - \lambda} - \frac{1}{2} \lambda \ln \left| \frac{\xi + \sqrt{\xi^2 - \lambda}}{\sqrt{\lambda}} \right|\end{aligned}\quad (53)$$

and

$$\int_{\xi}^{-\sqrt{\lambda}} \sqrt{\xi^2 - \lambda} d\xi = -\frac{1}{2} \xi \sqrt{\xi^2 - \lambda} + \frac{1}{2} \lambda \ln \left| \frac{\xi + \sqrt{\xi^2 - \lambda}}{\sqrt{\lambda}} \right| \quad (54)$$

Using Eqs (51a) and (51d) we obtain (for  $\lambda = 3$ ):

$$\begin{aligned}\psi(\xi) &= -\frac{A}{(\xi^2 - 3)^{1/4}} \exp \left[ \frac{1}{2} \xi \sqrt{\xi^2 - 3} - \frac{3}{2} \ln \left| \frac{\xi + \sqrt{\xi^2 - 3}}{\sqrt{3}} \right| \right] \quad \xi < -\sqrt{3} \\ &= \frac{A}{(\xi^2 - 3)^{1/4}} \exp \left[ -\frac{1}{2} \xi \sqrt{\xi^2 - 3} + \frac{3}{2} \ln \left| \frac{\xi + \sqrt{\xi^2 - 3}}{\sqrt{3}} \right| \right] \quad \xi > +\sqrt{3}\end{aligned}$$

which represents an antisymmetric function of  $\xi$ . In an exactly similar manner we can show that for  $\lambda = 7, 11, 15, \dots$   $\psi(\xi)$  will be antisymmetric and for  $\lambda = 1, 5, 9, 13, \dots$   $\psi(\xi)$  will be a symmetric function of  $\xi$ .

The JWKB wave functions are now completely determined except for an arbitrary multiplicative constant. We consider antisymmetric wave functions ( $n = 1, 3, 5, \dots$ ) and assume that  $\psi(\xi)$  has a unit slope at  $\xi = 0$ . This gives

$$A = \frac{(-1)^{(n-1)/2}}{\sqrt{2n+1}} ; \quad n = 1, 3, 5, \dots \quad (55)$$

The corresponding exact wave function would be (see Sec. 7.3)

*Exact wave function*

$$\psi_{\text{EXACT}}(\xi) = \frac{1}{2} (-1)^{(n-1)/2} \frac{(\frac{n-1}{2})!}{n!} H_n(\xi) \exp\left(-\frac{1}{2}\xi^2\right) \quad (56)$$

where we have chosen the multiplicative constant so that  $\psi'(0) = 1$ . In Figs 17.4 and 17.5 we have plotted the exact (viz., the Hermite-Gauss functions) and the JWKB wave functions for  $n = 3$  and 5. Except near the turning points, the JWKB wave functions agree well with the exact wave functions.

The JWKB solutions allow us to understand the general solution of the Schrödinger equation. Let us assume that  $E$  is not one of the eigenvalues, i.e.  $E \neq \frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \dots$ . Then, if we start with an exponentially decaying solution in the region  $x < a$ , we will end up with an exponentially amplifying solution in the region  $x > b$ . Similarly, if we start with an exponentially decaying solution in the region  $x > b$ , we will end up with an exponentially amplifying solution in the region  $x < a$ . These are the two independent solutions of the Schrödinger equation when  $E$  is not one of the eigenvalues.

**Example 17.2** Consider the potential energy variation given by (see Fig. 6.5)

*Potential corresponding to free fall under gravity*

$$\begin{aligned} V(x) &= \infty & x < 0 \\ &= \gamma x & x > 0 \end{aligned} \quad (57)$$

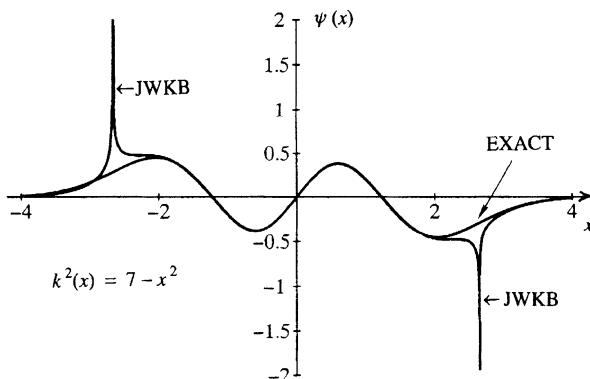


Figure 17.4. Exact and JWKB wave functions corresponding to  $n = 3$  [adapted from Ref. 3].

The above potential energy variation corresponds to the free fall of a particle in earth's gravitational field; obviously  $\gamma = \mu g$ . Since

$$k^2(x) = \frac{2\mu}{\hbar^2} [E - V(x)] \quad (58)$$

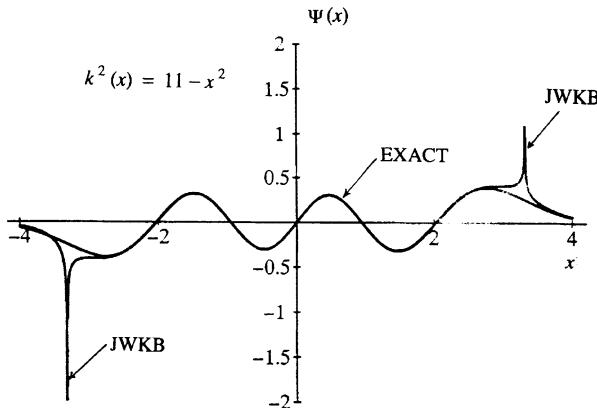


Figure 17.5. Exact and JWKB wave functions corresponding to  $n = 5$  [adapted from Ref. 3].

the turning points are  $x = 0$  and  $x = E/\gamma$ . Thus the eigenvalue equation [Eq. (44)] becomes

$$\begin{aligned} \left(n + \frac{1}{2}\right)\pi &= \int_0^{E/\gamma} k(x) \, dx \\ &= \left(\frac{2\mu}{\hbar^2}\right)^{1/2} \int_0^{E/\gamma} (E - \gamma x)^{1/2} \, dx = \frac{2}{3\gamma} \left(\frac{2\mu}{\hbar^2}\right)^{1/2} E^{3/2} \end{aligned} \quad (59)$$

implying

*Energy eigenvalues*

$$E = E_n = \left(\frac{\hbar^2\gamma^2}{2\mu}\right)^{1/3} \left[\frac{3}{4}(2n+1)\pi\right]^{2/3}; \quad n = 0, 1, 2, \dots \quad (60)$$

which represents the JWKB energy eigenvalues of the system. Thus

$$\mathcal{E}_n = \frac{E_n}{(\hbar^2\gamma^2/2\mu)^{1/3}} = \left[\frac{3}{4}(2n+1)\pi\right]^{2/3} \quad (61)$$

or

$$\mathcal{E}_n = 1.7707, 3.6838, 5.1775, \dots \quad (62)$$

corresponding to  $n = 0, 1, 2, \dots$ . It may be noted that the above values do not compare very well with the exact values which are (see Problem 6.8)

$$2.3381, 4.0879, 5.5206, \dots \quad (63)$$

The JWKB result does not compare very well with exact results because of the fact that there is an infinite discontinuity of  $V(x)$  [and hence of  $k^2(x)$ ] at  $x = 0$ . Now, because of  $V(x)$  becoming  $\infty$  at  $x = 0$ , the exact wave function must vanish there. Incorporating this condition, the JWKB wave function in the region  $0 < x < E/\gamma$  would be given by

$$\psi_{\text{JWKB}}(x) = \frac{A}{\sqrt{k(x)}} \sin \left[ \int_0^x k(x) dx \right] \quad 0 < x < E/\gamma \quad (64)$$

$$= \frac{A}{\sqrt{k(x)}} \sin \left[ \theta - \left( \int_x^b k(x) dx + \frac{\pi}{4} \right) \right] \quad (65)$$

where

$$\theta = \int_0^b k(x) dx + \frac{\pi}{4} \quad (66)$$

and

$$b = \frac{E}{\gamma} \quad (67)$$

Thus

$$\begin{aligned} \psi_{\text{JWKB}}(x) &= \frac{A}{\sqrt{k(x)}} \sin \theta \cos \left[ \int_x^b k(x) dx + \frac{\pi}{4} \right] \\ &\quad - \frac{A}{\sqrt{k(x)}} \cos \theta \sin \left[ \int_x^b k(x) dx + \frac{\pi}{4} \right] \end{aligned} \quad (68)$$

The first term on the right-hand side will go over to an exponentially amplifying solution in the region  $x > b$  and therefore we must have  $\sin \theta = 0$ , or,

$$\theta = n\pi \quad (69)$$

Thus

#### *Modified quantization condition*

$$\int_0^b k(x) dx = \left( n - \frac{1}{4} \right) \pi ; \quad n = 1, 2, \dots \quad (70)$$

The above equation represents the modified quantization condition and substituting for  $k(x)$  we will readily obtain

$$\varepsilon_n = \frac{E_n}{(\hbar^2 \gamma^2 / 2\mu)^{1/3}} = \left[ \frac{3}{4} \left( 2n - \frac{1}{2} \right) \pi \right]^{2/3} \quad (71)$$

or

$$\mathcal{E}_n = 2.3203, 4.0818, 5.5172, \dots \quad (72)$$

for  $n = 1, 2, 3, \dots$ . The above eigenvalues compare very well with the exact values [see Eq. (63)]. The corresponding JWKB wave functions would be given by Eq. (64) with

$$\begin{aligned} k(x) &= \left( \frac{2\mu}{\hbar^2} \right)^{1/2} (E - \gamma x)^{1/2} \\ &= \left( \frac{2\mu\alpha}{\hbar^2} \right)^{1/2} \xi^{1/2} \end{aligned} \quad (73)$$

where

$$\begin{aligned} \xi &\equiv \frac{E - \gamma x}{\alpha} = \mathcal{E} - X \\ X &\equiv \frac{\gamma}{\alpha} x \end{aligned} \quad (74)$$

and  $\alpha$  is to be defined later. Thus

$$\int_0^x k(x) dx = \left( \frac{2\mu\alpha^3}{\gamma^2\hbar^2} \right)^{1/2} \int_{\xi}^{\mathcal{E}} \xi^{1/2} d\xi \quad (75)$$

We choose  $\alpha$  such that the factor in front of the integral is unity, i.e.

$$\alpha \equiv \left( \frac{\hbar^2\gamma^2}{2\mu} \right)^{1/3} \quad (76)$$

[see Solution 6.8]. Thus

$$\begin{aligned} \int_0^x k(x) dx &= \frac{2}{3} [\mathcal{E}^{3/2} - \xi^{3/2}] \\ &= \frac{2}{3} [\mathcal{E}^{3/2} - (\mathcal{E} - X)^{3/2}] \end{aligned} \quad (77)$$

The JWKB solution [Eq. (64)] is therefore given by

$$\psi_{\text{JWKB}}(X) = \frac{1}{\mathcal{E}^{1/4}(\mathcal{E} - X)^{1/4}} \sin \left[ \frac{2}{3} \{ \mathcal{E}^{3/2} - (\mathcal{E} - X)^{3/2} \} \right] \quad 0 < X < \mathcal{E} \quad (78)$$

where we have chosen the constant such that  $d\psi/dX$  is unity at  $X = 0$ . For  $X > \mathcal{E}$ , the JWKB solution will be given by

$$\begin{aligned} \psi_{\text{JWKB}}(X) &= -\frac{\cos n\pi}{2\mathcal{E}^{1/4}(X-\mathcal{E})^{1/4}} \exp \left[ - \int_b^x \kappa(x) dx \right] \\ &= \frac{(-1)^{n+1}}{2\mathcal{E}^{1/4}(X-\mathcal{E})^{1/4}} \exp \left[ -\frac{2}{3} (X - \mathcal{E})^{3/2} \right], \quad X > \mathcal{E} \end{aligned} \quad (79)$$

Figure 17.6 gives a plot of the JWKB wave function for  $n = 2$  corresponding to which

$$\epsilon = \epsilon_2 = 4.0818 \quad (80)$$

Comparison has been made with the exact wave-function which is given by (see Solution 6.8)

*Exact wave function*

$$\psi_{\text{EXACT}}(x) = \frac{1}{Ai'(a_2)} Ai(x + a_2) \quad (81)$$

where  $a_2 = -4.08795$  represents the second zero of  $Ai(x)$ .

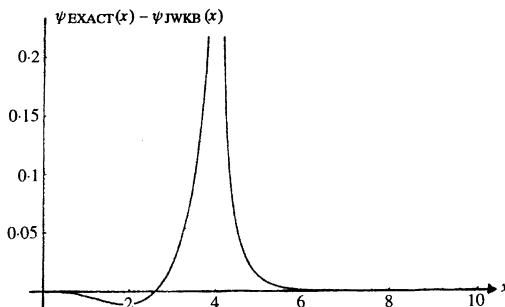
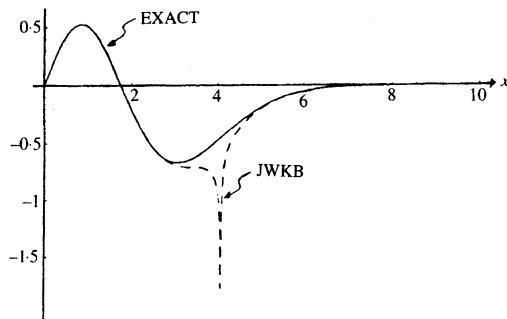


Figure 17.6. (a) Comparison of the JWKB wave function as given by Eqs (78) and (79) (shown as dashed curve) with the exact wave function as given by Eq. (81) (shown as solid curve) corresponding to the second energy state ( $n = 2$ ) for the potential energy variation given by Eq. (57). (b) A plot of  $\psi_{\text{EXACT}}(x) - \psi_{\text{JWKB}}(x)$  as a function of  $x$  [adapted from Ref. 3].

## 17.5. Application of the JWKB solutions to the tunnelling probability calculations

We next consider the tunnelling problem in quantum mechanics. Consider a potential energy variation of the type shown in Fig. 17.7(a). A particle of arbitrary (positive) energy  $E$  approaches the potential energy barrier from the left<sup>7</sup>. Our objective is to calculate the probability for the particle to tunnel through the barrier and also the probability for its reflection<sup>8</sup>.

In Fig. 17.7(b) we have shown the corresponding variation of  $k^2(x)$ ; the two turning points are denoted by  $a$  and  $b$ . In the regions  $x > b$  and  $x < a$ ,  $E$  would be greater than  $V(x)$  and the Schrödinger equation will be the form

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi(x) = 0 \quad (82)$$

where

$$k^2(x) = \frac{2\mu}{\hbar^2} [E - V(x)]$$

In order to describe incoming and outgoing waves, we will choose the JWKB solutions given by the exponential functions [see Eq. (24)] rather than sine and cosine solutions. Since in Region III we only have a wave propagating in the  $+x$  direction, the corresponding solution will be given by

$$\psi_{\text{III}}(x) = \frac{C}{\sqrt{k(x)}} \exp \left[ i \left( \int_b^x k(x) dx + \frac{\pi}{4} \right) \right] \quad (83)$$

where we have introduced a phase factor of  $\pi/4$  for convenience in using the connection formulae. Now in order to use the connection formulae [Eqs (32) and (33)], we rewrite Eq. (83) as

$$\begin{aligned} \psi_{\text{III}}(x) = & C \left[ \frac{1}{\sqrt{k(x)}} \cos \left( \int_b^x k(x) dx + \frac{\pi}{4} \right) \right] \\ & + \frac{iC}{2} \left[ \frac{2}{\sqrt{k(x)}} \sin \left( \int_b^x k(x) dx + \frac{\pi}{4} \right) \right] \end{aligned} \quad (84)$$

<sup>7</sup> This is typical of a scattering problem in which the energy is specified in advance and the behaviour of the wave function is found in terms of the energy. This is in contrast to the eigenvalue problem where the wave function vanishes as  $x \rightarrow \pm\infty$  leading to discrete values of the energy of the particle.

<sup>8</sup> The corresponding problem in electromagnetic theory would be when a light beam is incident on a thin layer of a rarer medium at an angle of incidence greater than the critical angle.

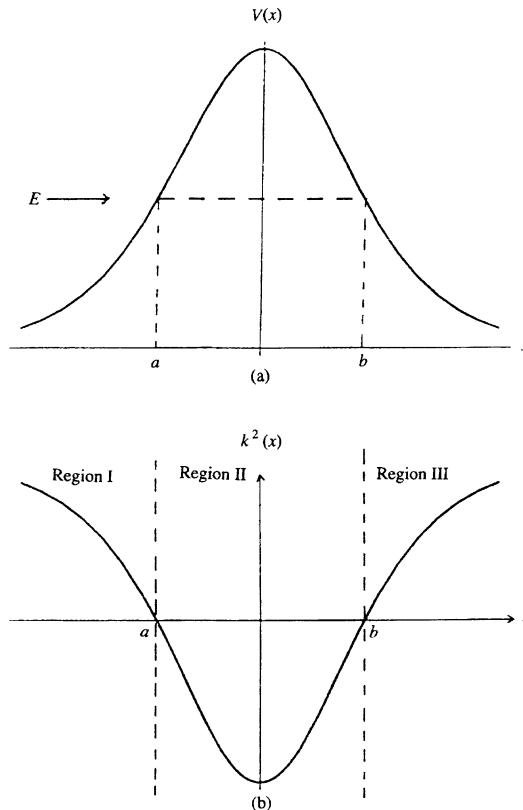


Figure 17.7. (a) A typical variation of  $V(x)$  corresponding to a scattering problem. A particle of energy  $E$  is incident from the left. The points  $x = a$  and  $x = b$  represent the turning points where  $V(x) = E$ . (b) The corresponding variation of  $k^2(x)$ .

We now use Eqs (32) and (33) to obtain the following JWKB solutions in Region II:

$$\begin{aligned} \psi_{\text{II}}(x) &= C \frac{1}{\sqrt{\kappa(x)}} \exp \left( + \int_x^b \kappa(x) dx \right) \\ &\quad + \frac{iC}{2} \left[ \frac{1}{\sqrt{\kappa(x)}} \exp \left( - \int_x^b \kappa(x) dx \right) \right] \end{aligned} \quad (85)$$

Now, in order to use the connection formulae [given by Eqs (30) and (31)] for obtaining the solution in Region I, we must have

$$\int_a^x \kappa(x) dx$$

in the exponent. Thus we write

$$\int_x^b \kappa(x) dx = \int_a^b \kappa(x) dx - \int_a^x \kappa(x) dx \quad (86)$$

so that  $\psi_{II}$  becomes<sup>9</sup>

$$\begin{aligned} \psi_{II}(x) &= \frac{C}{\theta} \frac{1}{\sqrt{\kappa(x)}} \exp \left( - \int_a^x \kappa(x) dx \right) \\ &\quad + \frac{iC\theta}{2} \left[ \frac{1}{\sqrt{\kappa(x)}} \exp \left( + \int_a^x \kappa(x) dx \right) \right] \end{aligned} \quad (87)$$

where

$$\theta \equiv \exp \left[ - \int_a^b \kappa(x) dx \right] \quad (88)$$

We can now use the connection formulae given by Eqs (30) and (31) to obtain

$$\begin{aligned} \psi_I(x) &= \frac{C}{\theta} \frac{2}{\sqrt{k(x)}} \sin \left( \int_x^a k(x) dx + \frac{\pi}{4} \right) \\ &\quad + \frac{iC\theta}{2} \frac{1}{\sqrt{k(x)}} \cos \left( \int_x^a k(x) dx + \frac{\pi}{4} \right) \end{aligned}$$

In order to express  $\psi_I$  as a superposition of incident and reflected waves, we write the sine and cosine functions as a sum of exponentials to obtain

$$\begin{aligned} \psi_I(x) &= \frac{A}{\sqrt{k(x)}} e^{-i \int_x^a k(x) dx} \\ &\quad [\text{incident wave propagating to the right}] \\ &\quad + \frac{B}{\sqrt{k(x)}} e^{i \int_x^a k(x) dx} \\ &\quad [\text{incident wave propagating to the left}] \end{aligned} \quad (89)$$

where

$$A = i C \left( \frac{1}{\theta} + \frac{\theta}{4} \right) e^{-i\pi/4} = C \left( \frac{1}{\theta} + \frac{\theta}{4} \right) e^{i\pi/4} \quad (90)$$

---

<sup>9</sup> Notice that the first term on the right-hand side of Eq. (85) is the exponentially amplifying term with respect to the point  $x = b$ ; this term becomes an exponentially decaying term with respect to the point  $x = a$  [see the first term on the right-hand side of Eq. (87)].

and

$$B = -i C \left( \frac{1}{\theta} - \frac{\theta}{4} \right) e^{i\pi/4} = C \left( \frac{1}{\theta} - \frac{\theta}{4} \right) e^{-i\pi/4} \quad (91)$$

### *Transmission and reflection coefficients*

Thus the transmission and reflection coefficients are given by

$$T = \left| \frac{C}{A} \right|^2 = \frac{1}{\left( \frac{1}{\theta} + \frac{\theta}{4} \right)^2} \quad (92)$$

$$R = \left| \frac{B}{A} \right|^2 = \frac{\left( \frac{1}{\theta} - \frac{\theta}{4} \right)^2}{\left( \frac{1}{\theta} + \frac{\theta}{4} \right)^2} \quad (93)$$

Notice that in spite of all the approximations made in the JWKB theory we still get

$$R + T = 1$$

In most practical cases  $\theta \ll 1$  and in this approximation

$$T \approx \theta^2 = e^{-2 \int_a^b \kappa(x) dx} \quad (94)$$

a formula that is widely used in literature.

**Example 17.3** *Transmission through a parabolic barrier* As a simple application of Eq. (94) we consider a parabolic barrier of the form

*Parabolic barrier potential*

$$\begin{aligned} V(x) &= V_0 \left[ 1 - \frac{x^2}{d^2} \right] & |x| < d \\ &= 0 & |x| > d \end{aligned} \quad (95)$$

(see Fig. 17.8). For  $E < V_0$ , the turning points are the roots of the equation

$$E = V_0 \left[ 1 - \frac{x^2}{d^2} \right]$$

implying

$$a = -d \left( 1 - \frac{E}{V_0} \right)^{1/2} \quad \text{and} \quad b = +d \left( 1 - \frac{E}{V_0} \right)^{1/2}$$

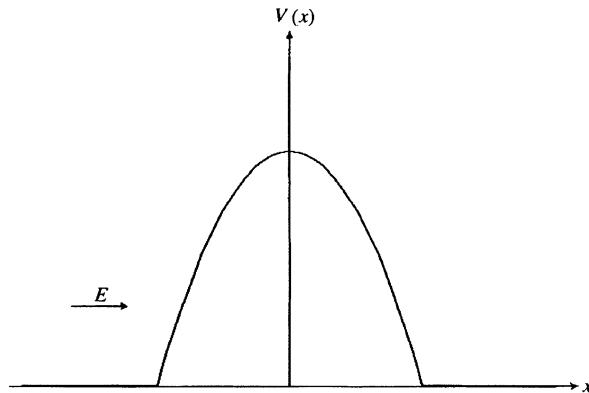


Figure 17.8. Parabolic variation of  $V(x)$  as given by Eq. (95).

Thus

$$\begin{aligned}\theta &= \exp \left\{ -\left(\frac{2\mu}{\hbar^2}\right)^{1/2} \int_a^b \left[ V_0 \left(1 - \frac{x^2}{d^2}\right) - E \right]^{1/2} dx \right\} \\ &= \exp \left\{ -\frac{\pi}{2} \left(\frac{2\mu V_0 d^2}{\hbar^2}\right)^{1/2} \left(1 - \frac{E}{V_0}\right) \right\} \\ T \approx \theta^2 &= \exp \left[ -\pi \left(\frac{2\mu V_0 d^2}{\hbar^2}\right)^{1/2} \left(1 - \frac{E}{V_0}\right) \right]\end{aligned}\quad (96)$$

It may be noted that  $E > V_0$ , there are no turning points and the JWKB formula [Eq. (94)] would predict  $T = 1$  which is not correct. Rigorous analysis will show that there is a finite reflection even for  $E > V_0$ .

**Example 17.4** In this example we will show how to use the connection formulae when there are more than two turning points. Although the analysis does get a bit involved, we urge the students to work it out in detail so that the *tricks* in using the connection formulae are completely understood.

We consider a  $V(x)$  variation of the type shown in Fig. 17.9(a) with the incident energy  $E$  such that

$$V_1 < E < V_0$$

so that the corresponding  $k^2(x)$  variation [shown in Fig. 17.9(b)] has four turning points<sup>10</sup>. For the sake of simplicity we assume a symmetric potential so that the turning points are at  $x = \pm a$  and at  $x = \pm b$ . In region V (i.e. for  $x > b$ ), we will

<sup>10</sup> For  $E < V_1$  we will have only two turning points and one can carry out an analysis similar to that in Sec. 17.5.

have an outgoing wave and hence the wave function will be of the form

$$\begin{aligned}\psi_V(x) &= \frac{C}{\sqrt{k}} \exp \left[ i \left( \int_b^x k(x) dx + \frac{\pi}{4} \right) \right] \\ &= \frac{C}{\sqrt{k}} \cos \left[ \int_b^x k(x) dx + \frac{\pi}{4} \right] + \frac{i C}{\sqrt{k}} \sin \left[ \int_b^x k(x) dx + \frac{\pi}{4} \right]\end{aligned}\quad (97)$$

which would go over to [cf. Eqs (84)–(88)]

$$\begin{aligned}\psi_{IV}(x) &= \frac{C}{\theta} \frac{1}{\sqrt{\kappa(x)}} \exp \left[ - \int_a^x \kappa(x) dx \right] \\ &\quad + \frac{i C \theta}{2} \frac{1}{\sqrt{\kappa(x)}} \exp \left[ + \int_a^x \kappa(x) dx \right]\end{aligned}\quad (98)$$

where

$$\theta \equiv \exp \left[ - \int_a^b \kappa(x) dx \right]\quad (99)$$

We again use the connection formulae [Eqs (30)–(31)] to obtain

$$\psi_{III}(x) = \frac{C}{\sqrt{k}} \left[ \frac{2}{\theta} \sin \left( \int_x^a k(x) dx + \frac{\pi}{4} \right) + \frac{i \theta}{2} \cos \left( \int_x^a k(x) dx + \frac{\pi}{4} \right) \right]$$

Writing

$$\int_x^a k(x) dx + \frac{\pi}{4} = \left( \int_{-a}^{+a} k(x) dx + \frac{\pi}{2} \right) - \left( \int_{-a}^x k(x) dx + \frac{\pi}{4} \right)$$

we get

$$\begin{aligned}\psi_{III}(x) &= \frac{C}{\sqrt{k}} \left[ \left( \frac{2}{\theta} \cos \alpha - \frac{i \theta}{2} \sin \alpha \right) \cos \left( \int_{-a}^x k dx + \frac{\pi}{4} \right) \right. \\ &\quad \left. + \left( \frac{2}{\theta} \sin \alpha + \frac{i \theta}{2} \cos \alpha \right) \sin \left( \int_{-a}^x k dx + \frac{\pi}{4} \right) \right]\end{aligned}\quad (100)$$

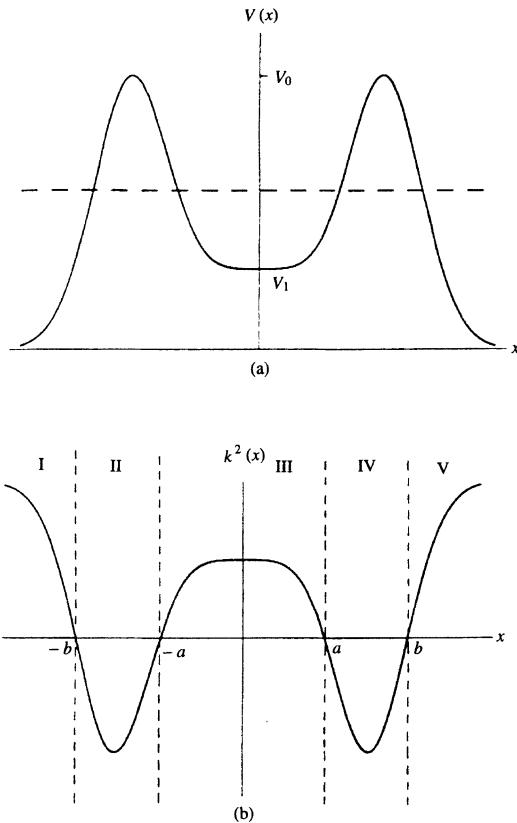


Figure 17.9. (a) A particle of energy  $E$  is incident on a symmetric potential well surrounded by a barrier. (b) The corresponding variation of  $k^2(x)$ .

where

$$\alpha \equiv \int_{-a}^{+a} k(x) \, dx \quad (101)$$

This would go over to

$$\begin{aligned} \psi_{II}(x) = & \frac{C}{\sqrt{k(x)}} \left[ \left( \frac{2}{\theta} \cos \alpha - \frac{i}{2} \frac{\theta}{2} \sin \alpha \right) \frac{1}{\theta} \exp \left( - \int_{-b}^x \kappa(x) \, dx \right) \right. \\ & \left. + \left( \frac{2}{\theta} \sin \alpha + \frac{i}{2} \frac{\theta}{2} \cos \alpha \right) \frac{\theta}{2} \exp \left( \int_{-b}^x \kappa(x) \, dx \right) \right] \end{aligned}$$

where we have used the fact that  $\kappa(x) = \kappa(-x)$  so that

$$\exp\left(-\int_{-b}^{-a} \kappa(x) dx\right) = \exp\left(-\int_a^b \kappa(x) dx\right) = \theta \quad [\text{see Eq. (99)}]$$

Further use of connection formulae gives

$$\begin{aligned} \psi_1(x) &= \frac{C}{\sqrt{k(x)}} \left[ \left( \frac{2}{\theta} \cos \alpha - \frac{i\theta}{2} \sin \alpha \right) \frac{2}{\theta} \sin \left( \int_x^b k(x) dx + \frac{\pi}{4} \right) \right. \\ &\quad \left. + \left[ \left( \frac{2}{\theta} \sin \alpha + \frac{i\theta}{2} \cos \alpha \right) \frac{\theta}{2} \cos \left( \int_x^b k(x) dx + \frac{\pi}{4} \right) \right] \right] \quad (102) \\ &= \frac{A}{\sqrt{k(x)}} \exp \left[ -i \left( \int_x^b k(x) dx + \frac{\pi}{4} \right) \right] \\ &\quad (\text{wave propagating to the right}) \\ &\quad + \frac{B}{\sqrt{k(x)}} \exp \left[ i \left( \int_x^b k(x) dx + \frac{\pi}{4} \right) \right] \\ &\quad (\text{wave propagating to the left}) \quad (103) \end{aligned}$$

where

$$A = \frac{1}{2} \left[ 2 \sin \alpha + i \cos \alpha \left( \frac{4}{\theta^2} + \frac{\theta^2}{4} \right) \right] C$$

and

$$B = \frac{i}{2} \cos \alpha \left( \frac{\theta^2}{4} - \frac{4}{\theta^2} \right) C \quad (104)$$

#### *Reflection and transmission coefficients*

Thus the reflection and transmission coefficients are given by

$$R = \left| \frac{B}{A} \right|^2 = \frac{\left( \frac{4}{\theta^2} - \frac{\theta^2}{4} \right)^2 \cos^2 \alpha}{4 \sin^2 \alpha + \left( \frac{4}{\theta^2} + \frac{\theta^2}{4} \right)^2 \cos^2 \alpha} \quad (105)$$

$$T = \left| \frac{C}{A} \right|^2 = \frac{4}{4 \sin^2 \alpha + \left( \frac{4}{\theta^2} + \frac{\theta^2}{4} \right)^2 \cos^2 \alpha} \quad (106)$$

It can be readily seen that  $R + T = 1$ . Further,

$$T = 1 \quad (R = 0) \quad (107)$$

when

$$\alpha = \int_{-a}^{+a} k(x) dx = \left( n + \frac{1}{2} \right) \pi \quad (108)$$

Equation (108) represents the eigenvalue condition for the potential well and Eq. (107) tells us that the *double barrier* is completely transparent for energies corresponding to the eigenvalues of the potential well.

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## 17.6. JWKB solutions for spherically symmetric potentials

For a spherically symmetric potential  $V(r)$ , the radial part of the wave function  $R(r)$  satisfies the equation

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)}{2\mu r^2} \right] R(r) = 0 \quad (109)$$

where  $E$  is the energy eigenvalue and the other symbols have their usual meanings (see Sec. 10.2). If we make the transformation

$$R(r) = \frac{u(r)}{r} \quad (110)$$

and consider the  $l = 0$  case, we readily obtain

$$\frac{d^2 u}{dr^2} + k^2(r) u(r) = 0, \quad (111)$$

where

$$k^2(r) = \frac{2\mu}{\hbar^2} [E - V(r)] \quad (112)$$

Since  $u(0)$  must be zero, the JWKB solution in the region  $0 < r < r_t$  is given by

$$u_1(r) = \frac{A}{\sqrt{k(r)}} \sin \left[ \int_0^r k(r) dr \right] \quad (113)$$

where  $r_t$  is the turning point where  $k(r)$  is zero. In order to obtain the JWKB solution in the region  $r > r_t$ , we carry out the usual manipulation:

$$\int_0^r k(r) dr = \left( \int_0^{r_t} k dr + \frac{\pi}{4} \right) - \left( \int_r^{r_t} k dr + \frac{\pi}{4} \right)$$

Thus

$$u_I(r) = \frac{A}{\sqrt{k(r)}} \left[ \sin \theta \cos \left( \int_r^{r_t} k(r) dr + \frac{\pi}{4} \right) - \cos \theta \sin \left( \int_r^{r_t} k(r) dr + \frac{\pi}{4} \right) \right] \quad (114)$$

where

$$\theta = \int_0^{r_t} k(r) dr + \frac{\pi}{4}$$

The first term on the right-hand side of Eq. (114) goes over to an exponentially amplifying solution and therefore we must have

$$\theta = n\pi$$

or

$$\int_0^{r_t} k(r) dr = \left( n - \frac{1}{4} \right) \pi ; \quad n = 1, 2, 3, \dots \quad (115)$$

The solution of the above equation would lead to the allowed energy eigenvalues [see Problem 17.8]. Further

$$u_{II}(r) = \frac{A(-1)^{n+1}}{\sqrt{k(r)}} \exp \left[ - \int_{r_t}^r k(r) dr \right] \quad (116)$$

## 17.7. Application of the JWKB method to alpha decay

In this section we will use results obtained by using the JWKB approximation to calculate the lifetime of nuclei emitting alpha particles. Now, the potential as seen by the  $\alpha$  particle is approximately given by (see Fig. 17.10)

$$\begin{aligned} V(r) &= -V_0 \quad r < R \\ &= \frac{zZq^2}{4\pi\epsilon_0 r} \quad r > R \end{aligned} \quad (117)$$

where  $R$  represents the radius of the nucleus,  $zq$  and  $Zq$  represent the charges of the alpha particle and of the daughter nucleus respectively (obviously  $z = 2$ ); we

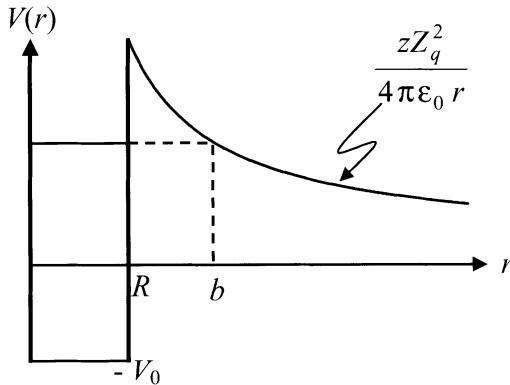
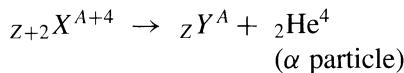


Figure 17.10a. The potential energy variation as seen by the alpha particle. Outside the nucleus (i.e., for  $r > R$ ) the alpha particle experiences a repulsive Coulomb force. The points  $r = R$  and  $r = b$  are the turning points.

have assumed that a nucleus of charge  $(Z + 2)q$  decays to a (daughter) nucleus of charge  $Zq$  and an alpha particle of charge  $2q$ :



The potential energy distribution given by Eq.(117) corresponds to the  $\alpha$  particle being free inside the nucleus and bound to it; outside the nucleus, the  $\alpha$ -particle experiences the repulsive Coulomb force. The tunnelling probability is given by

$$T \approx \exp(-2G) \quad (118)$$

where

$$\begin{aligned} G &= \sqrt{\frac{2\mu}{\eta^2}} \int_R^b \sqrt{\frac{zZq^2}{4\pi\epsilon_0 r} - E} dr \\ &= \left( \frac{2\mu z Z q^2}{4\pi\epsilon_0 \eta^2 E} \right)^{1/2} \int_R^b \sqrt{\frac{1}{r} - \frac{1}{b}} dr \end{aligned}$$

where

$$b = \frac{zZq^2}{4\pi\epsilon_0 E} \quad (119)$$

represents the outer turning point [see Fig. 17.10(a)]. Making the substitution  $r = b \cos^2 \theta$  we readily get

$$G = \sqrt{\frac{2\mu z Z q^2}{4\pi\epsilon_0 \eta^2} b} \left[ \cos^{-1} \sqrt{\frac{R}{b}} - \sqrt{\frac{R}{b} - \frac{R^2}{b^2}} \right] \quad (120)$$

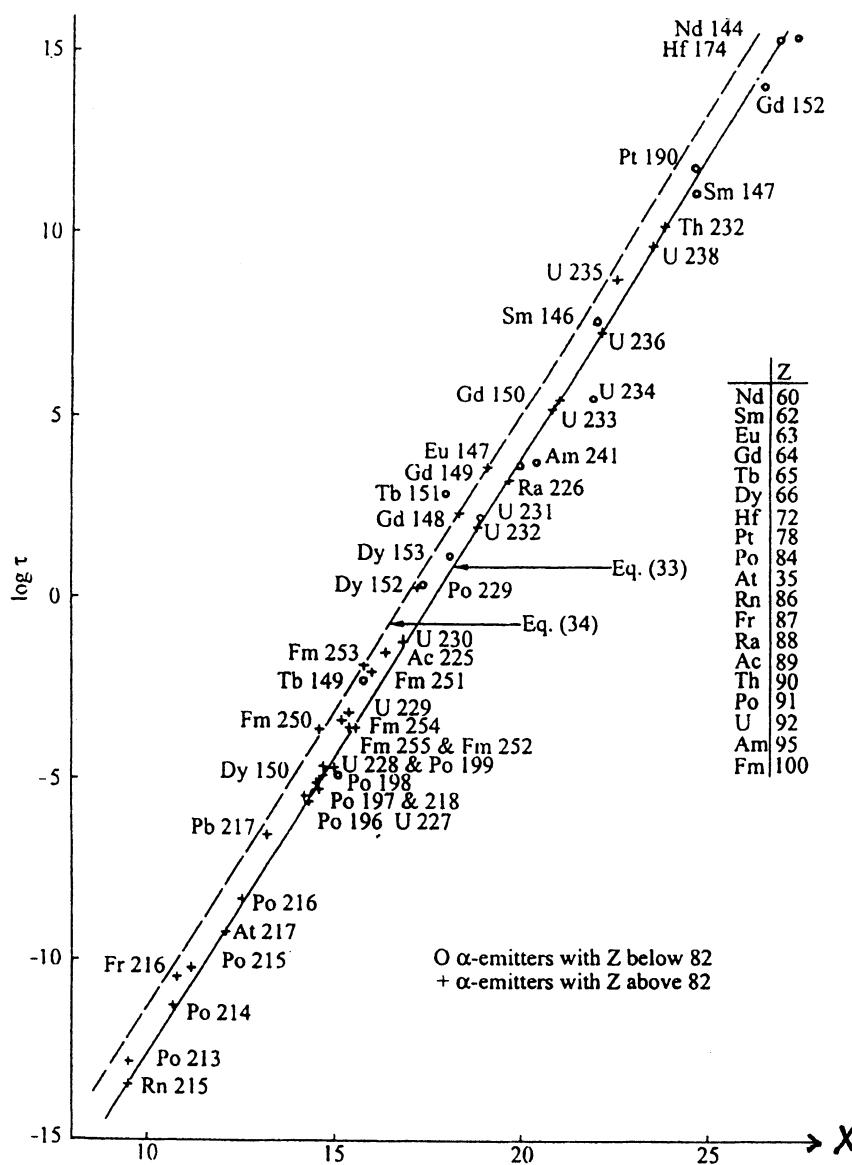


Figure 17.10b. Variation of  $\log \tau$  [where  $\tau$  is in years] with  $X [= (Z/\sqrt{E}) - Z^{2/3}]$ . [Adapted from Ref. 6].

Now, if the speed of the  $\alpha$  particles inside the nucleus is  $\sim v$  then

$$\text{Number of times the } \alpha\text{-particle hits the barrier per unit time} \sim \frac{v}{R} \quad (121)$$

Thus the probability per second of escape (which is the inverse of the mean life-time) is given by

$$\frac{1}{\tau} \approx \frac{v}{R} e^{-2G} \quad (122)$$

As we will show below, in most cases  $R/b \ll 1$  so that the quantity inside the square brackets of Eq.(120) can be written as

$$\begin{aligned} \cos^{-1} \sqrt{\frac{R}{b}} - \sqrt{\frac{R}{b} - \frac{R^2}{b^2}} &\approx \frac{\pi}{2} - \sqrt{\frac{R}{b}} - \sqrt{\frac{R}{b}} \\ &\approx \frac{\pi}{2} - 2\sqrt{\frac{R}{b}} \end{aligned}$$

Substituting the value of  $b$  from Eq.(119) we obtain

$$2G \approx 2zZ\alpha \left( \frac{2\mu c^2}{E} \right)^{1/2} \left[ \frac{\pi}{2} - 2\sqrt{\frac{R}{b}} \right] \quad (123)$$

where

$$\alpha = \frac{q^2}{4\pi\epsilon_0\eta c} \cong \frac{1}{137}$$

represents the fine structure constant. Now,

$$m_p c^2 \approx 938 \text{ MeV}$$

where  $m_p$  represents the mass of the proton and since  $\mu \approx 4m_p$  we get

$$2G \cong \frac{2.53Z}{\sqrt{E}} \left[ \frac{\pi}{2} - 2\sqrt{\frac{R}{b}} \right] \quad (124)$$

where  $E$  is measured in MeV and we have assumed  $z = 2$ . Also

$$\begin{aligned} b &= \frac{2Zq^2}{4\pi\epsilon_0 E} \\ &= \frac{2Z\alpha\eta}{m_p c} \left( \frac{m_p c^2}{E} \right) \\ &= \frac{2Z(1.05 \times 10^{-34})}{(1.67 \times 10^{-27})(3 \times 10^8)} \left( \frac{1}{137} \right) \left( \frac{938}{E} \right) \end{aligned}$$

or

$$b \approx 2.87 \times 10^{-15} \frac{Z}{E} \quad (125)$$

where  $b$  is measured in meters and  $E$  in MeV. Now, the radius of the nucleus is approximately given by

$$R \approx (1.07 \times 10^{-15}) A^{1/3} \text{ (m)} \quad (126)$$

where  $A$  represents the mass number and  $R$  is measured in meters. Thus we obtain

$$\sqrt{\frac{R}{b}} \approx 0.611 Z^{-1/2} A^{1/6} \sqrt{E} \quad (127)$$

Thus

$$2G \approx \sqrt{3.97Z} \sqrt{E} - 3.09 Z^{1/2} A^{1/6} \quad (128)$$

Now,

$$\begin{aligned} v &= \sqrt{\frac{2E}{\mu}} \\ &= c \sqrt{\frac{2E}{\mu c^2}} \end{aligned}$$

Since

$$\mu c^2 \approx 4m_p c^2 \approx 4 \times 938 \text{ MeV}$$

we obtain

$$v \approx 6.93 \times 10^6 \sqrt{E} \text{ (m/s)} \quad (129)$$

where  $E$  is measured in MeV and  $v$  is measured in meters/second. Thus

$$\frac{v}{R} \approx 6.47 \times 10^{21} E^{1/2} A^{-1/3} \text{ (s}^{-1}\text{)} \quad (130)$$

Substituting in Eq.(122) we get

$$\frac{1}{\tau} \approx [6.47 \times 10^{21} \sqrt{E} A^{-1/3}] \exp \left[ -\frac{3.97Z}{\sqrt{E}} + 3.09 Z^{1/2} A^{1/6} \right] \quad (131)$$

or

$$\log_{10} \tau \approx -21.8 - \frac{1}{2} \log_{10} E + \frac{1}{3} \log_{10} A + \frac{1.724Z}{\sqrt{E}} - 1.34 Z^{1/2} A^{1/6} \quad (132)$$

where  $\tau$  is measured in seconds and  $E$  in MeV. Let us next consider some examples: We consider the following radioactive decay



Thus  $Z = 82$ ,  $A = 208$  and  $E = 8.9$  MeV. Substituting in Eq.(132) we get

$$\begin{aligned}\log_{10} \tau &\approx -21.8 - 0.5 + 0.8 + 47.4 - 29.5 \\ &\approx -3.6\end{aligned}\quad (134)$$

giving

$$\tau \approx 10^{-4} \text{ s}$$

(The corresponding experimental value is  $\sim 3 \times 10^{-7}$  s.) On the other hand, for the radioactive decay



we get

$$\begin{aligned}\log_{10} \tau &\approx -21.8 - 0.3 + 0.8 + 75.7 - 31.6 \\ &\approx 23\end{aligned}\quad (136)$$

or

$$\tau \approx 10^{23} \text{ s}$$

The corresponding experimental value is  $10^{17}$  s. Although the theoretical values are not in agreement with the experimental values, one may note the enormous range in the values of  $\tau$ , from  $\sim 10^{17}$  s for  $\text{U}^{238}$  to  $\sim 3 \times 10^{-7}$  s for  $\text{Po}^{212}$  which is also predicted by our approximate theoretical analysis. One may note from Equations (134) and (135) that it is the term

$$\frac{1.724Z}{\sqrt{E}}$$

which is most important in Eq.(132). In Ref. 6, the empirical formula

$$\log_{10} \tau = C_1 \left[ \frac{Z}{\sqrt{E}} - Z^{2/3} \right] - C_2 \quad (137)$$

has been shown to agree well with the experimental data [see Fig. 17.10(b)]. In Eqs.(132) and (137)

$\tau$  is the half life in years

$Z$  is the atomic number of the daughter nucleus

and

$E$  is the energy of the  $\alpha$ -particle in MeV

The two lines in Fig. 17.10(b) correspond to

$$C_1 = 1.61(\text{MeV})^{1/2}, \quad C_2 = 28.9 \quad (138)$$

and

$$C_1 = 1.70(\text{MeV})^{1/2}, \quad C_2 = 30.0 \quad (139)$$

For example, for the radioactive decay given by Eq.(135)

$$E \approx 4.2 \text{ MeV} \quad \text{and} \quad Z = 90$$

Thus using Eqs.(138) and (139) we get

$$\tau \approx 10^{9.5} \text{ years} \approx 3 \times 10^{16.5} \text{ s}$$

and

$$\tau \approx 10^{10.5} \text{ years} \approx 3 \times 10^{17.5} \text{ s}$$

Similarly, for the decay given by Eq.(133) we would get [using Eq.(138)]

$$\tau \approx 10^{-15} \text{ years} \approx 3 \times 10^{-8} \text{ s}$$

Thus the empirical formula gives results close to the experimental values. It may be noted that if we assume  $A \approx 2Z$ , the term  $1.34Z^{1/2}A^{1/6}$  in Eq.(132) will give  $1.5Z^{2/3}$ .

We next show that in both the examples discussed above

$$\frac{R}{b} \ll 1$$

as was assumed earlier in the section. For example, corresponding to the radioactive decay given by Eq.(135), Eq.(126) gives

$$R \approx 6.59 \times 10^{-15} \text{ m}$$

Further, from Eq.(119)

$$b \approx 6.15 \times 10^{-14} \text{ m}$$

giving

$$\frac{R}{b} \approx 0.11$$

proving  $R/b \ll 1$ . Further, for the 4.2 MeV  $\alpha$ -particle

$$v \approx 1.42 \times 10^7 \text{ m/s}$$

This value of  $v$  may be compared with the value obtained from the uncertainty principle [see Chapter 3]

$$\begin{aligned} v &\sim \frac{h}{\mu R} \sim \frac{6.6 \times 10^{-34} \text{ J.s.}}{(4 \times 1.67 \times 10^{-27} \text{ kg}) \times (6.59 \times 10^{-15} \text{ m})} \\ &\approx 1.50 \times 10^7 \text{ m/s} \end{aligned}$$

## 17.8. Derivation of connection formulae

As mentioned earlier in Sections 17.1 and 17.2, the JWKB solutions are not valid near the turning points where  $k^2(x) = 0$ . Now, in the vicinity of a turning point, we may approximate  $k^2(x)$  by a linear function. Thus, referring to Fig. 17.1, in the neighbourhood of the turning point  $x = a$ , we may write

$$k^2(x) \approx -\alpha(x - a) \quad (140)$$

we assume  $\alpha$  to be positive. Substituting the above expression for  $k^2(x)$  in Eq.(1), we get

$$\frac{d^2\psi}{dx^2} - \alpha(x - a)\psi(x) = 0 \quad (141)$$

The above equation can be written in the form

$$\frac{d^2\psi}{dx^2} - z\psi(x) = 0 \quad (142)$$

where

$$z = \alpha^{1/3}(x - a) \quad (143)$$

We next write the JWKB solutions of Eq. (142).

For  $z > 0$ , we define  $\kappa^2(z) = z$  [cf. Eq. (26)]: thus the JWKB solutions are

$$\frac{1}{z^{1/4}} \exp[\pm \zeta] \quad (144)$$

where

$$\zeta = \int_0^z \kappa(z) dz = \frac{2}{3} z^{3/2} \quad (z > 0) \quad (145)$$

On the other hand, for  $z < 0$ ,

$$k^2(z) = -z = |z| \quad (146)$$

Thus the JWKB solutions are

$$\frac{1}{|z|^{1/4}} \cos \zeta \quad \text{and} \quad \frac{1}{|z|^{1/4}} \sin \zeta \quad (147)$$

where

$$\zeta = \int_z^0 (-z)^{1/2} dz = \frac{2}{3} (-z)^{3/2} \quad (z < 0) \quad (148)$$

Combining Eqs (145) and (148), we may write

$$\zeta = \frac{2}{3} |z|^{3/2} \quad (149)$$

Now, the exact solutions of Eq. (142) are  $Ai(z)$  and  $Bi(z)$  which have been discussed in Appendix D. The asymptotic forms of  $Ai(z)$  and  $Bi(z)$  are given by [see Eqs (22)–(25) of Appendix D]

$$Ai(z) \xrightarrow[z \rightarrow +\infty]{} \frac{1}{2\sqrt{\pi} z^{1/4}} e^{-\zeta} \quad (150)$$

$$\xrightarrow[z \rightarrow -\infty]{} \frac{1}{\sqrt{\pi} |z|^{1/4}} \sin\left(\zeta + \frac{\pi}{4}\right) \quad (151)$$

where  $\zeta = \frac{2}{3} |z|^{3/2}$ . Notice that the asymptotic forms are the JWKB solutions. Thus for  $k^2(z) = -z$ , the connection formula is given by

$$\frac{2}{|z|^{1/4}} \sin\left(\zeta + \frac{\pi}{4}\right) \leftrightarrow \frac{1}{z^{1/4}} e^{-\zeta} \quad (152)$$

implying that  $\sin\left(\zeta + \frac{\pi}{4}\right)$  goes over to the exponentially decaying solution. Similarly, the asymptotic forms of  $Bi(z)$  are given by

$$Bi(z) \xrightarrow[z \rightarrow +\infty]{} \frac{1}{2\sqrt{\pi} z^{1/4}} e^{+\zeta} \quad (153)$$

$$\xrightarrow[z \rightarrow -\infty]{} \frac{1}{\sqrt{\pi} |z|^{1/4}} \cos\left(\zeta + \frac{\pi}{4}\right) \quad (154)$$

yielding the connection formula

$$\frac{1}{|z|^{1/4}} \cos\left(\zeta + \frac{\pi}{4}\right) \leftrightarrow \frac{1}{z^{1/4}} e^{\zeta} \quad (155)$$

### *Connection formulae*

Since  $k^2(z) = -z$ , Eqs (152) and (155) can be generalized to

$$\frac{2}{\sqrt{k(z)}} \sin\left[\int_z^a k(z) dz + \frac{\pi}{4}\right] \leftrightarrow \frac{1}{\sqrt{\kappa(z)}} \exp\left[-\int_a^z \kappa(z) dz\right] \quad (156)$$

$$\frac{1}{\sqrt{k(z)}} \cos\left[\int_z^a k(z) dz + \frac{\pi}{4}\right] \leftrightarrow \frac{1}{\sqrt{\kappa(z)}} \exp\left[+\int_a^z \kappa(z) dz\right] \quad (157)$$

## 17.9. Some historical remarks

The approximate solutions of Eq. (1) as given by Eqs (24)–(28) are usually referred to as the WKB solutions. However, they were first put forward by Harold Jeffreys in a 1924 paper entitled *On certain approximate solutions of linear differential equations of the second order* (Ref. 7). Even the connection formulae were given by Jeffreys. Indeed this paper along with three other papers by Jeffreys formed part of a dissertation highly commended by the adjudicators for the Adams Prize of the University of Cambridge for the year 1923. The applications of the JWKB solutions to problems in quantum mechanics came much later and were given by Wentzel (Ref. 8), Kramers (Ref. 9) and Brillouin (Ref. 10). We feel that since the solutions were first put forward by Jeffreys, it should be referred to as the JWKB method; this is indeed what has been done by Fröman and Fröman (see Ref. 11).

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## 17.10. Problems

**Problem 17.1** Consider the symmetric linear profile given by

$$V(x) = \gamma |x|, \quad \gamma > 0 \quad (158)$$

Use the JWKB quantization condition [Eq. (44)] to obtain the following

$$E_n = \left[ \frac{3(n + \frac{1}{2})\pi\hbar\gamma}{4(2m)^{1/2}} \right]^{2/3}; \quad n = 0, 1, \dots \quad (159)$$

**Problem 17.2** In continuation of Problem 17.1, consider the more general power law profile given by

$$V(x) = \gamma |x|^\alpha; \quad \gamma > 0, \alpha > 0 \quad (160)$$

Show that the energy eigenvalues are given by

$$E_n = \left[ \frac{(n + \frac{1}{2})\pi\hbar\gamma^{1/\alpha}\Gamma(\frac{3}{2} + \frac{1}{\alpha})}{2(2m)^{1/2}\Gamma(\frac{3}{2})\Gamma(1 + \frac{1}{\alpha})} \right]^{2\alpha/(\alpha+2)} \quad (161)$$

**[Hint:** You may use the following relation

$$\int_0^1 t^{z-1} (1-t)^{w-1} dt = B(z, w) = \frac{\Gamma(z)\Gamma(w)}{\Gamma(z+w)} \quad (162)$$

**Problem 17.3** Show that the JWKB solution given by Eq. (23) would represent an accurate solution of Eq. (1) provided

$$\left| \frac{1}{2k} \frac{d^2 k}{dx^2} - \frac{3}{4k^2} \left( \frac{dk}{dx} \right)^2 \right| \ll k^2(x) \quad (163)$$

[Hint: Obtain the differential equation satisfied by  $\psi(x)$  as given by Eq. (23).]

**Problem 17.4** Show that the equation

$$\frac{d^2 y}{dx^2} + f(x) \frac{dy}{dx} + g(x) y(x) = 0 \quad (164)$$

can be transformed to the form given by Eq. (1) if we make the transformations

$$\psi(x) = y(x) \exp \left[ \frac{1}{2} \int^x f(x) dx \right] \quad (165)$$

with

$$k^2(x) = g(x) - \frac{1}{2} \frac{df}{dx} - \frac{1}{4} f^2(x) \quad (166)$$

**Problem 17.5** Consider a double well symmetric potential as shown in Fig. 17.11. Using the JWKB connection formulae, show that (for  $E < V_0$ ) the energy eigenvalues are determined by solving the following transcendental equation

$$\cot \left[ \int_a^b k(x) dx \right] = \pm \frac{1}{2} \exp \left[ - \int_{-a}^{+a} \kappa(x) dx \right] \quad (167)$$

where the  $+$  and  $-$  signs on the right-hand side correspond to symmetric and antisymmetric solutions respectively; in the above equation  $x = \pm a$  and  $x = \pm b$  represent the turning points. The above equation is not expected to give accurate results for  $E$  close to  $V_0$  (why?).

[Hint: Start with an exponentially decaying solution in Region V ( $x > b$ ) and use connection formulae to obtain solutions in Region III ( $-a < x < a$ ).]

**Problem 17.6**

- (a) Use the results of the previous problem to determine the energy levels of a double oscillator given by

$$V(x) = \frac{1}{2} m \omega^2 [|x| - d]^2 \quad (168)$$

- (b) Obtain the exact solution for the above potential energy distribution and compare the exact eigenvalues with the corresponding JWKB result.

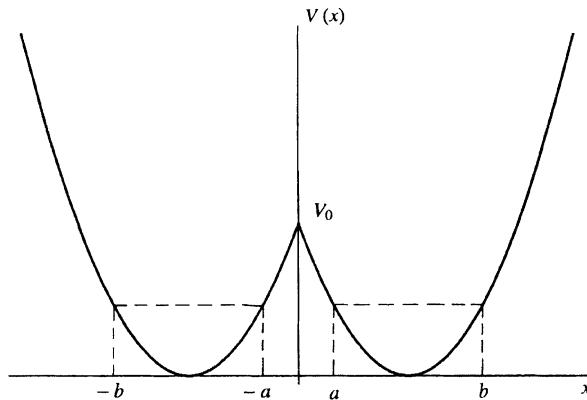


Figure 17.11. A double well potential which is symmetric about  $x = 0$ . The points  $x = \pm a$  and  $x = \pm b$  are the turning points [adapted from Ref. 3].

**Problem 17.7** Consider the three-dimensional isotropic oscillator for which (see Sec. 10.7):

$$V(r) = \frac{1}{2} \mu \omega^2 r^2$$

For  $l = 0$ , solve Eq. (115) to obtain

$$E = \left(2n + \frac{3}{2}\right) \hbar\omega ; \quad n = 0, 1, 2, \dots$$

which happens to be the exact result!

[Hint: The integration has to be carried out in a way similar to that given in Example 17.1.]

### Problem 17.8

- (a) The deuteron nucleus consists of a neutron and a proton and the neutron-proton interaction can be approximately described by the following potential energy variation:

$$V(r) = -V_0 e^{-r/a} \quad (169)$$

(see also Problem 10.8). Carry out the integration in Eq. (115) and derive the transcendental equation which would give the eigenvalues.

- (b) For the values of various parameters given in Problem 10.6, solve the transcendental equation to obtain the energy eigenvalue.
- (c) Plot the JWKB and exact solutions having the same slope at  $r = 0$ .

**Problem 17.9**

- (a) Consider the triangular barrier for which the potential energy variation is given by (see Fig. 17.12)

$$\begin{aligned} V(x) &= 0 & x < 0 \\ &= V_0 - \alpha x & 0 < x < a \\ &= 0 & x > a \end{aligned} \quad (170)$$

Show that (for  $E < V_0$ ) the JWKB tunnelling probability is given by

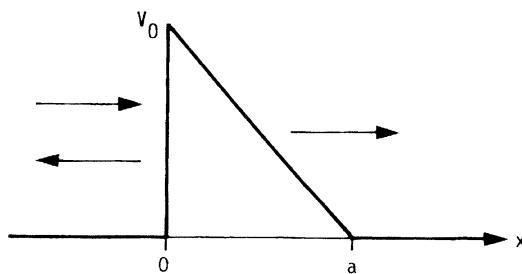


Figure 17.12. The triangular barrier.

$$T_{\text{JWKB}} = \exp \left[ -\frac{4}{3} g^{3/2} (1 - \varepsilon)^{3/2} \right] \quad (171)$$

where

$$g = \left( \frac{2m}{\hbar^2 \alpha^2} \right)^{1/3} V_0,$$

$$\varepsilon = \frac{E}{V_0}$$

- (b) The above potential energy variation is applicable to the field emission of electrons from a metal surface. Then  $V_0 = E_F + \phi$  and  $\alpha = (-q) F$  where  $E_F$  represents the Fermi energy,  $\phi$  the work function,  $q (< 0)$  the electronic charge and  $F$  the strength of the electric field. Assume  $T = 0$  K and calculate the dependence of the electric current on the electric field.

**Problem 17.10** The potential energy distribution given by Eq. (169) can also be (approximately) applied to a quantum well laser and to the  $\alpha$ -decay problem. For a quantum well laser

$$\alpha = \frac{V_0}{L_D} \quad (172)$$

where  $L_D$  is the Debye length and is typically few nanometers. Further  $50 \text{ meV} \lesssim V_0 \lesssim 500 \text{ meV}$ . Assuming

$$V_0 \simeq 50 \text{ meV} \quad \text{and} \quad L_D \simeq 1 \text{ nm}$$

show that  $g \simeq 1.1$ .

On the other hand, in the  $\alpha$ -decay problem for  $V_0 \approx 20 \text{ MeV}$  with  $a \approx 3R$  ( $R \approx 10^{-14} \text{ m}$  being the radius of the nucleus) show that  $g \simeq 15$ .

**Problem 17.11** For the potential energy function given by Eq. (169) one can obtain exact solutions of the Schrödinger equation in terms of the Airy functions. Calculate the corresponding tunnelling probability and compare with the corresponding JWKB results.

**Problem 17.12** Obtain the JWKB eigenvalues for the following potential energy distribution

$$V = -V_0 \operatorname{sech}^2\left(\frac{x}{a}\right) \quad (173)$$

**Problem 17.13** In the radial part of the Schrödinger equation [Eq. (109)] make the following transformations

$$R(r) = \frac{1}{r} u(r) \quad (174)$$

$$\frac{r}{a_0} = e^x \quad (175)$$

$$\chi(x) = u(x) e^{-x/2} \quad (176)$$

to obtain

$$\frac{d^2\chi}{dx^2} + k^2(x) \chi(x) = 0 \quad (177)$$

where

$$k^2(x) = \frac{2ma_0^2}{\hbar^2} e^{2x} \left[ E - V(a_0 e^x) - \frac{(l + \frac{1}{2})^2 \hbar^2}{2ma_0^2} e^{-2x} \right] \quad (178)$$

and  $a_0$  is a conveniently chosen length parameter. Notice that as  $r$  goes from 0 to  $\infty$ ,  $x$  goes from  $-\infty$  to  $+\infty$ . Thus show that the eigenvalue equation [Eq. (44)] leads to

$$\int_{r_1}^{r_2} k_1(r) dr = \left(n + \frac{1}{2}\right) \pi \quad (179)$$

where

$$k_1^2(r) = \frac{2m}{\hbar^2} \left[ E - V(r) - \frac{(l + \frac{1}{2})^2 \hbar^2}{2mr^2} \right] \quad (180)$$

and  $r_1$  and  $r_2$  are the turning points of  $k_1(r)$ .

**Problem 17.14** Using the results of the previous problem, find the eigenvalues corresponding to the Coulomb potential

$$V(r) = -\frac{Ze^2}{r} \quad (181)$$


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## 17.11. Solutions

**Solution 17.5** For  $V(x)$  as shown in Fig. 17.11, the corresponding variation of  $k^2(x)$  for  $E < V_0$  and  $E > V_0$  are shown in Figs 17.13 and 17.14 respectively. Notice that for  $E < V_0$ , there are 4 turning points and for  $E > V_0$  there are only 2 turning points. We assume  $E < V_0$  (see Fig. 17.13). We start with an exponentially

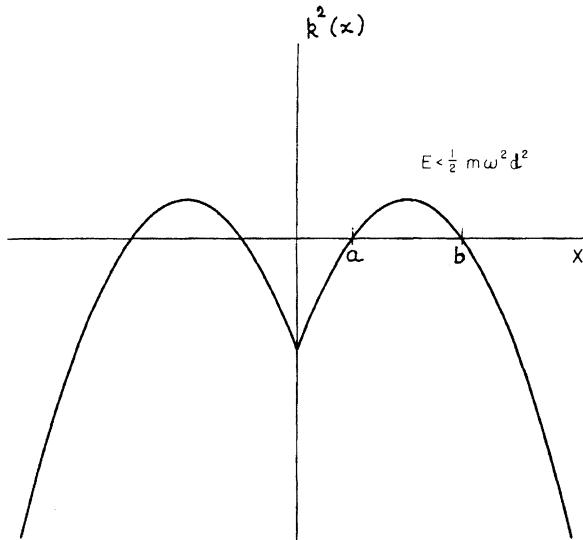


Figure 17.13. For the  $V(x)$  variation as shown in Fig. 17.11, the variation of  $k^2(x)$  with  $x$  for  $E < V_0$ .

decaying solution in Region V ( $x > b$ )

$$\psi_V(x) = \frac{A}{\sqrt{\kappa(x)}} \exp \left[ - \int_b^x \kappa(x) dx \right]; \quad x > b$$

This would go over to (in the region  $a < x < b$ )

$$\begin{aligned}\psi_{\text{IV}}(x) &= \frac{2A}{\sqrt{k}} \sin \left[ \int_x^b k(x) dx + \frac{\pi}{4} \right] \\ &= \frac{2A}{\sqrt{k}} \sin \left[ \left( \theta + \frac{\pi}{2} \right) - \left( \int_a^x k(x) dx + \frac{\pi}{4} \right) \right]; \quad a < x < b\end{aligned}$$

where

$$\theta = \int_a^b k(x) dx$$

Thus

$$\begin{aligned}\psi_{\text{IV}}(x) &= \frac{2A}{\sqrt{k}} \left[ \cos \theta \cos \left( \int_a^x k(x) dx + \frac{\pi}{4} \right) \right. \\ &\quad \left. + \sin \theta \sin \left( \int_a^x k(x) dx + \frac{\pi}{4} \right) \right]; \quad a < x < b\end{aligned}$$

which would go over to

$$\begin{aligned}\psi_{\text{III}}(x) &= \frac{2A}{\sqrt{\kappa}} \left[ \cos \theta \exp \left( \int_x^a \kappa dx \right) \right. \\ &\quad \left. + \frac{1}{2} \sin \theta \exp \left( - \int_x^a \kappa dx \right) \right]\end{aligned}$$

in the region  $-a < x < +a$ . The condition that the wave function has to be either a symmetric ( $\Rightarrow \psi'(0) = 0$ ) or an antisymmetric function of  $x$  ( $\Rightarrow \psi(0) = 0$ ) leads to Eq. (167).

**Solution 17.6** Figures 17.13 and 17.14 correspond to the double well potential with

$$V_0 = \frac{1}{2} m \omega^2 d^2 \quad (182)$$

We define

$$\alpha = \sqrt{\frac{2E}{\hbar \omega}} \quad \text{and} \quad \alpha_0 = \sqrt{\frac{2V_0}{\hbar \omega}} \quad (183)$$

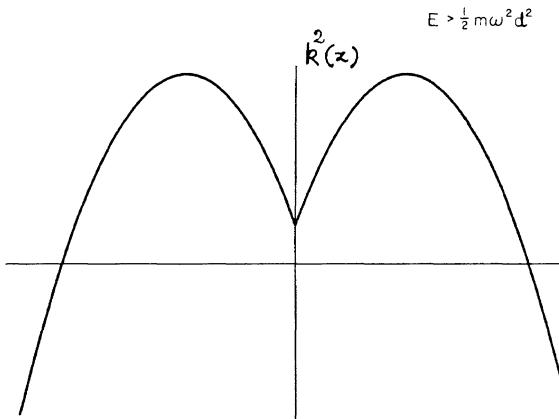


Figure 17.14. For the  $V(x)$  variation as shown in Fig. 17.11, the variation of  $k^2(x)$  with  $x$  for  $E > V_0$ .

We first assume  $E < V_0$  (i.e.  $\alpha < \alpha_0$ ). Now

$$\begin{aligned}\theta &= \int_a^b k(x) dx \\ &= \sqrt{\frac{2m}{\hbar^2}} \int_a^b [E - \frac{1}{2}m\omega^2(x-d)^2]^{1/2} dx \\ &= \int_{-\alpha}^{+\alpha} [\alpha^2 - \xi^2]^{1/2} d\xi = \frac{\pi}{2} \alpha^2\end{aligned}$$

where

$$\xi = \sqrt{\frac{m\omega}{\hbar}} (x - d)$$

Other integrations can easily be carried out. For  $E > V_0$ , we use Eq. (44). The final results are

(i) For  $E < V_0$  ( $0 < \alpha < \alpha_0$ )

$$\cot\left(\frac{\pi}{2}\alpha^2\right) = \pm \frac{1}{2} \exp\left[-\alpha_0(\alpha_0^2 - \alpha^2)^{1/2} + \alpha^2 \cosh^{-1}\frac{\alpha_0}{\alpha}\right] \quad (184)$$

and

(ii) For  $E > V_0$  ( $\alpha > \alpha_0$ )

$$\frac{\pi}{2}\alpha^2 + \alpha_0(\alpha^2 - \alpha_0^2)^{1/2} + \alpha^2 \sin^{-1}\frac{\alpha_0}{\alpha} = \left(m + \frac{1}{2}\right)\pi \quad (185)$$

The corresponding wave functions are given by (for  $E < V_0$ ):

$$\begin{aligned}\psi_V(\xi) = & \frac{C}{(\xi^2 - \alpha^2)^{1/4}} \exp\left[-\frac{1}{2}\xi(\xi^2 - \alpha^2)^{1/2}\right. \\ & \left. + \frac{1}{2}\alpha^2 \ln\left|\frac{\xi + (\xi^2 - \alpha^2)^{1/2}}{\alpha}\right|\right]\end{aligned}\quad (186)$$

Similarly,

$$\begin{aligned}\psi_{IV}(\xi) = & \frac{-2C}{(\alpha^2 - \xi^2)^{1/4}} \sin\left[\frac{\pi}{4} + \frac{\pi}{4}\alpha^2 - \frac{1}{2}\xi(\alpha^2 - \xi^2)^{1/2}\right. \\ & \left. - \frac{1}{2}\alpha^2 \sin^{-1}\frac{\xi}{\alpha}\right]\end{aligned}\quad (187)$$

and

$$\begin{aligned}\psi_{III}(\xi) = & \frac{C}{(\xi^2 - \alpha^2)^{1/4}} \left[ \cos\left(\frac{\pi}{2}\alpha^2\right) \exp(\xi) \right. \\ & \left. + \frac{1}{2} \sin\left(\frac{\pi}{2}\alpha^2\right) \exp(-\xi)\right]\end{aligned}\quad (188)$$

where

$$\begin{aligned}\zeta(\xi) = & \int_x^{x_1} \kappa(x) dx = \int_{-\xi}^{-\alpha} (\xi^2 - \alpha^2)^{1/2} d\xi \\ = & -\frac{1}{2}\xi(\xi^2 - \alpha^2)^{1/2} + \frac{1}{2}\alpha^2 \ln\left|\frac{\xi + \sqrt{\xi^2 - \alpha^2}}{\alpha}\right|\end{aligned}\quad (189)$$

Figure 17.15 shows the normalized energy eigenvalues  $\alpha^2$  for the double oscillator as a function of  $\alpha_0^2$ ; a large value of  $\alpha_0$  (and hence of  $a$ ) implies a large distance between the centers of the two oscillators. The solid and the dashed curves correspond to the exact and the JWKB calculations, respectively. As  $a \rightarrow \infty$ ,  $\alpha^2 (= 2E/\hbar\omega)$  approaches  $(2n + 1)$  and the levels become two-fold degenerate; thus the system becomes equivalent to two independent harmonic oscillators. Further, for  $a \rightarrow 0$ , we have the eigenvalue structure of a single harmonic oscillator. The exact solution for the double oscillator problem is given in terms of the confluent hypergeometric functions. For  $V(x)$  given by Eq. (167), the Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left\{ E - \frac{1}{2}m\omega^2[|x| - d]^2 \right\} \psi = 0 \quad (190)$$

In terms of the variables

$$\left. \begin{aligned} \sigma &= \left( \frac{2m\omega}{\hbar} \right)^{1/2} (x - d) \quad \text{for } x > 0 \\ \text{and} \quad \tau &= \left( \frac{2m\omega}{\hbar} \right)^{1/2} (x + d) \quad \text{for } x < 0 \end{aligned} \right\} \quad (191)$$

Eq. (189) becomes

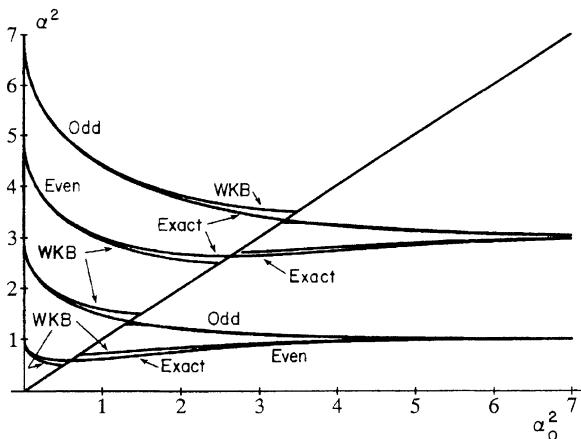


Figure 17.15. Normalized energy eigenvalues for the double oscillator as a function of  $\alpha_0^2$ .

$$\frac{d^2\psi}{d\sigma^2} + \left[ \nu + \frac{1}{2} - \frac{1}{4}\sigma^2 \right] \psi(\sigma) = 0 \quad \text{for } x > 0 \quad (192)$$

and

$$\frac{d^2\psi}{d\tau^2} + \left[ \nu + \frac{1}{2} - \frac{1}{4}\tau^2 \right] \psi(\tau) = 0 \quad \text{for } x < 0 \quad (193)$$

where

$$\nu = \frac{1}{2} \left( \frac{2E}{\hbar\omega} - 1 \right) = \frac{1}{2}(\alpha^2 - 1) \quad (194)$$

The boundary conditions for solving Eqs (191) and (192) are  $\psi \rightarrow 0$  as  $\sigma \rightarrow \infty$  and  $\tau \rightarrow -\infty$ . For  $a = 0$ ,  $\sigma = \tau$  and Eqs (191) and (192) become equivalent to the linear harmonic oscillator problem and  $\nu$  will then be  $0, 1, 2, \dots$ . The solution of Eq. (191) that vanishes for  $\sigma \rightarrow \infty$  is the parabolic cylinder functions  $D_\nu(\sigma)$ , (see Ref. 12) which are related to the confluent hypergeometric function through

the relation

$$D_v(\sigma) = 2^{v/2} \exp(-\sigma^2/4) \left[ \frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{1-v}{2})} {}_1F_1\left(-\frac{v}{2}; \frac{1}{2}; \frac{\sigma^2}{2}\right) + \frac{\sigma}{\sqrt{2}} \frac{\Gamma(-\frac{1}{2})}{\Gamma(-\frac{v}{2})} {}_1F_1\left(\frac{1-v}{2}; \frac{3}{2}; \frac{\sigma^2}{2}\right) \right] \quad (195)$$

Since  $D_v(\sigma) \rightarrow 0$  as  $\sigma \rightarrow \infty$  we must choose  $D_v(\sigma)$  for  $x > 0$  and  $D_v(-\tau)$  for  $\tau < 0$ . In any case, since  $V(-x) = V(x)$ , the wave functions will be either symmetric or antisymmetric in  $x$ ; thus, we need only the solution for  $x > 0$ . The eigenvalue equation for the symmetric and antisymmetric wave functions are

$$D'_v(\sigma)|_{x=0} = 0 \quad \text{symmetric} \quad (196)$$

and

$$D_v(\sigma)|_{x=0} = 0 \quad \text{antisymmetric} \quad (197)$$

The solution given by the above equations are plotted in Fig. 17.15. As mentioned earlier, for  $a \rightarrow 0$ , the solutions correspond to a single oscillator and for  $a \rightarrow \infty$  we have two-fold degeneracy corresponding to two non-interacting oscillators.

### Solution 17.8

$$\int_0^{r_t} k(r) dr = \sqrt{\frac{2\mu V_0}{\hbar^2}} \int_0^{r_t} \sqrt{e^{-r/a} - \epsilon} dr$$

where

$$\epsilon = -\frac{E}{V_0} \quad \text{and} \quad r_t = a \ln \frac{1}{\epsilon}$$

For a bound state  $-V_0 < E < 0$  implying  $0 < \epsilon < 1$ . If we make the substitution

$$\xi^2 = e^{-r/a} - \epsilon$$

we obtain

$$\int k(r) dr = -g \left[ \sqrt{e^{-r/a} - \epsilon} - \sqrt{\epsilon} \tan^{-1} \sqrt{\frac{e^{-r/a} - \epsilon}{\epsilon}} \right]$$

where

$$g = \sqrt{\frac{8\mu V_0 a^2}{\hbar^2}} \simeq 3.64$$

for the numerical values given in Problem 10.8. The transcendental equation determining the energy eigenvalues is given by

$$\sqrt{1 - \epsilon} - \sqrt{\epsilon} \tan^{-1} \sqrt{\frac{1 - \epsilon}{\epsilon}} = \left( n - \frac{1}{4} \right) \frac{\pi}{g}$$

For  $g = 3.64$  we obtain

$$\epsilon \simeq 0.0593$$

Thus

$$E \simeq -2.372 \text{ MeV}$$

which may be compared with the exact value of  $-2.223$  MeV. In Fig. 17.16 we have plotted the JWKB and exact wave functions having the same slope at  $r = 0$ .

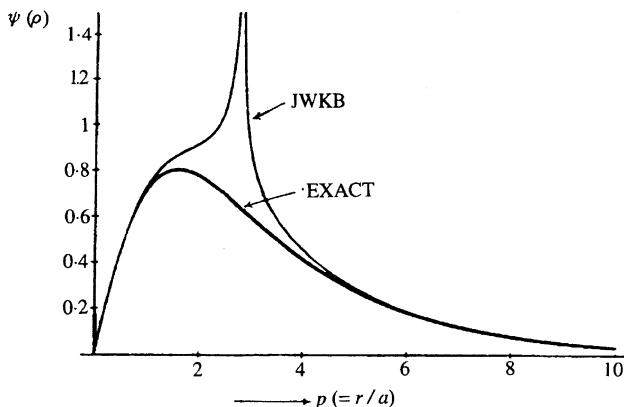


Figure 17.16. Exact and JWKB ground state wave functions corresponding to Eq. (111) ( $l = 0$ ) for the potential energy distribution given by Eq. (169) (adapted from Ref. 3).

### Solution 17.9

(b) The current density is given by

$$J = (-q_e) \int T \frac{p_x}{m} n(p_x) dp_x \quad (198)$$

where  $n(p_x) dp_x$  represents the number of electrons per unit volume whose  $p_x$  lies between  $p_x$  and  $p_x + dp_x$ . Now at low temperatures (i.e.  $T \ll E_F/k$ ), the Fermi function is approximately given by:

$$\begin{aligned} F(E) &= 1 && \text{for } E < E_{F_0} \\ &= 0 && \text{for } E > E_{F_0} \end{aligned}$$

(see Sec. 6.9). Using the expression for density of states (see Sec. 6.8.1), we get

$$\begin{aligned} n(p_x) dp_x &= \frac{2}{h^3} dp_x \iint dp_y dp_z \\ &= \frac{2}{h^3} dp_x \int_0^{2\pi} d\theta \int_0^{[2m(E_F - E_x)]^{1/2}} p_z dp_z \end{aligned}$$

where we have used polar coordinates and  $p_1 = (p_x^2 + p_y^2)^{1/2}$ . Thus

$$n(p_x) dp_x = \frac{4\pi m}{\hbar^3} (E_F - E_x) dp_x \quad (199)$$

Substituting this in Eq. (198), we get

$$J = \frac{4\pi m |q|}{\hbar^3} \int_0^{E_F} \exp \left[ -\beta \phi^{3/2} \left( 1 + \frac{\eta}{\phi} \right)^{3/2} \right] \eta d\eta$$

where  $\eta = E_{F_0} - E_x$ ,  $\phi = V_0 - E_{F_0}$ ,  $\beta = (4/3\alpha)(2m/\hbar^2)^{1/2}$ . Making a binomial expansion of  $(1 + \eta/\phi)^{3/2}$ , retaining up to the first-order term and extending the upper limit to  $\infty$ , we get

$$J \approx A_0 F^2 \exp(-B_0/F) \quad (200)$$

where we have used  $\alpha = |q| F$  and

$$A_0 = \frac{|q|^2}{8\pi\hbar\Phi} \simeq \frac{1.54 \times 10^{-6}}{\Phi} \text{ A/m}^2 \quad (201)$$

$$\begin{aligned} B_0 &= \frac{4}{3} |q|^{1/2} \left( \frac{2m}{\hbar^2} \right)^{1/2} \Phi^{3/2} \\ &\simeq 6.85 \times 10^9 \Phi^{3/2} \text{ V/m} \end{aligned} \quad (202)$$

$\Phi = \phi/|q|$  being the work function measured in electron volts. Equation (200) is known as the Fowler-Nordheim field emission formula and agrees with experimental data. Notice that the field emission (sometimes referred to as cold emission) is due to the tunnelling phenomenon and hence is a purely quantum mechanical effect.

**Solution 17.11** The solution of the one-dimensional Schrödinger equation is given by

$$\begin{aligned} \psi(x) &= A e^{ikx} + B e^{-ikx} & x < 0 \\ &= C Ai(\xi) + D Bi(\xi) & 0 < x < a \\ &= F e^{ik(x-a)} & x > a \end{aligned} \quad (203)$$

where

$$\xi = \left( \frac{2m}{\hbar^2 \alpha^2} \right)^{1/3} [V_0 - \alpha x - E]$$

and  $Ai(\xi)$  and  $Bi(\xi)$  are the Airy functions [see Appendix D]. Continuity of  $\psi(x)$  and  $d\psi/dx$  at  $x = 0$  and at  $x = a$  readily gives as tunnelling probability

$$T_{\text{exact}} = \left| \frac{F}{A} \right|^2 = \left| \frac{a_0 c_0^* - a_0^* c_0}{a_1 c_0^* - a_0^* c_1} \right|^2 \quad (204)$$

where

$$\begin{aligned} a_0 &= Bi'(\xi_0) + i\sqrt{g\varepsilon} Bi(\xi_0) \\ a_1 &= Bi'(\xi_1) + i\sqrt{g\varepsilon} Bi(\xi_1) \\ c_0 &= Ai'(\xi_0) + i\sqrt{g\varepsilon} Ai(\xi_0) \\ c_1 &= Ai'(\xi_1) + i\sqrt{g\varepsilon} Ai(\xi_1) \\ \xi_0 &= \xi(x=0) = g(1-\varepsilon) \\ \xi_1 &= -g\varepsilon \end{aligned}$$

and use has been made of the Wronskian [see, e.g. Ref. 13]

$$W[Ai, Bi] = Ai(\xi) Bi'(\xi) - Ai'(\xi) Bi(\xi) = \frac{1}{\pi} \quad (205)$$

In Figs 17.17 and 17.18 we have plotted the variations of  $T_{\text{exact}}$  and  $T_{\text{JWKB}}$  with

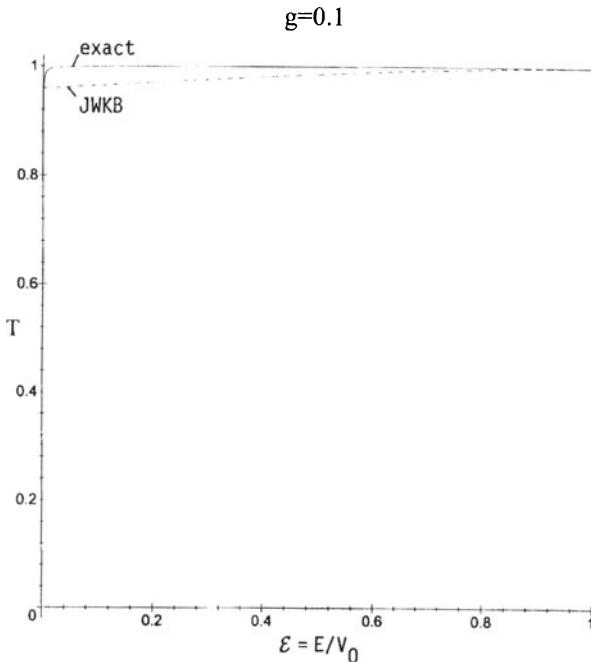


Figure 17.17. Variation of  $T_{\text{exact}}$  and  $T_{\text{JWKB}}$  with  $\varepsilon$  for  $g = 0.1$  [After Ref. 14].

$\varepsilon$  for  $g = 0.1$  and  $g = 1.0$ . In Ref. 14 it has been shown that the JWKB result is accurate for  $\tilde{g} \lesssim 0.1$ .

### Solution 17.12

$$k^2(x) = \frac{2mV_0}{\hbar^2} \left[ \frac{E}{V_0} + \operatorname{sech}^2\left(\frac{x}{a}\right) \right] \quad (206)$$

g=1

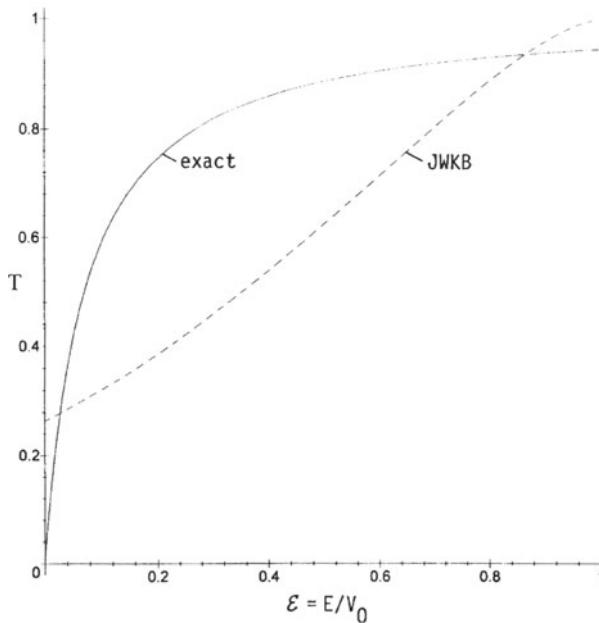


Figure 17.18. Variation of  $T_{\text{exact}}$  and  $T_{\text{JWKB}}$  with  $\mathcal{E}$  for  $g = 1.0$  [After Ref. 14].

and the quantization condition [Eq. (44)] becomes

$$\left(\frac{2mV_0a^2}{\hbar^2}\right)^{1/2} \int_{-\alpha(\mathcal{E})}^{+\alpha(\mathcal{E})} [\operatorname{sech}^2 \xi - \mathcal{E}]^{1/2} d\xi = \left(n + \frac{1}{2}\right)\pi \quad (207)$$

where

$$\xi = \frac{x}{a}, \quad \mathcal{E} = -\frac{E}{V_0} \quad \text{and} \quad \alpha = \operatorname{sech}^{-1} \sqrt{\mathcal{E}} \quad (208)$$

For bound states  $E < 0$  and, since  $E$  can never be less than the minimum value of  $V$ , we have

$$0 < \mathcal{E} < 1 \quad (209)$$

Equation (206) requires the solution of the integral

$$J(\mathcal{E}) = \int_{-\alpha(\mathcal{E})}^{+\alpha(\mathcal{E})} [\operatorname{sech}^2 \xi - \mathcal{E}]^{1/2} d\xi \quad (210)$$

If

$$J(x) = \int_{g(x)}^{f(x)} F(x, y) dy \quad (211)$$

then

$$\frac{dJ}{dx} = \int_{g(x)}^{f(x)} \frac{\partial F}{\partial x} dy + F[x, f(x)] \frac{df}{dx} - F[x, g(x)] \frac{dg}{dx} \quad (212)$$

Therefore

$$\frac{dJ}{d\varepsilon} = -\frac{1}{2} \int_{-\alpha}^{+\alpha} [\operatorname{sech}^2 \xi - \varepsilon]^{1/2} d\xi \quad (213)$$

In our case, the last two terms vanish because the limits are the turning points where the integrand vanishes. In fact, since this always happens, this technique is very often used in the evaluation of the integral appearing in the JWKB quantization condition. If we now make the transformation

$$\eta = \sinh \xi$$

then

$$d\eta = \cosh \xi d\xi \implies d\xi = \frac{d\eta}{(1 + \eta^2)^{1/2}}$$

and Eq. (212) becomes

$$\begin{aligned} \frac{dJ}{d\varepsilon} &= -\frac{1}{2} \int \frac{1}{\left(\frac{1}{1+\eta^2} - \varepsilon\right)^{1/2}} \frac{d\eta}{(1 + \eta^2)} \\ &= -\frac{1}{2\sqrt{\varepsilon}} \left[ \sin^{-1} \left( \sqrt{\frac{\varepsilon}{1-\varepsilon}} \sinh \xi \right) \right]_{-\alpha}^{+\alpha} \\ &= -\frac{\pi}{2\sqrt{\varepsilon}} \end{aligned}$$

Simple integration gives

$$J(\varepsilon) = \pi \left( 1 - \sqrt{\varepsilon} \right) \quad (214)$$

where we have used the condition  $J(1) = 0$  [see Eq. (209)]. Thus, the energy eigenvalues are given by

$$E_n = \frac{-\hbar^2}{2ma^2} \left[ \left( \frac{2mV_0a^2}{\hbar^2} \right)^{1/2} - \left( n + \frac{1}{2} \right) \right]^2 \quad (215)$$

In this case we can also obtain an exact solution of the Schrödinger equation; the final result is

$$E_n = \frac{-\hbar^2}{2ma^2} \left[ \frac{v}{2} - \left( n + \frac{1}{2} \right) \right]^2 \quad (216)$$

where

$$\nu = \left( \frac{8mV_0a^2}{\hbar^2} + 1 \right)^{1/2} \quad (217)$$

The JWKB eigenvalues are recovered if the first term in the brackets is large with respect to 1. The eigenfunctions are

$$\psi(\sigma) = [1 - \sigma]^{-(\nu-1)/2} W(\sigma) \quad (218)$$

where  $\sigma = -\sinh^2(x/a)$  and  $W(\sigma)$  is the polynomial solution of the hypergeometric equation.

**Solution 17.13** The JWKB quantization condition is given by

$$\sqrt{\frac{2m}{\hbar^2}} \int_{r_1}^{r_2} \left( E + \frac{Ze^2}{r} - \frac{(l + \frac{1}{2})^2 \hbar^2}{2mr^2} \right)^{1/2} dr = \left( n + \frac{1}{2} \right) \pi \quad (219)$$

or

$$\sqrt{2} J(\mathcal{E}) = \left( n + \frac{1}{2} \right) \pi \quad (220)$$

where

$$J(\mathcal{E}) = \int_{\xi_1}^{\xi_2} [-\mathcal{E} - V_{eff}(\xi)]^{1/2} d\xi \quad (221)$$

with

$$\begin{aligned} V_{eff}(\xi) &= -\frac{Z}{\xi} + \frac{\alpha}{\xi^2} \\ \mathcal{E} &= -\frac{E}{E_0}, \quad E_0 = \frac{me^4}{\hbar^2} \\ \xi &= \frac{r}{a_0}, \quad a_0 = \frac{\hbar^2}{me^2} \\ \alpha &= \frac{1}{2} \left( l + \frac{1}{2} \right)^2 \end{aligned}$$

Following the method used in the previous solution, we obtain

$$\frac{dJ}{d\mathcal{E}} = -\frac{\pi Z}{4\mathcal{E}^{3/2}} \quad (222)$$

Further, the minimum value of  $V_{eff}(\xi)$  is  $-Z^2/4\alpha$ , which occurs at  $\xi = 2\alpha/Z$ . Thus,

$$J \left( \mathcal{E} = -\frac{Z^2}{4\alpha} \right) = 0, \quad (223)$$

because  $\xi_1$  becomes equal to  $\xi_2$ . Equation (221) can now be integrated. Using Eq. (222), we obtain

$$\mathcal{E} = \frac{Z^2}{2(n + l + 1)^2} \quad (224)$$

which is also the *exact* result with total quantum number  $(n + l + 1)$ .

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# Chapter 18

## Addition of Angular Momenta: The Clebsch-Gordan Coefficients

*Quantum Mechanics is a framework theory which according to prevailing present opinion, applies to every kind of physical system . . .*

— ABNER SHIMONY<sup>1</sup>

### 18.1. Introduction

When a system is made of composite parts which interact with each other, it is the total angular momentum which is conserved and is of great importance. Indeed, the angular momenta to be combined may pertain to the same particle, namely, its orbital and spin angular momenta; or may pertain to the orbital (or spin) angular momenta of two different particles.

As an example, we consider the hydrogen atom problem. If we include the spin-orbit interaction, the Hamiltonian is given by (see Sec. 20.5)

$$H = H_0 + H' \quad (1)$$

where

$$\begin{aligned} H_0 &= -\frac{\hbar^2}{2m} \nabla^2 + V(r) \\ H' &= \xi(r) \mathbf{L} \cdot \mathbf{s} = \xi(r) (L_x s_x + L_y s_y + L_z s_z) \end{aligned}$$

and

$$\xi(r) = \frac{Ze^2}{2m^2c^2} \frac{1}{r^3}$$

<sup>1</sup> Abner Shimony in *Conceptual Foundations of Quantum Mechanics in The New Physics* (Editor: Paul Davis), Cambridge University Press, Cambridge, 1989.

It can be immediately seen that whereas  $L_z$  and  $s_z$  commute with  $H_0$ , they do not commute with  $H'$ . Indeed,

$$\begin{aligned} [L_z, H] &= [L_z, H_0] + [L_z, H'] \\ &= \xi(r) ([L_z, L_x] s_x + [L_z, L_y] s_y + [L_z, L_z] s_z) \\ &= i \hbar \xi(r) (L_y s_x - L_x s_y) \end{aligned}$$

where we have used the results of Sec. 9.4. Thus  $L_z$  does not commute with  $H$ . Similarly

$$[s_z, H] = i \hbar \xi(r) (L_x s_y - L_y s_x) = -[L_z, H]$$

immediately giving

$$[J_z, H] = 0 \quad (2)$$

where  $J_z = L_z + s_z$  represents the  $z$ -component of the total angular momentum operator. Thus  $J_z$  (and similarly  $J_x$  and  $J_y$ ) commute with  $H$  and are constants of motion.

We next consider the helium atom, the Hamiltonian of which is given by (see Sec. 22.2)

$$H = H_0 + H' \quad (3)$$

where

$$H_0 = -\frac{\hbar^2}{2m} [\nabla_1^2 + \nabla_2^2] - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}$$

and

$$H' = \frac{e^2}{r_{12}} = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Once again  $L_{1z}$  and  $L_{2z}$  commute with  $H_0$  but do not commute with  $H'$ ; indeed

$$[L_z, H] = [L_{1z} + L_{2z}, H] = 0 \quad (4)$$

implying that the components of the total angular momentum are constants of motion.

In this chapter we will consider the addition of angular momenta quite generally. Let  $\mathbf{J}_1$  and  $\mathbf{J}_2$  denote two angular momentum operators satisfying the commutation relations (see Eq. 3 of Chapter 13):

$$\begin{aligned} [J_{1x}, J_{1y}] &= i J_{1z} \\ [J_{2x}, J_{2y}] &= i J_{2z} \end{aligned} \quad (5)$$

and other equations can be written in cyclic order<sup>2</sup>; we are using a system of units in which  $\hbar = 1$ . We also have

$$[J_1^2, J_{1x}] = 0 = [J_2^2, J_{2x}], \text{ etc.}$$

---

<sup>2</sup> Often the commutation relations are written in the following form

$$\mathbf{J} \times \mathbf{J} = i\mathbf{J}$$

We assume that the components of  $\mathbf{J}_1$  and  $\mathbf{J}_2$  commute with each other, i.e.

$$[J_{1x}, J_{2x}] = 0 = [J_{1x}, J_{2y}], \text{ etc.}$$

We define the total angular momentum operator  $\mathbf{J}$ :

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \quad (6)$$

Now

$$\begin{aligned} [J_y, J_z] &= J_y J_z - J_z J_y \\ &= (J_{1y} + J_{2y})(J_{1z} + J_{2z}) - (J_{1z} + J_{2z})(J_{1y} + J_{2y}) \\ &= (J_{1y} J_{1z} - J_{1z} J_{1y}) + (J_{2y} J_{2z} - J_{2z} J_{2y}) \\ &= i(J_{1x} + J_{2x}) = i J_x \end{aligned} \quad (7)$$

implying that the components of  $\mathbf{J}$  satisfy the same commutation relations as that of an angular momentum operator. Thus (see also Problem 18.1)

$$[J^2, J_z] = 0, \text{ etc.} \quad (8)$$

where

$$\begin{aligned} J^2 &= J_x^2 + J_y^2 + J_z^2 = (J_{1x} + J_{2x})^2 + \dots + \dots \\ &= J_1^2 + J_2^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2 \end{aligned} \quad (9)$$

where we have used the relation  $\mathbf{J}_1 \cdot \mathbf{J}_2 = \mathbf{J}_2 \cdot \mathbf{J}_1$  because components of  $\mathbf{J}_1$  commute with components of  $\mathbf{J}_2$ . Since the total angular momentum vector is a constant of motion we will, in this chapter, construct vectors which are simultaneous eigenvectors of  $J^2$  and  $J_z$ .

Let  $\psi_1(j_1, m_1)$  be the simultaneous eigenvector of  $J_1^2$  and  $J_{1z}$ , i.e.

$$J_1^2 \psi_1(j_1, m_1) = j_1(j_1 + 1) \psi_1(j_1, m_1) \quad (10)$$

and

$$J_{1z} \psi_1(j_1, m_1) = m_1 \psi_1(j_1, m_1)$$

(see Sec. 13.2). Similarly let  $\psi_2(j_2, m_2)$  represent the simultaneous eigenvectors of  $J_2^2$  and  $J_{2z}$ . Now the operators  $J_1^2$ ,  $J_2^2$ ,  $J_{1z}$  and  $J_{2z}$  commute with each other and the product functions

$$\psi(j_1, j_2, m_1, m_2) = \psi_1(j_1, m_1) \psi_2(j_2, m_2) \quad (11)$$

represent a set of simultaneous eigenvectors of  $J_1^2$ ,  $J_2^2$ ,  $J_{1z}$  and  $J_{2z}$ . Further, for given values of  $j_1$  and  $j_2$  there will be  $(2j_1 + 1)$  possible values of  $m_1$  and  $(2j_2 + 1)$  possible values of  $m_2$ . Thus there will be  $(2j_1 + 1)(2j_2 + 1)$  possible eigenvectors.

because

$$(\mathbf{J} \times \mathbf{J})_x = J_y J_z - J_z J_y = i J_x, \text{ etc.}$$

Now, the operators  $J_1^2$ ,  $J_2^2$ ,  $J^2$  and  $J_z$  also commute with each other (see Problem 18.1) and thus one can construct vectors  $\phi(j_1, j_2, j, m)$  which are simultaneous eigenvectors of the operators  $J_1^2$ ,  $J_2^2$ ,  $J^2$  and  $J_z$  belonging to the eigenvalues  $j_1(j_1 + 1)$ ,  $j_2(j_2 + 1)$ ,  $j(j + 1)$  and  $m$  respectively. In Sec. 18.2 we will show that the allowed values of  $j$  are

*Allowed values of  $j$*

$$j_1 + j_2, j_1 + j_2 - 1, \dots |j_1 - j_2|$$

and since for each value of  $j$  there will be  $(2j + 1)$  values of  $m$ , the total number of  $\phi$  functions (for given values of  $j_1$  and  $j_2$ ) will be

$$\sum_{j=|j_1-j_2|}^{j=j_1+j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1) \quad (12)$$

which is the same as the number of  $\psi$  functions.

We can choose either the  $\psi$  functions or the  $\phi$  functions as the base states and can represent each of the  $\psi$  functions as a linear combination of  $\phi$  functions and conversely. Now the  $\psi$  functions as well as the  $\phi$  functions form orthonormal sets and if we normalize them then the transformation

$$\phi(j_1, j_2, j, m) = \sum_{m_1} \sum_{m_2} C(j_1, j_2; j, m, m_1, m_2) \psi(j_1, j_2, m_1, m_2) \quad (13)$$

is unitary and the coefficients

$$C(j_1, j_2; j, m, m_1, m_2) = \langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m \rangle \quad (14)$$

are known as the Clebsch-Gordan coefficients. The coefficients play an extremely important role in spectroscopy and also in scattering theory<sup>3</sup>. The general formulae for calculating these coefficients are complicated. In Sec. 18.3 we will calculate these coefficients for  $j_1 = j_2 = \frac{1}{2}$  and give tables for calculation of these coefficients for  $j_2 = \frac{1}{2}$  and  $j_2 = 1$  (for arbitrary values of  $j_1$ ). In Problem 18.3 we will calculate these coefficients for  $j_1 = 1$  and  $j_2 = \frac{1}{2}$ . It can be easily seen that  $\psi(j_1, j_2, m_1, m_2)$  are eigenfunctions of  $J_z$  belonging to the eigenvalue  $(m_1 + m_2)$  but, in general, they are not eigenfunctions of  $J^2$ . In Sec. 18.4 we discuss the isospin and show how Clebsch-Gordan coefficients can be used in pion-nucleon systems.

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<sup>3</sup> Some of the uses of Clebsch-Gordan coefficients in spectroscopy problems are discussed in Chapter 19. Applications in scattering theory can be found in Ref 1 and 2 and most of the texts in nuclear physics.

## 18.2. The possible values of $j$

Let us first consider the case  $j_1 = 1$  and  $j_2 = \frac{1}{2}$ ; thus  $m_1$  takes the values 1, 0 and  $-1$  and  $m_2$  takes the values  $\frac{1}{2}, -\frac{1}{2}$ . Consequently, there are six  $\psi$  functions

$$\begin{aligned} & \psi(1, \frac{1}{2}), \psi(0, \frac{1}{2}), \psi(-1, \frac{1}{2}) \\ & \psi(1, -\frac{1}{2}), \psi(0, -\frac{1}{2}) \text{ and } \psi(-1, -\frac{1}{2}) \end{aligned} \quad (15)$$

where we have omitted the values of  $j_1$  and  $j_2$ . The numbers inside the parenthesis denote the values of  $m_1$  and  $m_2$ . Clearly, the values of  $m (= m_1 + m_2)$  are

$$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, \text{ and } -\frac{3}{2}$$

respectively. The maximum value of  $m$  is  $\frac{3}{2}$  and thus one of the  $j$  values must be  $\frac{3}{2}$  which will give rise to four states with  $m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ . The remaining two states must correspond to  $j = \frac{1}{2}$  with  $m = \frac{1}{2}$  and  $-\frac{1}{2}$ . Thus the allowed values of  $j$  are  $\frac{3}{2}$  and  $\frac{1}{2}$  and the corresponding  $\phi$  vectors being

$$\phi(\frac{3}{2}, \frac{3}{2}), \phi(\frac{3}{2}, \frac{1}{2}), \phi(\frac{3}{2}, -\frac{1}{2}), \phi(\frac{3}{2}, -\frac{3}{2})$$

and

$$\phi(\frac{1}{2}, \frac{1}{2}), \phi(\frac{1}{2}, -\frac{1}{2})$$

where the numbers inside the parenthesis are the values of  $j$  and  $m$ ; once again we have omitted the values of  $j_1$  and  $j_2$ . Now

$$\psi(1, \frac{1}{2}) = \phi(\frac{3}{2}, \frac{3}{2})$$

because these are the only functions which correspond to  $m = \frac{3}{2}$ . Further, since  $\psi(0, \frac{1}{2})$  and  $\psi(1, -\frac{1}{2})$  correspond to  $m = \frac{1}{2}$ ,  $\phi(\frac{3}{2}, \frac{1}{2})$  and  $\phi(\frac{1}{2}, \frac{1}{2})$  should be linear combinations of  $\psi(0, \frac{1}{2})$  and  $\psi(1, -\frac{1}{2})$ . Similarly  $\phi(\frac{3}{2}, -\frac{1}{2})$  and  $\phi(\frac{1}{2}, -\frac{1}{2})$  should be linear combinations of  $\psi(0, -\frac{1}{2})$  and  $\psi(-1, \frac{1}{2})$  and finally

$$\phi(\frac{3}{2}, -\frac{3}{2}) = \psi(-1, -\frac{1}{2})$$

Let us next consider the general case and assume, without any loss of generality, that  $j_1 \geq j_2$ . The maximum values of  $m_1$  and  $m_2$  will be  $j_1$  and  $j_2$  and therefore the maximum value of  $j$  will be

$$j_{max} = (m_1 + m_2)_{max} = j_1 + j_2 \quad (16)$$

and there will be only one  $\psi$  vector and only one  $\phi$  vector which will correspond to  $m = j_1 + j_2$  which should be equal. Thus

$$\phi(j_1, j_2, j_1 + j_2, j_1 + j_2) = \psi(j_1, j_2, j_1, j_2) \quad (17)$$

The next largest value of  $m$  will be  $j_1 + j_2 - 1$  which will give rise to two  $\psi$  vectors

$$\psi(j_1, j_2 - 1) \text{ and } \psi(j_1 - 1, j_2) \quad (18)$$

and two  $\phi$  vectors

$$\phi(j_1 + j_2, j_1 + j_2 - 1) \text{ and } \phi(j_1 + j_2 - 1, j_1 + j_2 - 1) \quad (19)$$

where we have omitted  $j_1, j_2$  inside the brackets. The next value of  $m$  will be  $j_1 + j_2 - 2$  which give rise to three  $\psi$  vectors and three  $\phi$  vectors. In general, for  $m = j_1 + j_2 - k$ , we will have the following  $(k + 1)$   $\psi$  vectors

$$\psi(j_1 - k, j_2); \psi(j_1 - k + 1, j_2 - 1); \dots \psi(j_1, j_2 - k) \quad (20)$$

and the following  $\phi$  vectors

$$\begin{aligned} & \phi(j_1 + j_2, j_1 + j_2 - k); \phi(j_1 + j_2 - 1, j_1 + j_2 - k); \dots \\ & \phi(j_1 + j_2 - k, j_1 + j_2 - k) \end{aligned} \quad (21)$$

Each  $\phi$  vector can be expressed as a linear combination of the  $(k + 1)$   $\psi$  vectors, the constant coefficients being the Clebsch-Gordan coefficients. Now, since  $j_1 \geq j_2$  the maximum value of  $k$  should be such that  $j_2 - k$  equals  $-j_2$  [see Eq. (20)] or  $k_{max} = 2j_2$  and therefore

$$j_{min} = j_1 + j_2 - k_{max} = j_1 - j_2 \quad (22)$$

Thus the allowed values of  $j$  are

*Allowed values of  $j$*

$$j_1 + j_2, j_1 + j_2 - 1, \dots, j_1 - j_2 \quad (23)$$

### 18.3. Clebsch-Gordan coefficients for $j_1 = j_2 = \frac{1}{2}$

$$j_1 = j_2 = \frac{1}{2}$$

For  $j_1 = j_2 = \frac{1}{2}$ ,  $m_1 = \pm \frac{1}{2}$  and  $m_2 = \pm \frac{1}{2}$  giving four  $\psi$  functions

$$\psi\left(\frac{1}{2}, \frac{1}{2}\right), \psi\left(\frac{1}{2}, -\frac{1}{2}\right), \psi\left(-\frac{1}{2}, \frac{1}{2}\right) \text{ and } \psi\left(-\frac{1}{2}, -\frac{1}{2}\right)$$

The allowed values of  $j$  are 1 and 0 and hence the four  $\phi$  functions are

$$\phi(1, 1), \phi(1, 0), \phi(1, -1) \text{ and } \phi(0, 0)$$

Obviously

$$\phi(1, 1) = \psi\left(\frac{1}{2}, \frac{1}{2}\right) \quad (24)$$

and

$$\phi(1, -1) = \psi\left(-\frac{1}{2}, -\frac{1}{2}\right) \quad (25)$$

Further

$$\phi(1, 0) = c_1 \psi\left(\frac{1}{2}, -\frac{1}{2}\right) + c_2 \psi\left(-\frac{1}{2}, \frac{1}{2}\right) \quad (26)$$

and

$$\phi(0, 0) = c_3 \psi\left(\frac{1}{2}, -\frac{1}{2}\right) + c_4 \psi\left(-\frac{1}{2}, \frac{1}{2}\right) \quad (27)$$

Now

$$J_- \phi(1, 1) = J_- \psi\left(\frac{1}{2}, \frac{1}{2}\right) = (J_1)_- \psi\left(\frac{1}{2}, \frac{1}{2}\right) + (J_2)_- \psi\left(\frac{1}{2}, \frac{1}{2}\right)$$

or, using Eq. (31) of Chapter 13, we get

$$\sqrt{2} \phi(1, 0) = \psi\left(-\frac{1}{2}, \frac{1}{2}\right) + \psi\left(\frac{1}{2}, -\frac{1}{2}\right)$$

Thus

$$\phi(1, 0) = \frac{1}{\sqrt{2}} [\psi\left(-\frac{1}{2}, \frac{1}{2}\right) + \psi\left(\frac{1}{2}, -\frac{1}{2}\right)] \quad (28)$$

and since  $\phi(0, 0)$  must be orthogonal to  $\phi(1, 0)$  we must have [see also Problem 18.2(c)]

$$\phi(0, 0) = \frac{1}{\sqrt{2}} [-\psi\left(-\frac{1}{2}, \frac{1}{2}\right) + \psi\left(\frac{1}{2}, -\frac{1}{2}\right)] \quad (29)$$

(within an arbitrary phase factor). It can be easily seen that by using ladder operators on  $\phi(1, 0)$  or on  $\phi(1, -1)$  we cannot get  $\phi(0, 0)$  (see also Problem 18.2). We can thus write

$$\begin{pmatrix} \phi(1, 1) \\ \phi(1, 0) \\ \phi(1, -1) \\ \phi(0, 0) \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} \psi\left(\frac{1}{2}, \frac{1}{2}\right) \\ \psi\left(\frac{1}{2}, -\frac{1}{2}\right) \\ \psi\left(-\frac{1}{2}, \frac{1}{2}\right) \\ \psi\left(-\frac{1}{2}, -\frac{1}{2}\right) \end{pmatrix} \quad (30)$$

### *Singlet and triplet states*

The matrix elements are the Clebsch-Gordan coefficients. Corresponding to  $j = 0$  there is only one state  $\phi(0, 0)$  which is therefore known as a *singlet* state; for  $j = 1$  there are three states [ $\phi(1, 1)$ ,  $\phi(1, 0)$  and  $\phi(1, -1)$ ] and therefore  $j = 1$  is referred to as the *triplet* state. Notice that the singlet state is antisymmetric with respect to the interchange of  $m_1$  and  $m_2$  whereas the triplet state is symmetric (see also Sec. 22.6).

The Clebsch-Gordan coefficients for  $j_2 = \frac{1}{2}$  and  $j_2 = 1$  are tabulated<sup>4</sup> in Tables 18.1 and 18.2. We consider the case  $j_2 = \frac{1}{2}$ . For an arbitrary value of  $j_1$  the possible values of  $j$  would be

$$j_1 + \frac{1}{2} \quad \text{and} \quad j_1 - \frac{1}{2}$$

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<sup>4</sup> Tables 18.1 and 18.2 have been adapted from Ref. 3.

Table 18.1. Clebsch-Gordan Coefficients for  
 $j_2 = \frac{1}{2}; \langle j_1, \frac{1}{2}, m_1 m_2 | j_1, \frac{1}{2}, j m \rangle$

$j =$	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\sqrt{\frac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\frac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$
$j_1 - \frac{1}{2}$	$-\sqrt{\frac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\frac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$

Table 18.2. Clebsch-Gordan Coefficients for  $j_2 = 1; \langle j_1, 1, m_1 m_2 | j_1, 1, j m \rangle$

$j =$	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j_1 + 1$	$\sqrt{\frac{(j_1 + m)(j_1 + m + 1)}{(2j_1 + 1)(2j_1 + 2)}}$	$\sqrt{\frac{(j_1 - m + 1)(j_1 + m + 1)}{(2j_1 + 1)(j_1 + 1)}}$	$\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{(2j_1 + 1)(2j_1 + 2)}}$
$j_1$	$-\sqrt{\frac{(j_1 + m)(j_1 - m + 1)}{2j_1(j_1 + 1)}}$	$\frac{m}{\sqrt{j_1(j_1 + 1)}}$	$\sqrt{\frac{(j_1 - m)(j_1 + m + 1)}{2j_1(j_1 + 1)}}$
$j_1 - 1$	$\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{2j_1(2j_1 + 1)}}$	$\sqrt{\frac{(j_1 - m)(j_1 + m)}{j_1(2j_1 + 1)}}$	$\sqrt{\frac{(j_1 + m + 1)(j_1 + m)}{2j_1(2j_1 + 1)}}$

Thus using the top row of Table 18.1, we can write

$$\begin{aligned} \phi\left(j_1, \frac{1}{2}, j_1 + \frac{1}{2}, m\right) &= \sqrt{\frac{j_1 + \frac{1}{2} + m}{2j_1 + 1}} \psi\left(j_1, \frac{1}{2}, m_1 = m - \frac{1}{2}, m_2 = \frac{1}{2}\right) \\ &\quad + \sqrt{\frac{j_1 + \frac{1}{2} - m}{2j_1 + 1}} \psi\left(j_1, \frac{1}{2}, m_1 = m + \frac{1}{2}, m_2 = -\frac{1}{2}\right) \end{aligned} \quad (31)$$

If we assume  $j_1 = \frac{1}{2}$ , then we would readily get Eqs. (24), (25) and (28) corresponding to  $m = 1, -1$  and  $0$  respectively. Similarly, using the bottom row of the table, we can write for  $\phi(j_1, \frac{1}{2}, j_1 - \frac{1}{2}, m)$ . Now, for an electron in a hydrogen atom  $j_1 = l$  and

$$\psi\left(l, \frac{1}{2}, m_l, \frac{1}{2}\right) = R_{nl}(r) Y_{lm_l}(\theta, \phi) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} R_{nl} Y_{lm_l} \\ 0 \end{pmatrix} \quad (32)$$

corresponding to the spin up state of the electron. Similarly we can write the wave function for the spin down state.

**Example 18.1** As an example of using Table 18.1, let us consider the  $n = 3, l = 2$  state of the hydrogen atom. Since

$$j_1 = l = 2 \quad \text{and} \quad j_2 = s = \frac{1}{2}$$

we will have  $j = \frac{5}{2}$  and  $\frac{3}{2}$ . For the  $j = \frac{5}{2}$  state we will have to use the first row of Table 18.1 to obtain

$$\begin{aligned} & \phi \left( j_1 = 2, j_2 = \frac{1}{2}, j = j_1 + \frac{1}{2}, m \right) \\ &= \sqrt{\frac{2+m+\frac{1}{2}}{5}} \psi \left( j_1 = 2, j_2 = \frac{1}{2}, m_l = m - \frac{1}{2}, m_s = \frac{1}{2} \right) \\ &+ \sqrt{\frac{2-m+\frac{1}{2}}{5}} \psi \left( j_1 = 2, j_2 = \frac{1}{2}, m_l = m + \frac{1}{2}, m_s = -\frac{1}{2} \right) \end{aligned}$$

where for all wave functions we are assuming  $n = 3$ . Notice that  $m_l + m_s = m$  for both  $\psi$  functions. Thus

$$\begin{aligned} \phi \left( 2, \frac{1}{2}, \frac{5}{2}, m \right) &= \sqrt{\frac{\frac{5}{2}+m}{5}} R_{32}(r) Y_{2,m-\frac{1}{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{\frac{5}{2}-m}{5}} R_{32}(r) Y_{2,m+\frac{1}{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} \sqrt{\frac{\frac{5}{2}+m}{5}} R_{32} Y_{2,m-\frac{1}{2}} \\ \sqrt{\frac{\frac{5}{2}-m}{5}} R_{32} Y_{2,m+\frac{1}{2}} \end{pmatrix} \end{aligned}$$

Thus, for example, the wave function corresponding to the  $m = -\frac{3}{2}$  state of the  $3^2 D_{5/2}$  states would be

$$\phi \left( 2, \frac{1}{2}, \frac{5}{2}, -\frac{3}{2} \right) = \begin{pmatrix} \sqrt{\frac{1}{5}} R_{32}(r) Y_{2,-2}(\theta, \phi) \\ \sqrt{\frac{4}{5}} R_{32}(r) Y_{2,-1}(\theta, \phi) \end{pmatrix}$$

Similarly, the wave function corresponding to the  $m = +\frac{1}{2}$  state of the  $3^2 D_{3/2}$  would be (we will now have to use the second row of Table 18.1)

$$\phi \left( 2, \frac{1}{2}, \frac{3}{2}, +\frac{1}{2} \right) = \begin{pmatrix} -\sqrt{\frac{2}{5}} R_{32}(r) Y_{2,0}(\theta, \phi) \\ +\sqrt{\frac{3}{5}} R_{32}(r) Y_{2,1}(\theta, \phi) \end{pmatrix}$$

## 18.4. The concept of isospin

In this section we briefly introduce the concept of isospin and mention the use of Clebsch-Gordan coefficients while considering the addition of isospin; such considerations are of great importance in high energy scattering studies<sup>5</sup>.

It is well known that except for their differences in charge, neutrons and protons have similar properties. Thus neutron and proton can be thought of as eigenstates of the nucleon. Now a group of elementary particles can be thought of possessing isospin  $\tau$  if there are  $(2\tau+1)$  particles possessing nearly identical properties except for their charge. Thus protons and neutrons can be thought of possessing isospin  $\tau = \frac{1}{2}$  with  $\tau_z = +\frac{1}{2}$  and  $\tau_z = -\frac{1}{2}$  states corresponding to the proton and neutron respectively<sup>6</sup>. Similarly,  $\pi$ -mesons have an isospin of 1 since they occur in  $2\tau+1 (= 3)$  forms as positively charged  $\pi^+(\tau_z = 1)$ , uncharged  $\pi^0(\tau_z = 0)$  and negatively charged  $\pi^-(\tau_z = -1)$  mesons. The charge of the nucleons or mesons is given by

$$Q = |q| \left[ \tau_z + \frac{1}{2} B \right] \quad (33)$$

where  $B$  is known as the *baryon number* and has the value +1 for nucleons and 0 for mesons.

As an example, we consider the isospin of a system of two nucleons. Assuming that for isospin also, we can add the angular momenta in a manner similar to that discussed in Sections 18.2 and 18.3, we have four possible states

$$\phi(1, 1) = \psi \left( \frac{1}{2}, \frac{1}{2} \right) \quad (34)$$

$$\phi(1, 0) = \frac{1}{\sqrt{2}} \left[ \psi \left( \frac{1}{2}, -\frac{1}{2} \right) + \psi \left( -\frac{1}{2}, \frac{1}{2} \right) \right] \quad (35)$$

$$\phi(1, -1) = \psi \left( -\frac{1}{2}, -\frac{1}{2} \right) \quad (36)$$

$$\phi(0, 0) = \frac{1}{\sqrt{2}} \left[ \psi \left( \frac{1}{2}, -\frac{1}{2} \right) - \psi \left( -\frac{1}{2}, \frac{1}{2} \right) \right] \quad (37)$$

Obviously  $\psi(\frac{1}{2}, \frac{1}{2})$  corresponds to 2 protons because  $\tau_{1z} = \tau_{2z} = \frac{1}{2}$  and similarly  $\phi(1, -1)$  corresponds to 2 neutrons; both  $\phi(1, 0)$  and  $\phi(0, 0)$  correspond to one proton and one neutron. However,  $\phi(1, 0)$  is a symmetric function and  $\phi(0, 0)$  is

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<sup>5</sup> For a nice discussion on isospin the reader is referred to the books by Sachs (Ref. 4), Bethe and Morrison (Ref. 5), etc. A good discussion on the analysis of high energy nuclear scattering experiments can be found in Ref. 2 and 5.

<sup>6</sup> One may see the analogy with the spin angular momentum where  $s_z = +\frac{1}{2}$  and  $-\frac{1}{2}$  correspond to the spin up and spin down states (see Sec. 14.4).

antisymmetric. Now, the ground state of deuteron is a mixture of  ${}^3S_1$  and  ${}^3D_1$  states (see e.g., p 114 of Ref. 6), thus it is symmetric in coordinates. It corresponds to spin 1 and therefore it is also symmetric in spins of the two nucleons. The generalized Pauli principle (see e.g. Ref. 4 of Ch. 7) requires that the wave function should be antisymmetric in isospin variables and hence the isospin state must be  $\phi(0, 0)$ .

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## 18.5. Problems

**Problem 18.1** Show that the operators  $J_1^2$ ,  $J_2^2$ ,  $J^2$  and  $J_z$  commute with each other. In particular show that whereas  $J^2$  does not commute with  $J_{1z}$  and  $J_{2z}$  but it does commute with  $J_z = J_{1z} + J_{2z}$ .

### Problem 18.2

- (a) In Sec. 18.3, we had operated  $\phi(1, 1)$  by  $J_-$  and obtained the Clebsch-Gordan coefficients. Show that the same coefficients are obtained if we had operated  $\phi(1, -1)$  by  $J^+$ .
- (b) Operate  $\phi(1, 0)$  [see Eq. (28)] by  $J_-$  to obtain Eq. (25).
- (c) Operate Eq. (27) by  $J_-$  or  $J_+$  to show that  $c_3 = c_4$ .

**Problem 18.3** Calculate from the first principles the Clebsch-Gordan coefficients for  $j_1 = 1$  and  $j_2 = \frac{1}{2}$  and show that the results are consistent with Table 18.1. Use the calculated coefficients to write the wave functions for the  $p$ -states of an electron ( $l = 1, s = \frac{1}{2}$ ) for

$$j = \frac{3}{2} \left( m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \right)$$

and for

$$j = \frac{1}{2} \left( m_j = \frac{1}{2}, -\frac{1}{2} \right)$$

**Problem 18.4 (a)** Calculate from the first principles the Clebsch-Gordan coefficients for  $j_1 = 2$  and  $j_2 = \frac{1}{2}$  and show that the results are consistent with Table 18.2.

**(b)** Using Table 18.1 calculate the wave function for the following states of the hydrogen atom:

- (i)  $4^2D_{5/2}$  and  $4^2D_{3/2}$  states corresponding to  $m = \frac{3}{2}$ .
- (ii)  $4^2F_{7/2}$  and  $4^2F_{5/2}$  states corresponding to  $m = \frac{5}{2}$  and  $m = -\frac{1}{2}$ .

**Problem 18.5** In the electron spin-orbit interaction problem  $j_1 = l$ ,  $j_2 = s = \frac{1}{2}$  and  $j = l \pm \frac{1}{2}$  [see Eq. (23)]. Assuming that the system is in a state in which  $J_1^2$ ,  $J_2^2$ ,  $J^2$  and  $J_z$  are well-defined show that

$$\langle s_z \rangle = \pm \frac{m_j \hbar}{(2l + 1)} \quad (38)$$

where the upper and lower signs correspond to  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  respectively.

**Problem 18.6** For a state in which  $J_1^2$ ,  $J_2^2$ ,  $J_{1z}$  and  $J_{2z}$  have the well-defined values  $j_1(j_1 + 1)\hbar^2$ ,  $j_2(j_2 + 1)\hbar^2$ ,  $m_1\hbar$  and  $m_2\hbar$  show that

$$\langle J^2 \rangle = [j_1(j_1 + 1) + j_2(j_2 + 1) + 2m_1 m_2] \hbar^2 \quad (39)$$

**Problem 18.7** If  $j_1 (= 1)$  and  $j_2 (= \frac{1}{2})$  represent the isospin of pions and nucleons (see Sec. 18.4), then the total isospin of a pion nucleon system  $j$ , would be either  $\frac{3}{2}$  or  $\frac{1}{2}$ . Show that

$$|\pi^+ p\rangle = \left| j = \frac{3}{2}, j_z = \frac{3}{2} \right\rangle = \left| \frac{3}{2}, \frac{3}{2} \right\rangle \quad (40)$$

$$|\pi^+ n\rangle = \sqrt{\frac{1}{3}} \left| \frac{3}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad (41)$$

$$|\pi^0 p\rangle = \sqrt{\frac{2}{3}} \left| \frac{3}{2}, \frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad (42)$$

$$|\pi^0 n\rangle = \sqrt{\frac{2}{3}} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (43)$$

$$|\pi^- p\rangle = \sqrt{\frac{1}{3}} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (44)$$

$$|\pi^- n\rangle = \left| \frac{3}{2}, -\frac{3}{2} \right\rangle \quad (45)$$

## 18.6. Solutions

### Solution 18.1

$$J^2 = J_1^2 + J_2^2 + 2(J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z})$$

Since  $J_1^2$  and  $J_2^2$  commute with each other and also with  $J_{1x}$ ,  $J_{2x}$ ,  $J_{1y}$  . . . , etc.

$[J^2, J_1^2] = [J^2, J_2^2] = 0$ . Further,

$$[J_1^2, J_z] = [J_1^2, J_{1z}] + [J_1^2, J_{2z}] = 0$$

Similarly  $[J_2^2, J_z] = 0$ . However,  $[J^2, J_{1z}] \neq 0$ , indeed

$$\begin{aligned} [J^2, J_{1z}] &= [J_1^2, J_{1z}] + [J_2^2, J_{1z}] + 2(J_{1x}[J_{2x}, J_{1z}] + [J_{1x}, J_{1z}]J_{2x}) \\ &\quad + (J_{1y}[J_{2y}, J_{1z}] + [J_{1y}, J_{1z}]J_{2y}) + (J_{1z}[J_{2z}, J_{1z}] + [J_{1z}, J_{1z}]J_{2z}) \\ &= 2(-iJ_{1y}J_{2x} + iJ_{1x}J_{2y}) \end{aligned} \quad (46)$$

Similarly

$$[J^2, J_{2z}] = 2(-iJ_{1x}J_{2y} + iJ_{1y}J_{2x}) \quad (47)$$

Thus

$$[J^2, J_z] = [J^2, J_{1z} + J_{2z}] = 0$$

**Solution 18.3** We follow a procedure similar to that used in Sec. 18.3. Now,  $j_1 = 1$ ;  $j_2 = \frac{1}{2}$ ;  $m_1 = +1, 0, -1$ ;  $m_2 = \pm\frac{1}{2}$ ;  $j = \frac{3}{2}, \frac{1}{2}$  and

$$\phi\left(\frac{3}{2}, \frac{3}{2}\right) = \psi\left(1, \frac{1}{2}\right) \quad (48)$$

$$\phi\left(\frac{3}{2}, -\frac{3}{2}\right) = \psi\left(-1, -\frac{1}{2}\right) \quad (49)$$

Thus

$$J_- \phi\left(\frac{3}{2}, -\frac{3}{2}\right) = [(J_1)_- + J_2)_-] \psi\left(1, \frac{1}{2}\right)$$

If we use Eq. (31) of Chapter 13 we would get

$$\phi\left(\frac{3}{2}, \frac{1}{2}\right) = \frac{1}{\sqrt{3}} \psi\left(1, -\frac{1}{2}\right) + \sqrt{\frac{2}{3}} \psi\left(0, \frac{1}{2}\right) \quad (50)$$

If we operate again by  $J_-$  (or operate Eq. (50) by  $J_+$ ) we would get

$$\phi\left(\frac{3}{2}, -\frac{1}{2}\right) = \sqrt{\frac{2}{3}} \psi\left(0, -\frac{1}{2}\right) + \sqrt{\frac{1}{3}} \psi\left(-1, \frac{1}{2}\right) \quad (51)$$

Now  $\phi\left(\frac{1}{2}, \frac{1}{2}\right)$  has to be a linear combination of  $\psi\left(1, -\frac{1}{2}\right)$  and  $\psi\left(0, \frac{1}{2}\right)$  (because only these  $\psi$  functions give  $m = \frac{1}{2}$ ), thus we may write

$$\phi\left(\frac{1}{2}, \frac{1}{2}\right) = c_1 \psi\left(1, -\frac{1}{2}\right) + c_2 \psi\left(0, \frac{1}{2}\right)$$

Since it has to be orthogonal to  $\phi\left(\frac{3}{2}, \frac{1}{2}\right)$  we must have

$$\frac{c_1}{\sqrt{3}} + c_2 \sqrt{\frac{2}{3}} = 0$$

or

$$\phi\left(\frac{1}{2}, \frac{1}{2}\right) = c_1 \left[ \psi\left(1, -\frac{1}{2}\right) - \frac{1}{\sqrt{2}} \psi\left(0, \frac{1}{2}\right) \right]$$

Using the normalization condition we get  $c_1 = \sqrt{\frac{2}{3}}$ , giving

$$\phi\left(\frac{1}{2}, \frac{1}{2}\right) = \sqrt{\frac{2}{3}} \psi\left(1, -\frac{1}{2}\right) - \sqrt{\frac{1}{3}} \psi\left(0, \frac{1}{2}\right) \quad (52)$$

Operating  $\phi\left(\frac{1}{2}, \frac{1}{2}\right)$  by  $J_-$  we get

$$\phi\left(\frac{1}{2}, -\frac{1}{2}\right) = \frac{1}{\sqrt{3}} \psi\left(0, -\frac{1}{2}\right) - \sqrt{\frac{2}{3}} \psi\left(-1, \frac{1}{2}\right) \quad (53)$$

Equations (49)–(54) give that Clebsch-Gordan coefficients. Notice that the  $\phi$  functions automatically form an orthonormal set.

The Pauli wave functions can readily be written. For example, using Eq. (52) we obtain

$$\begin{aligned} \phi\left(\frac{3}{2}, -\frac{1}{2}\right) &= \sqrt{\frac{2}{3}} R_{n,1}(r) Y_{1,0} \begin{pmatrix} 0 \\ 1 \end{pmatrix} + \sqrt{\frac{1}{3}} R_{n,1}(r) Y_{1,-1} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= R_{n,1}(r) \begin{pmatrix} \sqrt{\frac{1}{3}} & Y_{1,-1}(\theta, \phi) \\ \sqrt{\frac{2}{3}} & Y_{1,0}(\theta, \phi) \end{pmatrix} \end{aligned}$$

Similarly one can obtain other wave functions.

**Solution 18.5** Writing  $l$  for  $j_1$ , in Eq. (31) we obtain

$$\langle s_z \rangle_{j=l+\frac{1}{2}} = \left[ \frac{l + \frac{1}{2} + m_j}{2l+1} \right] \left( \frac{1}{2} \hbar \right) + \left[ \frac{l + \frac{1}{2} - m_j}{2l+1} \right] \left( -\frac{1}{2} \hbar \right) = \frac{m_j \hbar}{2l+1} \quad (54)$$

and similarly for  $j = l - \frac{1}{2}$ .

**Solution 18.7**

$$\left| j = \frac{3}{2}, j_z = \frac{3}{2} \right\rangle = \left| j_{1z} = 1, j_{2z} = \frac{1}{2} \right\rangle = |\pi^+ p\rangle \quad (55)$$

$$\left| j = \frac{3}{2}, j_z = -\frac{3}{2} \right\rangle = \left| j_{1z} = -1, j_{2z} = -\frac{1}{2} \right\rangle = |\pi^- n\rangle \quad (56)$$

Now, using Eqs (51) and (52)

$$\begin{aligned} |j = \frac{3}{2}, j_z = \frac{1}{2}\rangle &= \sqrt{\frac{1}{3}} |j_{1z} = 1, j_{2z} = -\frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |j_{1z} = 0, j_{2z} = \frac{1}{2}\rangle \\ &= \sqrt{\frac{1}{3}} |\pi^+ n\rangle + \sqrt{\frac{2}{3}} |\pi^0 p\rangle \end{aligned} \quad (57)$$

and

$$\left| j = \frac{3}{2}, j_z = -\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| \pi^0 n \right\rangle + \sqrt{\frac{1}{3}} \left| \pi^- p \right\rangle, \text{ etc.} \quad (58)$$

Similarly we may use Eqs (53) and (54). Simple algebra will then give Eqs (42)–(45).

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### 18.7. References and suggested reading

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# Chapter 19

## Time Independent Perturbation Theory

We can imagine that this complicated array of moving things which constitute “the world” is something like a great chess game being played by the gods, and we are observers of the game. We do not know what the rules of the game are; all we are allowed to do is to watch the playing. Of course, if we watch long enough, we may eventually catch on to a few of the rules. **The rules of the game** are what we mean by **fundamental physics**. Even if we know every rule, however ... what we really can explain in terms of those rules is very limited, because almost all situations are so enormously complicated that we cannot follow the plays of the game using the rules, much less tell what is going to happen next. We must, therefore, limit ourselves to the more basic question of the rules of the game. If we know the rules, we consider that we “understand” the world.

— RICHARD FEYNMAN<sup>1</sup>

### 19.1. Introduction

In Chapters 6, 7, 10 and 16 we had obtained exact solutions of the Schrödinger equation for specific potential energy variations. However, for most problems in quantum mechanics, it is extremely difficult to obtain exact solutions of the Schrödinger equation and one has to resort to approximate methods. The three most important approximate methods are (i) the perturbation method, (ii) the variational method and (iii) the JWKB method; the perturbation method will be discussed in this chapter. We may mention here that the variational method (which is discussed in Chapter 21) can give good estimate of the ground state energy by choosing an appropriate trial function; however, the method becomes quite cumbersome when one has to apply to higher excited states. On the other hand, the JWKB method (discussed in Chapter 17) gives an approximate but direct solution of the Schrödinger equation. The JWKB method is applicable when the potential energy variation is smoothly varying and when the Schrödinger equation is separable to

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<sup>1</sup> The authors found this quotation in *The Making of the Atomic Bomb* by Richard Rhodes, Simon & Schuster, New York (1986).

a one-dimensional equation; if these conditions are satisfied, the method gives information about all the states of the problem.

The perturbation method, which is the subject matter of this chapter, is applicable when the Hamiltonian can be written as a sum of two parts

$$H = H_0 + H' \quad (1)$$

where the eigenvalues and eigenfunctions of  $H_0$  are known and the effect of  $H'$  can be assumed to be small;  $H_0$  is usually referred to as the unperturbed Hamiltonian and  $H'$  is known as the perturbation. We write the eigenvalue equation for the unperturbed Hamiltonian:

$$H_0 u_n = E_n u_n \quad (2)$$

where  $E_n$  and  $u_n$  are *known* eigenvalues and orthonormal eigenfunctions of  $H_0$  respectively. Our aim is to develop a perturbation method to solve the Schrödinger equation

$$H \psi_n = W_n \psi_n \quad (3)$$

and obtain approximate expressions for  $W_n$  and  $\psi_n$ . In Sec. 19.2 we will develop the perturbation theory for non-degenerate states which will be followed by considerations for degenerate states (Sec. 19.3). The theory that we will develop has been extensively applied to solve many problems in quantum mechanics; some of these applications will be discussed in this chapter. The effect of the magnetic field can also be studied by using perturbation theory which will be discussed in the next chapter.

## 19.2. Non-degenerate case

We introduce a parameter<sup>2</sup>  $g$  and write

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<sup>2</sup> This method is often used in mathematics. For example, if we wish to solve the equation

$$u = a + \epsilon u^2 \quad (i)$$

where  $\epsilon$  is a small number, we may write

$$u = u_0 + \epsilon u_1 + \epsilon^2 u_2 + \dots$$

If we substitute this series in, Eq. (i) above and equate powers of  $\epsilon$ , we obtain  $u_0 = a$ ,  $u_1 = u_0^2 = a^2$ ;  $u_2 = 2u_0u_1 = 2a^3$ , etc. Thus

$$u = a + \epsilon a^2 + 2\epsilon^2 a^3 + \dots$$

In this particular case, the exact solution of Eq. (i) can also be found:

$$u = \frac{1}{2\epsilon} \left[ 1 - (1 - 4a\epsilon)^{\frac{1}{2}} \right] = a + \epsilon a^2 + 2\epsilon^2 a^3 + \dots$$

where we have chosen that root which makes  $u \rightarrow a$  as  $\epsilon \rightarrow 0$ . Further, the series will be convergent only when  $4a\epsilon < 1$ . For further details on perturbation techniques, see References 1 and 2.

$$H = H_0 + g H' \quad (4)$$

Next, we express  $\psi_n$  and  $W_n$  as power series<sup>3</sup> in  $g$ , i.e. we write

$$\psi_n = \psi_n^{(0)} + g \psi_n^{(1)} + g^2 \psi_n^{(2)} + \dots \quad (5)$$

$$W_n = W_n^{(0)} + g W_n^{(1)} + g^2 W_n^{(2)} + \dots \quad (6)$$

where the superscripts 0, 1, 2, . . . refer to the zeroeth order, first order, second order perturbation and the parameter  $g$  is assumed to take a continuous range of values between 0 and 1. In the final result we will set  $g = 1$ . We substitute the expansions given by Eqs (5) and (6) in Eq. (3) to obtain

$$\begin{aligned} & (H_0 + g H') (\psi_n^{(0)} + g \psi_n^{(1)} + g^2 \psi_n^{(2)} + \dots) \\ &= (W_n^{(0)} + g W_n^{(1)} + g^2 W_n^{(2)} + \dots) (\psi_n^{(0)} + g \psi_n^{(1)} + g^2 \psi_n^{(2)} + \dots) \end{aligned} \quad (7)$$

Since the above equation is supposed to be valid for all values of  $g$  lying between 0 and 1, the coefficients of equal powers of  $g$  on either side of the equation must be same i.e.

$$H_0 \psi_n^{(0)} = W_n^{(0)} \psi_n^{(0)} \quad (8)$$

$$H_0 \psi_n^{(1)} + H' \psi_n^{(0)} = W_n^{(0)} \psi_n^{(1)} + W_n^{(1)} \psi_n^{(0)} \quad (9)$$

$$H_0 \psi_n^{(2)} + H' \psi_n^{(1)} = W_n^{(0)} \psi_n^{(2)} + W_n^{(1)} \psi_n^{(1)} + W_n^{(2)} \psi_n^{(0)} \quad (10)$$

etc. Equation (8) tells us that  $\psi_n^{(0)}$  and  $W_n^{(0)}$  are the eigenfunctions and eigenvalues of the unperturbed Hamiltonian. Thus

$$\psi_n^{(0)} = u_n \quad (11)$$

and

$$W_n^{(0)} = E_n \quad (12)$$

We will be considering the effect of the perturbation  $H'$  on the  $n^{th}$  state which will be assumed to be discrete and non-degenerate<sup>4</sup>; however, other states need neither be discrete nor be non-degenerate.

<sup>3</sup> For example, if  $H'$  is proportional to the strength of the electric field  $\mathcal{E}$  then  $\psi_n^{(1)}, \psi_n^{(2)}, \psi_n^{(3)} \dots$  will be proportional to  $\mathcal{E}, \mathcal{E}^2, \mathcal{E}^3$ , respectively;  $\psi_n^{(0)}$  will be independent of  $\mathcal{E}$ . In some cases, such a power series may not be convergent [see, e.g. Eq. (37)]; indeed if it is an asymptotic series (see Appendix K), the first few terms may give fairly good results.

<sup>4</sup> The corresponding theory for degenerate states is discussed in Sec. 19.3.

### 19.2.1. FIRST ORDER PERTURBATION

We assume that the eigenfunctions of the unperturbed Hamiltonian,  $H_0$ , form a complete set; thus we may express  $\psi_n^{(1)}$  as a linear combination of the functions  $u_n$ :

$$\psi_n^{(1)} = \sum_m a_m^{(1)} u_m \quad (13)$$

where the superscript refers to the fact that we are considering first order perturbation. The summation appearing in the above equation actually represents a summation over discrete states and integration over the continuum. If we substitute the above expansion in Eq. (9), we would obtain

$$H_0 \sum_m a_m^{(1)} u_m + H' \psi_n^{(0)} = W_n^{(0)} \psi_n^{(1)} + W_n^{(1)} \psi_n^{(0)} \quad (14)$$

or

$$\sum_m a_m^{(1)} E_m u_m + H' u_n = E_n \sum_m a_m^{(1)} u_m + W_n^{(1)} u_n \quad (15)$$

where we have used Eqs (2) and (11). If we now multiply the above equation by  $u_k^*$  and integrate, we would get

$$\sum_m a_m^{(1)} E_m \delta_{km} + H'_{kn} = E_n \sum_m a_m^{(1)} \delta_{km} + W_n^{(1)} \delta_{kn}$$

or, carrying out the summations we get

$$a_k^{(1)} (E_n - E_k) + W_n^{(1)} \delta_{kn} = H'_{kn} \quad (16)$$

where

$$H'_{kn} \equiv \int u_k^* H' u_n d\tau = \langle k | H' | n \rangle \quad (17)$$

and we have used the orthonormality condition

$$\langle k | m \rangle = \int u_k^* u_m d\tau = \delta_{km};$$

the integrations are over the entire space. For  $k = n$ , Eq. (16) gives

$$W_n^{(1)} = H'_{nn} = \int u_k^* H' u_n d\tau = \langle n | H' | n \rangle \quad (18)$$

which represents the first order perturbation to the energy. For  $k \neq n$ , Eq. (16) gives

$$a_k^{(1)} = \frac{H'_{kn}}{(E_n - E_k)}, \quad k \neq n \quad (19)$$

Notice that we have not been able to determine  $a_n^{(1)}$ . However, it can be easily seen from Eq. (9) that if we add an arbitrary multiple of  $u_n$  to  $\psi_n^{(1)}$ , the equation remains unaltered. Hence, without any loss of generality, we may assume

$$a_n^{(1)} = 0 \quad (20)$$

Such a choice implies

$$\int u_n^* \psi_n^{(1)} d\tau = 0 \quad (21)$$

### 19.2.2. SECOND ORDER PERTURBATION

We next expand  $\psi_n^{(2)}$  as a linear combination of the eigenfunctions of  $H_0$ ; thus, we write

$$\psi_n^{(2)} = \sum_m a_m^{(2)} u_m \quad (22)$$

where the superscripts refer to the fact that we are considering second order perturbation. Substituting the above expansion in Eq. (10) we get

$$\begin{aligned} & H_0 \sum_m a_m^{(2)} u_m + H' \sum_m a_m^{(1)} u_m \\ &= W_n^{(0)} \sum_m a_m^{(2)} u_m + W_n^{(1)} \sum_m a_m^{(1)} u_m + W_n^{(2)} u_n \end{aligned}$$

Multiplying by  $u_k^*$  and integrating we obtain

$$\begin{aligned} & \sum_m a_m^{(2)} E_m \delta_{km} + \sum_m a_m^{(1)} H'_{km} \\ &= E_n \sum_m a_m^{(2)} \delta_{km} + H'_{nn} \sum_m a_m^{(1)} \delta_{km} + W_n^{(2)} \delta_{kn} \end{aligned}$$

or

$$a_k^{(2)} (E_n - E_k) + W_n^{(2)} \delta_{kn} = \sum_m a_m^{(1)} H'_{km} - a_k^{(1)} H'_{nn} \quad (23)$$

For  $k = n$ , we get

$$\begin{aligned} W_n^{(2)} &= \sum_m a_m^{(1)} H'_{nm} - a_n^{(1)} H'_{nn} \\ &= \sum_m^{(m \neq n)} a_m^{(1)} H'_{nm} \end{aligned}$$

where the prime over the summation indicates that we have omitted the term  $m = n$ . Thus, using Eq. (19), we get

$$W_n^{(2)} = \sum_{\substack{m \\ (m \neq n)}} \frac{|H'_{mn}|^2}{E_n - E_m} \quad (24)$$

where we have used the relation  $H'_{nm} = (H'_{mn})^*$ . The above equation gives the second order perturbation to the energy eigenvalue. Further, for  $k \neq n$ , Eq. (23) gives

$$a_k^{(2)} = \sum_m' \frac{H'_{km} H'_{mn}}{(E_n - E_k)(E_n - E_m)} - \frac{H'_{kn} H'_{nn}}{(E_n - E_k)^2} \quad (25)$$

Similarly, we may obtain  $W_n^{(3)}$ . The final result is

$$W_n = W_n^{(0)} + W_n^{(1)} + W_n^{(2)} + W_n^{(3)} + \dots \quad (26)$$

$$\begin{aligned} &= E_n + H'_{nn} + \sum_m' \frac{|H'_{mn}|^2}{E_n - E_m} \\ &\quad + \left[ \sum_m' \frac{|H'_{mn}|^2 (H'_{mm} - H'_{nn})}{(E_n - E_m)^2} \right] \end{aligned}$$

$$+ \frac{1}{3} \sum_m' \sum_{\substack{k \\ k \neq n \\ k \neq m}} \left\{ \frac{1}{E_m - E_k} + \frac{1}{E_n - E_k} \right\} \frac{H'_{nk} H'_{km} H'_{mn} + H'_{nm} H'_{mk} H'_{kn}}{E_n - E_m} \quad (27)$$

### 19.2.3. TWO SIMPLE EXAMPLES

In order to illustrate the use of the perturbation theory to non-degenerate states we consider a perturbation of the form  $\frac{1}{2}bx^2$  to the linear harmonic oscillator problem. Thus

$$H_0 = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad (28)$$

and

$$H' = \frac{1}{2}bx^2 \quad (29)$$

The eigenvalues and eigenfunctions of  $H_0$  are well known (see Sec. 7.2)

$$H_0 u_n = E_n u_n \quad (30)$$

where

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega; \quad n = 0, 1, 2, 3 \dots \quad (31)$$

$$u_n = N_n H_n(\xi) \exp(-\frac{1}{2}\xi^2) \quad (32)$$

$$\begin{aligned} \omega &= \sqrt{\frac{k}{\mu}}, \quad N_n = \left[ \frac{\gamma}{\sqrt{\pi} 2^n n!} \right]^{1/2} \\ \xi &= \gamma x, \quad \gamma = \sqrt{\frac{\mu\omega}{\hbar}} = \left[ \frac{\mu k}{\hbar^2} \right]^{1/4} \end{aligned} \quad (33)$$

Notice that the exact solution can easily be obtained; all that one has to do is replace  $k$  by  $k + b$ . Thus if we write

$$H\psi_n = W_n \psi_n \quad (34)$$

where

$$H = H_0 + H' \quad (35)$$

then

$$W_n = \left( n + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu}} \left[ 1 + \frac{b}{k} \right]^{1/2} \quad (36)$$

or

$$W_n = \left( n + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu}} \left[ 1 + \frac{1}{2} \frac{b}{k} - \frac{1}{8} \frac{b^2}{k^2} + \dots \right] \quad (37)$$

the binomial expansion being valid when  $\frac{b}{k} < 1$ . If we compare Eq. (37) with Eq. (6), we obtain

$$W_n^{(0)} = \left( n + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu}} = E_n \quad (38)$$

$$W_n^{(1)} = \frac{1}{2} \left( n + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu}} \frac{b}{k} \quad (39)$$

$$W_n^{(2)} = -\frac{1}{8} \left( n + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu}} \frac{b^2}{k^2}, \text{ etc.} \quad (40)$$

where  $W_n^{(0)}$  represent the unperturbed eigenvalue, and  $W_n^{(1)}$  and  $W_n^{(2)}$  represent the first and the second order perturbations respectively. Notice that  $W_n^{(1)}$  is linear in  $b$ ,  $W_n^{(2)}$  is quadratic in  $b$ , etc. Further, the power series is convergent only when  $b/k < 1$ .

Let us now employ perturbation theory to calculate  $W_n^{(1)}$ ,  $W_n^{(2)}$ , etc. Now,

$$\begin{aligned} W_n^{(1)} &= \frac{1}{2} b \int_{-\infty}^{\infty} u_n^*(x) x^2 u_n(x) dx = \frac{1}{2} b \langle n | x^2 | n \rangle \\ &= \frac{1}{2} \left( n + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu}} \frac{b}{k} \end{aligned} \quad (41)$$

where we have used the results derived in Solution 12.4. Equation (41) agrees with Eq. (39). In order to calculate  $W_n^{(2)}$  we note that

$$H'_{mn} = \langle m | H' | n \rangle = \frac{1}{2} b \langle m | x^2 | n \rangle \quad (42)$$

is non-zero only when  $m = n - 2$ ,  $m = n$  or  $m = n + 2$  (see Solution 12.4). Thus

$$\begin{aligned} W_n^{(2)} &= \sum_m' \frac{|H'_{mn}|^2}{E_n - E_m} \\ &= \left( \frac{1}{2} b \right)^2 \left[ \frac{|\langle n - 2 | x^2 | n \rangle|^2}{E_n - E_{n-2}} + \frac{|\langle n + 2 | x^2 | n \rangle|^2}{E_n - E_{n+2}} \right] \\ &= -\frac{1}{8} b^2 \frac{\hbar}{\mu^2 \omega^3} \left( n + \frac{1}{2} \right) \end{aligned} \quad (43)$$

which agrees with Eq. (40).

Another simple example is to consider a linear harmonic oscillator of charge  $Q$  perturbed by an electric field  $\mathcal{E}$  in the  $+x$ -direction. Thus

$$H_0 = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu \omega^2 x^2 \quad (44)$$

and

$$H' = -Q \mathcal{E} x \quad (45)$$

Now,

$$\langle m | H' | n \rangle = -Q \mathcal{E} \langle m | x | n \rangle$$

is non-zero only when  $m = n \pm 1$  (see Problem 12.3). Thus  $W_n^{(1)} = 0$  and

$$\begin{aligned} W_n^{(2)} &= \sum_m' \frac{|H'_{mn}|^2}{E_n - E_m} = Q^2 \mathcal{E}^2 \left[ \frac{|\langle n - 1 | x | n \rangle|^2}{E_n - E_{n-1}} - \frac{|\langle n + 1 | x | n \rangle|^2}{E_{n+1} - E_n} \right] \\ &= -\frac{Q^2 \mathcal{E}^2}{2\mu \omega^2} \end{aligned}$$

In this case also one can find an exact solution of the problem by shifting the origin. This can easily be seen because

$$\begin{aligned} H &= H_0 + H' = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}\mu\omega^2x^2 - Q\mathcal{E}x \\ &= -\frac{\hbar^2}{2\mu} \frac{d^2}{d\xi^2} + \frac{1}{2}\mu\omega^2\xi^2 - \frac{Q^2\mathcal{E}^2}{2\mu\omega^2} \end{aligned}$$

where  $\xi = x - \frac{Q\mathcal{E}}{\mu\omega^2}$ . Thus the exact eigenvalue spectrum is

$$W_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{Q^2\mathcal{E}^2}{2\mu\omega^2} \quad (46)$$

It may be noted that in this case the second order theory happens to give the exact results.

### 19.3. Perturbation theory for degenerate states

In the perturbation theory developed in Sec. 19.2, the zeroeth order wave function satisfies the equation

$$H_0\psi_n^{(0)} = W_n^{(0)}\psi_n^{(0)} \quad (47)$$

(see Eq. 8). The above equation implies that  $\psi_n^{(0)}$  is the eigenfunction corresponding to the unperturbed Hamiltonian. If we consider the perturbation to the  $n^{th}$  state then we put

$$W_n^{(0)} = E_n \text{ and } \psi_n^{(0)} = u_n \quad (48)$$

where  $u_n$  and  $E_n$  represent the eigenfunction and the energy eigenvalue for the  $n^{th}$  state respectively. Now, for a degenerate state, any linear combination of the eigenfunctions is also a possible eigenfunction (see Sec. 6.3); consequently,  $\psi_n^{(0)}$  cannot be completely specified by its unperturbed energy. Further, we notice from Eq. (16) that corresponding to a degenerate state if  $k \neq n$  but  $E_k = E_n$  then  $H'_{kn}$  must be zero (otherwise  $a_k^{(1)}$  will be infinite, see Eq. 19). Hence, we must choose<sup>5</sup>

<sup>5</sup> This also follows from the fact that in calculating the first order perturbation when we use the expansion

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \dots$$

we must know precisely  $\psi^{(0)}$  which represents the eigenfunction to which  $\psi$  will collapse when the perturbation is made to go to zero. However, for a degenerate state, we have no *a priori* knowledge which would allow us to predict as to which linear combination will  $\psi$  collapse to. Indeed, Eq. (16) tells us that we must choose such linear combinations so that  $H'_{kn} = 0$  for  $k \neq n$  (among the degenerate eigenfunctions).

for  $\psi_n^{(0)}$  such linear combinations of  $u_n$  so that  $H'_{kn} = 0$  for  $k \neq n$ . Obviously, the choice of the linear combination will depend on the form of  $H'$ . We illustrate the procedure by considering the splitting of the first excited state of the H-atom by an electric field; the splitting of spectral lines due to an electric field is known as Stark effect. The  $n = 2$  state of the H-atom is 4-fold degenerate. The eigenfunctions<sup>6</sup> are (see Sec. 10.4):

$$\left. \begin{aligned} u_1 &= R_{20}Y_{00} = \frac{1}{\sqrt{4\pi}} R_{20}(r); & (n = 2, l = 0, m = 0) \\ u_2 &= R_{21}Y_{10} = \sqrt{\frac{3}{4\pi}} R_{21}(r) \cos \theta; & (n = 2, l = 1, m = 0) \\ u_3 &= R_{21}Y_{11} = -\sqrt{\frac{3}{8\pi}} R_{21}(r) \sin \theta e^{i\phi}; & (n = 2, l = 1, m = 1) \\ u_4 &= R_{21}Y_{1-1} = \sqrt{\frac{3}{8\pi}} R_{21}(r) \sin \theta e^{-i\phi}; & (n = 2, l = 1, m = -1) \end{aligned} \right\} \quad (49)$$

where

$$R_{20}(r) = \frac{1}{\sqrt{2}} \frac{1}{a_0^{3/2}} \left( 1 - \frac{r}{2a_0} \right) e^{-r/2a_0} \quad (50)$$

and

$$R_{21}(r) = \frac{1}{2\sqrt{6}} \frac{1}{a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \quad (51)$$

The corresponding (unperturbed) eigenvalue is [see Sec. 10.4]

$$W_2^{(0)} = -\frac{\mu\alpha^2c^2}{8} = -\frac{1}{4} E_H$$

where  $-E_H$  ( $\approx -13.6$  eV) represents the ground state energy of the hydrogen atom; the corresponding ground state wave function is denoted by  $u_0$ . Let the required linear combination be

$$\psi^{(0)} = c_1 u_1 + \dots + c_4 u_4$$

If we substitute this linear combination in the following equation (see Eq. 9)

$$H_0\psi^{(1)} + H'\psi^{(0)} = W^{(0)}\psi^{(1)} + W^{(1)}\psi^{(0)}$$

---

<sup>6</sup> It should be noted that we could have started with linear combinations of  $u_1, u_2, u_3$  and  $u_4$ ; however, the functions should form an orthonormal set.

we would obtain

$$\begin{aligned} H_0 \sum_m a_m^{(1)} u_m + H' [c_1 u_1 + c_2 u_2 + c_3 u_3 + c_4 u_4] \\ = W_2^{(0)} \sum_m a_m^{(1)} u_m + W_2^{(1)} [c_1 u_1 + c_2 u_2 + c_3 u_3 + c_4 u_4] \end{aligned} \quad (52)$$

where we have assumed

$$\psi_2^{(1)} = \sum_m a_m^{(1)} u_m$$

Thus

$$\begin{aligned} \sum_m a_m^{(1)} E_m u_m + H' [c_1 u_1 + \dots + c_4 u_4] \\ = W_2^{(0)} \sum_m a_m^{(1)} u_m + W_2^{(1)} [c_1 u_1 + \dots + c_4 u_4] \end{aligned}$$

Multiplying by  $u_1^*$  and integrating we obtain

$$a_1^{(1)} W_2^{(0)} + [c_1 H'_{11} + c_2 H'_{12} + c_3 H'_{13} + c_4 H'_{14}] = W_2^{(0)} a_1^{(1)} + W_2^{(1)} c_1$$

where we have used the fact that  $E_m (= W_2^{(0)})$  represents the unperturbed energy eigenvalue. Further

$$H'_{ij} = \int u_i^* H' u_j d\tau$$

Rearranging we obtain

$$c_1 (H'_{11} - W_2^{(1)}) + c_2 H'_{12} + c_3 H'_{13} + c_4 H'_{14} = 0 \quad (53)$$

Similarly, if we multiply Eq. (52) by  $u_2^*$ ,  $u_3^*$  and  $u_4^*$  and integrate, we would obtain respectively the following equations

$$c_1 H'_{21} + c_2 (H'_{22} - W_2^{(1)}) + c_3 H'_{23} + c_4 H'_{24} = 0 \quad (54)$$

$$c_1 H'_{31} + c_2 H'_{32} + c_3 (H'_{33} - W_2^{(1)}) + c_4 H'_{34} = 0 \quad (55)$$

$$c_1 H'_{41} + c_2 H'_{42} + c_3 H'_{43} + c_4 (H'_{44} - W_2^{(1)}) = 0 \quad (56)$$

Obviously, for a  $g$ -fold degenerate state, we will obtain a set of  $g$  equations. Now for nontrivial solutions

$$\left| \begin{array}{cccc} H'_{11} - W_2^{(1)} & H'_{12} & H'_{13} & H'_{14} \\ H'_{21} & H'_{22} - W_2^{(1)} & H'_{23} & H'_{24} \\ H'_{31} & H'_{32} & H'_{33} - W_2^{(1)} & H'_{34} \\ H'_{41} & H'_{42} & H'_{43} & H'_{44} - W_2^{(1)} \end{array} \right| = 0 \quad (57)$$

which is known as the secular equation.

Now, for the hydrogen atom, if  $\mathbf{r}_1$  and  $\mathbf{r}_2$  represent the position coordinates of the electron and proton respectively, then

$$\mathbf{P} = q(\mathbf{r}_2 - \mathbf{r}_1) = -q\mathbf{r} \quad (58)$$

would represent the electric dipole moment of the atom. In the above equation  $q$  ( $> 0$ ) represents the charge of the proton and  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$  represents the relative coordinate [see Sec. 10.3]. Thus, in the presence of the electric field  $\boldsymbol{\epsilon}$  the interaction energy would be given by

$$H' = -\mathbf{P} \cdot \boldsymbol{\epsilon} \quad (59)$$

Assuming a static electric field (of magnitude  $\epsilon$ ) in the  $z$ -direction we get

$$H' = q\epsilon z = q\epsilon r \cos \theta \quad (q > 0) \quad (60)$$

Now

$$\begin{aligned} H'_{23} &= \int u_2^* H' u_3 d\tau \\ &= \iiint \left[ \sqrt{\frac{3}{4\pi}} R_{21}(r) \cos \theta \right] [q\epsilon r \cos \theta] \\ &\quad \times \left[ -\sqrt{\frac{3}{8\pi}} R_{31}(r) \sin \theta e^{i\phi} \right] r^2 dr \sin \theta d\theta d\phi \\ &= 0 \end{aligned}$$

because  $\int_0^{2\pi} e^{i\phi} d\phi = 0$ . Due to the same reason, the matrix elements  $H'_{32}$ ,  $H'_{13}$ ,  $H'_{31}$ ,  $H'_{14}$ ,  $H'_{41}$  and  $H'_{32}$  would vanish. By carrying out the integration over  $\theta$ , it can easily be shown that  $H'_{11}$ ,  $H'_{22}$ ,  $H'_{33}$ ,  $H'_{44}$  and  $H'_{34}$  would vanish. The only non-vanishing<sup>7</sup> matrix elements would be  $H'_{12}$  and  $H'_{21}$ . Now

$$\begin{aligned} H'^*_2 &= H'_{12} = \int u_1^* H' u_2 d\tau \\ &= \frac{\sqrt{3}(q\epsilon)}{4\pi} \int_0^\infty \frac{1}{\sqrt{2}} \frac{1}{2\sqrt{6}} \frac{1}{a_0^3} \frac{r^2}{a_0} \left( 1 - \frac{r}{2a_0} \right) e^{-r/a_0} r^2 dr \end{aligned}$$

---

<sup>7</sup> This could have been directly deduced from the following reasoning: since all the wave functions have definite parities and since  $H'$  has odd parity

$$\int u_1^* H' u_1 d\tau = \dots = \int u_1^* H' u_4 d\tau = 0$$

$$\begin{aligned} & \times \int_0^\infty \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi \\ & = -3q\epsilon a_0 = -g \end{aligned} \quad (61)$$

where  $g = 3q\epsilon a_0$ . Thus the secular equation becomes

$$\begin{vmatrix} -W_2^{(1)} & -g & 0 & 0 \\ -g & -W_2^{(1)} & 0 & 0 \\ 0 & 0 & -W_2^{(1)} & 0 \\ 0 & 0 & 0 & -W_2^{(1)} \end{vmatrix} = 0 \quad (62)$$

The roots are

$$W_2^{(1)} = +g, -g, 0, 0$$

Now, if we substitute the values of the matrix elements, Eqs.(53)-(56) become

$$-c_1 W_2^{(1)} - c_2 g = 0$$

$$-c_1 g - c_2 W_2^{(1)} = 0$$

$$c_3 W_2^{(1)} = 0$$

$$c_4 W_2^{(1)} = 0$$

Clearly for  $W_2^{(1)} = g$ ,  $c_1 = -c_2$ ,  $c_3 = c_4 = 0$  and the required linear combination is

$$\phi_1 = \frac{1}{\sqrt{2}}(u_1 - u_2) \quad (63)$$

where the factor  $1/\sqrt{2}$  is such that  $\phi_1$  is normalized. Similarly for  $W_2^{(1)} = -g$ ,  $c_1 = c_2$ ,  $c_3 = c_4 = 0$  and the required linear combination is

$$\phi_2 = \frac{1}{\sqrt{2}}(u_1 + u_2) \quad (64)$$

For the root  $W_2^{(1)} = 0$ ,  $c_1 = c_2 = 0$  and  $c_3$  and  $c_4$  are indeterminate. Thus

$$\phi_3 \text{ and } \phi_4 = c_3 u_3 + c_4 u_4 \quad (65)$$

The splitting of the level is shown in Fig. 19.1. As can be seen the levels characterized by the wave functions  $u_3$  and  $u_4$  remain degenerate and the degeneracy is said to be partially lifted. The above theoretical predictions agree with corresponding experimental values for electric field strengths less than about  $10^6$  volts/m. For higher fields, the quadratic Stark effect has to be taken into account. Eventually,

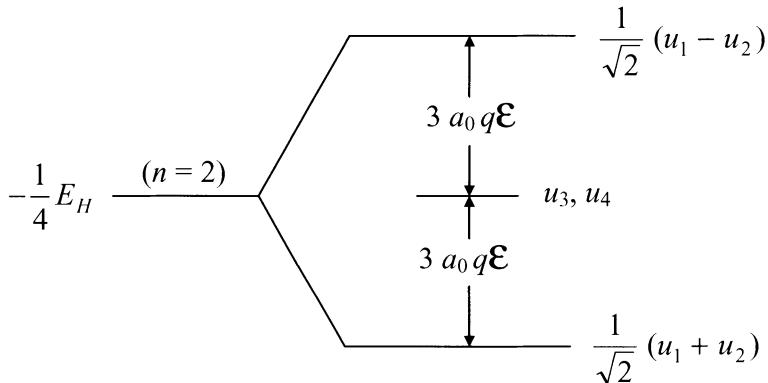


Figure 19.1. The splitting of the  $n = 2$  level of the hydrogen atom by the electric field.

for field strengths greater than  $10^7$  volts/m, autoionization occurs and Stark effect disappears.

#### 19.4. Examples from matrix algebra

The use of the perturbation approach can be illustrated by considering examples from matrix algebra. We will discuss first the non-degenerate case and then the degenerate case. Obviously, while considering examples from matrix algebra one must always have Hermitian matrices.

##### Case 1: Non-degenerate case

Let us consider the matrix

$$H = \begin{pmatrix} 1 + \varepsilon & \varepsilon \\ \varepsilon & -1 + \varepsilon \end{pmatrix}$$

We write  $H = H_0 + H'$ , where

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad H' = \begin{pmatrix} \varepsilon & \varepsilon \\ \varepsilon & \varepsilon \end{pmatrix}$$

$H_0$  is assumed to represent the unperturbed matrix and  $H'$  represents the perturbation and we assume  $\varepsilon \ll 1$ . The eigenvalues of  $H_0$  are  $+1$  and  $-1$ ; the corresponding orthonormal eigenfunctions are

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Now

$$H'_{11} = (1 \ 0) \begin{pmatrix} \varepsilon & \varepsilon \\ \varepsilon & \varepsilon \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \varepsilon$$

and

$$H'_{22} = (0 \ 1) \begin{pmatrix} \varepsilon & \varepsilon \\ \varepsilon & \varepsilon \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \varepsilon$$

Thus, in the first-order perturbation theory, the eigenvalues are

$$1 + \varepsilon \quad \text{and} \quad -1 + \varepsilon$$

The exact eigenvalues of  $H$  are given by

$$\begin{aligned} \lambda &= \varepsilon \pm (1 + \varepsilon^2)^{1/2} \\ &= 1 + \varepsilon + \frac{1}{2}\varepsilon^2 + \mathcal{E}; \quad \text{and} \quad -1 + \varepsilon - \frac{1}{2}\varepsilon^2 + \mathcal{E} \end{aligned}$$

which agrees with the perturbation theory result.

### Case 2: Degenerate case

As before, we write  $H = H_0 + H'$  with

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad H' = \begin{pmatrix} \varepsilon & \varepsilon \\ \varepsilon & \varepsilon \end{pmatrix}$$

and assume  $\varepsilon \ll 1$ . Clearly the matrix  $H_0$  has only one eigenvalue, viz., +1, which is two fold-degenerate. Further, any column matrix  $\begin{pmatrix} a \\ b \end{pmatrix}$  is an eigenvector. We may choose

$$|u_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |u_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

as the base vectors. Thus

$$H'_{11} = (1 \ 0) \begin{pmatrix} \varepsilon & \varepsilon \\ \varepsilon & \varepsilon \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \varepsilon$$

Similarly

$$H'_{22} = H'_{12} = H'_{21} = \varepsilon$$

Therefore, the secular equation is

$$\begin{vmatrix} \varepsilon - W & \varepsilon \\ \varepsilon & \varepsilon - W \end{vmatrix} = 0$$

which gives

$$W = 0 \quad \text{and} \quad W = 2\varepsilon$$

The degeneracy is lifted and according to first order perturbation theory the eigenvalues are

$$1 \quad \text{and} \quad 1 + 2\varepsilon$$

If we denote the eigenfunction by

$$|\phi\rangle = c_1|u_1\rangle + c_2|u_2\rangle$$

then

$$c_1(\varepsilon - W) + c_2\varepsilon = 0$$

and

$$c_1\varepsilon + c_2(\varepsilon - W) = 0$$

For

$$W = 0, \quad c_1 = -c_2$$

and

$$|\phi_1\rangle = \frac{1}{\sqrt{2}}(|u_1\rangle - |u_2\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

For

$$W = 2\varepsilon, \quad c_1 = -c_2$$

and

$$|\phi_2\rangle = \frac{1}{\sqrt{2}}(|u_1\rangle + |u_2\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Notice that

$$\langle\phi_1|H'|\phi_2\rangle = \langle\phi_2|H'|\phi_1\rangle = 0$$

i.e., we have chosen such linear combinations in which  $H'$  is diagonal. It is easy to show that if we try to directly determine the eigenvalues and eigenfunctions of  $H$ , we would obtain

$$(1 + \varepsilon - \lambda)^2 = \varepsilon^2$$

or

$$\lambda = 1 + \varepsilon \pm \varepsilon$$

Thus, it so happens that the first order perturbation theory gives the exact results.

## 19.5. Fine structure of the hydrogen atom

**Important Note:** In this section, in order to be consistent with the notation used in most books on spectroscopy, we will be using CGS units. In order to get the corresponding formulae in the MKS units, we must replace

$$e^2 \text{ by } \frac{q^2}{4\pi\epsilon_0}$$

Alternatively, we can replace  $e^2$  by  $\alpha\hbar c$  where  $\alpha (= 1/137)$  is the fine structure constant. Then the formulae will be valid both in MKS and CGS units.

The theory of the hydrogen atom developed in Chapter 10 was based on the non-relativistic expression for the Hamiltonian given by

$$H = H_0 = \frac{p^2}{2m} + V(r) \quad (66)$$

where

$$V(r) = -\frac{Ze^2}{r} \quad (67)$$

(67) In Sec. 10.4 we had solved the eigenvalue equation

$$H_0\psi = E\psi \quad (68)$$

and had shown that the discrete energy levels corresponding to the Hamiltonian  $H_0$  are given by

$$E = E_n = -\frac{Z^2 mc^2 \alpha^2}{2n^2} = -\frac{Z^2 E_H}{n^2}; \quad n = 1, 2, 3, \dots \quad (69)$$

where

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137.036} \quad (70)$$

is the fine structure constant and other symbols have been defined in Sections 10.3 and 10.4. The corresponding orthonormal wavefunctions are given by (see Sec. 10.4)

$$\psi = \psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) \quad (71)$$

where  $R_{nl}(r)$  are the radial part of the wave function (see Sec. 10.4 and Appendix I) and  $Y_{lm}(\theta, \phi)$  are the spherical harmonics (see Chapters 9 and 15). Transitions between states (corresponding to different values of  $n$ ) lead to Lyman series, Balmer series, etc., (see Fig. 10.1). However, if these spectral lines are seen through a high resolution spectroscope then usually each line is seen to consist of more than one line. This splitting is usually referred to as the fine structure of the spectral lines which is due to a combination of the effect due to relativity and also due to the interaction of the spin angular momentum of the electron with its orbital angular momentum—we will use first order perturbation theory to study the effects due to relativity and also due to spin-orbit interactions. We may mention here that when the atoms are put in a magnetic field then the spectral lines undergo further splitting—this is known as Zeeman effect. This will be discussed in the next chapter.

### 19.5.1. RELATIVISTIC EFFECTS

Now, according to the special theory of relativity, the relation between the energy and momentum for a free particle is given by

$$E^2 = c^2 p^2 + m^2 c^4 \quad (72)$$

where  $m$  represents the rest mass of the particle and  $c$  the speed of light in free space. In the presence of the potential  $V(r)$ , the above equation modifies to

$$[E - V(r)]^2 = c^2 p^2 + m^2 c^4 \quad (73)$$

We replace  $\mathbf{p}$  by  $-i\hbar$  to obtain the relativistic Schrödinger equation

$$[-\hbar^2 c^2 \nabla^2 + m^2 c^4] \psi = [E - V(r)]^2 \psi \quad (74)$$

If we write  $E = E' + mc^2$ , the above equation can be written as

$$(H_0 + H') \psi = E' \psi \quad (75)$$

where

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (76)$$

and

$$H' = -\frac{[E' - V(r)]^2}{2mc^2} \quad (77)$$

If we neglect  $H'$ , we get the non-relativistic Schrödinger equation

$$H_0 = \psi = E' \psi \quad (78)$$

which is the same as Eq.(68). We will now use first order perturbation theory to study the effect of  $H'$ . Now, if  $\psi_{nlm}$  represent the hydrogen atom wave functions (see Sec. 10.4) then

$$\begin{aligned} \iiint \psi_{nl'm'}^* H' \psi_{nlm} d\tau &= -\frac{1}{2mc^2} \iiint \psi_{nl'm'}^* [E_n - V(r)]^2 \psi_{nlm} d\tau \\ &= -\frac{1}{2mc^2} \left\{ \int_0^\infty \left[ E_n + \frac{Ze^2}{r} \right]^2 |R_{nl}(r)|^2 r^2 dr \right\} \delta_{ll'} \delta_{mm'} \end{aligned}$$

where  $E_n$  represents the energy levels of the hydrogen atom [see Eq.(69)]. The above equation tells us that we already have a representation in which  $H'$  is diagonal. Thus the relativity correction would be given by

$$\Delta E_{\text{rel}} = W_{\text{rel}}^{(1)} = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n Ze^2 \left\langle \frac{1}{r} \right\rangle + Z^2 e^4 \left\langle \frac{1}{r^2} \right\rangle \right]$$

where

$$\left\langle \frac{1}{r^p} \right\rangle \equiv \int_0^\infty \frac{1}{r^p} [R_{nl}(r)]^2 r^2 dr \quad (79)$$

Substituting the expression for  $\langle \frac{1}{r} \rangle$  and  $\langle \frac{1}{r^2} \rangle$  from Appendix I we obtain

$$\begin{aligned} \Delta E_{\text{rel}} &= -\frac{1}{2mc^2} \left[ \frac{Z^4}{n^4} E_H^2 - \frac{2Z^2}{n^2} E_H Z e^2 \frac{Z}{a_0 n^2} + 4Z^4 E_H^2 \frac{1}{n^3 (l + \frac{1}{2})} \right] \\ &= -\frac{Z^2 E_H}{n^2} \left( \frac{\alpha Z}{n} \right)^2 \left[ \frac{n}{l + \frac{1}{2}} - \frac{3}{4} \right] \end{aligned}$$

Thus

$$\Delta E_{\text{rel}} = E_n \left( \frac{\alpha Z}{n} \right)^2 \left[ \frac{n}{l + \frac{1}{2}} - \frac{3}{4} \right] \quad (80)$$

In wavenumber units we get

$$\Delta T_{\text{rel}} = \frac{\Delta E_{\text{rel}}}{hc} = -\frac{\alpha^2 Z^4}{n^4} R \left[ \frac{n}{l + \frac{1}{2}} - \frac{3}{4} \right] \text{cm}^{-1} \quad (81)$$

where

$$R = \frac{mc\alpha^2}{2h} \quad (82)$$

represents the Rydberg constant whose numerical values are given in Sec. 10.3. For the hydrogen atom  $Z = 1$ , and substituting the values of  $R$  and  $\alpha$  we obtain

$$\Delta T_{\text{rel}} \approx -\frac{5.845}{n^4} \left[ \frac{n}{l + \frac{1}{2}} - \frac{3}{4} \right] \text{cm}^{-1} \quad (83)$$

Thus because of relativistic effects, the eigenstates corresponding to a particular value of  $n$  will split and the degeneracy will be partially removed. For the  $n = 2$  state we have

$$\begin{aligned} \Delta T_{\text{rel}} &\approx -1.1870 \text{ cm}^{-1} \quad \text{for } n = 2, l = 0 \\ &\approx -0.2130 \text{ cm}^{-1} \quad \text{for } n = 2, l = 1 \end{aligned}$$

Similarly, the  $n = 3$  state will split into 3 levels corresponding to  $l = 0, 1$  and  $2$ . Figure 19.2 which corresponds to the  $n = 2$  state of the hydrogen atom. However, the results are not in agreement with the experimental data; one has to take into account the spin-orbit interaction which will be discussed next.

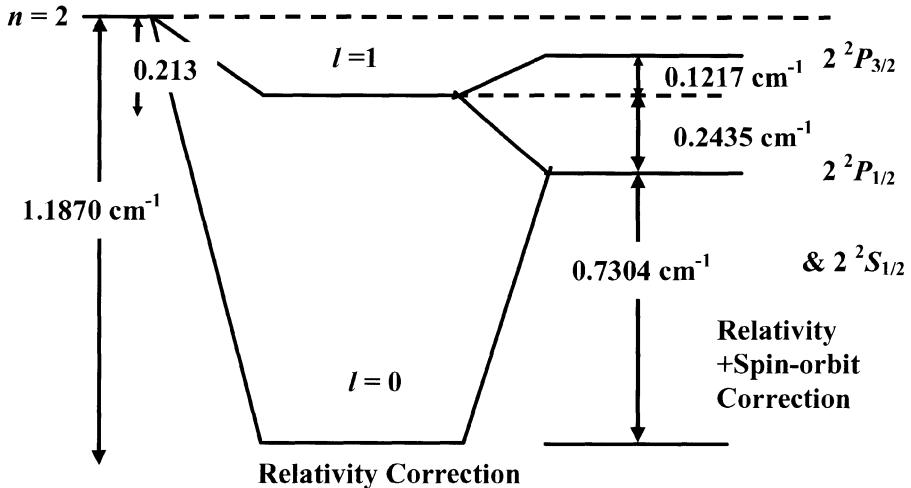


Figure 19.2. The perturbation due to relativistic effects and spin-orbit interaction for the  $n = 2$  state of the hydrogen atom.

### 19.5.2. THE SPIN-ORBIT INTERACTION

In a hydrogen-like atom the spin-orbit interaction  $H'$  is given by (see Sec. 20.5)

$$H' = \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{s} = \frac{Z\hbar\alpha}{2m^2c} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{s} \quad (84)$$

Since

$$J^2 = L^2 + s^2 + 2\mathbf{L} \cdot \mathbf{s}$$

we get  $2\mathbf{L} \cdot \mathbf{s} = J^2 - L^2 - s^2$ ; thus we will have to choose a representation in which  $J^2$ ,  $L^2$  and  $s^2$  are well-defined and calculate the spin-orbit correction. The Pauli Operator for (see Sec. 13.6) is given by

$$(H')_P = \frac{Z\alpha\hbar}{4m^2c} \frac{1}{r^3} [(J^2)_P - (L^2)_P - (s^2)_P] \quad (85)$$

Thus, the Pauli wave equation is given by

$$(H)_P \psi_P = [(H_0)_P + (H')_P] \psi_P = W \psi_P \quad (86)$$

where

$$(H_0)_P = \begin{pmatrix} H_0 & 0 \\ 0 & H_0 \end{pmatrix} = \begin{pmatrix} -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} & 0 \\ 0 & -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \end{pmatrix}$$

and

$$\psi_P = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$$

represents the Pauli wave function. The Pauli wave equation for the unperturbed Hamiltonian is given by (see Sec. 13.6)

$$\begin{pmatrix} H_0 & 0 \\ 0 & H_0 \end{pmatrix} \begin{pmatrix} \psi_+^{(0)} \\ \psi_-^{(0)} \end{pmatrix} = W^{(0)} \begin{pmatrix} \psi_+^{(0)} \\ \psi_-^{(0)} \end{pmatrix}$$

or

$$H_0 \psi_{\pm}^{(0)} = W^{(0)} \psi_{\pm}^{(0)} \quad (87)$$

Consequently,  $W^{(0)}$  will simply represent the energy levels of hydrogen like atom problem:

$$W^{(0)} = E_n = -\frac{Z^2 me^4}{2n^2 \hbar^2} = -\frac{Z^2 E_H}{n^2} \quad (88)$$

and  $\psi_{\pm}^{(0)}$  will be the hydrogen atom wave functions which are simply  $R_{nl} Y_{lm_l}(\theta, \phi)$ ; we have put a subscript  $l$  to  $m$  to distinguish it from  $m_s$  and  $m_j$  which correspond to spin and total angular momentum quantum numbers. Thus the Pauli wave functions for the spin up and the spin down states would be given by

$$\begin{aligned} (\psi_+^{(0)})_P &= \psi \left( n, l, m_l, m_s = +\frac{1}{2} \right) = R_{nl} Y_{lm_l} |\uparrow\rangle = R_{nl} Y_{lm_l} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} R_{nl} Y_{lm_l} \\ 0 \end{pmatrix} \end{aligned} \quad (89)$$

and

$$\begin{aligned} (\psi_-^{(0)})_P &= \psi \left( n, l, m_l, m_s = -\frac{1}{2} \right) = R_{nl} Y_{lm_l} |\downarrow\rangle = R_{nl} Y_{lm_l} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 \\ R_{nl} Y_{lm_l} \end{pmatrix} \end{aligned} \quad (90)$$

In the absence of the spin-orbit interaction, both the wave functions correspond to the same energy. Thus, in order to determine the splitting due to spin-orbit interaction we must choose a representation in which  $H'$  is diagonal, i.e. we must choose such linear combinations of  $(\psi_+^{(0)})_P$  and  $(\psi_-^{(0)})_P$  in which  $\mathbf{L} \cdot \mathbf{s}$  or  $J^2$ ,  $L^2$  and  $s^2$  are well defined. This can easily be obtained by using Clebsch-Gordon coefficients (see Table 18.1)

$$(\phi_1)_P = \phi \left( n, l, j = 1 + \frac{1}{2}, m_j \right)$$

$$\begin{aligned}
&= \sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}} \psi \left( n, l, m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2} \right) \\
&\quad + \sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}} \psi \left( n, l, m_l = m_j + \frac{1}{2}, m_s = -\frac{1}{2} \right) \\
&= \left( \begin{array}{l} \sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}} R_{nl} Y_{l,m_j-\frac{1}{2}} \\ \sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}} R_{nl} Y_{l,m_j+\frac{1}{2}} \end{array} \right) \tag{91}
\end{aligned}$$

A similar expression can be written down for

$$(\phi_2)_P = \phi \left( n, l, j = l - \frac{1}{2}, m_j \right)$$

Now

$$\left. \begin{array}{l} (J^2)_P \phi = j(j+1)\hbar^2 \phi \\ (L^2)_P \phi = l(l+1)\hbar^2 \phi \\ (s^2)_P \phi = \frac{3}{4}\hbar^2 \phi \end{array} \right\} \tag{92}$$

Thus, the first order perturbation due to the spin-orbit interaction would be given by

$$\begin{aligned}
\Delta E_{s-o} &= W_{s-o}^{(1)} = \int d\tau \phi^+ (H')_P \phi \\
&= \frac{Z\hbar\alpha}{4m^2c} \int d\tau \frac{1}{r^3} \phi^+ [(J^2)_P - (L^2)_P - (s^2)_P] \phi \\
&= \frac{z\hbar\alpha}{4m^2c} \left[ j(j+1) - l(l+1) - \frac{3}{4} \right] \hbar^2 \int d\tau \frac{1}{r^3} \\
&\times \left[ \frac{l \pm m_j + \frac{1}{2}}{2l+1} |R_{nl}|^2 |Y_{l,m_j-\frac{1}{2}}|^2 + \frac{l \mp m_j + \frac{1}{2}}{2l+1} |R_{nl}|^2 |Y_{l,m_j+\frac{1}{2}}|^2 \right]
\end{aligned}$$

where the upper and lower signs correspond to  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  respectively. Carrying out the integration over the angles we obtain:

$$\Delta E_{s-o} = \frac{Z\hbar^3\alpha}{4m^2c} \left[ j(j+1) - l(l+1) - \frac{3}{4} \right] \left\langle \frac{1}{r^3} \right\rangle \tag{93}$$

Using the expression for  $\langle \frac{1}{r^3} \rangle$  from Appendix I we get

$$\left. \begin{aligned} \Delta E_{s-o} &= \frac{Z^4 \alpha^4 m c^2}{2n^3(l+1)(2l+1)} && \text{for } j = l + \frac{1}{2} \\ &= -\frac{Z^4 \alpha^4 m c^2}{2n^3 l (2l+1)} && \text{for } j = l - \frac{1}{2} \end{aligned} \right\} \quad (94)$$

In wavenumber units

$$\Delta T_{s-o} = \frac{1}{hc} \Delta E_{s-o}$$

or,

$$\Delta T_{s-o} = \left\{ \begin{array}{ll} \frac{Z^4 \alpha^2 R}{n^3(l+1)(2l+1)} & \text{for } j = l + \frac{1}{2} \\ -\frac{Z^4 \alpha^2 R}{n^3 l (2l+1)} & \text{for } j = l - \frac{1}{2} \end{array} \right. \quad (95)$$

Thus for the hydrogen atom ( $Z = 1$ ), one obtains for  $n = 2$  [see Fig. 19.2].

$$\begin{aligned} \Delta T_{s-o} \left( n = 2, l = 1, j = \frac{3}{2} \right) &= \frac{1.097 \times 10^5}{48} \left( \frac{1}{137} \right)^2 \text{ cm}^{-1} \\ &\approx 0.1217 \text{ cm}^{-1} \end{aligned}$$

Similarly

$$\begin{aligned} \Delta T_{s-o} \left( n = 2, l = 1, j = \frac{1}{2} \right) &\approx -0.2435 \text{ cm}^{-1} \\ \Delta T_{s-o} \left( n = 2, l = 0, j = \frac{1}{2} \right) &= +0.7304 \text{ cm}^{-1} \\ \Delta T_{s-o} \left( n = 1, l = 0, j = \frac{1}{2} \right) &= +5.8435 \text{ cm}^{-1} \end{aligned}$$

The sum of the relativity and spin orbit correction is referred to as the fine structure splitting which we will denote by  $\Delta T_{fs}$ :

$$\Delta T_{fs} = \Delta T_{rel} + \Delta T_{s-o}$$

For  $j = l + \frac{1}{2}$

$$\Delta T_{fs} = -\frac{\alpha^2 Z^4}{n^4} R \left[ \frac{n}{l + \frac{1}{2}} - \frac{3}{4} - \frac{n}{(l+1)(2l+1)} \right]$$

where we have used Eqs. (81) and (95). Simple manipulations and use of the relation  $j = l + \frac{1}{2}$  would give

$$\Delta T_{\text{fs}} = -\frac{\alpha^2 Z^4}{n^4} R \left[ \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right]; \quad j = l \pm \frac{1}{2} \quad (96)$$

Even for  $j = l - \frac{1}{2}$ , the above expression is valid. We must mention here that the selection rules for transitions between doublets are

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta j = 0, \pm 1 \quad (97)$$

The total quantum number may change by any integral amount.

### 19.5.3. FINE STRUCTURE OF THE HYDROGEN ATOM

For the hydrogen atom  $Z = 1$  and substituting the values of  $\alpha$  and  $R$  we get

$$\Delta T_{\text{fs}} \approx -\frac{5.845}{n^4} \left[ \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right] \text{ cm}^{-1} \quad (98)$$

The fine structure of various levels of the hydrogen atom are shown in Fig. 19.3. Now, the  $n = 3 \rightarrow n = 2$  transition corresponds to the  $H_\alpha$  line of the Balmer

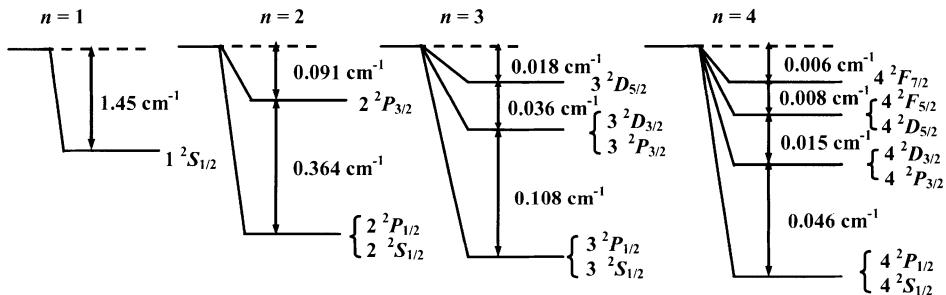


Figure 19.3. Fine structure of various levels of the hydrogen atom.

series of the hydrogen atom ( $\lambda \approx 6564.7 \text{ \AA}$ ). The fine structure leads to 5 lines corresponding to the following transitions (see, e.g., Ref. 3):

	$\Delta T(\text{cm}^{-1})$
$3^2 S_{1/2} \rightarrow 2^2 P_{3/2}$	-0.071
$3^2 D_{3/2} \rightarrow 2^2 P_{3/2}$	+0.037
$3^2 D_{5/2} \rightarrow 2^2 P_{3/2}$	+0.073
$3^2 P_{1/2} \rightarrow 2^2 S_{1/2}$	+0.294
$3^2 D_{3/2} \rightarrow 2^2 P_{1/2}$	+0.402

The third and the fifth lines are the most intense—separated by  $0.329\text{ cm}^{-1}$  consistent with experimental findings.

#### 19.5.4. SPECTRA OF THE IONIZED HELIUM ATOM

We consider the  $n = 4$  to  $n = 3$  transition for the  $\text{He}^+$  atom. Substituting the value of  $R$  [as given in Sec. 10.4] we get

$$T(n = 4) - T(n = 3) = -43889.6 \left[ \frac{1}{16} - \frac{1}{9} \right]$$

or,

$$T_{43} \approx 21335\text{ cm}^{-1}$$

which corresponds to  $\lambda \approx 4687.2\text{ \AA}$ . Now, from Eq.(96)

$$\Delta T_{\text{fs}} \approx -\frac{93.49}{n^4} \left[ \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right] \text{ cm}^{-1}$$

Various lines corresponding to the fine structure of the  $4687\text{ \AA}$  line are shown in Fig. 19.4; they are

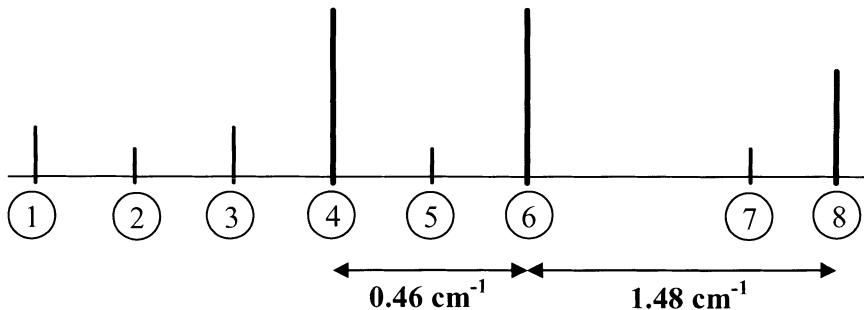


Figure 19.4. Fine structure of the  $n = 4$  to  $n = 3$  transition of the ionized helium atom.

$$\Delta T(\text{cm}^{-1})$$

$$1 \Rightarrow 4^2S_{1/2} \rightarrow 3^2D_{3/2} \quad -0.321$$

$$2 \Rightarrow 4^2P_{3/2} \rightarrow 3^2D_{5/2} \quad -0.168$$

$$3 \Rightarrow 4^2F_{5/2} \rightarrow 3^2D_{5/2} \quad +0.755$$

$$4 \Rightarrow 4^2F_{7/2} \rightarrow 3^2D_{5/2} \quad +0.197$$

$$5 \Rightarrow 4^2D_{3/2} \rightarrow 3^2P_{3/2} \quad +0.409$$

$$6 \Rightarrow 4^2F_{5/2} \rightarrow 3^2D_{3/2} \quad +0.653$$

$$7 \Rightarrow 4^2P_{1/2} \rightarrow 3^2S_{1/2} \quad +1.410$$

$$8 \Rightarrow 4^2D_{3/2} \rightarrow 3^2P_{1/2} \quad +2.140$$

The wavenumber difference between the two most intense lines (4 and 6) would be

$$0.653 - 0.197 \approx 0.46 \text{ cm}^{-1}$$

which agrees with experimental data; the experimental data has been given in Sec. 9.5 of Ref. 3.

### 19.6. Almost degenerate perturbation theory

We next consider the case when the levels are *almost degenerate*, i.e. the corresponding energy eigenvalues are very nearly equal. For such a case the perturbation theory for non-degenerate states is strictly not valid because the corresponding expansion coefficient would become very large (see Eq.19). We give here an approximate perturbation theory for a group of two levels which are almost degenerate. Let  $u_1$  and  $u_2$  represent the eigenfunctions of the two levels with energy eigenvalues  $E_1$  and  $E_2$  i.e.,

$$H_0 u_{1,2} = E_{1,2} u_{1,2} \quad (99)$$

We write

$$\psi \approx c_1 u_1 + c_2 u_2 \quad (100)$$

and substitute in the eigenvalue equation

$$H\psi = W\psi$$

to obtain

$$c_1 H_{11} + c_2 H_{12} = W c_1 \quad (101)$$

and

$$c_1 H_{21} + c_2 H_{22} = W c_2 \quad (102)$$

where

$$\begin{aligned} H_{ij} &= \int u_i^* H u_j d\tau = \int u_i^* (H_0 + H') u_j d\tau \\ &= E_j \delta_{ij} + H'_{ij} \end{aligned} \quad (103)$$

Equations (101) and (102) give us the secular determinant

$$\begin{vmatrix} H_{11} - W & H_{12} \\ H_{21} & H_{22} - W \end{vmatrix} = 0 \quad (104)$$

which gives us

$$W_{1,2} = \frac{1}{2}[H_{11} + H_{22}] \pm \frac{1}{2}[(H_{11} - H_{22})^2 + 4|H_{12}|^2]^{1/2} \quad (105)$$

It is to be noted that when  $E_1 = E_2$  one obtains the result for degenerate states (see Sec.19.3). On the other hand, when  $|H_{11} - H_{22}| \gg |H_{12}|$ , one gets (by making a binomial expansion)

$$W_{1,2} \approx \frac{1}{2}[H_{11} + H_{22}] \pm \frac{1}{2} \left[ (H_{11} - H_{22}) + \frac{1}{2} \frac{|H_{12}|^2}{H_{11} - H_{22}} \right] \quad (106)$$

Thus

$$W_1 = E_1 + H'_{11} + \frac{|H'_{12}|^2}{(E_1 + H'_{11}) - (E_2 + H'_{22})} \quad (107)$$

(and a similar expression for  $W_2$ ) which agree with the result obtained by using non-degenerate perturbation theory to order  $g^2$  because the term  $(H'_{11} - H'_{22})$  in the denominator of the third term is itself of order  $g$ ;  $g$  is the parameter introduced in Eq.(4). Thus Eq.(105) represents the general expression which in the appropriate limiting forms go over to the expressions corresponding to non-degenerate and degenerate state perturbation theory.

## 19.7. Dalgarno's method

If it becomes necessary to calculate the second order correction (viz.,  $W_n^{(2)}$ ) one has to evaluate the infinite sum given by Eq.(24) which, in general, is extremely difficult to carry out. However, in some cases it is possible to directly solve Eq.(9) and obtain an analytical expression for  $\psi_n^{(1)}$  using which one can evaluate  $W_n^{(2)}$  by using the following expression:

$$W_n^{(2)} = \int \psi_n^{(0)*} H' \psi_n^{(1)} d\tau - W_n^{(1)} \int \psi_n^{(0)*} \psi_n^{(1)} d\tau \quad (108)$$

The above equation is obtained by multiplying Eq.(10) by  $\psi_n^{(0)*}$  and integrating. This method is due to Dalgarno and is known as Dalgarno's method (see Ref. 4). We will illustrate its use by considering the Stark effect problem for the ground state of the hydrogen atom<sup>8</sup>. The perturbation is  $H' = q\epsilon r \cos \theta$  (see Eq.58). Now  $W_1^{(0)} = -E_H$  and it is easy to show that  $W_1^{(1)} = 0$ . We rewrite Eq.(9) as

$$H_0 \psi_1^{(1)} - W_1^{(0)} \psi_1^{(1)} = -H' \psi_1^{(0)} + W_1^{(1)} \psi_1^{(0)} \quad (109)$$

Thus

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{q^2}{4\pi\epsilon_0 r} + E_H \right] \psi_1^{(1)} = -q\epsilon r \cos \theta \frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-r/a_0} \quad (110)$$

<sup>8</sup> Epstein has given another method for calculating the Stark effect problem in hydrogen atom. The method has been discussed in Ref. 5, p. 195.

where we have substituted the ground state wave function from Eqs.(36) and (59) of Chapter 10. Since  $\psi_1^{(1)}$  should go to zero as  $\epsilon \rightarrow 0$ , we need find only the solution to the inhomogeneous part of the equation. We assume

$$\psi_1^{(1)} = R(r) \cos \theta \quad (111)$$

Thus

$$\begin{aligned} \nabla^2 \psi_1^{(1)} &= \left[ \frac{1}{r^2} \frac{d}{dr} \left( r \frac{dR}{dr} \right) \cos \theta + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \cos \theta \right) R(r) \right] \\ &= \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2}{r^2} R(r) \right] \cos \theta \end{aligned} \quad (112)$$

We substitute in Eq.(110) and introduce the variable [see Eq.(54) of Chapter 10]  $\xi = r/a_0$ , where  $a_0$  is the Bohr radius. Simple manipulations would give

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{dR}{d\xi} \right) - \frac{2}{\xi^2} R(\xi) + \left( \frac{2}{\xi} - 1 \right) R(\xi) = C\xi e^{-\xi} \quad (113)$$

where

$$C = \frac{q\epsilon}{E_H \sqrt{\pi a_0}} \quad (114)$$

Let us introduce  $F(\xi)$  such that

$$R(\xi) = \xi F(\xi) e^{-\xi} \quad (115)$$

On substitution in Eq.(113), we obtain

$$\xi \frac{d^2 F}{d\xi^2} + (4 - 2\xi) \frac{dF}{d\xi} - 2F(\xi) = C\xi \quad (116)$$

We are interested in determining the inhomogeneous part of the solution. We find that  $F(\xi) = a + b\xi$  satisfies Eq.(116) provided we choose  $a = 2b = C/2$ . Thus we obtain

$$R(\xi) = -\frac{C}{2}\xi \left( 1 + \frac{1}{2}\xi \right) e^{-\xi}$$

and therefore

$$\psi_1^{(1)} = -\frac{C}{2}\xi \left( 1 + \frac{1}{2}\xi \right) e^{-\xi} \cos \theta \quad (117)$$

Substituting in Eq.(108) we get

$$\begin{aligned} W_1^{(2)} &= \int \psi_1^{(0)} H' \psi_1^{(1)} d\tau \\ &= \iiint \left[ \frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-r/a_0} \right] [q\epsilon r \cos \theta] \\ &\quad \times \left[ -\frac{C}{2}\xi \left( 1 + \frac{1}{2}\xi \right) e^{-\xi} \cos \theta \right] r^2 dr \sin \theta d\theta d\phi \end{aligned} \quad (118)$$

where  $E_H (\approx 13.6 \text{ eV})$  is a positive number. The above result is in MKS units. In CGS units (which is often used in such problems), the result is

$$W_1^{(2)} = -\frac{9}{8} \frac{a_0^2}{E_H} e^2 \epsilon^2 = -\frac{9}{4} a_0^3 \epsilon^2$$

where we have used the result  $E_H = e^2/2a_0$ . Thus we may write

$$W_1 = W_1^{(0)} - \frac{9}{4} a_0^3 \epsilon^2 \text{ (CGS units)} \quad (119)$$

Thus the polarizability<sup>9</sup> for the normal hydrogen atom is given by

$$\alpha = \frac{9}{2} a_0^3 = 0.677 \times 10^{-24} \text{ cm}^3 \quad (120)$$

Similarly, one can obtain expressions for  $\psi_1^{(2)}(r)$  and  $W_1^{(4)}$  (see, e.g. Ref. 4).

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## 19.8. Problems

**Problem 19.1** Consider an electron inside an infinitely deep one dimensional potential well:

$$\begin{aligned} V(x) &= 0 \quad \text{for } 0 < x < L \\ &= \infty \quad \text{for } x < 0 \text{ and } x > L \end{aligned}$$

(see Sec.6.6.1). Assuming a perturbation of the form  $H' = -Q\epsilon ex$  show that in the first order perturbation theory each level gets shifted by  $-\frac{1}{2} Q\epsilon L$ . Further, show that for the ground state ( $n = 1$ )

$$\psi^{(1)}(n = 1) = c_2 \psi^{(0)}(n = 2) + c^3 \psi^{(0)}(n = 3) + \epsilon$$

where

$$c_2 = \frac{32}{27\pi^4} \left( \frac{\mu a^2}{\hbar^2} \right) (-Q\epsilon L), \text{ etc.}$$

**Problem 19.2** Consider the one-dimensional harmonic oscillator problem. Assuming perturbation  $H' = \beta x^4$  show that

$$W_n^{(1)} = \frac{3\beta}{2(\mu\omega/\hbar)^2} \left( n^2 + n + \frac{1}{2} \right) \quad (121)$$

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<sup>9</sup> For details on polarizability one may refer to Ref. 5, Sec. 29e and 49f; Ref. 6, Sec. 5.3.

[Hint: see Problem 12.5].

**Problem 19.3** Let the matrix

$$P = \begin{pmatrix} 1 & \varepsilon \\ \varepsilon & 3 \end{pmatrix}$$

be written in the form  $P = P_0 + P'$ , where

$$P_0 = \begin{pmatrix} 1 & 0 \\ 0 & 3 \end{pmatrix} \quad \text{and} \quad P' = \begin{pmatrix} 0 & \varepsilon \\ \varepsilon & 0 \end{pmatrix}$$

Consider  $P'$  as the perturbation and use second order perturbation theory to calculate the eigenvalues of  $P$ . Compare the results with the ones obtained by diagonalizing the matrix  $P$ .

**Problem 19.4** Let the matrix

$$P = \begin{pmatrix} 1 & \varepsilon & 0 \\ \varepsilon & 1 & 0 \\ 0 & 0 & 2 + \varepsilon \end{pmatrix}$$

be written in the form  $P = P_0 + P'$  where

$$P = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 1 & 2 \end{pmatrix} \quad \text{and} \quad P' = \begin{pmatrix} 1 & \varepsilon & 0 \\ \varepsilon & 0 & 0 \\ 0 & 0 & \varepsilon \end{pmatrix}$$

Consider  $P'$  as the perturbation and use degenerate state perturbation theory to calculate the eigenvalues of  $P$ .

**Problem 19.5** Consider a particle in an infinitely deep potential well inside a cube of dimension  $L$  (see Sec. 6.8). Consider a perturbation of the form

$$H' = kx^2$$

Apply first order perturbation theory to the first excited state which is 3-fold degenerate. Is the degeneracy completely lifted?

**Problem 19.6** Consider a Hamiltonian of the form

$$H = H_0 + H'$$

where

$$H_0 = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{1}{2}k(x_1^2 + x_2^2) \quad (122)$$

and

$$H' = \lambda x_1 x_2 \quad (123)$$

The above Hamiltonian represents two identical oscillators (along the same axis) with an interaction between the two. (If we replace  $x_1$  by  $x$ , and  $x_2$  by  $y$ , we would have a two-dimensional oscillator which has been discussed in Problem 10.13). Treat  $H'$  as a perturbation and calculate the first order shift in the energy level of the first excited state. This problem can also be solved exactly. Obtain the exact solution and compare with the result obtained by using perturbation theory.

**Problem 19.7** In continuation of the previous problem, consider again two identical oscillators with an interaction given by

$$H' = \frac{1}{2}k\varepsilon x_1 x_2(x_1^2 + x_2^2) \quad (124)$$

Treat  $H'$  as a perturbation and show that in the first order perturbation theory, the ground state is not shifted and the 2-fold degenerate first excited state split whose energies are

$$\left(2 \pm \frac{3}{4}\frac{\varepsilon\hbar}{\sqrt{\mu k}}\right)\hbar\omega;$$

The corresponding eigenfunctions being

$$\frac{1}{\sqrt{2}}(\psi_{0,1} \pm \psi_{1,0})$$

**Problem 19.8** Using first order perturbation theory calculate the ground state energy of a helium-like atom; assume the interaction between the two electrons to represent the perturbation. Show that the first ionization potential for a single electron is given by

$$\left(\frac{1}{2}Z^2 - \frac{5}{8}Z\right)E_H \quad (125)$$

Assume the nucleus to be infinitely heavy.

**Problem 19.9** While solving the Schrödinger equation for a hydrogen-like atom one assumes the nucleus to be a point charge. Using first order perturbation theory calculate the effect of the finite size of the nucleus assuming the nucleus to be a sphere of radius  $R_N$  with its charge uniformly distributed throughout its volume. (The effect of the finite size of the nucleus is usually referred to as volume effect and is important while considering *isotope shift*).

**Problem 19.10** The previous problem has an important application in muonic atoms<sup>10</sup> which consists of a  $\mu$ -meson and a nucleus ( $m_\mu \approx 207m_e$ ). First show that the Bohr radius for the muonic atom is comparable to the nuclear radius for  $Z \approx 45$ ; thus for  $Z \approx 45$  the muon orbit may be inside the nucleus. Assuming the

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<sup>10</sup> Muonic atoms may be formed when a muon slows down through matter. Such atoms have been obtained for  $Z = 1$  to heavy elements like uranium.

Coulomb potential to be a perturbation, calculate the energy levels of the muonic atom.

**Problem 19.11** In the  $n = 4$  to  $n = 3$  transition of the  $\text{He}^+$ -atom calculate the separation between the three lines corresponding to the following transitions

$$\begin{aligned} 4^2F_{7/2} &\rightarrow 3^2D_{5/2} \\ 4^2F_{5/2} &\rightarrow 3^2D_{3/2} \end{aligned}$$

and

$$4^2D_{3/2} \rightarrow 3^2P_{1/2}$$

[Ans:  $\approx 0.45 \text{ cm}^{-1}$ ,  $1.48 \text{ cm}^{-1}$ ]

**Problem 19.12** (a) In the  $n = 3$  to  $n = 2$  transition of the hydrogen atom (the  $H_\alpha$  line of the Balmer series) calculate the separation between the two lines corresponding to the following transitions

$$\begin{aligned} 3^2D_{5/2} &\rightarrow 2^2P_{3/2} \\ 3^2D_{3/2} &\rightarrow 2^2P_{1/2} \end{aligned}$$

(b) The  $H_\beta$  line of the Balmer series of the hydrogen atom corresponds to the  $n = 4 \rightarrow n = 2$  transition. The two most intense lines of the fine structure of the  $H_\beta$  line corresponds to

$$4^2D_{5/2} \rightarrow 2^2P_{3/2}$$

and

$$4^2D_{3/2} \rightarrow 2^2P_{1/2}$$

transitions. Calculate the separation between the two lines.

(c) Show that there would be 3 lines resulting from the  ${}^2D \rightarrow {}^2P$  transition.

**Problem 19.13** A plane rotator is defined by the Hamiltonian  $H = M_z^2/2I$  where  $I$  is the moment of inertia and  $M_z$  is the operator of the component of angular momentum along the axis of rotation  $z$ . Replace  $M_z$  by  $-i\hbar \frac{\partial}{\partial \phi}$  and find the eigenvalues and normalized eigenfunctions of  $H$ . (You will only have to assume that the wave functions should be single-valued.) If the rotator be perturbed by a constant field in its plane, in which its potential energy is  $\epsilon \cos \phi$ , show that to the order  $\epsilon^2$ , the displacement of the level  $E_m$  is

$$\frac{\epsilon^2 I}{\hbar^2(4m^2 - 1)}$$

**Problem 19.14** A particle moves in a potential that is central except for a small non-central perturbation

$$F(r)(3 \cos^2 \theta - 1)$$

Show that in first order perturbation theory, the energies of the states  $s$  of the system are unaffected and that the three  $p$  states ( $l = 1; m = 1, 0, -1$ ) are respectively perturbed by  $\frac{1}{2}A$ ,  $A$  and  $-\frac{1}{2}A$  where  $A$  is determined from the form of the central potential and of  $F(r)$ .

[Hint: The unperturbed eigenfunctions of the  $p$  states are of the form  $R(r)Y_{1,1}(\theta, \phi)$ ;  $R(r)Y_{1,0}(\theta, \phi)$  and  $R(r)Y_{1,-1}(\theta, \phi)$ ].

**Problem 19.15** Consider the interaction between two hydrogen atoms in their ground state (this kind of interaction is known as Van der Waal's interaction). Let  $A$  and  $B$  denote the positions of the nuclei of the two atoms; these nuclei are assumed to be fixed in space and separated by a distance  $R$ —see Fig. 19.5. Show that the

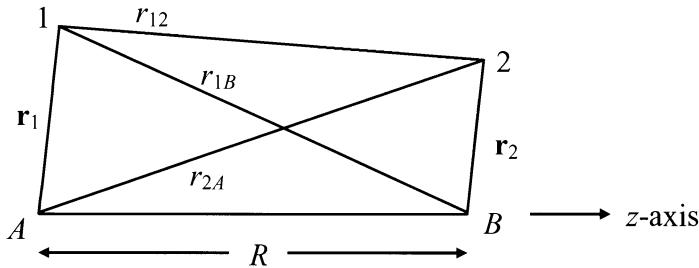


Figure 19.5. The hydrogen atom molecule;  $A$  and  $B$  denote the positions of the two nuclei.

Hamiltonian can be written in the form

$$H = H_0 + H' \quad (126)$$

where

$$H_0 = -\frac{\hbar^2}{2\mu}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_1} - \frac{e^2}{r_2} \quad (127)$$

and

$$H' \approx \frac{e^2}{R}(x_1x_2 + y_1y_2 - 2z_1z_2) \quad (128)$$

$x_1, x_2$ , etc. represent the  $x$ -coordinates of the electrons 1 and 2 with respect to the nuclei  $A$  and  $B$  respectively. Use perturbation theory to calculate the effect of  $H'$ . (The variational analysis of the hydrogen molecule and the hydrogen molecule ion is discussed in Sec. 21.7, Problems 21.4 and 21.5).

## 19.9. Solutions

**Solution 19.5** If we refer to Sec. 6.8 then the energy eigenvalue corresponding to the first excited state is given by

$$W_1^{(0)} = \frac{6\pi^2\hbar^2}{2\mu L^2}$$

The state is 3-fold degenerate; the wave functions are

$$u_1 = \sqrt{\frac{8}{L^3}} \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{\pi z}{L}; \quad [n_x = 2, n_y = 1, n_z = 1]$$

$$u_2 = \sqrt{\frac{8}{L^3}} \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L} \sin \frac{\pi z}{L}; \quad [n_x = 1, n_y = 2, n_z = 1]$$

$$u_3 = \sqrt{\frac{8}{L^3}} \sin \frac{\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{2\pi z}{L}; \quad [n_x = 1, n_y = 1, n_z = 2]$$

Now

$$H'_{ij} = \int u_i^* H' u_j d\tau = k \iiint u_i^* x^2 u_j dx dy dz$$

Simple integrations show that

$$H'_{ij} = 0 \quad \text{for } i \neq j$$

Thus we already have a representation in which  $H'$  is diagonal. Further

$$H'_{ij} = kL^2 \left( \frac{1}{3} - \frac{1}{8\pi^2} \right) = g_1 \quad (\text{say})$$

and

$$H'_{22} = H'_{33} = kL^2 \left( \frac{1}{3} - \frac{1}{2\pi^2} \right) = g_2 \quad (\text{say})$$

Hence the secular determinant is

$$\begin{vmatrix} g_1 - W_1^{(1)} & 0 & 0 \\ 0 & g_2 - W_1^{(1)} & 0 \\ 0 & 0 & g_2 - W_1^{(1)} \end{vmatrix} = 0$$

The roots are  $g_1, g_2, g_2$ ; the degeneracy is partially lifted and the perturbed energy levels are

$$W_1^{(0)} + g_1, \quad W_1^{(0)} + g_2 \quad \text{and} \quad W_1^{(0)} + g_2$$

**Solution 19.6** The normalized eigenfunctions of  $H_0$  are

$$\psi_{n_1 n_2}^{(0)} = N H_{n_1}(\xi_1) H_{n_2}(\xi_2) \exp \left[ -\frac{1}{2} (\xi_1^2 + \xi_2^2) \right]; \quad n_1, n_2 = 0, 1, 2, \dots$$

where

$$\xi_1 = \gamma x_1, \quad \xi_2 = \gamma x_2 = \gamma = \left[ \frac{\mu k}{\hbar^2} \right]^{1/4}$$

The corresponding eigenvalues are [see also Problem 10.11]

$$W_{n_1, n_2}^{(0)} = (n_1 + n_2 + 1)\hbar\omega$$

The first excited state is two-fold degenerate ( $n_1 = 0, n_2 = 1$  and  $n_1 = 1, n_2 = 0$ ) the corresponding eigenvalue being  $2\hbar\omega$ . If we write  $u_1 = \psi_{0,1}^{(0)}$ ,  $u_2 = \psi_{1,0}^{(0)}$  and

$$H'_{ij} = \iint u_j^* H' u_i dx_1 dx_2, \quad i, k = 1, 2$$

then  $H'_{11} = H'_{22} = 0$  and

$$\begin{aligned} H'_{21} &= \iint_{-\infty}^{+\infty} u_1^* \frac{\xi_1 \xi_2}{\gamma^2} u_2 \frac{d\xi_1 d\xi_2}{\gamma} \\ &= \left( \frac{\gamma}{\sqrt{\pi}} \right)^2 \frac{1}{2} \frac{\lambda}{\gamma^4} \int_{-\infty}^{\infty} 2\xi_1^2 e^{-\xi_1^2} d\xi_1 \int_{-\infty}^{\infty} 2\xi_2^2 e^{-\xi_2^2} d\xi_2 \\ &= \frac{\lambda}{2\gamma^2} = \frac{\lambda}{2k} \hbar\omega = H'_{21} \end{aligned}$$

On solving the secular equation, we obtain

$$W^{(1)} = \pm \frac{\lambda}{2k} \hbar\omega$$

the corresponding eigenfunctions being

$$\frac{1}{\sqrt{2}}(u_1 \pm u_2) = \frac{1}{\sqrt{2}}(\psi_{0,1}^{(0)} \pm \psi_{1,0}^{(0)})$$

The exact eigenvalues of  $H$  can be determined if we introduce the new variables

$$\eta_1 = \frac{x_1 + x_2}{\sqrt{2}} \quad \text{and} \quad \eta_2 = \frac{x_1 - x_2}{\sqrt{2}}$$

Thus

$$H = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial \eta_1^2} + \frac{\partial^2}{\partial \eta_2^2} \right) + \frac{1}{2}(k + \lambda)\eta_1^2 + \frac{1}{2}(k - \lambda)\eta_2^2$$

The exact energy levels of which are given by [see Problem 10.13]

$$\left( n_1 + \frac{1}{2} \right) \hbar \sqrt{\frac{k + \lambda}{\mu}} + \left( n_2 + \frac{1}{2} \right) \hbar \sqrt{\frac{k - \lambda}{\mu}}; \quad n_1, n_2 = 0, 1, 2, \dots$$

If we make a binomial expansion of the square root in powers of  $\lambda/k$  then the first order terms will be the same as obtained from the perturbation theory.

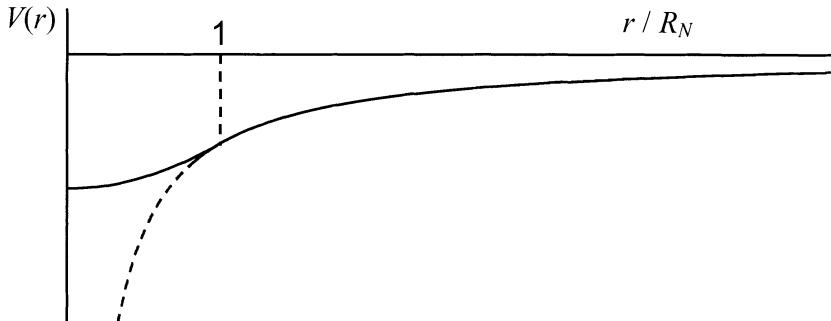


Figure 19.6. The solid curve shows the variation of  $V(r)$  [as given by Eq. (130)] when the effect of the finite size of the nucleus has been taken into account. The dashed curve in the region  $r < R_N$  is the extension of the  $1/r$  variation.

**Solution 19.9**<sup>11</sup> The charge density inside the nucleus is

$$\frac{Ze}{\frac{4\pi}{3}R_N^3}$$

Thus the force acting on the electron will be given by

$$\left. \begin{aligned} F(r) &= -\frac{Ze^2}{\frac{4\pi}{3}R_N^3} \frac{4\pi}{3}r^3 \frac{1}{r^2} \quad \text{for } 0 \leq r \leq R_N \\ &= -\frac{Ze^2}{r^2} \quad \text{for } r \geq R_N \end{aligned} \right\} \quad (129)$$

Since  $F(r) = -\partial V/\partial r$ , we obtain (see Fig. 19.6)

$$\left. \begin{aligned} V(r) &= -\frac{Ze^2}{R_N} \left( \frac{3}{2} - \frac{1}{2} \frac{r^2}{R_N^2} \right) \quad \text{for } 0 \leq r \leq R_N \\ &= -\frac{Ze^2}{r} \quad \text{for } r \geq R_N \end{aligned} \right\} \quad (130)$$

where the zero of the potential energy has been assumed at  $r = \infty$  and use has been made of the fact that  $V(r)$  is continuous at  $r = R_N$ . The perturbation is therefore given by

$$\begin{aligned} H' &= -\frac{Ze^2}{R_N} \left( \frac{3}{2} - \frac{1}{2} \frac{R_N^2}{R_N^2} \right) + \frac{Ze^2}{r} \quad \text{for } 0 \leq r \leq R_N \\ &= 0 \quad \text{for } r \geq R_N \end{aligned}$$

---

<sup>11</sup> Solutions 19.9 and 19.10 have been adapted from Ref. 7.

Consequently

$$W_n^{(1)} = \int_0^{R_N} r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi [\psi_n^{(0)}]^* H' \psi_n^{(0)}$$

Since the radius of the nucleus is usually much smaller than the Bohr radius, we may assume the wave function to remain constant over the region of integration; thus we may replace  $\psi_n^{(0)}$  by its value at  $r = 0$ . Consequently

$$\begin{aligned} W_n^{(1)} &\approx [R_{nl}(0)]^2 \int_0^{R_N} H' r^2 dr \iint |Y_{lm}(\theta, \phi)|^2 \sin \theta d\theta d\phi \\ &\approx \frac{4}{5} \frac{Z^4}{n^3} \left( \frac{R_N}{a_0} \right)^2 E_H \delta_{l0} \end{aligned}$$

where we have used the relation

$$[R_{nl}(0)]^2 = \left( \frac{Z}{a_0} \right)^3 \frac{4}{n^3} \delta_{l0}$$

and  $E_H \approx 13.6$  eV. A positive value of  $W_n^{(1)}$  was expected because the potential energy increases due to the finite size of the nucleus (see Fig. 19.6). Thus

$$W_n \approx W_n^{(0)} + W_n^{(1)} = -\frac{Z^2 E_H}{n^2} \left[ 1 - \frac{4}{5} \frac{Z^2 R_0^2 A^{2/3}}{a_0^2 n} \delta_{l0} \right] \quad (131)$$

where we have used the relation  $R_N = R_0 A^{1/3}$ ,  $A$  being the mass number of the nucleus and  $R_0 \approx 1.07 \times 10^{-15}$  m. For hydrogen,

$$W_1^{(0)} \approx -13.6 \text{ eV} \quad \text{and} \quad W_1^{(1)} \approx 4 \times 10^{-9} \text{ eV} \quad (132)$$

which is indeed a very small correction.

**Solution 19.10** For orbits inside the nucleus, we may write [see Eq. (130)]

$$H_0 = -\frac{\hbar^2}{2m_\mu} \nabla^2 - \frac{Ze^2}{R_N} \left( \frac{3}{2} - \frac{1}{2} \frac{r^2}{R_N^2} \right)$$

and

$$\begin{aligned} H' &= 0 \quad \text{for } 0 \leq r \leq R_N \\ &= \frac{Ze^2}{R_N} \left( \frac{3}{2} - \frac{1}{2} \frac{r^2}{R_N^2} \right) - \frac{Ze^2}{r} \quad \text{for } r \geq R_N \end{aligned}$$

where  $m_\mu$  represents the mass of the muon. Now,  $H_0$  is the same as one obtains in the 3-dimensional harmonic oscillator problem (see Solution 10.12). The radial part of the Schrödinger equation is of the form

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m_\mu}{\hbar^2} \left[ E + \frac{3}{2} \frac{Ze^2}{R_N} - \frac{1}{2} \frac{Ze^2}{R_N^3} r^2 - \frac{l(l+1)\hbar^2}{2m_\mu r^2} \right] R(r) = 0$$

The energy levels are given by

$$E = -\frac{3}{2} \frac{Ze^2}{R_N} + \left( 2p + l + \frac{3}{2} \right) \hbar\omega; \quad (133)$$

where

$$l = 0, 1, 2, \dots; \quad p = 0, 1, 2, \dots$$

and

$$\omega = \left[ \frac{Ze^2}{m_\mu R_N^3} \right]^{1/2} = \left[ \frac{Z\alpha\hbar c}{m_\mu R_N^3} \right]^{1/2} \quad (134)$$

Further

$$W^{(1)} = Ze^2 \int_{R_N}^{\infty} |R_{pl}|^2 \left[ \frac{1}{R_N} \left( \frac{3}{2} - \frac{r^2}{2R_N^2} \right) - \frac{1}{r} \right] r^2 dr \quad (135)$$

where the wave functions can be expressed in terms of confluent hypergeometric functions (see Solution 10.12 and Appendix F).

As an example<sup>12</sup>, if we consider the  $2P \rightarrow 1S$  transition in lead ( $Z = 82$ ) and assume the nucleus to be a point charge, the energy liberated would be

$$\frac{m_\mu}{m_e} Z^2 E_H \left[ \frac{1}{1^2} - \frac{1}{2^2} \right] = 207 Z^2 E_H \frac{3}{4} \approx 14 \text{ MeV}$$

If we take into account the effect due to spin and due to relativistic effects, the above value increases by 2 MeV to give 16 MeV; however, the experiments show that a photon of energy  $\sim 6$  MeV is emitted. If we calculate the  $1S$  energy level from Eq.(133) and the  $2P$  energy level from the expression

$$\frac{m_\mu Z^2 E_H}{m_e n^2}$$

then the energy difference between the  $2P$  and  $1S$  states comes out to be 3.6 MeV. If we now use Eq.(135) to incorporate the correction for the  $1S$  energy state one obtains a value of 5 MeV which is close to the experimental value.

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<sup>12</sup> Data taken from Ref. 7. A nice discussion on muonic atoms has been given by these authors.

**Solution 19.15**<sup>13</sup> The perturbation  $H'$  is given by

$$H' = \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{R_{1B}} - \frac{e^2}{R_{2A}} \quad (136)$$

The terms  $e^2/R$ ,  $e^2/r_{12}$ ,  $-e^2/r_{1B}$  and  $-e^2/r_{2A}$  represents the interaction between the two protons, the two electrons, the first electron with the nucleus at  $B$  and the second electron with the nucleus at  $A$  respectively. We expand  $H'$  in powers of  $1/R$ :

$$\begin{aligned} H' &= \frac{e^2}{R} \left[ 1 + R \left\{ \frac{1}{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 + R - z_1)^2} \right\}^{1/2} \right. \\ &\quad \left. - R \left\{ \frac{1}{x_1^2 + y_1^2 + (R - z_1)^2} \right\}^{1/2} - R \left\{ \frac{1}{x_2^2 + y_2^2 + (z_2 + R)^2} \right\}^{1/2} \right] \\ &= \frac{e^2}{R} \left[ 1 + \left\{ 1 + \frac{2(z_2 - z_1)}{R} + \frac{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}{R^2} \right\}^{-1/2} \right. \\ &\quad \left. - \left\{ 1 - \frac{2z_1}{R} + \frac{x_1^2 + y_1^2 + z_1^2}{R^2} \right\}^{-1/2} - \left\{ 1 + \frac{2z_2}{R} + \frac{x_2^2 + y_2^2 + z_2^2}{R^2} \right\}^{-1/2} \right] \\ &\approx \frac{e^2}{R^3} (x_1 x_2 + y_1 y_2 - 2z_1 z_2) \end{aligned} \quad (137)$$

Let  $\psi_k^{(0)}$  represent the wave functions of the unperturbed Hamiltonian and let  $|k\rangle$  represent the corresponding eigenket; the ground state is assumed to correspond to  $k = 1$ . Thus

$$\psi_1^{(0)} = u_{100}(\mathbf{r}_1)u_{100}(\mathbf{r}_2) \quad (138)$$

where  $u_{nlm}$  represent the hydrogen atom wave functions. Obviously

$$W_1^{(1)} = \langle 1 | H' | 1 \rangle = \iint d\tau_1 d\tau_2 [\psi_1^{(0)}]^* H' \psi_1^{(0)} = 0 \quad (139)$$

because integral like

$$\iint d\tau_1 x_1 [u_{100}(\mathbf{r}_1)]^2$$

would vanish. Now

$$W_1^{(2)} = \sum_k' \frac{|\langle 1 | H' | k \rangle|^2}{E_1 - E_k} > \frac{1}{E_1 - E_p} \sum_k' |\langle 1 | H' | k \rangle|^2 \quad (140)$$

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<sup>13</sup> This solution is adapted from Ref. 9.

where the prime on  $\sum$  indicates that the term  $k = 1$  has been omitted from the summation.<sup>14</sup> Further the  $p$ th state ( $p \neq 1$ ) corresponds to the lowest state for which  $\langle 1|H'|p\rangle$  does not vanish and the inequality follows from that fact that  $E_k \geq E_p$ . Now

$$\begin{aligned}\sum'_k |\langle 1|H'|k\rangle|^2 &= \sum_k |\langle 1|H'|k\rangle|^2 - |\langle 1|H'|1\rangle|^2 \\ &= \sum_k |\langle 1|H'|k\rangle|^2 |\langle k|H'|1\rangle|^2 \\ &= |\langle 1|H'^2|1\rangle|\end{aligned}\quad (141)$$

where we have used Eq.(139) and the relation

$$\sum_k |k\rangle\langle k| = 1$$

(see Eq.(40) of Chapter 11), Now

$$\begin{aligned}|\langle 1|H'^2|1\rangle| &= \frac{e^4}{R^6} \langle 1|x_1^2x_2^2 + y_1^2y_2^2 + 4z_1^2z_2^2 + 2x_1x_2y_1y_2 \\ &\quad - 4x_1x_2z_1z_2 - 4y_1y_2z_1z_2|1\rangle \\ &= \frac{e^4}{R^6} 6\langle x_1^2 \rangle^2 = \frac{6e^2a_0^4}{R^6}\end{aligned}\quad (142)$$

Further

$$E_1 = -\frac{me^4}{2\hbar^2} - \frac{me^4}{2\hbar^2} = -\frac{e^4}{a_0}$$

and the lowest state for which  $|\langle 1|H'|k\rangle| \neq 0$  corresponds to  $n_1 = n_2 = 2$ . Thus

$$E_p = -\frac{me^4}{8\hbar^2} - \frac{me^4}{8\hbar^2} = -\frac{e^2}{4a_0}$$

and

$$E_1 - E_p = -\frac{3e^2}{4a_0}$$

Hence

$$W_1^{(2)} > -\frac{1}{\frac{3e^2}{4a_0}} \frac{6e^4a_0^4}{R^6} = -\frac{8e^2a_0^5}{R^6}$$

or

$$W_1 \approx W_1^{(0)} + W_1^{(2)} > -\frac{e^2}{a_0} \left[ 1 + \frac{8a_0^6}{R^6} \right] \quad (143)$$

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<sup>14</sup> The  $\sum$  actually represents summation over discrete states and integration over continuum.

### 19.10. References and suggested reading

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# Chapter 20

## Effects of Magnetic Field

*... On the basis of my earlier results on the classification of spectral terms in a strong magnetic field, the general formulation of the exclusion principle became clear to me.*

— WOLFGANG PAULI in his Nobel lecture.

### 20.1. Introduction

Studies on the interaction of magnetic field with particles are of immense importance in many diverse areas. For example, in spectroscopy, the splitting of lines in a magnetic field (which leads to Zeeman and Paschen-Back effects, see Problems 20.1–20.4) is a subject of considerable importance (see, e.g. Ref. 1). In solid state physics, the calculation of diamagnetic and paramagnetic susceptibilities (see Problem 20.11) and the experiments on electron spin resonance and nuclear magnetic resonance (see Chapter 14), have immense practical importance (see, e.g. Ref 2–5).

In this chapter we will discuss the interaction of magnetic field with particles. We will first develop the Hamiltonian of a charged particle in an electromagnetic field (Sec. 20.2) and will then discuss the interaction of the magnetic field with the orbital angular momentum and spin angular momentum of the electron (Secs 20.3 and 20.4). For example, we will show that the possible values of the magnetic moment component of the electron (because of its orbital motion) along the direction of the magnetic field are

$$-m_l \mu_B \quad (1)$$

where<sup>1</sup>

---

<sup>1</sup> In Chapter 10, the magnetic quantum number is denoted by  $m$ , here it is denoted by  $m_l$  to avoid confusion with the electron mass  $m$ .

$$\begin{aligned}\mu_B &\equiv \frac{q\hbar}{2m} = 9.274 \times 10^{-24} \text{ Joule/tesla} \\ &= 9.274 \times 10^{-28} \text{ Joule/gauss} \\ &(1 \text{ tesla} = 10^4 \text{ gauss})\end{aligned}\tag{2}$$

is known as the Bohr magneton,  $m_l$  is the magnetic quantum number; the charge of the electron has been assumed to be  $-q$  ( $q \simeq 1.602 \times 10^{-19} \text{ C}$ ). Thus for a  $d$ -electron ( $l = 2$ ) the possible values of orbital magnetic moment along the direction of the magnetic field are

$$-2\mu_B, -\mu_B, 0, +\mu_B, +2\mu_B$$

corresponding to  $m_l = +2, +1, 0, -1$  and  $-2$  respectively.

On the other hand, the magnetic moment components due to the spin angular momentum of the electron, along the direction of the magnetic field are (see Secs 14.3 and 14.4).

$$\pm \frac{1}{2}g\mu_B \simeq \pm\mu_B\tag{3}$$

where  $g$  is known as the *Lande's g factor*<sup>2</sup> ( $\simeq 2.0023$ ). The corresponding proton magnetic moment is

$$\pm \frac{1}{2}g_p\mu_p\tag{4}$$

where  $g_p \simeq 5.56$ , and

$$\mu_p = \frac{q\hbar}{2M} \simeq 5.051 \times 10^{-31} \text{ Joule/gauss.}$$

In Sec. 20.5 we will discuss the spin-orbit interaction.

## 20.2. The Hamiltonian

We first define the vector and scalar potentials. From the Maxwell's equation

$$\nabla \cdot \mathbf{B} = 0\tag{5}$$

<sup>2</sup> The relativistic theory of Dirac predicts  $g = 2$ ; however, relativistic quantum electrodynamics shows that

$$g = 2 + \frac{\alpha}{2\pi} + O(\alpha^2)$$

where  $\alpha \left( \frac{q^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137} \right)$  is the fine structure constant. For the proton,  $g$  is very much different from 2 and hence it is not really a pure Dirac particle. It may be mentioned that neutral particles like neutrons;  $\Lambda$ ,  $\Sigma^0$  (which have spin  $\frac{1}{2}$ ) have finite magnetic moments; e.g. for the neutron  $\mu_n = 3.83 (q/2m_n)\mathbf{s}$ , where  $m_n$  is the neutron mass. Physically this arises from internal current distributions.

it immediately follows that  $\mathbf{B}$  can be expressed as the curl of a vector

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (6)$$

where  $\mathbf{A}$  is known as the vector potential. Further, if we substitute this in the equation

$$\nabla \times \mathcal{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (7)$$

we would get

$$\nabla \times \left( \mathcal{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = 0 \quad (8)$$

Thus we may set

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} - \nabla \phi \quad (9)$$

where  $\phi$  is known as the scalar potential.

We next consider the motion of a charged particle (of charge  $Q$ ) in an electromagnetic field. The force acting on the charged particle is given by

$$\mathbf{F} = Q [\mathcal{E} + \mathbf{v} \times \mathbf{B}] \quad (10)$$

or

$$m \frac{d\mathbf{v}}{dt} = \mathbf{F} = Q \left[ -\frac{\partial \mathbf{A}}{\partial t} - \nabla \phi + \mathbf{v} \times (\nabla \times \mathbf{A}) \right]$$

Now

$$\begin{aligned} (\mathbf{v} \times \nabla \times \mathbf{A})_x &= v_y \left( \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) - v_z \left( \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) \\ &= \frac{\partial}{\partial x}(\mathbf{v} \cdot \mathbf{A}) - \frac{dA_x}{dt} + \frac{\partial A_x}{\partial t} \end{aligned}$$

where use has been made of the following relation

$$\frac{dA_x}{dt} = \frac{\partial A_x}{\partial t} + \left( v_x \frac{\partial A_x}{\partial x} + v_y \frac{\partial A_x}{\partial y} + v_z \frac{\partial A_x}{\partial z} \right)$$

Thus

$$\frac{d}{dt} [m\mathbf{v} + Q\mathbf{A}] = \nabla (-Q\phi + Q(\mathbf{v} \cdot \mathbf{A})) \quad (11)$$

The above equation can be written in the form

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{x}} \right) = \frac{\partial L}{\partial x} \quad (12)$$

(and similar equations with  $x$  replaced by  $y$  and  $z$ ) where

$$L = \frac{1}{2}m\mathbf{v} \cdot \mathbf{v} - Q\phi + Q\mathbf{A} \cdot \mathbf{v} \quad (13)$$

Equation (12) is the Lagrangian equation of motion (see, e.g. Ref. 6) and  $L$  denotes the Lagrangian. The conjugate momenta are given by

$$p_x = \frac{\partial L}{\partial \dot{x}} = mv_x + QA_x$$

or

$$\mathbf{p} = m\mathbf{v} + Q\mathbf{A} \quad (14)$$

The Hamiltonian is given by

$$\begin{aligned} H &= \mathbf{p} \cdot \mathbf{v} - L \\ &= \mathbf{p} \cdot \left[ \frac{1}{m}(\mathbf{p} - Q\mathbf{A}) \right] - \frac{1}{2}m \left[ \frac{1}{m}(\mathbf{p} - Q\mathbf{A}) \right]^2 \\ &\quad + Q\phi - Q\mathbf{A} \cdot \frac{1}{m}(\mathbf{p} - Q\mathbf{A}) \\ &= \frac{1}{2m} [\mathbf{p} - Q\mathbf{A}]^2 + Q\phi \end{aligned} \quad (15)$$

Equation (15) represents the Hamiltonian describing the non-relativistic motion of a charged particle in an electromagnetic field.

In order to write the Schrödinger equation, we replace the operator  $\mathbf{p}$  by  $-i\hbar\nabla$  to obtain

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (16)$$

where

$$H = \frac{1}{2m} [-i\hbar\nabla - Q\mathbf{A}]^2 + Q\phi \quad (17)$$

### 20.3. The Schrödinger equation corresponding to a static electromagnetic field

For a static electromagnetic field the wave function can be written in the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar} \quad (18)$$

where  $\psi(\mathbf{r})$  satisfies the equation

$$\frac{1}{2m} [-i\hbar\nabla - Q\mathbf{A}]^2 \psi + Q\phi\psi = E\psi$$

or

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \frac{iQ\hbar}{2m}[\nabla \cdot (\mathbf{A}\psi) + \mathbf{A} \cdot \nabla\psi] + \left[\frac{Q^2}{2m}A^2 + Q\phi\right]\psi = E\psi \quad (19)$$

Now, in the Coulomb gauge<sup>3</sup>,  $\nabla \cdot \mathbf{A} = 0$  and we have

$$\nabla \cdot (\mathbf{A}\psi) = (\nabla \cdot \mathbf{A})\psi + \mathbf{A} \cdot \nabla\psi = \mathbf{A} \cdot \nabla\psi$$

which gives

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \frac{iQ\hbar}{m}\mathbf{A} \cdot \nabla\psi + \left[\frac{Q^2}{2m}A^2 + Q\phi\right]\psi = E\psi \quad (20)$$

Further, for a uniform magnetic field, we can always write<sup>4</sup>

$$\mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) \quad (21)$$

Thus the second term in Eq. (20) becomes

$$\begin{aligned} \frac{iQ\hbar}{m}\mathbf{A} \cdot \nabla\psi &= \frac{iQ\hbar}{2m}(\mathbf{B} \times \mathbf{r}) \cdot \nabla\psi \\ &= -\frac{Q}{2m}\mathbf{B} \cdot [\mathbf{r} \times (-i\hbar\nabla)]\psi \\ &= -\frac{Q}{2m}\mathbf{B} \cdot (\mathbf{r} \times \mathbf{p})\psi = -\frac{Q}{2m}(\mathbf{B} \cdot \mathbf{L})\psi \\ &= -\boldsymbol{\mu}_o \cdot \mathbf{B}\psi \end{aligned} \quad (22)$$

where  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$  represents the orbital angular momentum and

$$\boldsymbol{\mu}_o = \frac{Q}{2m}\mathbf{L} \quad (23)$$

<sup>3</sup> From Eq. (6) we see that  $\mathbf{B}$  is left unchanged if we add gradient of a scalar to  $\mathbf{A}$ :

$$\mathbf{A} \rightarrow \mathbf{A}' + \nabla\chi$$

We may choose  $\chi$  such that  $\nabla \cdot \mathbf{A} = 0$ ; this is known as the Coulomb gauge (for further details, see, for example, Ref. 7):

<sup>4</sup>

$$\begin{aligned} \nabla \times \mathbf{A} &= \frac{1}{2}\nabla \times (\mathbf{B} \times \mathbf{r}) = \frac{1}{2}[(\nabla \cdot \mathbf{r})\mathbf{B} - (\mathbf{B} \cdot \nabla)\mathbf{r}] \\ &= \frac{1}{2}[3\mathbf{B} - \mathbf{B}] = \mathbf{B} \end{aligned}$$

Also notice that

$$\nabla \cdot \mathbf{A} = \frac{1}{2}\nabla \cdot (\mathbf{B} \times \mathbf{r}) = \frac{1}{2}[\mathbf{r} \cdot (\nabla \times \mathbf{B}) - \mathbf{B} \cdot (\nabla \times \mathbf{r})] = 0$$

because the field is uniform.

can be interpreted as the magnetic moment associated with the orbital motion of the charged particle<sup>5</sup> (the subscript  $o$  signifies that the magnetic moment refers to the orbital motion). This follows from the fact that the interaction energy of a magnet (with magnetic moment  $\mu_o$ ) in a uniform magnetic field is given by<sup>6</sup>

$$U = -\mu_o \cdot \mathbf{B} \quad (24)$$

Equation (20) therefore assumes the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \left(\frac{Q}{2m}\mathbf{L} \cdot \mathbf{B}\right)\psi + \frac{Q^2}{8m}(\mathbf{B} \times \mathbf{r})^2\psi + Q\phi\psi = E\psi \quad (25)$$

The second term has just been physically interpreted as the magnetic interaction energy associated with the circulatory motion of the charged particle; the third term can also be interpreted in terms of a potential energy function (see, e.g., Ref. 10, Section 10.6), however the considerations are rather involved. Further, since the term is proportional to the square of the magnetic field, it makes a negligible contribution unless the fields are extremely high.

## 20.4. The interaction of the magnetic field with the spin angular momentum of the electron

In Sec. 14.3 we had discussed that the electron is endowed with an intrinsic spin angular momentum given by

$$\mathbf{s} = \frac{1}{2}\hbar\boldsymbol{\sigma} \quad (26)$$

where  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$  are the Pauli matrices. Further, the magnetic moment associated with the spin angular momentum of a particle of charge  $Q$  has the form [cf. Eq. (23)]

$$\boldsymbol{\mu} = g\frac{Q}{2m}\mathbf{s} \quad (27)$$

As mentioned earlier, for the electron  $g \simeq 2$  and  $Q = -q$ ; on the other hand, for the proton  $g \simeq 5.56$ ,  $Q = +q$  and  $m$  has to be replaced by the proton mass.

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<sup>5</sup> Equation (23) can be physically understood by noting that a charge  $Q$  rotating (in the anticlockwise direction) in a circle of radius  $r$  with speed  $v$  constitutes a current  $I = Q/(2\pi r/v)$  and therefore the magnetic moment associated with the motion is given by (see, e.g. Ref. 8, Section 34-3).

$$\boldsymbol{\mu} = \frac{Qv}{2\pi r}\mathbf{A} = \frac{Qv}{2\pi r}\pi r^2\hat{\mathbf{z}} = \frac{Q}{2m}\mathbf{r} \times \mathbf{p} = \frac{Q}{2m}\mathbf{L}$$

where we have assumed the circular motion to be in the  $x$ - $y$  plane and the area vector  $\mathbf{A}$  points in the positive  $z$ -direction for anticlockwise motion.

<sup>6</sup> See, e.g. Ref. 9, p.19.

Thus the total magnetic moment of the electron is given by

$$\boldsymbol{\mu}_{\text{total}} = -\frac{q}{2m} [\mathbf{L} + g\mathbf{s}] \simeq -\frac{q}{2m} [\mathbf{L} + 2\mathbf{s}] \quad (28)$$

## 20.5. The spin-orbit interaction

In order to physically understand the spin-orbit interaction we note that an observer who is at rest with the electron sees the nucleus moving around him; the circulating nucleus constitutes a current and produces a magnetic field at the electron given by

$$\mathbf{B} = -(\epsilon_0 \mu_0) \mathbf{v} \times \mathbf{E}$$

where  $\mathbf{E}$  represents the electric field produced at the electron by the nucleus and  $\mathbf{v}$  the velocity of the electron. For a central potential

$$-q\mathbf{E} = -\nabla V = -\frac{1}{r} \frac{dV}{dr} \mathbf{r} \quad (29)$$

Thus

$$\mathbf{B} = \frac{1}{qc^2} \frac{1}{r} \frac{dV}{dr} \frac{1}{m} \mathbf{L} \quad (30)$$

where  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$  represents the angular momentum. The interaction energy with the magnetic moment of the electron is given by

$$\begin{aligned} H_{s-o} &= -\frac{1}{2} \boldsymbol{\mu} \cdot \mathbf{B} = -\frac{1}{2} \left[ -g \frac{q}{2m} \mathbf{s} \right] \cdot \left[ \frac{1}{qc^2} \frac{1}{r} \frac{dV}{dr} \frac{1}{m} \mathbf{L} \right] \\ &= \frac{g}{4m^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{s} \end{aligned} \quad (31)$$

where an additional factor of  $\frac{1}{2}$  has been introduced; this is known as the Thomas procession factor and comes from a proper relativistic treatment (Ref. 11). The subscript s-o on  $H$  implies spin-orbit interaction. For the Coulomb potential

$$V(r) = -\frac{Zq^2}{4\pi\epsilon_0 r}$$

and

$$H_{s-o} = \frac{gZ\hbar\alpha}{4m^2 c} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{s} \quad (32)$$

where

$$\alpha = \frac{q^2}{4\pi\epsilon_0 \hbar c} \simeq \frac{1}{137}$$

represents the fine structure constant. It may be mentioned that the spin-orbit interaction comes out automatically through a proper relativistic treatment.

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## 20.6. Problems

**Problem 20.1** For a hydrogen atom placed in a weak uniform magnetic field (in the  $z$ -direction) the Hamiltonian will be of the form

$$H = H_0 + H' \quad (33)$$

where

$$H_0 = \frac{p^2}{2m} + V(r) \quad (34)$$

and

$$H' = \frac{q}{2m} \mathbf{B} \cdot \mathbf{L} = \frac{\mu_B B}{\hbar} L_z \quad (35)$$

represents the interaction with the magnetic field [see Eq. (24)]; we have neglected the effects due to spin angular momentum of the electron (see Problem 20.2). Treat  $H'$  as perturbation and show that  $s$  states ( $l = 0$ ) are not split whereas the  $p$ -states ( $l = 1$ ) are split into three states separated by the energy interval  $\mu_B B$ . This is known as the *normal Zeeman effect*.

[**Note:** In this particular problem the perturbation calculation gives the exact results.]

**Problem 20.2** In continuation with the previous problem, if we take into account the effects due to spin angular momentum of the electron, the Hamiltonian will be of the form

$$H = H_0 + H' + H'' \quad (36)$$

where  $H_0$  is given by Eq. (34),  $H'$  represents the spin-orbit interaction [see Eq. (32)]

$$H' = f(r) \mathbf{L} \cdot \mathbf{s}, \quad f(r) = \frac{gZ\hbar\alpha}{4m^2c} \frac{1}{r^3} \quad (37)$$

and

$$H'' = \frac{qB}{2m} [L_z + gs_z] = \frac{\mu_B B}{\hbar} [L_z + gs_z] \quad (38)$$

represents the interaction with the magnetic field (see Eq. (28)). Assume that the effect of  $H''$  to be small in comparison to the effect of  $H'$ , use the wave functions corresponding to  $H'$  as the perturbation (see Solution 19.12) to calculate the effect of  $H''$ . This is known as the weak-field *anomalous Zeeman effect*, or just *Zeeman effect*.

**Problem 20.3** Consider again the hydrogen-like atom in a magnetic field  $\mathbf{B}$ . Assume the magnetic field to be so strong that the effect of the spin-orbit interaction to be small compared to the effect of the magnetic field. Using the eigenfunctions of  $H_0 + H''$ , calculate the perturbation due to spin-orbit interaction. This is known as the *Paschen-Back effect*.

**Problem 20.4** The previous two problems correspond to weak magnetic field and strong magnetic fields respectively. For the intermediate field case,  $H' + H''$  has to be treated as perturbation to  $H_0$ . Use degenerate state perturbation theory to calculate the effect of  $H' + H''$ .

**Problem 20.5** In the following problem we will consider the effect of the proton magnetic moment and hence the hyperfine structure. However, before we do so, we note that the electron and proton can ever their spin up or down; thus there are four possible spin states

$$|e \uparrow p \uparrow\rangle, |e \uparrow p \downarrow\rangle, |e \downarrow p \uparrow\rangle \text{ and } |e \downarrow p \downarrow\rangle \quad (39)$$

where the state  $|e \uparrow p \downarrow\rangle$  corresponds to electron spin up and proton spin down, etc. Show that the operator

$$P = \frac{1}{2} [1 + \boldsymbol{\mu}_e \cdot \boldsymbol{\sigma}_p] \quad (40)$$

is the spin exchange operator, i.e. when  $P$  operates on any of the 4 states, the spin directions are exchanged. Thus

$$P |e \uparrow p \downarrow\rangle = |e \downarrow p \uparrow\rangle, \text{ etc.}$$

In Eq. (40)  $\boldsymbol{\sigma}_e$  and  $\boldsymbol{\sigma}_p$  represent the Pauli spin matrices for electron and proton respectively; further  $\boldsymbol{\sigma}_e$  acts only on the electron spin and  $\boldsymbol{\sigma}_p$  acts only on the proton spin.

**Problem 20.6** The magnetic field due to the proton magnetic moment interacts with the magnetic moment of the electron to give rise to the following interaction energy for  $s$  states [see Eq. (23-193) of Ref.12]:

$$H' \simeq \frac{\epsilon}{n^3} \boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p \quad (41)$$

where

$$\epsilon = \frac{8}{3a_0^3} \mu_p \mu_B = \frac{8}{3a_0^3} \left( g_p \frac{q \hbar}{4M_p} \right) \left( g_e \frac{q \hbar}{4m} \right) \quad (42)$$

$g_p (\simeq 5.56)$  and  $g_e (\simeq 2.0)$  represent the  $g$  factors of proton and electron respectively;  $a_0$  represents the Bohr radius and  $M_p$  represents the proton mass. Show for the ground state ( $n = 1$ )  $H'$  leads to the (hyperfine) splitting of  $4\epsilon$  which leads to the 21 cm line.

**Problem 20.7** In continuation of the previous problem, if we put the hydrogen atom in a magnetic field, the interaction energy (for  $n = 1$ ) is

$$H' = \mu_B \sigma_{ez} B - \mu_p \sigma_{pz} B + \epsilon \boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p \quad (43)$$

Calculate the corresponding splitting and the spin wave functions.

**Problem 20.8** In Example 14.1, instead of solving the time dependent Schrödinger equation, solve the Heisenberg equation of motion for  $s_x$ ,  $s_y$  and  $s_z$ . For

$$|\Psi(0)\rangle = \cos\left(\frac{1}{2}\phi\right) |\hat{\mathbf{z}}\uparrow\rangle + \sin\left(\frac{1}{2}\phi\right) |\hat{\mathbf{z}}\downarrow\rangle \quad (44)$$

calculate  $\langle s_x(t) \rangle$ ,  $\langle s_y(t) \rangle$  and  $\langle s_z(t) \rangle$  and interpret the results physically.

**Problem 20.9** For a uniform magnetic field in the  $z$ -direction, we may assume

$$A_x = 0, A_y = xB, A_z = 0 \quad (45)$$

(Notice that  $\nabla \times \mathbf{A} = B\hat{\mathbf{z}}$  and  $\nabla \cdot \mathbf{A} = 0$ ). Write down the corresponding Schrödinger equation for an electron and obtain an exact solution of the same<sup>7</sup>. How would the eigenvalues get modified if the magnetic moment associated with the spin angular momentum is also taken into account.

**Problem 20.10** In the above problem, if we assume  $\mathbf{A}$  to be given by Eq. (21), show that the same values for the energy eigenvalues are obtained; the wave functions however differ by an unimportant phase factor.

**Problem 20.11** In continuation of Problem 20.10, consider an electron in a spherically symmetric potential experiencing a uniform magnetic field in the  $z$ -direction for which  $\mathbf{A}$  may be assumed to be of the form

$$A_x = -\frac{1}{2}yB, A_y = \frac{1}{2}xB, A_z = 0 \quad (46)$$

Carry out a perturbation analysis and show that if  $\langle H_1 \rangle$  and  $\langle H_2 \rangle$  represent the perturbations proportional to  $B$  and  $B^2$  then whenever  $\langle H_1 \rangle \neq 0$ ,

$$\langle H_2 \rangle \ll \langle H_1 \rangle \quad (47)$$

Derive expressions for diamagnetic and paramagnetic susceptibilities.

**Problem 20.12** In the above problem if we assume  $\mathbf{A}$  to be given by Eq. (45) show that the final results are the same.

**Problem 20.13** The potential energy of a two-dimensional harmonic oscillator can be written as

$$V = \frac{1}{2}\mu\omega_0^2(x^2 + y^2) \quad (48)$$

---

<sup>7</sup> This solution leads to the orbital diamagnetism of free electrons (see, e.g. Ref. 2, Chapter XVI).

Determine the energy levels and wave functions of the oscillator placed in a uniform magnetic field along the  $z$ -direction

[Hint: Assuming  $\mathbf{A}$  to be given by Eq. (46), solve Eq. (20) or Eq. (25)].

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## 20.7. Solutions

**Solution 20.1** The perturbation is

$$H' = \frac{\mu_B B}{\hbar} L_z = -i \mu_B B \frac{\partial}{\partial \phi} \quad (49)$$

The eigenfunctions of  $H_0$  are (see Sec. 10.4)

$$u(n, l, m_l) = R_{nl}(r) Y_{lm_l}(\theta, \phi) \quad (50)$$

Since

$$L_z Y_{lm_l} = m_l \hbar Y_{lm_l} \quad (51)$$

we get

$$H' u(n, l, m_l) = m_l \hbar u(n, l, m_l) \quad (52)$$

and, consequently the off-diagonal elements are zero<sup>8</sup>. The Zeeman splitting is therefore given by

$$\Delta = \int u^*(n, l, m_l) H' u(n, l, m_l) d\tau = \mu_B B m_l \quad (53)$$

Thus a level characterised by the orbital angular quantum number  $l$  splits up into  $(2l + 1)$  levels. However, because of the selection rule

$$\Delta m_l = 0, \pm 1 \quad (54)$$

we get three lines of frequencies

$$\omega_0 - \frac{\mu_B B}{\hbar}, \omega_0, \omega_0 + \frac{\mu_B B}{\hbar} \quad (55)$$

which is known as the *normal Zeeman effect*.

**Solution 20.2** Because of the spin-orbit interaction, the levels split and each level is characterised by definite values of  $J^2$ ,  $L^2$  and  $S^2$  (see Problem 19.12);

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<sup>8</sup> Indeed  $u(n, l, m_l)$  are the *exact* eigenfunctions of  $H (= H_0 + H')$  corresponding to the eigenvalue  $E_n + \mu_B B m_l$ .

the corresponding Pauli wave functions are given by

$$\phi(n, l, j_+, m_j) = \begin{pmatrix} \left[ \frac{l + \frac{1}{2} + m_j}{2l + 1} \right]^{1/2} R_{nl}(r) Y_{l, m_j - \frac{1}{2}} \\ \left[ \frac{l + \frac{1}{2} - m_j}{2l + 1} \right]^{1/2} R_{nl}(r) Y_{l, m_j + \frac{1}{2}} \end{pmatrix}_{\text{for } j = l + \frac{1}{2}} \quad (56)$$

and

$$\phi(n, l, j_-, m_j) = \begin{pmatrix} - \left[ \frac{l + \frac{1}{2} - m_j}{2l + 1} \right]^{1/2} R_{nl}(r) Y_{l, m_j - \frac{1}{2}} \\ \left[ \frac{l + \frac{1}{2} + m_j}{2l + 1} \right]^{1/2} R_{nl}(r) Y_{l, m_j + \frac{1}{2}} \end{pmatrix}_{\text{for } j = l - \frac{1}{2}} \quad (57)$$

where

$$j_{\pm} = l \pm \frac{1}{2}$$

The states corresponding to  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  are  $(2l + 2)$  and  $2l$ -fold degenerate. Now, the Pauli operator for  $H''$  is

$$(H'')_P = \frac{\mu_B B}{\hbar} \begin{pmatrix} L_z + \frac{1}{2}g\hbar & 0 \\ 0 & L_z - \frac{1}{2}g\hbar \end{pmatrix} \quad (58)$$

Since

$$L_z Y_{l, m_j - \frac{1}{2}} = -i\hbar \frac{\partial}{\partial\phi} Y_{l, m_j - \frac{1}{2}} = (m_j - \frac{1}{2})\hbar Y_{l, m_j - \frac{1}{2}}$$

we immediately have (for  $j = l + \frac{1}{2}$ )

$$(H'')_P \phi(j_+, m_j) = \mu_B B \begin{pmatrix} \left[ \frac{l + \frac{1}{2} + m_j}{2l + 1} \right]^{1/2} (m_j - \frac{1}{2} + \frac{1}{2}g) R_{nl}(r) Y_{l, m_j - \frac{1}{2}} \\ \left[ \frac{l + \frac{1}{2} - m_j}{2l + 1} \right]^{1/2} (m_j + \frac{1}{2} - \frac{1}{2}g) R_{nl}(r) Y_{l, m_j + \frac{1}{2}} \end{pmatrix}$$

The off-diagonal elements are obviously zero and the perturbation is thus given by

$$\begin{aligned} \Delta &= \int \phi^*(j_+, m_j) (H'')_P \phi(j_+, m_j) d\tau \\ &= \mu_B B \frac{(2l + g)m_j}{(2l + 1)} \text{ for } j = l + \frac{1}{2} \end{aligned} \quad (59)$$

and similarly,

$$\Delta = \mu_B B \frac{(2l+2-g)m_j}{(2l+1)} \text{ for } j = l - \frac{1}{2} \quad (60)$$

Thus the  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$  split into  $(2l+2)$  and  $2l$  levels. Further, if we assume  $g = 2$ , Eqs (59) and (60) can be combined to give

$$\Delta = \mu_B B \frac{j + \frac{1}{2}}{l + \frac{1}{2}} m_j ; \quad j = l \pm \frac{1}{2} \quad (61)$$

Figure 20.1 shows the splitting of the  $P$ -state of an alkali atom. For the  $P$ -state,  $l = 1$  and we may have  $j = 3/2$  and  $1/2$ . Thus

$$\begin{aligned} \frac{\Delta}{\mu_B B} &= \frac{4}{3}m_j \text{ for } j = \frac{3}{2} \\ &= \frac{2}{3}m_j \text{ for } j = \frac{1}{2} \end{aligned}$$

Thus the  $j = 3/2$  level will split into 4 states ( $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ ) and the  $j = \frac{1}{2}$  level will split into 2 states ( $m_j = -\frac{1}{2}, \frac{1}{2}$ ) as shown in Fig. 20.1. In the figure the two states corresponding to  $B = 0$  represent the fine structure splitting given by Eq. (117) of Chapter 19 (see Problem 19.12).

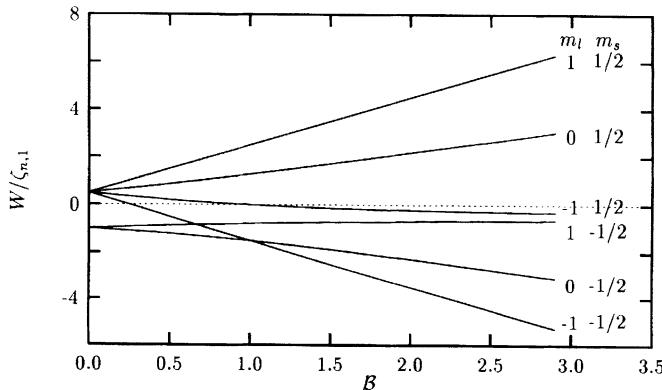


Figure 20.1. The splitting of the  $P$ -state of an alkali atom by magnetic field. The two states corresponding to  $B = 0$  represent the fine structure splitting.

**Solution 20.3** It is obvious that the functions

$$|\psi(n, l, m_l, \frac{1}{2})\rangle = |n, l, m_l, \hat{\mathbf{z}} \uparrow\rangle \quad (62)$$

and

$$|\psi(n, l, m_l, -\frac{1}{2})\rangle = |n, l, m_l, \hat{\mathbf{z}} \downarrow\rangle \quad (63)$$

are the exact eigenfunctions of  $H_0 + H''$  belonging to the eigenvalues

$$E_n + \frac{\mu_B B}{\hbar} \left[ m_l \hbar + \frac{1}{2} g \hbar \right]$$

and

$$E_n + \frac{\mu_B B}{\hbar} \left[ m_l \hbar - \frac{1}{2} g \hbar \right]$$

respectively. The above equations can be combined to give

$$E_n + \mu_B B(m_l + 2m_s) \quad (64)$$

where  $m_s = \frac{1}{2}$  and  $m_s = -\frac{1}{2}$  correspond to the spin up and spin down states and we have assumed  $g = 2$ . Now, for the two states given by Eqs (62) and (63),  $L_z$  and  $s_z$  are well-defined and expectation values of  $L_x$ ,  $s_x$ ,  $L_y$  and  $s_y$  are zero (see Problem 13.1). Thus the perturbation is given by

$$\begin{aligned} \langle f(r) \mathbf{L} \cdot \mathbf{s} \rangle &= \langle f(r) \rangle \langle L_z s_z \rangle \\ &= \zeta_{n,l} m_l m_s \end{aligned} \quad (65)$$

where

$$\begin{aligned} \zeta_{n,l} &= \langle f(r) \rangle \hbar^2 = \frac{g Z \hbar \alpha \hbar^2}{4m^2 c} \int \frac{1}{r^3} |R_{nl}(r)|^2 r^2 dr \\ &= \frac{Z^4 \alpha^4 m c^2}{2n^3 l(l + \frac{1}{2})(l + 1)} \end{aligned} \quad (66)$$

where we have used Eq. (11) of Appendix I. Thus the energy levels are given by

$$E = E_n + \mu_B B(m_l + 2m_s) + \zeta_{n,l} m_l m_s \quad (67)$$

where

$$m_l = -l, \dots, l \text{ and } m_s = +\frac{1}{2} \text{ and } -\frac{1}{2} \quad (68)$$

Equation (67) represents the *Paschen-Back effect* and as can be seen the operators  $L^2$ ,  $S^2$ ,  $L_z$  and  $s_z$  have well-defined values for each state; this is referred to as by saying that  $S^2$ ,  $L^2$ ,  $L_z$  and  $s_z$  are good quantum numbers. The splitting for the  $P$ -state of an alkali atom is shown in Fig. 20.1. In the figure  $\mathcal{B} = \mu_B B / \zeta_{n,l}$ . At  $B = 0$ , we have the fine structure splitting. For small values of  $B$ , Eq. (66) is to be used and for large values of  $B$ , Eq. (67) is to be used. Both equations are limiting forms of Eq. (76) which should be used for intermediate values of  $B$ .

**Solution 20.4** We should first mention that for weak fields  $s^2$ ,  $L^2$ ,  $J^2$  and  $J_z$  are good quantum numbers, and on the other hand, for strong fields  $s^2$ ,  $L^2$ ,  $L_z$  and  $s_z$  are good quantum numbers. However, for intermediate fields neither of them are good quantum numbers and one must calculate the off-diagonal elements as is done in degenerate state perturbation theory.

We choose as our representation, the eigenstates for the strong field case<sup>9</sup>; these are given by Eqs (62) and (63). Now, from Eq. (67)

$$\begin{aligned} &\langle \psi(n, l, m_l, \pm \frac{1}{2}) | H'' | \psi(n, l, m_l, \pm \frac{1}{2}) \rangle \\ &= (m \pm \frac{1}{2}) \mu_B B \end{aligned} \quad (69)$$

---

<sup>9</sup> We could have equally well chosen the eigenstates for the weak field case.

where<sup>10</sup>

$$m = m_l + m_s = \begin{cases} m_l + \frac{1}{2} & \text{for } m_s = \frac{1}{2} \\ m_l - \frac{1}{2} & \text{for } m_s = -\frac{1}{2} \end{cases}$$

The off diagonal elements like

$$\langle \psi(n, l, m_l, \pm \frac{1}{2}) | H'' | \psi(n, l, m_l, \mp \frac{1}{2}) \rangle$$

would vanish because  $|\psi(n, l, m_l, \pm \frac{1}{2})\rangle$  are eigenstates of  $H''$ .

Next in order to calculate the matrix elements of

$$\mathbf{L} \cdot \mathbf{s} = \frac{J^2 - L^2 - s^2}{2} \quad (70)$$

we write

$$\begin{aligned} |\psi(n, l, m_l = m - \frac{1}{2}, + \frac{1}{2})\rangle &= \left( \frac{l+m+\frac{1}{2}}{2l+1} \right)^{1/2} |\phi(n, l, j_+, m)\rangle \\ &\quad - \left( \frac{l-m+\frac{1}{2}}{2l+1} \right)^{1/2} |\phi(n, l, j_-, m)\rangle \end{aligned} \quad (71)$$

$$\begin{aligned} |\psi(n, l, m_l = m + \frac{1}{2}, - \frac{1}{2})\rangle &= \left( \frac{l-m+\frac{1}{2}}{2l+1} \right)^{1/2} |\phi(n, l, j_+, m)\rangle \\ &\quad + \left( \frac{l+m+\frac{1}{2}}{2l+1} \right)^{1/2} |\phi(n, l, j_-, m)\rangle \end{aligned} \quad (72)$$

where  $j_{\pm} = l \pm \frac{1}{2}$ . Further,  $\phi$  are eigenfunctions in the representation  $L^2, s^2, J^2$  and  $J_z$  and we have used the Clebsch-Gordan coefficients from Chapter 18 (see Table 18.1). Now

$$J^2 |\phi(n, l, j_+, m)\rangle = (l + \frac{1}{2})(l + \frac{3}{2}) \hbar^2 |\phi(n, l, j_+, m)\rangle \quad (73)$$

$$J^2 |\phi(n, l, j_-, m)\rangle = (l - \frac{1}{2})(l + \frac{1}{2}) \hbar^2 |\phi(n, l, j_-, m)\rangle \quad (74)$$

---

<sup>10</sup> The quantity  $m$  is denoted by  $m_j$  in Problem 20.2. For convenience, we are dropping the subscript  $j$ .

The operator  $L^2$  has the eigenvalues  $l(l+1)\hbar^2$  and  $s^2$  has the eigenvalue  $\frac{1}{2}(\frac{3}{2})\hbar^2 = \frac{3}{4}\hbar^2$ . Thus (omitting the subscripts  $n, l$ ):

$$\begin{aligned} & \langle \psi(m_l = m - \frac{1}{2}, \frac{1}{2}) | \frac{J^2 - L^2 - s^2}{2} | \psi(m_l = m - \frac{1}{2}, \frac{1}{2}) \rangle \\ &= \left[ \left( \frac{l+m+\frac{1}{2}}{2l+1} \right)^{1/2} \langle \phi(j_+, m) | - \left( \frac{l-m+\frac{1}{2}}{2l+1} \right)^{1/2} \langle \phi(j_-, m) | \right] \frac{J^2 - L^2 - s^2}{2} \\ &\times \left[ \left( \frac{l+m+\frac{1}{2}}{2l+1} \right)^{1/2} | \phi(j_+, m) \rangle - \left( \frac{l-m+\frac{1}{2}}{2l+1} \right)^{1/2} | \phi(j_-, m) \rangle \right] \\ &= \frac{l+m+\frac{1}{2}}{2l+1} \frac{1}{2} \left\{ j_+(j_+ + 1) - l(l+1) - \frac{3}{4} \right\} \hbar^2 \\ &+ \frac{l-m+\frac{1}{2}}{2l+1} \frac{1}{2} \left\{ j_-(j_- + 1) - l(l+1) - \frac{3}{4} \right\} \hbar^2 = \frac{1}{2} \left( m - \frac{1}{2} \right) \hbar^2 \end{aligned}$$

Further, the only non-vanishing, non-diagonal matrix elements are

$$\begin{aligned} & \langle \psi(m_l = m - \frac{1}{2}, \frac{1}{2}) | \mathbf{L} \cdot \mathbf{s} | \psi(m_l = m + \frac{1}{2}, -\frac{1}{2}) \rangle \\ &= \langle \psi(m_l = m + \frac{1}{2}, -\frac{1}{2}) | \mathbf{L} \cdot \mathbf{s} | \psi(m_l = m - \frac{1}{2}, \frac{1}{2}) \rangle \\ &= \frac{1}{2} \left[ \left( l+m+\frac{1}{2} \right) \left( l-m+\frac{1}{2} \right) \right]^{1/2} \hbar^2 \end{aligned}$$

Thus, considering  $H' + H''$  as perturbation, secular determinant is (see Sec. 19.3):

$$\left| \begin{array}{cc} \frac{1}{2} \left( m - \frac{1}{2} \right) \zeta_{n,l} + \left( m + \frac{1}{2} \right) \mu_B B - W & \frac{1}{2} \zeta_{n,l} \left[ \left( l+m+\frac{1}{2} \right) \left( l-m+\frac{1}{2} \right) \right]^{1/2} \\ \frac{1}{2} \zeta_{n,l} \left[ \left( l+m+\frac{1}{2} \right) \left( l-m+\frac{1}{2} \right) \right]^{1/2} & -\frac{1}{2} \left( m + \frac{1}{2} \right) \zeta_{n,l} + \left( m - \frac{1}{2} \right) \mu_B B - W \end{array} \right| = 0 \quad (75)$$

where  $\zeta_{n,l}$  is given by Eq. (66). Equation (75) gives

$$\begin{aligned} W^2 + W \left[ \frac{1}{2} \zeta_{n,l} - 2m\mu_B B \right] + \left[ - \left( \frac{1}{2} \zeta_{n,l} \right)^2 l(l+1) \right. \\ \left. - m\mu_B B \zeta_{n,l} + \mu_B^2 B^2 \left( m^2 - \frac{1}{4} \right) \right] = 0 \end{aligned}$$

The solutions are

$$\begin{aligned} W = -\frac{1}{4} \zeta_{n,l} + m_j \mu_B B \pm \frac{1}{4} \left[ 4\mu_B^2 B^2 + 8\zeta_{n,l} m_j \mu_B B \right. \\ \left. + \zeta_{n,l}^2 (2l+1)^2 \right]^{1/2} \end{aligned} \quad (76)$$

where we have reintroduced the subscript  $j$  on  $m$ . It may be noted that

(i) For  $B = 0$

$$W = \frac{1}{4}\zeta_{n,l} [-1 \pm (2l + 1)] \quad (77)$$

which is the fine structure splitting (see Problem 19.12).

(ii) For small  $B$

$$\begin{aligned} W &\rightarrow -\frac{1}{4}\zeta_{n,l} + (m_j\mu_B B) \pm \frac{1}{4}\zeta_{n,l}(2l+1) \left[ 1 + \frac{8(m_j\mu_B B)}{\zeta_{n,l}(2l+1)^2} \right]^{1/2} \\ &\simeq \frac{1}{4}\zeta_{n,l} [-1 \pm (2l+1)] + \frac{2l+1 \pm 1}{2l+1} m_j\mu_B B \end{aligned} \quad (78)$$

which is the Zeeman effect (see Problem 20.2).

(iii) For large  $B$

$$\begin{aligned} W &\rightarrow -\frac{1}{4}\zeta_{n,l} + m_j\mu_B B \pm \frac{1}{2}\mu_B B \left[ 1 + \frac{m_j\zeta_{n,l}}{\mu_B B} \right]^{1/2} \\ &\simeq \left[ -\frac{1}{4} \pm \frac{1}{2}m_j \right] \zeta_{n,l} + \left( m_j \pm \frac{1}{2} \right) \mu_B B \end{aligned} \quad (79)$$

which is the same as given by Eq. (67) provided we note that  $m_j = m_l + m_s$  and the upper and lower signs in Eq. (79) correspond to  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$  respectively.

For the  $P$ -state of an alkali atom,  $l = 1$ , and we may write Eq. (76) in the form

$$\frac{W}{\zeta_{n,l}} = -\frac{1}{4} + m_j \mathcal{B} \pm \frac{1}{4} \sqrt{4\mathcal{B}^2 + 8m_j \mathcal{B} + 9} \quad (80)$$

where  $\mathcal{B} = \mu_B B / \zeta_{n,l}$ . In Fig. 20.1 we have plotted the splitting of the  $P$ -state of an alkali atom.

**Solution 20.5** We first note that

$$\sigma_x |\uparrow\rangle = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\downarrow\rangle$$

and

$$\sigma_y |\uparrow\rangle = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = i |\downarrow\rangle$$

where  $|\uparrow\rangle$  and  $|\downarrow\rangle$  states are the  $|\widehat{\mathbf{z}}\downarrow\rangle$  and  $|\widehat{\mathbf{z}}\downarrow\rangle$  states respectively. Similarly,

$$\sigma_x |\downarrow\rangle = |\uparrow\rangle \text{ and } \sigma_y |\downarrow\rangle = -i |\uparrow\rangle$$

Since the components of  $\sigma_e$  operate only on the electron spin state and the components of  $\sigma_p$  operate only on the proton spin state we have, for example,

$$\begin{aligned}\sigma_{ex}\sigma_{px}|e\uparrow p\downarrow\rangle &= \sigma_{ex}|e\uparrow p\uparrow\rangle = |e\downarrow p\uparrow\rangle \\ \sigma_{ey}\sigma_{py}|e\uparrow p\downarrow\rangle &= -i\sigma_{ey}|e\uparrow p\uparrow\rangle = |e\downarrow p\uparrow\rangle \\ \sigma_{ez}\sigma_{pz}|e\uparrow p\downarrow\rangle &= -\sigma_{ez}|e\uparrow p\downarrow\rangle = -|e\uparrow p\downarrow\rangle\end{aligned}$$

Thus

$$\begin{aligned}\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p |e\uparrow p\downarrow\rangle &= \sigma_{ex}\sigma_{px}|e\uparrow p\downarrow\rangle + \sigma_{ey}\sigma_{py}|e\uparrow p\downarrow\rangle + \sigma_{ez}\sigma_{pz}|e\uparrow p\downarrow\rangle \\ &= 2|e\downarrow p\uparrow\rangle - |e\uparrow p\downarrow\rangle\end{aligned}$$

Therefore

$$P|e\uparrow p\downarrow\rangle = \frac{1}{2}[1 + \boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p]|e\uparrow p\downarrow\rangle = |e\downarrow p\uparrow\rangle$$

Similarly one can consider other operations to obtain

$$P|e\uparrow p\uparrow\rangle = |e\uparrow p\uparrow\rangle, P|e\downarrow p\downarrow\rangle = |e\downarrow p\downarrow\rangle \quad (81)$$

and

$$P|e\downarrow p\uparrow\rangle = |e\uparrow p\downarrow\rangle$$

which shows that  $P$  is the spin exchange operator.

**Solution 20.6** Since  $H'$  is proportional to  $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$ , we have to look for a representation in which  $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$  is diagonal. Introducing the angular momentum operators

$$\mathbf{s}_1 = \frac{1}{2}\hbar\boldsymbol{\sigma}_e, \mathbf{s}_2 = \frac{1}{2}\hbar\boldsymbol{\sigma}_p \text{ and } \mathbf{s} = \mathbf{s}_1 + \mathbf{s}_2 \quad (82)$$

we have

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \frac{1}{4}\hbar^2\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p = \frac{1}{2}[s^2 - s_1^2 - s_2^2] \quad (83)$$

We have to look for a representation in which  $s^2$ ,  $s_1^2$  and  $s_2^2$  are diagonal. This is easily obtained from the Clebsch-Gordan coefficients (see Table 18.1) and one has the four states

$$\left. \begin{aligned}|1\rangle &= |e\uparrow p\uparrow\rangle \\ |2\rangle &= |e\downarrow p\downarrow\rangle \\ |3\rangle &= \frac{1}{\sqrt{2}}[|e\uparrow p\downarrow\rangle + |e\downarrow p\uparrow\rangle]\end{aligned}\right\} \quad (84)$$

$$|4\rangle = \frac{1}{\sqrt{2}}[|e\uparrow p\downarrow\rangle - |e\downarrow p\uparrow\rangle] \quad (85)$$

The first three states represent the triplet state and the fourth state represents the singlet state. For the triplet state the values of  $s^2$ ,  $s_1^2$  and  $s_2^2$  are  $2\hbar^2$ ,  $\frac{3}{4}\hbar^2$  and

$\frac{3}{4}\hbar^2$  respectively; the corresponding values for the singlet state are  $0$ ,  $\frac{3}{4}\hbar^2$  and  $\frac{3}{4}\hbar^2$  respectively. Thus the values of  $\mathbf{s}_1 \cdot \mathbf{s}_2$  are:

$$\frac{1}{2} \left[ 2 - \frac{3}{4} - \frac{3}{4} \right] \hbar^2 = \frac{1}{4} \hbar^2 \text{ for the triplet state}$$

and

$$\frac{1}{2} \left[ -\frac{3}{4} - \frac{3}{4} \right] \hbar^2 = -\frac{3}{4} \hbar^2 \text{ for the singlet state}$$

Consequently for  $n = 1$ , the energy for the triplet and singlet states are

$$E_1 + \epsilon \text{ and } E_1 - 3\epsilon \quad (86)$$

the separation is

$$4\epsilon = \frac{32}{3a_0^3} \left( g_p \frac{q\hbar}{4M_p} \right) \left( g \frac{q\hbar}{4m} \right) \quad (87)$$

the corresponding wavelength ( $= hc/4\epsilon$ ) is about 21 cm which is the famous 21 cm *line* used by the radio astronomers to measure the amount of hydrogen in the galaxy. The measured value of the frequency is (quoted from Ref. 13)

$$\nu = (1420405751.800 \pm .028) \text{ Hz}$$

which is one of the most accurately determined quantities.

**Solution 20.7** The states  $|e \uparrow p \uparrow\rangle$  and  $|e \downarrow p \downarrow\rangle$  are eigenstates of  $H'$  belonging to the eigenvalues

$$\mu_B B - \mu_p B + \epsilon$$

and

$$-\mu_B B + \mu_p B + \epsilon$$

It is easy to see that  $|e \uparrow p \downarrow\rangle$  and  $|e \downarrow p \uparrow\rangle$  are not eigenstates. We write

$$|a\rangle = |e \uparrow p \downarrow\rangle \text{ and } |b\rangle = |e \downarrow p \uparrow\rangle$$

Now

$$\begin{aligned} H' |a\rangle &= H' |e \uparrow p \downarrow\rangle = \mu_B B |e \uparrow p \downarrow\rangle + \mu_p B |e \uparrow p \downarrow\rangle + \epsilon(2P - 1) |e \uparrow p \downarrow\rangle \\ &= (\mu_B B + \mu_p B - \epsilon) |a\rangle + 2\epsilon |b\rangle \end{aligned}$$

Thus

$$\langle a | H' | a \rangle = (\mu_B B + \mu_p B - \epsilon), \quad \langle b | H' | b \rangle = 2\epsilon$$

Similarly,

$$\langle b | H' | b \rangle = (-\mu_B B - \mu_p B - \epsilon), \quad \langle a | H' | b \rangle = 2\epsilon$$

The secular determinant is

$$\begin{vmatrix} \langle a | H' | a \rangle - W & \langle b | H' | a \rangle \\ \langle a | H' | b \rangle & \langle b | H' | b \rangle - W \end{vmatrix} = 0$$

which gives

$$W = -\epsilon \pm \sqrt{4\epsilon^2 + (\mu_B + \mu_P)^2 B^2} \quad (88)$$

the corresponding wave functions can easily be found. For  $B \rightarrow 0$  we get the results of the previous problem.

**Solution 20.8** In the Heisenberg representation (see Sec. 12.9)

$$\left. \begin{array}{l} i \hbar \frac{ds_x}{dt} = [s_x, H] = \omega_0 [s_x, s_z] = -i \hbar \omega_0 s_y(t) \\ i \hbar \frac{ds_y}{dt} = [s_y, H] = \omega_0 [s_y, s_z] = +i \hbar \omega_0 s_x(t) \\ i \hbar \frac{ds_z}{dt} = 0 \end{array} \right\} \quad (89)$$

Thus

$$\frac{d^2 s_x}{dt^2} = -\omega_0 \frac{ds_y}{dt} = -\omega_0^2 s_x \quad (90)$$

The solutions are therefore

$$s_x(t) = s_x(0) \cos \omega_0 t + s_y(0) \sin \omega_0 t \quad (91)$$

$$s_y(t) = -s_x(0) \sin \omega_0 t + s_y(0) \cos \omega_0 t \quad (92)$$

$$s_z(t) = s_z(0) \quad (93)$$

The expectation values are

$$\langle s_x(t) \rangle = \langle \Psi(0) | s_x(t) | \Psi(0) \rangle = \langle s_x(0) \rangle \cos \omega_0 t + \langle s_y(0) \rangle \sin \omega_0 t \quad (94)$$

etc. For  $|\Psi(0)\rangle = |\hat{\mathbf{x}} \uparrow\rangle$

$$\langle s_x(0) \rangle = \frac{1}{2} \hbar, \quad \langle s_y(0) \rangle = 0 = \langle s_z(0) \rangle \quad (95)$$

and we obtain the same result as in Example 14.1. For

$$|\Psi(0)\rangle = \cos \frac{\phi}{2} |\hat{\mathbf{z}} \uparrow\rangle + \sin \frac{\phi}{2} |\hat{\mathbf{z}} \downarrow\rangle \quad (96)$$

$$s_x(0) |\Psi(0)\rangle = \frac{1}{2} \hbar \cos \frac{\phi}{2} \sigma_x \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{2} \hbar \sin \frac{\phi}{2} \sigma_x \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= \frac{1}{2} \hbar \cos \frac{\phi}{2} |\hat{\mathbf{z}} \downarrow\rangle + \frac{1}{2} \hbar \sin \frac{\phi}{2} |\hat{\mathbf{z}} \uparrow\rangle$$

Thus

$$\langle s_x(0) \rangle = \frac{1}{2} \hbar \sin \phi$$

Similarly  $\langle s_y(0) \rangle = 0$  and  $\langle s_z(0) \rangle = \frac{1}{2} \hbar \cos \phi$ . Physically this implies that at  $t = 0$ , the spin is in the  $x$ - $z$  plane at an angle with the  $z$ -axis. Using Eqs (91)–(93), we get

$$\langle s_x(t) \rangle = \frac{1}{2} \hbar \sin \phi \cos \omega_0 t \quad (97)$$

$$\langle s_y(t) \rangle = -\frac{1}{2} \hbar \sin \phi \sin \omega_0 t \quad (98)$$

$$\langle s_z(t) \rangle = \frac{1}{2} \hbar \cos \phi \quad (99)$$

which shows the precessional motion (see Example 14.2).

**Solution 20.9** Equation (20) with  $\phi = 0$ ,  $Q = -q$  and  $\mathbf{A}$  given by Eq. (45) becomes

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left[ E + \frac{iq\hbar}{m} Bx \frac{\partial \psi}{\partial y} - \frac{1}{2m} q^2 B^2 x^2 \right] \psi = 0 \quad (100)$$

The solution of Eq. (100) is of the form

$$\psi(z) = u(x) \exp \left[ \frac{i}{\hbar} (P_y y + P_z z) \right] \quad (101)$$

where  $u(x)$  satisfies the following equation

$$\frac{d^2 u(x)}{dx^2} + \frac{2m}{\hbar^2} \left[ E - \frac{P_z^2}{2m} - \frac{q^2 B^2}{2m} \left( x + \frac{P_y}{qB} \right)^2 \right] u(x) = 0 \quad (102)$$

Equation (102) is very similar to the linear harmonic oscillator problem (see Sec. 7.2). The energy eigenvalues are

$$E = \frac{P_z^2}{2m} + \left( n + \frac{1}{2} \right) \hbar \frac{qB}{m} = \frac{P_z^2}{2m} + (2n + 1)\mu_B B \quad (103)$$

where  $n = 0, 1, 2, \dots$ . The corresponding  $u(x)$  are the Hermite-Gauss functions. For a fixed value of  $n$ , the continuous energy bands are called Landau bands (see, e.g. Ref. 14). Notice that Eq. (103) is independent of  $P_y$  and hence there is infinite degeneracy. If spin angular momentum is also taken into account, we would get

$$E = \frac{P_z^2}{2m} + \left( 2n + 1 \pm \frac{1}{2} \right) \mu_B B \quad (104)$$

**Solution 20.11** Equation (20) (for  $Q = -q$  and  $\mathbf{A}$  given by Eq. (46)) gives the following expression for the Hamiltonian

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\nabla^2 + V(r) - \frac{iq\hbar B}{2m} \left( x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) + \frac{q^2B^2}{8m}(x^2 + y^2) \\ &= H_0 + H_1 + H_2 \end{aligned} \quad (105)$$

where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \quad (106)$$

$$H_1 = \frac{qB}{2m}L_z \quad (107)$$

$$H_2 = \frac{q^2B^2}{8m}(x^2 + y^2) \quad (108)$$

The term  $H_1$  represents the interaction between the magnetic moment of the atom and the external magnetic field and gives rise to paramagnetism. The term  $H_2$  can be interpreted as the interaction of the magnetic moment induced in the atom with the magnetic field (see, e.g. Ref. 15, Sec. 18.3); this gives rise to diamagnetism. Treating  $H_1$  and  $H_2$  as perturbations we get

$$\langle H_1 \rangle = \frac{qB}{2m}m_l\hbar = m_l\mu_B B \quad (109)$$

and

$$\langle H_2 \rangle = \frac{q^2B^2}{8m} \langle r^2 \sin^2 \theta \rangle \quad (110)$$

If  $\langle H_1 \rangle \neq 0$  then (assuming  $m_l \sim 1$ )

$$\frac{\langle H_2 \rangle}{\langle H_1 \rangle} = \frac{qB}{4\hbar} \langle r^2 \sin^2 \theta \rangle \sim \frac{qB}{4\hbar} a_0^2 \quad (111)$$

where  $a_0 (\simeq 0.5 \times 10^{-10} \text{ m})$  represents the Bohr radius. Thus

$$\begin{aligned} \frac{\langle H_2 \rangle}{\langle H_1 \rangle} &\sim \frac{1.6 \times 10^{-19}}{4 \times 10^{-34}} \times 0.25 \times 10^{-20} B \\ &\sim 10^{-6} B \text{ (B measured in tesla)} \\ &\sim 10^{-10} B \text{ (B measured in Gauss)} \end{aligned}$$

Since the laboratory magnetic fields almost never exceed  $10^5$  Gauss,

$$\frac{\langle H_2 \rangle}{\langle H_1 \rangle} \ll 1 \quad (112)$$

hence whenever the paramagnetic term is non-zero, it dominates over the diamagnetic term. Thus for  $l > 0$ ,  $\langle H_2 \rangle$  dominates and for  $l = 0$ , the diamagnetic term determines the magnetic behaviour. Indeed, for such a case  $\langle \sin^2 \theta \rangle = \frac{2}{3}$  and

$$\langle H_2 \rangle = \frac{q^2 B^2}{12m} \langle r^2 \rangle \quad (113)$$

The induced magnetic moment is therefore  $-\frac{q^2}{6m} \langle r^2 \rangle B$ ; thus if there are  $N$  atoms per unit volume with each atom having  $Z$  electrons, we get the following expression for the diamagnetic susceptibility

$$\chi_{dia} = -\frac{NZq^2}{6m} \langle r^2 \rangle \quad (114)$$

consistent with the classical result (see, e.g. Ref. 15, Sec. 18.3). The diamagnetic susceptibility therefore depends on the charge distribution in the atoms. For further details and comparison with experimental data, see, e.g. Ref. 4. In order to calculate the paramagnetic susceptibility, we note that the magnetic moment per unit volume,  $P$ , is the statistical average over all possible states:

$$\begin{aligned} P &= N \frac{\sum m_l \mu_B \exp[-\Gamma m_l]}{\sum \exp[-\Gamma m_l]} \\ &= N \mu_B \frac{\sum m_l (1 - \Gamma m_l + \dots)}{\sum (1 - \Gamma m_l + \dots)} \approx -N \mu_B \left( \frac{N \mu_B}{kT} \right) \frac{1}{3} l(l+1) \end{aligned} \quad (115)$$

where  $N$  represents the number of atoms per unit volume and the summation over  $m_l$  goes from  $-l$  to  $+l$ . Further,

$$\Gamma = \frac{\mu_B B}{kT}$$

which has been assumed to be very small compared to unity and use has been made of the relation

$$\sum_{m_l=-l}^{+l} m_l = 0, \quad \sum_{m_l=-l}^{+l} m_l^2 = \frac{1}{3} l(l+1)(2l+1)$$

Thus

$$\chi_{para} = \frac{N \mu_B^2}{3kT} l(l+1) \quad (116)$$

If we take into account the effect of spin in a multi-electron atom,  $m_l$ , has to be replaced by  $M_l + 2M_s$  to obtain

$$\begin{aligned}\chi &= \frac{N\mu_B^2}{kT} \left[ \frac{\Sigma M_l^2}{2L+1} + \frac{4\Sigma M_s^2}{2S+1} \right] \\ &= \frac{N\mu_B^2}{3kT} [L(L+1) + 4S(S+1)]\end{aligned}\quad (117)$$

The  $1/T$  dependence of the susceptibility [see, Eqs (116) and (117)] is known as Curie law. For further details, see Ref. 4.

**Solution 20.13** We assume  $\mathbf{A}$  to be given by Eq. (46), i.e.

$$A_x = -\frac{1}{2} yB, \quad A_y = \frac{1}{2} xB, \quad A_z = 0 \quad (118)$$

We can then use either Eq. (20) or Eq. (25). If we use Eq. (20) then the second term on the LHS would become

$$\begin{aligned}\frac{iQ\hbar}{\mu} \mathbf{A} \cdot \nabla \psi &= \frac{iQ\hbar B}{2\mu} \left[ -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y} \right] \\ &= -\frac{QB}{2\mu} [xp_y - yp_x] \\ &= -\frac{QB}{2\mu} L_z = +\frac{i\hbar QB}{2\mu} \frac{\partial}{\partial \phi}\end{aligned}\quad (119)$$

Thus Eq. (20) [or Eq. (25)] takes the following form in the 2-dimensional polar coordinates  $(\rho, \phi)$ :

$$\begin{aligned}-\frac{\hbar^2}{2\mu} \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial \psi}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 \psi}{\partial \phi^2} \right] \\ + \left[ \frac{i\hbar QB}{2\mu} \frac{\partial \psi}{\partial \phi} + \frac{Q^2 B^2}{8\mu} \rho^2 \psi + V(\rho) \psi \right] = E\psi(\rho, \phi)\end{aligned}\quad (120)$$

Now for  $\psi$  to be single value we must have

$$\psi(\rho, \phi) = \left[ \frac{1}{\sqrt{2\pi}} e^{im\phi} \right] R(\rho); \quad m = 0, \pm 1, \pm 2 \quad (121)$$

Thus  $R(\rho)$  will satisfy the equation

$$\frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{dR}{d\rho} \right) + \frac{2\mu}{\hbar^2} \left[ \left( E + \frac{QBm\hbar}{2\mu} \right) + \frac{1}{2} \mu \omega^2 \rho^2 - \frac{m^2}{\rho^2} \right] R(\rho) = 0 \quad (122)$$

where

$$\omega = \left( \omega_0^2 + \frac{Q^2 B^2}{4\mu^2} \right)^{1/2} \quad (123)$$

Equation (122) is of the same form as that of a 2-dimensional harmonic oscillator and we can solve either using Cartesian coordinates (see Sec. 10.6) or using cylindrical coordinates (see Problem 10.12). If we use Cartesian coordinates, the energy eigenvalues would be given by

$$E = (n_1 + n_2 + 1) \hbar\omega - \frac{mQ\hbar B}{2\mu}; \quad n_1, n_2 = 0, 1, 2, \dots \quad (124)$$

The corresponding eigenfunctions would be appropriate linear combinations of the Hermite-Gauss functions which are also eigenfunctions of  $L_z$ ; i.e. the  $\phi$  dependence of the wave function must be of the form of  $\exp(im\phi)$ .

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# Chapter 21

## The Variational Method

*All science is either physics or stamp collecting.*

— ERNST RUTHERFORD

### 21.1. Introduction

In many cases stationary perturbation theory cannot be applied successfully as there may not be a closely related problem which is capable of exact solution.

In this chapter, we shall describe the variational method for evaluating the energies of the ground state and the first few discrete states of a bound system, approximately. We shall then apply it to calculate the ground state energy of the helium atom and the hydrogen molecular ion.

### 21.2. The basic principle

Let  $\Psi_n$  denote the exact set of eigenfunctions of the hamiltonian  $H$

$$H\Psi_n = E_n \Psi_n \quad (1)$$

These eigenfunctions constitute a complete set of functions in the sense that an arbitrary bounded quadratically integrable function  $\phi$  can be expanded in terms of the eigenfunctions. Thus we may write

$$\phi = \sum_n a_n \Psi_n \quad (2)$$

Evidently, the quantity

$$\langle H \rangle = \int \Psi_n^* H \Psi_n d\tau \quad (3)$$

yields the energy  $E_n$ , assuming that the  $\Psi_n$  are normalised. Consider, now, the quantity

$$E_\phi = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \quad (4)$$

(If we use normalized functions  $\phi$ ,  $E_\phi$  resembles  $\langle H \rangle$ ).

We can show that  $E_\phi$  will always be larger than  $E_0$ , the lowest of the spectrum  $E_n$ . ( $E_0$  is the ground state energy).

Before proving this simple result, one can see how this comes about. The effect of  $H$  on the ket vector  $| \phi \rangle$  is, in general, to rotate it, except when  $| \phi \rangle$  is one of the eigenkets of  $H$ . Thus the scalar product, formed with the bra  $\langle \phi |$  and  $H | \phi \rangle$  will be an extremum for the precise case when  $H | \phi \rangle$  and  $| \phi \rangle$  point in the same direction.

We have, on substitution for  $\phi$  from Eq. (2) in Eq. (3)

$$E_\phi = \frac{\int (\sum a_n^* \Psi_n^* H \sum a_n \Psi_n) d\tau}{\int \left( \sum_n a_n^* \Psi_n^* \right) \left( \sum_n a_n \Psi_n \right) d\tau} \quad (5)$$

Since

$$\int \psi_n^* \psi_m d\tau = \delta_{nm} \quad (6)$$

we obtain

$$E_\phi = \frac{\sum_n a_n^* a_n E_n}{\sum_n a_n^* a_n} \quad (7)$$

Subtracting  $E_0$ , the energy of the ground state, from both sides of the equation, we have

$$E_\phi - E_0 = \frac{\sum_n |a_n|^2 (E_n - E_0)}{\sum_n |a_n|^2} \quad (8)$$

Now

$$E_n \geq E_0$$

because by definition  $E_0$  is the ground state energy, and since  $|a_n|^2 \geq 0$  for all  $n$ , we must have

$$E_\phi - E_0 \geq 0$$

or

$$E_\phi \geq E_0 \quad (9)$$

This important inequality can be used to obtain an upper bound to the ground state energy  $E_0$ . We choose a suitable function  $\phi$  known as the trial function which depends on a number of variable parameter  $c_i$  ( $i = 1, \dots, p$ ). This trial function is

substituted in Eq. (3) and the parameters are chosen so as to make  $E_\phi$  a minimum by solving the  $p$  equations

$$\frac{\partial E_\phi}{\partial c_i} = 0 \quad (i = 1, 2, \dots, p) \quad (10)$$

The minimum value of  $E$  determined in this way provides an upper bound to  $E_0$ , which will be close to the actual value if the trial function has a form closely resembling that of the actual ground state function  $\psi_0$ . Many different types of trial functions have been tried for the simple atoms and molecules, and some of these have been applied to much more complicated systems.

### 21.3. The hydrogen atom as an example

In order to illustrate the use of the variational method, we apply it to the hydrogen atom problem. If we choose

$$\phi = A_1 \exp \left( -\alpha \frac{r}{a_0} \right)$$

we already have the correct form of the wave function (see Sec. 10.4). We will calculate

$$E(\alpha) = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau}$$

and set  $\partial E / \partial \alpha = 0$ , this will give us the value of  $\alpha$  for which  $E$  is a minimum. We first normalize  $\phi$ :

$$1 = \int_0^\infty 4\pi r^2 dr \phi^* \phi = 4\pi |A_1|^2 \int_0^\infty \exp \left[ -\frac{2\alpha r}{a_0} \right] r^2 dr$$

giving

$$A_1 = \left( \frac{\alpha^3}{\pi a_0^3} \right)^{1/2}$$

Thus

$$\phi = \left( \frac{\alpha^3}{\pi a_0^3} \right)^{1/2} \exp \left( -\alpha \frac{r}{a_0} \right)$$

Since  $\phi(r)$  is now normalized,  $E(\alpha) = \int \phi^* H \phi d\tau$ . Further, since  $\phi$  depends only on  $r$ , we need only keep the part of  $H$  which depends on  $r$ , i.e.

$$H_{radial} = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{e^2}{r} \quad (11)$$

The integrals are easy to evaluate and one obtains

$$E(\alpha) = \left[ \frac{\hbar^2 \alpha^2}{2ma_0^2} - \frac{e^2 \alpha}{a_0} \right]$$

Setting  $dE/d\alpha = 0$  gives  $\alpha = (me^2/\hbar^2) a_0 = 1$ . Thus

$$E(\alpha) |_{\min} = -\frac{e^2}{2a_0} \quad (12)$$

which is the exact result, as it indeed should be, because we had started out with the correct form of  $\phi$ .

It is instructive to see what we would obtain if we use other forms of the trial function (see also Problem 21.1). We choose

$$\phi = A \exp \left[ -\alpha \left( \frac{r}{a_0} \right)^2 \right]$$

Normalizing, we get

$$A = \left( \frac{2\alpha}{\pi a_0^2} \right)^{3/4}$$

The integrals are again easy to evaluate and one obtains

$$E(\alpha) = \left[ \frac{3}{2}\alpha - 2^{2/3} \left( \frac{\alpha}{\pi} \right)^{1/2} \right] \frac{e^2}{a_0}$$

The minimum value of  $E$  is obtained when  $\alpha = 8/9\pi$ , the corresponding energy being

$$E(\alpha) |_{\min} = -0.85 \frac{e^2}{2a_0} \quad (13)$$

In Fig. 21.1 we have plotted the following normalized functions

$$\psi_1 = \left( \frac{\alpha^3}{\pi a_0^3} \right)^{1/2} \exp \left( -\alpha \frac{r}{a_0} \right), \alpha = 1 \quad (14)$$

$$\psi_2 = \left( \frac{2\alpha}{\pi a_0^2} \right)^{3/4} \exp \left( -\alpha \frac{r^2}{a_0^2} \right), \alpha = \frac{8}{9\pi} \quad (15)$$

$$\psi_3 = \left( \frac{\alpha^5}{3\pi a_0^3} \right)^{1/2} \frac{r}{a_0} \exp \left( -\alpha \frac{r}{a_0} \right), \alpha = \frac{3}{2} \quad (16)$$

the values of  $\alpha$  are such that one obtains minimum energies for that particular form of function.

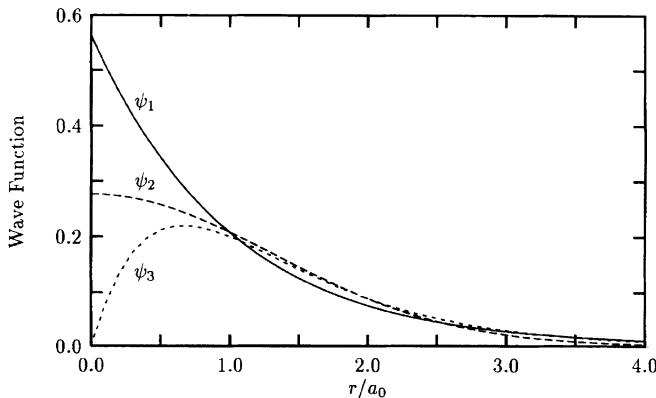


Figure 21.1. The variation of the normalized trial functions as given by Eqs (14), (15) and (16).

It can be seen that although  $\psi_3$  is closer to the actual wave function  $\psi_1$  than  $\psi_2$  for large  $r$ , the energy obtained for  $\psi_2$  is a better estimate. The reason is that for calculating energy eigenvalues, the wave function for large  $r$  does not contribute as much as for smaller values of  $r$ .

This observation illustrates an important point, namely, that the ‘best’ form of wave function depends on the particular problem at hand. If, we are interested primarily in the large  $r$  behaviour of the wave function for calculating a physical quantity for the system, the function that yields a better energy estimate may not nevertheless be an appropriate wave function.

## 21.4. The helium atom

Another illustration of the variational method is the application to the ground state of helium. If we assume that the two  $1s$  electrons move independently in the field of the nucleus (i.e. neglecting their mutual repulsion), the wave function will be

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \left( \frac{Z^3}{\pi a_0^3} \right) e^{-Zr_1/a_0} e^{-Zr_2/a_0}$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the coordinates of the two electrons, with the origin at the nucleus and  $Z = 2$ , the nuclear charge (see Fig. 22.1).

The interaction of the electrons will result in their being held little more loosely by the nucleus. We therefore choose a trial function of the form

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z'^3}{\pi a_0^3} \exp\left[-\frac{Z'r_1}{a_0}\right] \exp\left[-\frac{Z'r_2}{a_0}\right] \quad (17)$$

with  $Z'$  representing an effective nuclear charge and regard it as a variational parameter; we expect the best value of  $Z'$  to be somewhat less than the nuclear charge. Since  $\phi$  is normalized,

$$E(Z') = \iint \phi^* H \phi d\tau_1 d\tau_2$$

The above integral has been evaluated in Sec. 22.4 and Problem 22.2, the minimum value is

$$E_0 = -2 \left( Z - \frac{5}{16} \right)^2 \frac{e^2}{2a_0} = -2 \left( Z - \frac{5}{16} \right)^2 \times 13.6 \text{ eV} \quad (18)$$

which occurs when

$$Z' = Z - \frac{5}{16} \quad (19)$$

This value of the energy is better than the value obtained from first order perturbation theory (see Sec. 22.3). Putting  $Z = 2$ , we get

$$E_0 = - \left( \frac{27}{16} \right)^2 \frac{e^2}{a_0} = -2.85 \frac{e^2}{a_0} \quad (20)$$

The experimental value for the minimum energy required to remove both the electrons from a helium atom is  $2.904 e^2/a_0$ . It is worthwhile pointing out that a large number of trial functions have been used to obtain the ground state energy of the helium atom. Some of the trial functions used and the corresponding ground state energies are tabulated in Table 21.1.

It should be noted that in general, the accuracy of the calculated value of the ground state energy increases with increase in the number of terms.

## 21.5. Application to excited states

Suppose we choose a ket  $|\phi\rangle$  which has no component along the *ground state axis*, i.e.  $|\phi\rangle$  lies entirely in the ‘plane’ of the remaining eigenkets in the Hilbert space. If we now vary  $|\phi\rangle$ , (keeping the variation within this ‘plane’), we ought to arrive at the best estimate for the energy of the first excited state.

Table 21.1. Variation Functions for the Normal Helium Atom\*

(Symbols  $s = \frac{r_1+r_2}{a_0}$ ,  $t = \frac{r_1-r_2}{a_0}$ ,  $u = r_{12}/a_0$   
 Experimental value\*\*  $W = -5.8736 R_{\text{He}} hc$ )

Variation function, with best values of constants***	Energy (in units of $-R_{\text{He}} hc$ )	Deviation from experiment (in units of $-R_{\text{He}} hc$ )
1. $e^{-2s}$	5.50	0.31
2. $e^{-Z'^s}$ , $Z' = \frac{27}{16} = 1.6875$	5.6953	0.1120
3. $e^{-Z'^s} \cosh ct$ , $Z' = 1.67$ , $c = 0.48$	5.7508	0.0565
4. $e^{-Z'^s}(1 + c_2 t^2)$ , $Z' = 1.69$ , $c_2 = 0.142$	5.7536	0.0537
5. $e^{-Z'^s} e^{cu}$ , $Z' = 1.86$ , $c = 0.26$	5.7792	0.0281
6. $e^{-Z'^s}(1 + c_1 u)$ , $Z' = 1.849$ , $c_1 = 0.364$	5.7824	0.0249
7. $e^{-Z'^s}(1 + c_1 u + c_2 t^2)$ , $Z' = 1.816$ , $c_1 = 0.30$ , $c_2 = 0.13$	5.80488	0.00245
8. $e^{-Z'^s}(1 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2)$ , $Z' = 1.816$ , $c_1 = 0.353$ , $c_2 = 0.128$ , $c_3 = -0.101$ , $c_4 = 0.033$ , $c_5 = -0.032$	5.80648	0.00085

\* Adapted from Sec. VIII-29d of Ref. 1.

\*\*  $R_{\text{He}} = \frac{2\pi^2 \mu e^4}{h^3 c} = 109722.4 \text{ cm}^{-1}$ . ( $\mu$  is the reduced mass of the electron and the nucleus).

\*\*\* The normalization factor is omitted of these functions, 1 is due to Unsold, 2 to Kellner, 3 to Eckart and Hylleraas and the remainder to Hylleraas.

We do this by first restricting our choice  $\phi$  to be orthogonal to  $\psi_0$ . Let

$$\phi = \chi - \psi_0 \int \psi_0^* \chi \, d\tau \quad (21)$$

Since  $\phi$  is now orthogonal to  $\psi_0$  (as can be easily seen by evaluating  $\int \phi^* \psi_0 \, d\tau$ ), we have

$$\phi = \sum_1^\infty a_n \psi_n$$

the coefficient  $a_0$  being zero.

We can now evaluate  $E_\phi$  as before and show that

$$E_\phi - E_1 = \frac{\sum_1^\infty |a_n|^2 (E_n - E_1)}{\sum_1^\infty |a_n|^2}$$

and conclude  $E_\phi > E_1$  using the same arguments as before.

Thus, one chooses an appropriate form  $\chi$  with a set of variable parameters, then define  $\phi$  as in Eq. (21) and go through the variation procedure.

Evidently, this procedure can be continued for higher states; we define

$$\phi = \chi - \sum_{n=0}^{N-1} \psi_n \int \psi_n^* \chi \, d\tau \quad (22)$$

$\phi$  is now orthogonal to the lowest  $N - 1$  states and we can estimate the energy of the  $N^{\text{th}}$  state. However, the procedure is quite cumbersome as one goes to higher levels. It is sometimes possible to choose a trial function  $\phi$  directly from symmetry considerations so that orthogonality to lower state eigenfunctions is ensured.

## 21.6. Linear variation functions

A trial function can also be chosen as a linear combination of a set of complete orthonormal function  $u_n$ :

$$\psi = \sum_{n=1}^m c_n u_n \quad (23)$$

The variational energy is therefore given by

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \frac{\sum_n \sum_m c_n^* c_m H_{nm}}{\sum_n |c_n|^2}$$

or

$$E \sum_n |c_n|^2 = \sum_n \sum_m c_n^* c_m H_{nm} \quad (24)$$

where

$$H_{nm} = \int u_n^* H u_m \, d\tau \quad (25)$$

Differentiating Eq. (24) with respect to  $c_k$  and setting  $\partial E / \partial c_k = 0$ , we obtain<sup>1</sup>

$$\sum_n c_n^* H_{nk} - E c_k^* = 0 \quad (26)$$

For non-trivial solutions the determinant must vanish. Thus

$$|H_{ij} - E \delta_{ij}| = 0; i, j = 1, 2, \dots, m \quad (27)$$

---

<sup>1</sup> What would be the equation if we had differentiated Eq. (24) with respect to  $c_k^*$ ?

Eq. (27) is known as the secular equation. Eq. (27) will, in general, give  $m$  roots of  $E$ . For a particular value of  $E$ , the coefficient  $c_k$  can be found by using Eq. (26) and the normalization condition

$$\sum_n |c_n|^2 = 1 \quad (28)$$

The lowest root of  $E$  and the corresponding wave function represent approximations to the energy and the wave function of the ground state of the system. Other roots and the corresponding wave functions represent approximation to the excited states.

Often, it is more convenient to use a set of basis functions which are not necessarily orthogonal. In that case, the secular equation takes the form

$$|H_{ij} - S_{ij}E| = 0 \quad (29)$$

where

$$S_{ij} = \int u_i^* u_j d\tau \quad (30)$$

is known as the overlap integral.

## 21.7. The $\text{H}_2^+$ ion

As an example of the linear combination method, we consider the  $\text{H}_2^+$  ion. The Hamiltonian, neglecting the nuclear kinetic energy and the spin-orbit interaction, is given by

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \quad (31)$$

where  $r_A = |\mathbf{r} - \mathbf{R}_A|$ ,  $r_B = |\mathbf{r} - \mathbf{R}_B|$ ,  $R = |\mathbf{R}_A - \mathbf{R}_B|$ ,  $\mathbf{r}$  being the position of the electron,  $\mathbf{R}_A$  and  $\mathbf{R}_B$  being the positions of the two protons.

If  $R$  is large, then there will be a large probability for the electron to be either near  $A$  or near  $B$  but not both. Indeed, in the former case we have approximately a  $1s$  hydrogen atom wave function centred at  $A$  and in the latter case at  $B$ . This suggests that we use a linear combination as a trial function, i.e.

$$\psi = c_A u_{1A} + c_B u_{1B} \quad (32)$$

Note that the wave functions  $u_{1A}$  and  $u_{1B}$  which are the  $1s$  wave functions at  $A$  and  $B$  are *not* orthogonal. A single electron wave function as above is called a molecular orbital. This particular form of a linear combination of atomic ‘orbitals’ making a molecular orbital is called LCAO-MO for short. We now use Eq. (29). The normalised wave functions are given by

$$\begin{aligned} u_{1A} &= \left( \frac{1}{\pi a_0^3} \right)^{1/2} \exp[-r_A/a_0] \\ u_{1B} &= \left( \frac{1}{\pi a_0^3} \right)^{1/2} \exp[-r_B/a_0] \end{aligned} \quad (33)$$

The integrals in Eq. (29) should now be evaluated

$$\begin{aligned} S_{AA} &= \frac{1}{\pi a_0^3} \int \exp[-(2r_A/a_0)] d\tau = 1 = S_{BB} \\ S_{AB} = S_{BA} &= \frac{1}{\pi a_0^3} \int \exp[(-r_A/a_0) - (r_B/a_0)] d\tau \\ &= S, \text{ say} \\ H_{AA} = H_{BB} &= \frac{1}{\pi a_0^3} \int \exp(-r_A/a_0) \left[ -\frac{\hbar^2}{2m} \nabla^2 \right. \\ &\quad \left. - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \right] \exp(-r_A/a_0) d\tau \\ &= \frac{e^2}{R} - \frac{e^2}{2a_0} - \frac{e^2}{\pi a_0^3} \int \frac{1}{r_B} \exp(-2r_A/a_0) d\tau \end{aligned}$$

and

$$\begin{aligned} H_{AB} = H_{BA} &= \frac{1}{\pi a_0^3} \int \exp(r_A/a_0) \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_A} \right. \\ &\quad \left. - \frac{e^2}{r_B} + \frac{e^2}{R} \right] \exp(-r_B/a_0) d\tau \\ &= \left( \frac{e^2}{R} - \frac{e^2}{2a_0} \right) S_{AB} - \frac{e^2}{\pi a_0^3} \int \frac{1}{r_A} \exp(-r_A/a_0) \\ &\quad \times \exp(-r_B/a_0) d\tau \end{aligned}$$

In order to evaluate the integrals in the expressions for  $S_{AB}$ ,  $H_{AA}$  and  $H_{AB}$ , it is convenient to introduce the confocal elliptic coordinates

$$\mu = \frac{r_A + r_B}{R}, \nu = \frac{r_A - r_B}{R} \quad (34)$$

and the azimuthal angle  $\phi$ . Obviously,

$$1 \leq \mu < \infty; -1 \leq \nu \leq +1; 0 \leq \phi \leq 2\pi$$

and

$$\int F d\tau = \int_1^\infty d\mu \int_{-1}^{+1} d\nu \int_0^{2\pi} d\phi \frac{R^3}{8} (\mu^2 - \nu^2) F(\mu, \nu, \phi) \quad (35)$$

The integrations can easily be carried out. The results are as follows:

$$S_{AB} = S_{BA} = \left[ 1 + \xi + \frac{1}{3}\xi^2 \right] e^{-\xi} \quad (36)$$

$$H_{AA} = H_{BB} = \left[ -\frac{1}{2} + \left( \frac{1}{\xi} + 1 \right) e^{-2\xi} \right] \frac{e^2}{a_0}$$

$$H_{AB} = H_{BA} = \left[ \left( \frac{1}{\xi} - \frac{1}{2} \right) S_{AB} - (1 + \xi) e^{-\xi} \right] \frac{e^2}{a_0}$$

where  $\xi = R/a_0$ . Now the secular equation [Eq. (29)] is of the form

$$\begin{vmatrix} H_{AA} - S_{AA}E & H_{AB} - S_{AB}E \\ H_{BA} - S_{BA}E & H_{BB} - S_{BB}E \end{vmatrix} = 0 \quad (37)$$

Thus

$$(H_{AA} - E)^2 = (H_{AB} - S_{AB}E)^2 \quad (38)$$

or

$$E_\pm = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} \quad (39)$$

The corresponding wave functions can easily be found

$$\psi_+ = \frac{1}{\sqrt{2}(1 + S_{AB})^{1/2}} (u_{1A} + u_{1B}) \quad (40)$$

$$\psi_- = \frac{1}{\sqrt{2}(1 - S_{AB})^{1/2}} (u_{1A} - u_{1B}) \quad (41)$$

Obviously  $\psi_+$  is symmetric with respect to the interchange of the nuclei and  $\psi_-$  is antisymmetric.

Since the dissociation energy is  $E_H + E_{H^+} - E_{H_2^+}$  we define

$$\mathcal{E}_\pm = E_\pm + \frac{e^2}{2a_0} = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} + \frac{e^2}{2a_0} \quad (42)$$

We substitute the expressions for  $H_{AA}$ ,  $H_{AB}$  and  $S_{AB}$  from Eq. (36) and calculate  $\mathcal{E}_{\pm}$  as a function of  $\xi$  (see Fig. 21.2). The quantity  $\mathcal{E}_+$  (which corresponds to the symmetric state) has a minimum value<sup>2</sup> for  $\xi \approx 2.4$  giving  $R \approx 1.3 \text{ \AA}$ , the corresponding value of  $\mathcal{E}_+$  being -1.76 eV. Experimentally  $R \approx 1.06 \text{ \AA}$  and the dissociation energy is 2.8 eV. A better agreement between theory and experiment is obtained by introducing a variational parameter in the trial function (see Problem 21.4).

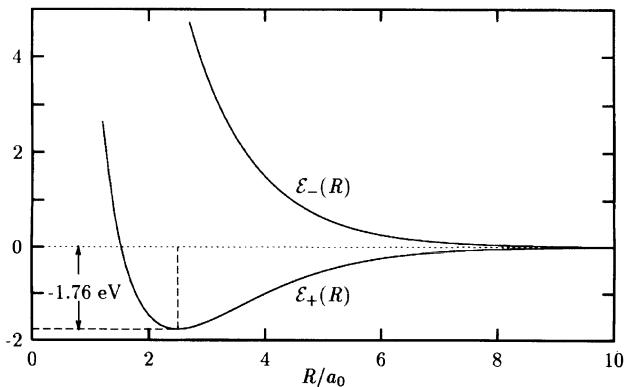


Figure 21.2. The variation of  $\mathcal{E}_{\pm}$  as a function of  $R/a_0$ . The minimum of  $\mathcal{E}_+$  occurs at  $R \approx 2.45a_0 \approx 1.3\text{\AA}$  at which  $\mathcal{E}_+ \approx -1.76 \text{ eV}$ .

We may point out certain shortcomings of the chosen trial function. For example, if we let  $R \rightarrow 0$  we should obtain the  $\text{He}^+$  ion the ground state energy of which is  $-2e^2/a_0$ , whereas Eqs (39) and (36) will give

$$E_+ \rightarrow -1.5e^2/a_0 \text{ as } R \rightarrow 0$$

The discrepancy is due to the choice of the trial function which, for  $R \rightarrow 0$ , becomes the 1s hydrogen atom wave function which is obviously incorrect. This is the reason why we find the binding too weak.

We should, however, point out that for  $R \rightarrow \infty$ ,  $\psi_+$  should describe the system accurately.

<sup>2</sup> The wave function  $\psi_+$  which leads to negative energy values is known as a ‘bounding orbital’; on the other hand, since  $\psi_-$  leads to positive energy values, it is known as an ‘anti-bonding orbital’.

## 21.8. Problems

**Problem 21.1** For the ground state of the hydrogen atom use the following as trial wave functions

$$\phi_1 \sim r \exp\left[-\alpha \frac{r}{a_0}\right], \quad \phi_2 \sim \frac{1}{\alpha^2 + (r/a_0)^2} \quad (43)$$

where  $\alpha$  is the parameter to be varied and  $a_0$  is Bohr radius. Show that the values of  $\alpha$  for which minimum energy is obtained are 1.5 and  $\pi/4$  respectively, the corresponding energies being  $-0.75 E_H$  and  $-0.81 E_H$ . Discuss with the results obtained in Sec. 21.3.

**Problem 21.2** The neutron-proton short-range interaction can be approximately described by the square well potential

$$\begin{aligned} V &= -V_0 & 0 < r < a \\ &= 0 & r > a \end{aligned} \quad (44)$$

(a) For  $l = 0$  obtain the exact solution of the Schrodinger equation and show that for  $V_0 = 40$  MeV and  $a = 1.896 \times 10^{-13}$  cm, the ground state energy is given by  $E = -2.223$  MeV which is the experimental value for the binding energy of the deuteron<sup>3</sup>.

(b) Next assume a trial wave function of the form

$$\phi \sim \exp[-\beta r/a] \quad (45)$$

Using the values of  $V_0$  and  $a$  given in part (a) carry out a variational analysis (with  $\beta$  as the variational parameter) to obtain the ground state energy of the deuteron and compare with the exact result.

**Problem 21.3** The neutron-proton interaction can also be described by the exponential potential

$$V = -V_0 e^{-r/a} \quad (46)$$

(a) For  $l = 0$  has exact solution of the Schrodinger equation can be obtained in terms of Bessel functions (see Problem 10.8). Show that for  $V_0 = 40$  MeV and  $a = 1.854 \times 10^{-13}$  cm, the ground state energy is given by  $E = -2.223$  MeV.

(b) Assuming a trial function of the form given by Eq. (45) carry out a variational analysis to obtain the ground state energy of the deuteron.

**Problem 21.4 (a)** In Sec. 21.4 we have solved the  $H_2^+$  ion problem assuming linear combination of the  $1s$  hydrogen atom wave functions as trial function. In order to

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<sup>3</sup> In Problems 21.2(a) and 21.3(a) the values of  $V_0$  and  $a$  are chosen such that the minimum energy eigenvalue agrees with the experimental value.

obtain a better estimate of  $E_{\pm}$ , assume the trial function to be a linear combination of the following functions (see Eqs 32 and 33)

$$u_{1A} = \left(\alpha/\pi a_0^3\right)^{1/2} \exp\left[-\alpha \frac{r_A}{a_0}\right] \quad (47)$$

$$u_{1B} = \left(\alpha/\pi a_0^3\right)^{1/2} \exp\left[-\alpha \frac{r_B}{a_0}\right] \quad (48)$$

with  $\alpha$  as the variational parameter. Show that for  $\alpha \approx 1.238$  the minimum value of  $E_+$  ( $= -15.95$  eV) is obtained; Calculate the corresponding dissociation energy and the separation between the two protons and compare with the experimental values given in Sec. 21.4.

(b) If the minimum value of  $E_+$  is obtained for  $R = R_0$  then

$$\frac{dE_+}{dR} \Big|_{R=R_0} = 0 \quad (49)$$

and we may write

$$E_+ = E_0 + \frac{1}{2} k (R - R_0)^2 \quad (50)$$

where  $E_0 \approx -15.95$  eV. From the calculations in part (a) of the problem, obtain the value of  $k$ . Compare the above equation with Eq. (90) of Chapter 10 and obtain the zero-point energy corresponding to the vibrational motion. Add this to  $E_+$  to obtain a better estimate for the dissociation energy. The discussion of the hydrogen ion problem (Solution 21.4) is based on the analysis given in Ref. 3.

**Problem 21.5** For the hydrogen molecule problem discussed in Problem 19.15, estimate the ground state energy by assuming a trial function of the form

$$\phi = u_0(\mathbf{r}_1, \mathbf{r}_2) (1 + AH') \quad (51)$$

where  $H'$  is given by Eq. (96) of Chapter 19,  $A$  is the variational parameter<sup>4</sup> (assumed to be real) and

$$u_0(\mathbf{r}_1, \mathbf{r}_2) = u_{100}(\mathbf{r}_1) u_{100}(\mathbf{r}_2) \quad (52)$$

$u_{100}(\mathbf{r}_1)$  and  $u_{100}(\mathbf{r}_2)$  being the wave functions corresponding to the ground state of the hydrogen atom, the coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are defined in Fig. 19.2.

<sup>4</sup> This problem is adapted from Ref. 2; the justification for such a choice of the trial function is also given there.

## 21.9. Solutions

**Solution 21.2 (a)** The solution of the radial part of the Schrodinger equation for the square well potential is discussed in Problem 10.4 (with  $b = 0$ ). We write  $E = -B$  where  $B$  is the binding energy of the deuteron. The equation that determines the energy eigenvalues for  $l = 0$  is

$$\cot k_1 a = -\kappa/k_1 = -[B/(V_0 - B)]^{1/2} \quad (53)$$

where  $\kappa^2 = 2\mu B/\hbar^2$  and  $k_1^2 = 2\mu(V_0 - B)/\hbar^2$ . Now  $\mu = (m_n m_p)/(m_n + m_p) \approx 0.8369 \times 10^{-24}$  gm. For  $V_0 \simeq 40$  MeV,  $a \simeq 1.896 \times 10^{-13}$  cm we obtain  $B \simeq 2.223$  MeV.

**(b)** The normalized trial wave function is given by

$$\phi = \left[ \frac{\beta^3}{\pi a^3} \right]^{1/2} \exp[-\beta r/a] \quad (54)$$

Thus

$$E_\beta = \frac{\beta^3}{\pi a^3} \int_0^\infty e^{-\beta r/a} \left[ -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) - V(r) \right] e^{-\beta r/a} 4\pi r^2 dr \quad (55)$$

Substituting for  $V(r)$  from Eq. (44) and carrying out the integration, we get

$$E_\beta = \frac{\hbar^2}{2\mu a^2} [\beta^2 - 2\gamma \{1 - (1 + 2\beta + 2\beta^2) e^{-2\beta}\}] \quad (56)$$

where

$$\gamma = \frac{\mu V_0 a^2}{\hbar^2} \simeq 1.73 \quad (57)$$

The minimum occurs when  $dE_\beta/d\beta = 0$  giving

$$\beta e^{-2\beta} = \frac{1}{4\gamma} = 0.1445 \quad (58)$$

On solving the above equation we get  $\beta \simeq 0.93$ . Thus

$$E_\beta \simeq -1.43 \text{ MeV}$$

As can be seen the error is quite large which is due to the fact that the choice of the trial function is poor.

**Solution 21.3 (a)** Referring to the solution of Problem 10.8, we have

$$g = \left[ \frac{8\mu V_0 a^2}{\hbar^2} \right]^{1/2} \simeq 3.64 \quad (59)$$

The solution of the equation  $J_v(g) = 0$  gives

$$v = \left[ \frac{8\mu Ba^2}{\hbar^2} \right]^{1/2} \simeq 0.858 \quad (60)$$

giving  $B = 2.223$  MeV.

**(b)** We substitute for  $V(r)$  from Eq. (46) in Eq. (55) and carry out the integration to obtain

$$E_\beta = \frac{\hbar^2}{2\mu a^2} \left[ \beta^2 - \frac{8\gamma\beta^3}{(1+2\beta)^3} \right] \quad (61)$$

where

$$\gamma = \frac{\mu V_0 a^2}{\hbar^2} \simeq 1.655$$

The minimum occurs when  $dE_\beta/d\beta = 0$  giving

$$\frac{(1+2\beta)^4}{\beta} = 24\gamma = 39.73 \quad (62)$$

On solving the above equation we get  $\beta = 0.6088$ . Thus

$$E_\beta = -2.14 \text{ MeV}$$

**Solution 21.4** The analysis is similar to the one given in Sec. 21.4; the result for  $E_+$  is

$$E_+ = \left[ -\frac{\alpha^2}{2} + \frac{\alpha(\alpha-1) - \frac{\alpha}{\zeta} \left\{ 1 - (1+\zeta)e^{-2\zeta} \right\} + \alpha(\alpha-2)(1+\zeta)e^{-\zeta}}{1 + \left( 1 + \zeta + \frac{1}{3}\zeta^2 \right) e^{-\zeta}} + \frac{\alpha}{\zeta} \right] \frac{e^2}{a_0} \quad (63)$$

where  $\zeta = \alpha\xi = \alpha R/a_0$ . For  $\alpha = 1$  we will get the results of Sec. 21.4. Now we may write the above equation in the form

$$E_+ = \alpha F_1(\zeta) + \alpha^2 F_2(\zeta) \quad (64)$$

where

$$F_1(\zeta) = \left[ \frac{-1 - \frac{1}{\zeta} \left\{ 1 - (1+\zeta)e^{-2\zeta} \right\} - 2(1+\zeta)e^{-\zeta}}{1 + \left( 1 + \zeta + \frac{1}{3}\zeta^2 \right) e^{-\zeta}} + \frac{1}{\zeta} \right] \frac{e^2}{a_0} \quad (65)$$

and

$$F_2(\zeta) = \left[ -\frac{1}{2} + \frac{1 + (1+\zeta)e^{-\zeta}}{1 + \left( 1 + \zeta + \frac{1}{3}\zeta^2 \right) e^{-\zeta}} \right] \frac{e^2}{a_0} \quad (66)$$

We take  $\alpha$  and  $\zeta$  as two independent parameters. Setting  $dE_+/d\alpha = 0$ , we get

$$\alpha = -F_1(\zeta)/2F_2(\zeta) \quad (67)$$

Thus

$$E_+ = -\frac{[F_1(\zeta)]^2}{4F_2(\zeta)} \quad (68)$$

The above two equations enable us to plot  $\alpha$  and  $E_+$  as a function of  $\zeta$  (see Fig. 21.3) the minimum value of  $E_+$  ( $\simeq -0.5865 \frac{e^2}{a_0} \simeq -15.95$  eV) occurs at

$$\zeta \simeq 2.48 \quad \text{for which } \alpha \simeq 1.238$$

Thus

$$\text{Dissociation energy} = E_H - E_{H_2^+} \simeq -13.6 + 15.95 \text{ eV} = 2.35 \text{ eV}$$

$$R = \frac{\zeta}{\alpha} a_0 \simeq 2.003 a_0 \approx 1.06 \text{ \AA}$$

(b) Following Ref. 3, we fit the curve for  $E_+$  to a parabola (around the minimum value) and one can show

$$\begin{aligned} E_+ &\approx [-0.5865 + 0.050(\zeta - 2.48)^2] \frac{e^2}{a_0} \\ &\approx [-0.5865 + 2.74 \times 10^{15}(R - 1.06 \times 10^{-8})^2] \frac{e^2}{a_0} \end{aligned}$$

where  $R$  is in centimeters. Thus

$$\frac{d^2E_+}{dR^2} \approx 1.19 \times 10^5 \text{ ergs/cm}^2$$

Since  $\mu = m_n m_p / (m_n + m_p) \approx 0.837 \times 10^{-24}$  gm, we have using Eq. (99) of Chapter 10, the following value for the zero-point energy

$$\begin{aligned} E_{vib} &= \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \approx \frac{1}{2} \times 10^{-27} \times \sqrt{\frac{1.19 \times 10^5}{0.837 \times 10^{-24}}} \\ &\approx 1.89 \times 10^{-13} \text{ erg} \approx 0.12 \text{ eV} \end{aligned}$$

Thus the dissociation energy becomes 2.23 eV.

### Solution 21.5

$$E_\phi = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau}$$

where  $H = H_0 + H'$  (see Problem 19.15),  $d\tau = d\mathbf{r}_1, d\mathbf{r}_2$  and the integral is over a six-dimensional space. Now

$$u_0 = u_{100}(\mathbf{r}_1) u_{100}(\mathbf{r}_2) = \frac{1}{\pi a_0^3} \exp\left(-\frac{r_1 + r_2}{a_0}\right)$$

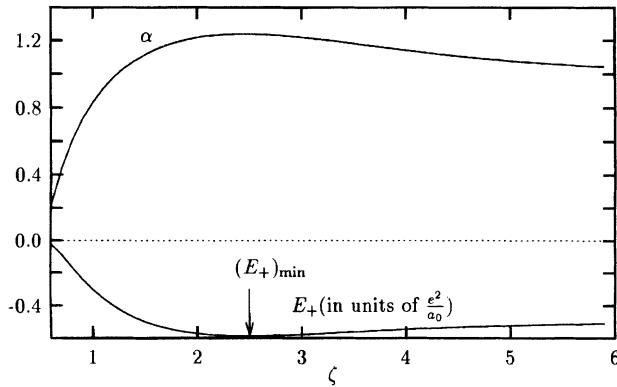


Figure 21.3. The variation of  $E_+$  and  $\alpha$  with  $\zeta$ . The minimum value of  $E_+$  ( $\simeq -0.5865 \frac{e^2}{a_0} \simeq -15.95 \text{ eV}$ ) occurs at  $\zeta = 2.48$  at which  $\alpha = 1.238$ .

and

$$H_0 u_0 = E_0 u_0, \quad E_0 = -\frac{e^2}{2a_0} - \frac{e^2}{2a_0} = -\frac{e^2}{a_0}$$

Thus

$$\begin{aligned} \int \phi^* \phi \, d\tau &= \int u_0^2 \, d\tau + 2A \int u_0 H' u_0 \, d\tau + A^2 \int u_0 H'^2 u_0 \, d\tau \\ &= 1 + A^2 \int u_0 H'^2 u_0 \, d\tau \end{aligned}$$

where we have used the relation

$$\int u_0 H' u_0 \, d\tau = 0$$

which can be verified by direct integration. Further,

$$\begin{aligned} \int \phi^* H \phi \, d\tau &= \int u_0 (1 + AH') (H_0 + H') u_0 (1 + AH') \, d\tau \\ &= \int u_0 H_0 u_0 \, d\tau + \int u_0 H' u_0 \, d\tau \\ &\quad + A \left[ \int u_0 H' H_0 u_0 \, d\tau + \int u_0 H_0 (u_0 H') \, d\tau \right] \\ &\quad + \int u_0 H' u_0 H' \, d\tau + \int u_0 H'^2 u_0 \, d\tau \Big] \\ &\quad + A^2 \left[ \int u_0 H' H_0 (u_0 H') \, d\tau + \int u_0 H'^3 u_0 \, d\tau \right] \\ &= E_0 + \left[ E_0 + A \int u_0 H' u_0 \, d\tau + E_0 \int u_0 u_0 H' \, d\tau \right] \end{aligned}$$

$$\begin{aligned}
 & + 2 \int u_0 H'^2 u_0 d\tau \Big] \\
 & = E_0 + 2A \int u_0 H'^2 u_0 d\tau
 \end{aligned}$$

the other integrals going to zero. Thus

$$\begin{aligned}
 E_\phi &= \frac{E_0 + 2A \int u_0 H'^2 u_0 d\tau}{1 + A^2 \int u_0 H'^2 u_0 d\tau} \\
 &\approx E_0 + (2A - A^2 E_0) \int u_0 H'^2 u_0 d\tau
 \end{aligned}$$

Setting  $dE/dA = 0$ , we get  $A = 1/E_0$  thus the minimum value of  $E_\phi$  is given by

$$E_\phi = E_0 + \frac{1}{E_0} \int u_0 H'^2 u_0 d\tau$$

The integral is evaluated in Problem 19.15, on substitution we get

$$E_\phi = E_0 - \frac{6e^2 a_0^5}{R^6}$$

Combining the result of Problem 19.15 we may write

$$E_0 - \frac{8e^2 a_0^5}{R^6} < \text{Ground state Energy} < E_0 - \frac{6e^2 a_0^5}{R^6}$$


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## 21.10. References and suggested reading

1. L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Co., New York (1935).
2. L.I. Schiff, *Quantum Mechanics*, McGraw-Hill Book Co., New York (1968).
3. S. Flugge, *Practical Quantum Mechanics*, Springer Verlag, New York (1974).

# Chapter 22

## The Helium Atom and the Exclusion Principle

... According to this point of view the doublet structure of alkali spectra as well as the deviation from Larmor's theorem is due to a particular two-valuedness of the quantum theoretic properties of the electron, which cannot be described from the classical point of view.

— WOLFGANG PAULI (1924).

### 22.1. Introduction

Schrödinger's equation, as we have seen in chapter 10, gives the same energies for the hydrogen atom as the Bohr model. It is only when we consider many electron systems that new effects are manifest, the most important being those due to the Pauli exclusion principle which is fundamental to an understanding of the building up of the periodic table. In this chapter, we shall first consider the ground state of a two-electron system, namely the helium atom and then go on to examine a few excited states in order to understand the basic principles of the study of atomic structure.

### 22.2. The independent particle approximation

The potential energy of the helium-like atom contains an extra term, apart from the-electron nucleus interaction: namely, the repulsive energy of the two electrons. The Hamiltonian is

$$\begin{aligned} H &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \\ &= -\frac{\hbar^2}{2m} [\nabla_1^2 + \nabla_2^2] - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \end{aligned} \quad (1)$$

Here  $\mathbf{r}_1$  and  $\mathbf{r}_2$  represent the coordinates of the two electrons with respect to the nucleus (which is assumed to be stationary) and  $\mathbf{r}_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  is the distance between the two electrons—see Fig. 22.1; for the helium atom,  $Z = 2$ . Now the term  $e^2/r_{12}$  is of the same order of magnitude as the other two terms in the potential energy; nevertheless, we shall begin by neglecting it. (We shall see, later, how to incorporate this term). The resulting approximation may be called the *independent particle model*. In this approximation, the Schrödinger equation

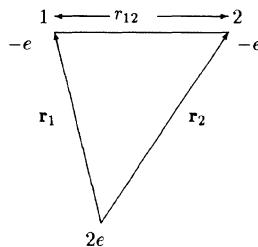


Figure 22.1. The helium atom consists of a nucleus of charge  $2e$  and two electrons.

$$\left( -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} \right) u(\mathbf{r}_1, \mathbf{r}_2) = E u(\mathbf{r}_1, \mathbf{r}_2) \quad (2)$$

may be separated by writing

$$u(\mathbf{r}_1, \mathbf{r}_2) = u_a(\mathbf{r}_1) u_b(\mathbf{r}_2) \quad (3)$$

giving identical equations for  $u_a$  and  $u_b$ :

$$\left( -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{r_1} \right) u_a(\mathbf{r}_1) = E_a u_a(\mathbf{r}_1) \quad (4)$$

$$\left( -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{r_2} \right) u_b(\mathbf{r}_2) = E_b u_b(\mathbf{r}_2) \quad (5)$$

with

$$E = E_a + E_b \quad (6)$$

Equations (4) and (5) tell us that the two electrons 1 and 2 move independently of each other and the total energy of the system is simply the sum of the energies of the non-interacting electrons.

Since Eqs. (4) and (5) are the same as for a hydrogen-like atom, the solutions are immediately written down (see Sec. 10.2)

$$u_a(\mathbf{r}_1) = R_{n_1 l_1}(r_1) Y_{l_1 m_1}(\theta_1, \phi_1) \quad (7)$$

and a similar expression for  $u_b(\mathbf{r}_2)$ . A particular eigenstate is characterised by specifying  $a$  and  $b$ , i.e. by specifying the two sets of quantum numbers  $n_1, l_1, m_1$  and  $n_2, l_2, m_2$ .

Similarly, the energy eigenvalues can easily be written down. Both  $E_a$  and  $E_b$  would be of the form<sup>1</sup>

$$E_n = -\frac{Z^2}{n^2} \frac{me^4}{2\hbar^2} = -\frac{Z^2}{n^2} E_H \quad (8)$$

where

$$E_H = \frac{me^4}{2\hbar^2} \simeq 13.605 \text{ eV} \quad (9)$$

represents the ionization energy of the hydrogen atom. In this approximation, then the ground state is the one with both electrons in the 1s state (designated as the  $1s^2$  configuration), the total energy being (for  $Z = 2$ )

$$-4 E_H - 4 E_H = -108.8 \text{ eV} \quad (10)$$

This is to be compared with the observed value of  $-79.0 \text{ eV}$ .

### 22.3. Electron interaction energy

One way to estimate this is to regard  $e^2/r_{12}$  as a perturbation. The first order correction to the ground state energy is, then

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \iint u_{100}^*(\mathbf{r}_1) u_{100}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} u_{100}(\mathbf{r}_1) u_{100}(\mathbf{r}_2) d\tau_1 d\tau_2 \quad (11)$$

which has been evaluated in Problem 22.1, the result is

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{5Z}{4} E_H \approx 34.02 \text{ eV} \quad (12)$$

where we have assumed  $Z = 2$ . Thus the total energy is  $-74.8 \text{ eV}$ , only  $4.2 \text{ eV}$  above the experimental value. Such a large “correction” makes the perturbation approach suspect and we turn to other methods.

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<sup>1</sup> The Hamiltonian given by Eq. (1) assumes infinite mass of the nucleus. The effect of the finite mass of the nucleus can be approximately taken into account by replacing the electron mass  $m$  by the reduced mass  $\mu$  ( $= mM/(m + M)$ ) where  $M$  is the mass of the nucleus – see Problem 22.6 (cf. Sec. 10.2).

## 22.4. Variational method

The effect of the repulsive term,  $e^2/r_{12}$ , is to reduce the nuclear attraction on each electron. One way to accommodate this is to assume hydrogen-like wave functions corresponding to an effective nuclear charge  $Z'$ , which will be assumed to be a variable parameter. Thus, we assume the (normalized) wave function as [cf. Eq. (65) of chapter 10]:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \left( \frac{Z'^3}{\pi a_0^3} \right) e^{-Z'r_1/a_0} e^{-Z'r_2/a_0} \quad (13)$$

The Hamiltonian, however, remains as in Eq. (1) with  $Z$  as a *fixed* number; for He,  $Z = 2$ . We have to minimise the integral (see Secs 21.2 and 21.4):

$$\begin{aligned} E(Z') = \iint \Phi^* \left[ -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - Ze^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \right. \\ \left. + \frac{e^2}{r_{12}} \right] \Phi(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2 \end{aligned} \quad (14)$$

which has been evaluated in Problem 22.2. The result is

$$E(Z') = \left[ -2Z'^2 + 4Z'(Z' - Z) + \frac{5}{4}Z' \right] E_H \quad (15)$$

The minimum of  $E(Z')$  occurs when

$$Z' = Z_{\text{eff}} = Z - \frac{5}{16} \approx 1.69 \quad (16)$$

so that

$$\begin{aligned} E &= -2 Z_{\text{eff}}^2 E_H \\ &\approx -76.2 \text{ eV} \end{aligned} \quad (17)$$

Other trial functions (having more complicated forms) have also been used, some yielding values within 0.01% of the observed one—see Table 21.1.

## 22.5. Exchange degeneracy and identical particles

In Sec. 22.2 we saw that in the independent particle model, the wave function

$$u_a(\mathbf{r}_1) u_b(\mathbf{r}_2) \quad (18)$$

is a solution of the Schrödinger equation corresponding to the energy  $E = E_a + E_b$ . Since the Schrödinger equation [Eq. (2)] is completely symmetrical in the two electrons, it is obvious that the wave function<sup>2</sup>

$$u_b(\mathbf{r}_1) u_a(\mathbf{r}_1) \quad (19)$$

is also a solution of the Schrödinger equation corresponding to the *same* eigenvalue  $E_a + E_b$ . Thus we have a degeneracy which is known as the *exchange degeneracy* because it arises due to the possibility of exchanging the two electrons.<sup>3</sup> We could also construct the linear combinations

$$u_+ = \frac{1}{\sqrt{2}} [u_a(\mathbf{r}_1) u_b(\mathbf{r}_2) + u_a(\mathbf{r}_2) u_b(\mathbf{r}_1)] \quad (20)$$

$$u_- = \frac{1}{\sqrt{2}} [u_a(\mathbf{r}_1) u_b(\mathbf{r}_2) - u_a(\mathbf{r}_2) u_b(\mathbf{r}_1)] \quad (21)$$

which are also solutions of Eq. (2) belonging to the same energy  $E_a + E_b$ ; the factor  $\frac{1}{\sqrt{2}}$  has been introduced so that the wave functions are normalized. The solutions  $u_+$  and  $u_-$  are known as the symmetric and antisymmetric solutions because when the indices 1 and 2 are interchanged,  $u_+$  remains the same whereas  $u_-$  changes sign. We will shortly see that it is essential that we use either the symmetrical or antisymmetrical solution rather than solutions given by Eq. (18) and Eq. (19) which are neither symmetric nor antisymmetric. This is due to the indistinguishability of identical particles like electrons. It may be mentioned that in classical mechanics, identical particles are always distinguishable in the sense that it is possible to keep track of individual particles. However, in quantum mechanics, since it is not possible to keep track of individual particles (without disturbing the system), identical particles are indistinguishable. Thus considering a two-electron system, if the two electrons are interchanged, we must get the same wave function except (possibly) for an unimportant phase factor<sup>4</sup>, i.e.

$$u(\mathbf{r}_1, \mathbf{r}_2) = e^{i\phi} u(\mathbf{r}_2, \mathbf{r}_1) \quad (22)$$

where  $\phi$  is a real constant. Now, if  $P_{12}$  represents the particle interchange operator then

$$P_{12} u(\mathbf{r}_1, \mathbf{r}_2) = u(\mathbf{r}_2, \mathbf{r}_1) \quad (23)$$

<sup>2</sup> The wave function given by Eq. (18) corresponds to the state where the first electron is in the state  $a$  and the second electron in the state  $b$  whereas Eq. (19) corresponds to the first electron in state  $b$  and the second electron in state  $a$ .

<sup>3</sup> The exchange degeneracy exists as long as we neglect the electron-electron interaction. If the interaction between electrons is taken into account, the levels, in general, will split up (see Sec. 22.6).

<sup>4</sup> One could also argue that the probability of finding the first electron at  $\mathbf{r}_1$  and the second electron at  $\mathbf{r}_2$  must be equal to the probability of finding the first electron at  $\mathbf{r}_2$  and the second electron at  $\mathbf{r}_1$  giving

$$|u(\mathbf{r}_1, \mathbf{r}_2)|^2 = |u(\mathbf{r}_2, \mathbf{r}_1)|^2$$

which would lead to Eq. (22).

and

$$P_{12}^2 u(\mathbf{r}_1, \mathbf{r}_2) = P_{12} u(\mathbf{r}_2, \mathbf{r}_1) = u(\mathbf{r}_1, \mathbf{r}_2) \quad (24)$$

Further

$$\begin{aligned} P_{12}^2 u(\mathbf{r}_1, \mathbf{r}_2) &= P_{12} u(\mathbf{r}_2, \mathbf{r}_1) = e^{-i\phi} P_{12} u(\mathbf{r}_1, \mathbf{r}_2) \\ &= e^{-i\phi} u(\mathbf{r}_2, \mathbf{r}_1) \\ &= e^{-2i\phi} u(\mathbf{r}_1, \mathbf{r}_2) \end{aligned}$$

Thus

$$e^{-2i\phi} = +1 \text{ or } e^{i\phi} = \pm 1$$

giving

$$u(\mathbf{r}_1, \mathbf{r}_2) = \pm u(\mathbf{r}_2, \mathbf{r}_1) \quad (25)$$

The above equation shows that the wave function should be either symmetrical or antisymmetrical with respect to the interchange of the indices.

It may be mentioned that if the two particles are in the symmetric (or antisymmetric) state then they will remain in the symmetric (or antisymmetric) state for all times. This follows from the Schrödinger equation

$$\dot{\Psi} = \frac{1}{i\hbar} H \Psi \quad (26)$$

implying that  $\dot{\Psi}$  has the same symmetry as  $\Psi$  (because  $H$  is always symmetrical with respect to the change of indices as the two electrons are identical; see, e.g. Eq. (1)). Hence if  $\Psi(\mathbf{r}_1, \mathbf{r}_2, t = 0)$  is symmetric then it will remain symmetric at  $\Delta t$  and so on.

## 22.6. The Pauli exclusion principle

Till now we have not considered the spin angular momentum associated with the electron. We denote the spin functions by  $|\chi_{\pm}\rangle$  where  $|\chi_+\rangle$  and  $|\chi_-\rangle$  represent the spin up and spin down states.<sup>5</sup> For the two electron system, the spin functions are  $|\chi_{\pm}(1)\rangle$  and  $|\chi_{\pm}(2)\rangle$  where the numbers in the parenthesis refer to the first and second electron. Because of the indistinguishability of the electrons, we must construct appropriate linear combinations which are either symmetric or antisymmetric with respect to the interchange of indices; these states are denoted by

$$|\chi_t^+\rangle = |\chi_+(1)\chi_+(2)\rangle = |1\uparrow 2\uparrow\rangle \quad (27)$$

---

<sup>5</sup> Thus, if the electron is in the spin up (or spin down) state then the measurement of the  $z$ -component of the spin angular momentum will lead to  $+\frac{1}{2}\hbar$  (or  $-\frac{1}{2}\hbar$ ). At some places it will be convenient to designate the states  $|\chi_+\rangle$  and  $|\chi_-\rangle$  as  $|\uparrow\rangle$  and  $|\downarrow\rangle$  respectively.

$$|\chi_t^-\rangle = |\chi_-(1)\chi_-(2)\rangle = |1\downarrow 2\downarrow\rangle \quad (28)$$

$$\begin{aligned} |\chi_t^0\rangle &= \frac{1}{\sqrt{2}} [|\chi_+(1)\chi_-(2)\rangle + |\chi_-(1)\chi_+(2)\rangle] \\ &= \frac{1}{\sqrt{2}} [|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle] \end{aligned} \quad (29)$$

$$\begin{aligned} |\chi_s\rangle &= \frac{1}{\sqrt{2}} [|\chi_+(1)\chi_-(2)\rangle - |\chi_-(1)\chi_+(2)\rangle] \\ &= \frac{1}{\sqrt{2}} [|1\uparrow 2\downarrow\rangle - |1\downarrow 2\uparrow\rangle] \end{aligned} \quad (30)$$

the first three functions being symmetric and the last one being antisymmetric. The first function, for example, corresponds to both the functions being in the spin up state and so on.

Now, in Sec. 18.3 we had seen that the first three states (known as the triplet state) corresponds to total spin  $S = 1$  and the fourth state (known as the singlet state) corresponds to the total spin  $S = 0$ ; in Eqs (27)–(29),  $\chi_t^+$ ,  $\chi_t^0$  and  $\chi_t^-$  correspond to  $S = 1$  (with  $m_s = 1, 0, -1$ ) and  $\chi_s$  correspond to  $S = 0$ .

We consider the ground state ( $1s^2$ ) of the helium atom. The total wave function will be

$$u_{100}(\mathbf{r}_1) u_{100}(\mathbf{r}_2) \quad (31)$$

multiplied by the appropriate spin function. Now, it is an experimental fact that the ground state of the helium atom does not split up in a magnetic field; consequently it must be a singlet rather than a triplet state, i.e. we must have the following wave function representing the ground state

$$u_{100}(\mathbf{r}_1) u_{100}(\mathbf{r}_2) \frac{1}{\sqrt{2}} [|\chi_+(1)\chi_-(2)\rangle - |\chi_-(1)\chi_+(2)\rangle] \quad (32)$$

Thus the ground state wave function is antisymmetric.<sup>6</sup> Analysis of higher excited states of helium (and also of other atoms) shows that *the wave function for a system of electrons must be antisymmetric with respect to the interchange of two electrons*. Consequently, if the space dependent function is symmetric then the spin function should be antisymmetric and vice versa. The general wave function (for a 2 electron system) should therefore be of the form

<sup>6</sup> The ground state is denoted by  ${}^1S_0$ . The superscript 1 denotes a singlet (total spin = 0), S denotes  $L = 0$ , the subscript 0 is to indicate  $J = 0$ . It is unfortunate that an S state here may be confused with total spin; certain conventions have to be adhered to, however!

$$\psi = \frac{1}{\sqrt{2}} [\psi_a(1) \psi_b(2) - \psi_b(1) \psi_a(2)] \quad (33)$$

where the subscripts  $a$  and  $b$  include the spin state, i.e. they represent  $n, l, m$  and  $m_s$ . It is obvious that if  $a = b$  (i.e. if both the electrons have the same set of values of  $n, l, m$  and  $m_s$ ) then

$$\psi = 0$$

which is the Pauli exclusion principle<sup>7</sup> according to which in an atom no two electrons can have the same set of values of the four quantum numbers  $n, l, m$  and  $m_s$ . Thus the antisymmetric nature of the total wave function leads automatically to the Pauli exclusion principle.

For a system of  $N$  electrons, the antisymmetric wave function is given by the Slater determinant

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{a_1}(1) & \psi_{a_1}(2) & \dots & \psi_{a_1}(N) \\ \psi_{a_2}(1) & \psi_{a_2}(2) & \dots & \\ \vdots & & & \\ \psi_{a_N}(1) & \dots & & \psi_{a_N}(N) \end{vmatrix} \quad (34)$$

It is immediately obvious that if  $a_1 = a_2$  then the two rows would become the same and the determinant would vanish.

Particles that are described by antisymmetric wave functions are known as Fermions and they are said to obey Fermi-Dirac statistics; examples of such particles are electrons, protons, neutrons, etc. On the other hand, particles which are

<sup>7</sup> At this stage it may be worthwhile to mention that Pauli had put forward the exclusion principle before Uhlenbeck and Goudsmidt had introduced the idea of the spinning electron. In order to give satisfactory explanations of the spectra of alkali atoms and of the anomalous Zeeman effect, Pauli argued that for a general classification of each of the electron in an atom, four quantum numbers are needed. In his Nobel lecture, Pauli mentions that "I proposed the assumption of a new quantum theoretic property of the electron, which I called *a two valuedness not describable classically*". He then put forward his exclusion principle according to which there can never be two or more equivalent electrons in an atom which have the same values of all four quantum numbers. Pauli in his Nobel lecture also mentions that "the physicists found it difficult to understand the exclusion principle, since no meaning in terms of a model was given to the fourth degree of freedom of the electron. The gap was filled by Uhlenbeck and Goudsmidt's idea of the electron spin which made it possible to understand the anomalous Zeeman effect simply by assuming that the spin quantum number of one electron is  $\frac{1}{2}$  and that the quotient of the magnetic moment to the mechanical angular moment has for the spin a value twice as large as for the ordinary orbit of the electron". For a nice discussion on the historical development, the reader is referred to the Nobel lecture of Pauli and to Ref 1 and 2; the original article of Pauli has been reprinted in Ter Haar's book (Ref. 1).

described by symmetric wave functions are known as *Bosons* and they are said to obey Bose-Einstein statistics; examples of such particles are photons, pions, etc. Pauli has proved that particles with half integral spin are Fermions and particles with integral spin are Bosons; the proof is, however, much beyond the scope of this book.

## 22.7. Excited states of helium<sup>8</sup>

For the first excited state, we have the possible configurations  $1s2s$  and  $1s2p$ . Once again, if we ignore the electron-electron interaction, we have the independent particle model and the spatial part of the wave functions would be of the form

$$u_{100}(\mathbf{r}_1) \ u_{2l0}(\mathbf{r}_2) \quad (35)$$

where  $l = 0$  for  $2s$  and  $l = 1$  for  $2p$  states. This wave function, however, does not have the symmetry property required and the correct combinations are

$$u_+ = \frac{1}{\sqrt{2}} [u_{100}(\mathbf{r}_1) \ u_{2l0}(\mathbf{r}_2) + u_{100}(\mathbf{r}_2) \ u_{2l0}(\mathbf{r}_1)] \quad (36)$$

and

$$u_- = \frac{1}{\sqrt{2}} [u_{100}(\mathbf{r}_1) \ u_{2l0}(\mathbf{r}_2) - u_{100}(\mathbf{r}_2) \ u_{2l0}(\mathbf{r}_1)] \quad (37)$$

(For the ground state  $1s^2$  configuration,  $u_-$  would vanish identically).

We now incorporate spin wave functions. We have already seen that the singlet state  $|\chi_s\rangle$  is antisymmetric and the triplet state is symmetric  $|\chi_t\rangle$  (see Eqs (27)–(30)). In accordance with the exclusion principle, only the following antisymmetric combinations are permissible

$$\psi_s = u_+ |\chi_s\rangle \quad (\text{singlet}) \quad (38)$$

$$\psi_t = u_- |\chi_t\rangle \quad (\text{triplet}) \quad (39)$$

where the subscripts  $s$  and  $t$  refer to the singlet and triplet states respectively. Now, if we ignore the interaction of the electrons, these four states are degenerate; its inclusion lifts the degeneracy. Qualitatively, we can see this as follows. For a space symmetric wave function, there is a considerable probability for the two electrons to come close together (i.e.  $u_+$  can be large for  $\mathbf{r}_1 \approx \mathbf{r}_2$ ) whereas for the space antisymmetric state, this probability is quite small. Thus, the repulsive energy of the two electrons gives a larger positive contribution for  $u_+$  than for  $u_-$ .

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<sup>8</sup> The ground state of lithium and the corresponding exchange correction has been discussed Ref. 3.

One, therefore, expects triplet states to lie lower than the singlet ones. We must emphasize that this difference in energy is *not* due to spin dependent forces but is a consequence of the exclusion principle and the electrostatic interaction of the two electrons.

The configuration  $1s2s$  gives the singlet state  ${}^1S_0$  and the triplet  ${}^3S_1$  since we have  $L = 0$  and  $S = 0$  or  $1$ , the subscript gives the  $J$  value. One can estimate the difference in their energies by a perturbation calculation. The first order correction to their energy is

$$\Delta E_s = \iint u_+^* \frac{e^2}{r_{12}} u_+ d\tau_1 d\tau_2 \quad (\text{singlet}) \quad (40)$$

$$\Delta E_t = \iint u_-^* \frac{e^2}{r_{12}} u_- d\tau_1 d\tau_2 \quad (\text{triplet}) \quad (41)$$

where

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| = r_{21}$$

Since<sup>9</sup>

$$\langle \chi_s | \chi_s \rangle = 1 = \langle \chi_t | \chi_t \rangle \quad (42)$$

and since  $e^2/r_{12}$  does not involve spin, only the space part of the wave function appears in the perturbation calculation. Next, we substitute for  $u_+$  and  $u_-$  (from Eqs (36) and (37) with  $l = 0$ ) in Eqs (40) and (41) to obtain

$$\Delta E_s = J_0 + K_0 \quad (43)$$

$$\Delta E_t = J_0 - K_0 \quad (44)$$

where

$$J_l = e^2 \iint u_{100}^*(\mathbf{r}_1) u_{2l0}^*(\mathbf{r}_2) \frac{1}{r_{12}} u_{100}(\mathbf{r}_1) u_{2l0}(\mathbf{r}_2) d\tau_1 d\tau_2 \quad (45)$$

and

$$K_l = e^2 \iint u_{100}^*(\mathbf{r}_1) u_{2l0}^*(\mathbf{r}_2) \frac{1}{r_{12}} u_{100}(\mathbf{r}_2) u_{2l0}(\mathbf{r}_1) d\tau_1 d\tau_2 \quad (46)$$

and in arriving at Eqs (43) and (44) we have used the fact that in the integrals  $J_l$  and  $K_l$ , we can interchange  $\mathbf{r}_1$  and  $\mathbf{r}_2$ .

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<sup>9</sup> It is because of the relation  $\langle \chi_s | \chi_s \rangle = 1$  that the perturbation to the ground state energy will be simply Eq. (11) although the ground state wave function is given by Eq. (32).

The integral  $J_l$  (for  $l = 0$ ) is of the same type as we had encountered in the ground state energy shift calculation, the term  $K_l$  is known as the *exchange integral*. The evaluation is tedious but straightforward and yields

$$\begin{aligned} J_0 &\approx 9.1 \text{ eV} \\ K_0 &\approx 0.4 \text{ eV} \end{aligned} \quad (47)$$

A similar treatment can be given for the  $1s2p$  configuration. Since  $l_1 = 0$  and  $l_2 = 1$ ,  $L = 1$  and for the singlet state ( $S = 0$ )  $J$  takes the value 1; on the other hand, for the triplet state ( $S = 1$ )  $J$  takes the values 2, 1, 0. Thus the possible states are

$$^1P_1 \text{ and } ^3P_{2,1,0}$$

(to be read as ‘singlet P one’ and ‘triplet P two, one and zero’). Again the triplet levels lie lower than the singlet state, in fact

$$J_1 \approx 10.2 \text{ eV} \quad K_1 \approx 0.1 \text{ eV} \quad (48)$$

The corresponding energy levels are given in Fig. 22.2 (see also Problem 22.4).

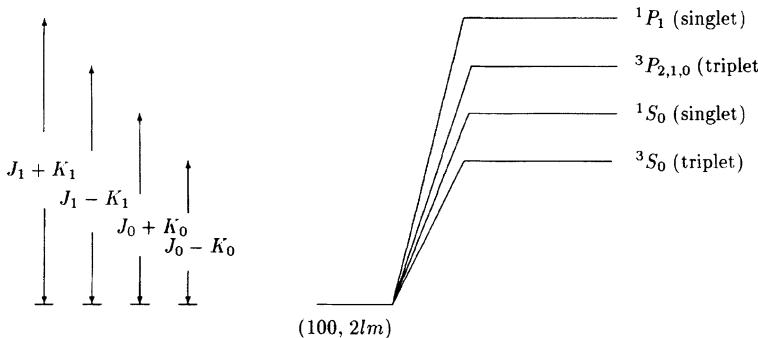


Figure 22.2. The splitting of the first excited state of the helium atom.

## 22.8. Fine structure

In order to remove the degeneracy within the triplet levels, it is necessary to include the spin-orbit interaction. This is the interaction between the magnetic moment (associated with spin) and the orbital motion of the electron and is represented by a term of the form<sup>10</sup>

$$\sum_i \xi(r_i) \mathbf{L} \cdot \mathbf{S} \quad (49)$$

<sup>10</sup>  $\mathbf{L}$ ,  $\mathbf{S}$  are the orbital and spin quantum numbers of the atom.

in the Hamiltonian. For a state with a particular value of  $L$ ,  $S$  and  $J$  we have

$$\langle \mathbf{L} \cdot \mathbf{S} \rangle = \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \quad (50)$$

which gives, 1, -1 and -2 for the  ${}^3P_2$ ,  ${}^3P_1$  and  ${}^3P_0$  states respectively. Writing

$$2\Gamma = \int d\tau \Psi^* \left( \sum_i \xi(r_i) \right) \Psi \quad (51)$$

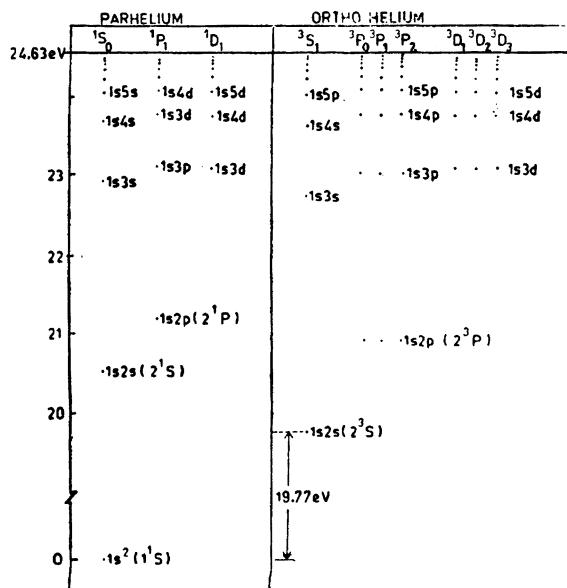
we have, for the spin-orbit correction,  $2\Gamma$ ,  $-2\Gamma$  and  $-4\Gamma$  for the above three terms giving the so called fine structure splitting which is  $\sim 10^{-4}$  eV. Finally, it may be pointed out that there is a further  $2J + 1$  degeneracy in each of these terms which can be removed by the application of a magnetic field. The total number of  ${}^3P$  states is  $5 + 3 + 1 = 9$ ; this is  $(2S+1)(2L+1)$  as may be expected.

## 22.9. Helium spectra

In order to compare the foregoing theory with experiment, we have to state the rules governing transitions between the various states. In the dipole approximation (to be discussed in Sec. 26.3), it can be shown that no transition occurs between singlet and triplet states. As a result, the energy level diagram of helium splits into two parts as shown in Fig. 22.3. The figure shows the energy levels when one of the electrons is in the  $1s$  state and the other in  $nl$  state. Note the following features.

1. Singlet levels, belonging to a particular value of  $n$  and  $l$  have higher energy than triplet levels of the same  $n$  and  $l$ .
2. For  $n = 2$ , the difference  $|S - {}^3S|$  is larger than  $|P - {}^3P|$  difference. This is because the exchange integral  $K$  for the  $P$  state is smaller; there is a smaller contribution from those regions where  $1/r_{12}$  is large.
3. The states  $2{}^3S$  and  $2{}^1S$  are *metastable*. The  $2{}^1S \rightarrow 1{}^1S$  transition is forbidden because of the selection rule  $\Delta l = \pm 1$  for dipole transitions and the  $2{}^3S \rightarrow 1{}^1S$  for this reason as well as the one mentioned earlier, forbidden triplet-singlet transitions. Thus helium exists as two ‘gases’ as it were, parahelium<sup>11</sup> atoms with  $S = 0$  and orthohelium with  $S = 1$ .

<sup>11</sup> Some earlier books called it parhelium.



*Figure 22.3.* The energy levels of the helium atom.

### 22.10. Problems

**Problem 22.1** Evaluate the integral in Eq. (11) and calculate the ground state energy of 2 electron systems like He, Li<sup>+</sup>, Be<sup>++</sup> and B<sup>+++</sup>. Determine the ionisation energy and compare with the corresponding experimental values which are 24.63 eV, 75.64 eV, 153.87 eV and 259.31 eV respectively.

**Problem 22.2** Evaluate the integral in Eq. (14) and calculate the ionisation energy for 2-electron systems. Compare with the corresponding result obtained by using perturbation theory.

### Problem 22.3

## Using the expressions

$$u_{100}(\mathbf{r}) = \frac{1}{\sqrt{4\pi}} \left( \frac{Z}{a_0} \right)^{3/2} 2 e^{-Zr/a_0} \quad (52)$$

$$u_{200}(\mathbf{r}) = \frac{1}{\sqrt{4\pi}} \left( \frac{Z}{2a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \quad (53)$$

and

$$u_{210}(\mathbf{r}) = \left( \frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{a_0\sqrt{3}} e^{-Zr/2a_0} \sqrt{\frac{3}{4\pi}} \cos\theta \quad (54)$$

evaluate the integrals in Eqs (45) and (46). [You will have to use the relation given by Eq. (63)]. For  $Z = 2$  show that

$$J_0 \approx 9.1 \text{ eV}$$

$$K_0 \approx 0.4 \text{ eV}$$

$$J_1 \approx 10.2 \text{ eV}$$

$$K_1 \approx 0.1 \text{ eV}$$

**Problem 22.4** Using the above values of  $J_0$ ,  $K_0$ ,  $J_1$  and  $K_1$  draw the energy levels of the  $1s2s$  and  $1s2p$  states of helium atom (see Fig. 22.2) and calculate the ionization energies of the corresponding states.

**Problem 22.5** In the independent particle model (see Sec. 22.2), the first excited state of the helium atom is 8-fold degenerate<sup>12</sup> (we are neglecting spin). In order to evaluate the electron interaction energy  $\langle e^2/r_{12} \rangle$  we must choose a representation in which the perturbation is diagonal. Show that, in order to make  $H'$  ( $= e^2/r_{12}$ ) diagonal we must choose the appropriate symmetric and antisymmetric forms [see Eqs (36) and (37)]. [Pauling and Wilson (Ref.4) have explicitly shown this by solving a  $8 \times 8$  determinant].

### Problem 22.6

(a) In the hydrogen atom problem we had shown that the two body problem can be reduced to a one body problem with electron mass replaced by the reduced mass. In the helium atom problem (which is a 3 body problem) one can approximately take into account the effect of nuclear motion in the following manner:

If  $\mathbf{R}_1$  and  $\mathbf{R}_2$  represent the position of the two electrons and  $\mathbf{R}_n$  that of the nucleus (of mass M) then the Hamiltonian is of the form

$$H = \frac{1}{2M} P_n^2 + \frac{1}{2m} (P_1^2 + P_2^2) - e^2 \left( \frac{2}{|\mathbf{R}_1 - \mathbf{R}_n|} + \frac{2}{|\mathbf{R}_2 - \mathbf{R}_n|} - \frac{1}{|\mathbf{R}_1 - \mathbf{R}_2|} \right) \quad (55)$$

where

$$\begin{aligned} P_i^2 &= -\hbar^2 \left[ \frac{\partial^2}{\partial X_i^2} + \frac{\partial^2}{\partial Y_i^2} + \frac{\partial^2}{\partial Z_i^2} \right] \\ &= -\hbar^2 \frac{\partial^2}{\partial \mathbf{R}_i^2} \quad i = n, 1 \text{ and } 2 \end{aligned} \quad (56)$$

Introduce the coordinates

$$\mathbf{r}_1 = \mathbf{R}_1 - \mathbf{R}_n, \mathbf{r}_2 = \mathbf{R}_2 - \mathbf{R}_n \quad (57)$$

and the center of mass coordinate  $\mathbf{R}$

$$(M + 2m) \mathbf{R} = M \mathbf{R}_n + m (\mathbf{R}_1 + \mathbf{R}_2) \quad (58)$$

---

<sup>12</sup> There will be 4 wave functions like  $u_{100}(\mathbf{r}_1) u_{2lm}(\mathbf{r}_2)$  and 4 like  $u_{2lm}(\mathbf{r}_1) u_{100}(\mathbf{r}_2)$ .

and show that

$$H = \frac{P^2}{2(M+2m)} + \frac{1}{2\mu} (p_1^2 + p_2^2) + \frac{1}{M} \mathbf{p}_1 \cdot \mathbf{p}_2 + e^2 \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \quad (59)$$

where

$$\mu = \frac{mM}{m+M} \quad (60)$$

is the reduced mass of an electron with the nucleus. Since  $M \gg \mu$  the term  $\frac{1}{M} \mathbf{p}_1 \cdot \mathbf{p}_2$  will be small in comparison to the preceding term and in the first approximation can be neglected. In this approximation, the resulting Hamiltonian is of the same form as Eq. (1) except for  $m$  being replaced by  $\mu$  and for an additional term involving the translational motion of the center of mass.

(b) Use first order perturbation theory to show that using a wave function of the form given by Eq. (3), the effect of the term  $\frac{1}{M} \mathbf{P}_1 \cdot \mathbf{P}_2$  is zero.

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## 22.11. Solutions

**Solution 22.1** The normalized hydrogen atom ground state wave function is given by Eq. (52). Thus

$$u_{100}(\mathbf{r}_1) u_{100}(\mathbf{r}_2) = \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 \exp \left[ -Z \frac{(r_1 + r_2)}{a_0} \right] \quad (61)$$

Substituting in Eq. (11) we get

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{Z^6 e^2}{\pi^2 a_0^6} \int d\tau_1 e^{-2Zr_1/a_0} \int d\tau_2 e^{-2Zr_2/a_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (62)$$

Now

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \begin{cases} \frac{1}{r_1} \sum_l \left( \frac{r_2}{r_1} \right)^l P_l(\cos \theta) & \text{for } r_1 \geq r_2 \\ \frac{1}{r_2} \sum_l \left( \frac{r_1}{r_2} \right)^l P_l(\cos \theta) & \text{for } r_2 \geq r_1 \end{cases} \quad (63)$$

where  $\theta$  is the angle between  $\mathbf{r}_1$  and  $\mathbf{r}_2$  (see, e.g. Ref. 5, p. 176). Further, in evaluating the second integral, if we choose the  $z_2$ -axis along  $\mathbf{r}_1$ , then

$$d\tau_2 = r_2^2 dr_2 \sin \theta \, d\theta \, d\phi$$

Introducing

$$\rho_1 = \frac{2Zr_1}{a_0} \text{ and } \rho_2 = \frac{2Zr_2}{a_0}$$

we get

$$\begin{aligned}
 \left\langle \frac{e^2}{r_{12}} \right\rangle &= \frac{Ze^2}{32\pi^2 a_0} \iiint \rho_1^2 d\rho_1 \sin \theta_1 d\theta_1 d\phi_1 e^{-\rho_1} \left[ \frac{1}{\rho} \int_0^{\rho_1} \rho_2^2 d\rho_2 e^{-\rho_2} \right. \\
 &\quad \times \frac{1}{\rho_1} \sum_l \left( \frac{\rho_2}{\rho_1} \right)^l \iint P_l(\cos \theta) \sin \theta d\theta d\phi + \int_{\rho_1}^{\infty} \rho_2^2 d\rho_2 e^{-\rho_2} \\
 &\quad \times \frac{1}{\rho_2} \sum_l \left( \frac{\rho_1}{\rho_2} \right)^l \iint P_l(\cos \theta) \sin \theta d\theta d\phi \left. \right] \\
 &= \frac{Ze^2}{8\pi a_0} \iiint \rho_1^2 d\rho_1 \sin \theta_1 d\theta_1 d\phi_1 e^{-\rho_1} \left[ \frac{1}{\rho_1} \int_0^{\rho_1} \rho_2^2 e^{-\rho_2} d\rho_2 \right. \\
 &\quad \left. + \int_{\rho_1}^{\infty} \rho_2 e^{-\rho_2} d\rho_2 \right] \\
 &= \frac{5}{8} Z \frac{e^2}{a_0} = \frac{5Z}{4} E_H
 \end{aligned} \tag{64}$$

where we have used the relation

$$\begin{aligned}
 \int_0^\pi P_l(\cos \theta) \sin \theta d\theta &= 2 \text{ for } l = 0 \\
 &= 0 \text{ for } l \geq 1
 \end{aligned} \tag{65}$$

Thus, according to the first order perturbation theory, the ground state energy is given by

$$\begin{aligned}
 W^{(1)} &= -2Z^2 E_H + \frac{5}{4} Z E_H = \left( -Z^2 + \frac{5}{8} Z \right) 2E_H \\
 &= \left( -Z^2 + \frac{5}{8} Z \right) \times 27.21 \text{eV}
 \end{aligned} \tag{66}$$

The calculated values are tabulated in Table 22.1. Since the ground state energy of a one-electron atom is  $-Z^2 E_H$ , the ionisation energy is given by

$$\begin{aligned}
 &\left[ \left( Z^2 - \frac{5}{8} Z \right) 2E_H - Z^2 E_H \right] \\
 &= \left[ Z^2 - \frac{5}{4} Z \right] E_H
 \end{aligned} \tag{67}$$

Table 22.1. Ground State and Ionization Energies of Two Electron Atoms

Atom	Z	Ground State			Difference between Experimental Values and Perturbation Theory Results	
		Ionization Energy				
		Perturbation Theory	Experi- mental value	Perturbat- ion Theory		
		[Eq. (66)]	[Eq. (67)]	[Eq. (73)]		
He	2	-74.83 eV	24.63 eV	20.40 eV	23.06 eV	4.23 eV
Li <sup>+</sup>	3	-193.87 eV	75.64 eV	71.43 eV	74.08 eV	4.21 eV
Be <sup>++</sup>	4	-367.30 eV	153.87 eV	149.66 eV	152.31 eV	4.21 eV
B <sup>+++</sup>	5	-595.20 eV	259.31 eV	255.09 eV	257.75 eV	4.22 eV

In Table 22.1 we have tabulated the ionization energy as given by the above equation and compared with the corresponding experimental values. It is interesting to note that the absolute error remains almost the same; however, the percentage error decreases with increase in  $Z$ . Physically this is due to the fact that for large  $Z$ , the term  $-Ze^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$  would dominate over the term  $e^2/r_{12}$ .

**Solution 22.2** Since  $\exp[-Z'r/a_0]$  is the ground state wave function for a hydrogen-like atom with charge  $Z'e$ , we must have

$$\left[ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z'e^2}{r_1} \right] \phi(\mathbf{r}_1, \mathbf{r}_2) = -Z'^2 E_H \phi(\mathbf{r}_1, \mathbf{r}_2) \quad (68)$$

Thus

$$E(Z') = \iint \phi^* \left[ -2Z'^2 E_H + (Z' - Z)e^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_{12}} \right] \phi d\tau_1 d\tau_2 \quad (69)$$

Now

$$\begin{aligned} e^2 \iint \phi^* \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \phi d\tau_1 d\tau_2 &= 2e^2 \iint \frac{|\phi|^2}{r_1} d\tau_1 d\tau_2 \\ &= 2Z' \frac{e^2}{a_0} = 4Z' E_H \end{aligned} \quad (70)$$

and

$$\iint \phi^* \frac{e^2}{r_{12}} \phi d\tau_1 d\tau_2 = \frac{5}{4} Z' E_H \quad (71)$$

[see Eq. (64)]. On substitution we get Eq. (15) and the condition  $\frac{dE}{dZ'} = 0$  leads to

$$Z' = Z_{eff} = Z - \frac{5}{16}$$

Thus the ground state energy is

$$E = -2 \left( Z - \frac{5}{16} \right)^2 E_H \quad (72)$$

and the corresponding ionization energy is

$$\left[ 2 \left( Z - \frac{5}{16} \right)^2 - Z^2 \right] E_H \quad (73)$$

which gives a much better estimate than the perturbation theory result (see Table 22.1).

**Solution 22.4** According to the first order perturbation theory the energy levels for the  $1s2s$  and  $1s2p$  configurations are given by

$$\begin{aligned} W^{(1)} &= \left( -Z^2 E_H - \frac{Z^2}{4} E_H \right) + J_l \pm K_l \\ &= -5E_H + J_l \pm K_l \end{aligned} \quad (74)$$

where we have assumed  $Z = 2$  and the upper and lower states correspond to singlet (parahelium) and triplet (orthohelium) states respectively. Substituting the values we get

$$\begin{aligned} W_{1s2s}^{(1)} &\approx -58.9 \pm 0.4 \text{ eV} \\ &\approx -58.5 \text{ eV and } -59.3 \text{ eV} \end{aligned} \quad (75)$$

$$\begin{aligned} W_{1s2p}^{(1)} &\approx -57.8 \pm 0.1 \text{ eV} \\ &\approx -57.7 \text{ eV and } -57.9 \text{ eV} \end{aligned} \quad (76)$$

The ionization energies are given by

$$\left. \begin{aligned} -Z^2 E_H - W^{(1)} &\approx 4.1 \text{ eV for the } 1s2s \text{ parahelium state } (^1S_0) \\ &\approx 4.9 \text{ eV for the } 1s2s \text{ orthohelium state } (^3S_0) \\ &\approx 3.3 \text{ eV for the } 1s2p \text{ parahelium state } (^1P_1) \\ &\approx 3.5 \text{ eV for the } 1s2p \text{ orthohelium state } (^3P_{210}) \end{aligned} \right\} \quad (77)$$

The corresponding experimental values are 3.97 eV, 4.76 eV, 3.368 eV and 3.623 eV respectively.

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## 22.12. References and suggested reading

1. D. Ter Harr, *The Old Quantum Theory*, Pergamon Press, Oxford (1967).

2. M. Jammer, *The Conventional Development of Quantum Mechanics*, McGraw-Hill Book Co., New York (1966).
3. S. Flugge, *Practical Quantum Mechanics*, Springer Verlag, Berlin (1971).
4. L. Pauling and E.B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Co., New York (1935).
5. J. Irving and N. Mullineux, *Mathematics in Physics and Engineering*, Academic Press, New York (1959).

# Chapter 23

## Some Select Topics

*I saw a medley of haphazard facts fall into line and order . . . “But it’s true,” I said to myself. “It’s very beautiful. And it’s true.”*

— C.P. SNOW<sup>1</sup>.

### 23.1. Introduction

In this chapter we will discuss in detail some select topics which are of considerable importance in quantum mechanics. In Sec. 23.2 we will discuss the semi-classical as well as the more rigorous method for calculating the lifetime of quasi-bound states. In Sec. 23.3 we will present a perturbation analysis of a periodic structure characterized with a sinusoidal variation of potential energy variation. In Sec. 23.4 we will describe a versatile matrix method for the analysis of a quantum mechanical problems. Finally, in Sec. 23.5 we will discuss the Thomas-Fermi model of the atom.

### 23.2. Tunnelling lifetime calculations

#### 23.2.1. SEMI-CLASSICAL APPROXIMATE ANALYSIS

We first consider the bound states corresponding to the following potential energy variation (see Fig. 23.1)

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < a \\ V_0 & x > a \end{cases} \quad (1)$$

---

<sup>1</sup> The authors found this quotation in John Gribbin’s book *In Search of Schrödinger Cat*, Black Swan Books (1984).

In Sec. 16.2 we had discussed the solution of the Schrödinger equation for the above profile and had shown that the energy eigenvalues are determined by solving the following transcendental equation

$$L = \sin ka + \frac{k}{\kappa} \cos ka = 0 \quad (2)$$

where

$$k^2 = \frac{2\mu E}{\hbar^2} \quad \text{and} \quad \kappa^2 = \frac{2\mu(V_0 - E)}{\hbar^2} \quad (3)$$

Equation (2) can be written in the form

$$-\xi \cot \xi = \sqrt{\alpha^2 - \xi^2} \quad (4)$$

where

$$\xi = ka = \left[ \frac{2\mu E a^2}{\hbar^2} \right]^{1/2} \quad \text{and} \quad \alpha = \left[ \frac{2\mu V_0 a^2}{\hbar^2} \right]^{1/2} \quad (5)$$

Let us assume  $\alpha = 7$ . The solution of the transcendental equation [Eq. (2)] gives us bound states for which

$$\xi = 2.739488 \quad \text{and} \quad 5.401717$$

We define the normalized energy eigenvalue

$$\epsilon = \frac{E}{V_0} = \left( \frac{\xi}{\alpha} \right)^2 \quad (6)$$

Thus the corresponding discrete values of  $\epsilon$  are given by

$$\epsilon \simeq 0.153159 (= \epsilon_1) \quad \text{and} \quad 0.595480 (= \epsilon_2) \quad (7)$$

The corresponding wave function is given by

$$\psi_b(x) = \begin{cases} A_b \sin k_b x & 0 < x < a \\ A_b \sin k_b a e^{-\kappa_b(x-a)} & x > a \end{cases} \quad (8)$$

where the subscript  $b$  refers to the fact that we are considering particular bound states. If we normalize the wave function we would readily get

$$A_b = \left[ \frac{2\kappa_b}{1 + \kappa_b a} \right]^{1/2} \quad (9)$$

The discrete eigenvalues and corresponding eigenfunctions are shown in Fig. 23.1.

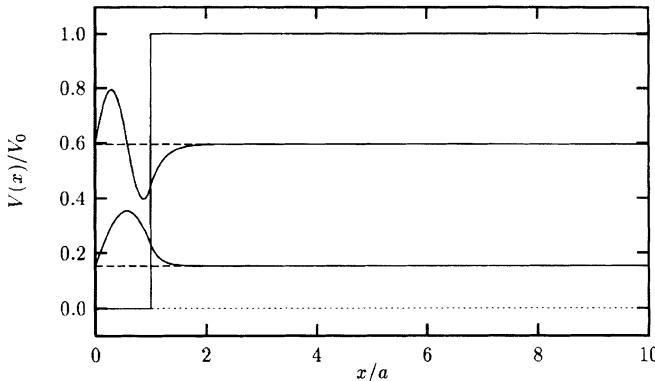


Figure 23.1. The discrete eigenvalues and eigenfunctions corresponding to the potential energy distribution given by Eq. (1) with  $\alpha = 7$ .

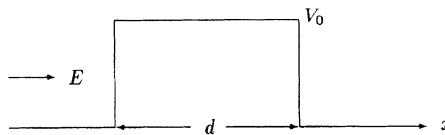


Figure 23.2. Tunnelling through a rectangular potential barrier of height  $V_0$  and width  $d$ .

We next consider tunnelling through a rectangular potential barrier (of width  $d$ ) as shown in Fig. 23.1. We had discussed this in Sec. 8.3 and had shown that tunnelling probability is given by

$$T = \frac{4\epsilon(1-\epsilon)}{\sinh^2(\kappa d) + 4\epsilon(1-\epsilon)} \quad (10)$$

For  $\kappa d \gg 1$ , the expression for the tunnelling probability takes the form

$$T \approx 16\epsilon(1-\epsilon)e^{-2\kappa d} \quad (11)$$

We next consider a potential energy variation of the type shown in Fig. 23.3:

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < a \\ V_0 & a < x < a+d \\ 0 & x > a \end{cases} \quad (12)$$

Now, according to the semi-classical theory, a particle confined inside the well (i.e. within the region  $0 < x < a$ ) will hit the barrier  $v/2a$  times a second, where  $v$  is the speed of the particle. Thus the probability per second of escape (which is the inverse of the mean lifetime) is given by

$$\frac{1}{\tau} \approx \frac{v}{2a} T$$

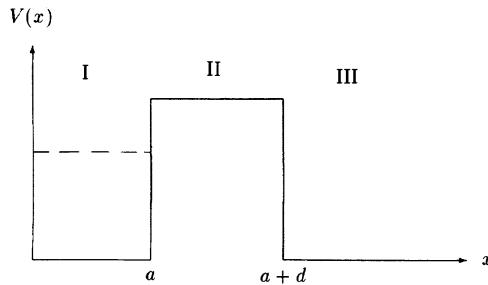


Figure 23.3. A tunnelling potential energy variation as given by Eq. (12).

which can be simplified to the following form

$$\tau \approx \frac{1}{16} \left[ \frac{2\mu a^2}{\hbar^2} \right] \frac{\kappa a}{[\epsilon(1-\epsilon)]^{3/2}} e^{2\kappa d} \quad (13)$$

(this analysis is similar to the one that we had carried out while studying the alpha decay problem in Sec. 17.7).

### 23.2.2. QUASI-BOUNDED STATES

In above we have given a very simple semi-classical analysis for the calculation of the lifetime for a particle to tunnel through a barrier. For a more rigorous analysis, we must understand the concept of quasi-bound states which we will now discuss. We consider again the leaky structure shown in Fig. 23.3. For such a structure, if we solve the Schrödinger equation we would find that there are no discrete energy eigenstates and all values of  $E > 0$  are allowed; these form the continuum eigenstates of the system. The solution of the Schrödinger equation in the three regions can be written in the form

$$\psi_E(x) = \begin{cases} A \sin kx & 0 < x < a \\ Be^{\kappa(x-a)} + Ce^{-\kappa(x-a)} & a < x < a+d \\ D_+e^{ik(x-a-d)} + D_-e^{-ik(x-a-d)} & x > a+d \end{cases} \quad (14)$$

where (without any loss of generality) we have assumed  $E < V_0$ . Continuity of the wave function and its derivative at  $x = a$  and at  $x = a + d$  give us

$$B = \frac{1}{2}A \left[ \sin ka + \frac{k}{\kappa} \cos ka \right] \quad (15)$$

$$C = \frac{1}{2}A \left[ \sin ka - \frac{k}{\kappa} \cos ka \right] \quad (16)$$

$$D_-^* = D_+ = \frac{1}{2}B \left[ 1 + \frac{\kappa}{ik} \right] e^{\kappa d} + \frac{1}{2}C \left[ 1 - \frac{\kappa}{ik} \right] e^{-\kappa d} \quad (17)$$

The orthogonality condition for these continuum eigenstates are given by

$$\int_0^\infty \psi_{E'}^*(x) \psi_E(x) dx = \delta(E - E') \quad (18)$$

which gives us

$$|D_+| = |D_-| = \frac{1}{\hbar} \left[ \frac{\mu}{2\pi k} \right]^{1/2} \quad (19)$$

Now, if we assume  $\kappa d \gg 1$ , then the exponentially decaying term in Eq. (17) can be neglected, and in this approximation

$$D_-^* = D_+ \approx \frac{1}{4} L A \left( 1 + \frac{\kappa}{ik} \right) e^{\kappa d} \quad (20)$$

where  $L$  has already been defined in Eq. (2). It is readily seen that since  $\kappa d \gg 1$ , unless  $L \approx 0$ ,

$$\left| \frac{D_\pm}{A} \right| \gg 1 \quad (21)$$

implying that the amplitude of the wave function is large in the region  $x > (a+d)$ . However, for values of  $E$  such that  $L = 0$  [i.e. when the condition for discrete bound states (corresponding to Fig. 23.1) are satisfied], then  $B = 0$  and we have only the exponentially decaying solution in the region  $a < x < a+d$  [see Eq. (14)] and the amplitude of the oscillatory solution in the region  $x > (a+d)$  is very weak. Thus when

$$L = 0 = B \quad (22)$$

the wave function has the properties of a discrete eigenfunction in regions I and II having very weak oscillations in the region III. We refer the eigenfunctions corresponding to  $B = 0$  as quasi-bound states. In Figs 23.4(a) and 23.5(a) we have plotted the eigenfunctions corresponding to  $\alpha = 7$  with

$$\epsilon = 0.153159 (= \epsilon_1) \quad \text{and} \quad 0.595480 (= \epsilon_2)$$

respectively. As can be seen the wave functions are the same as for the bound state except for the weak oscillatory solution in the region  $x > (a+d)$ . These are the quasi-bound states of the system. In Figs 23.4(b) and 23.5(b) we have plotted the eigenfunctions corresponding to

$$\epsilon = 0.157159 \quad \text{and} \quad 0.675480$$

respectively. Thus, we find that if we go slightly away from the quasi-bound state, there is a drastic change in the behaviour of the eigenfunction. In fact, if we plot

$$\left| \frac{A}{D_\pm} \right|^2$$

as a function of  $E$  (see Fig. 23.6), we will get very sharply peaked Lorentzians, the width of which is directly related to the lifetime of the quasi-bound state. All the plots correspond to  $d/a = 0.75$ .

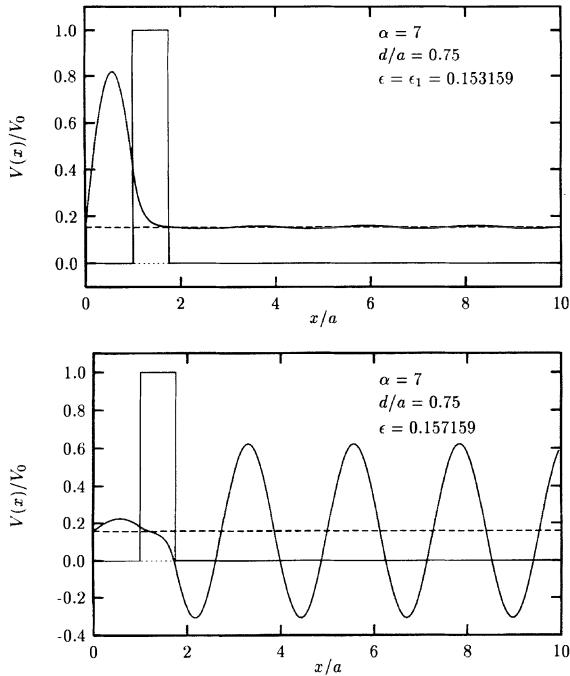


Figure 23.4. (a) The quasi- bound state corresponding to  $\epsilon = \epsilon_1 = 0.153159$ . (b) The eigenfunction corresponding to  $\epsilon = 0.157159$

### 23.2.3. LIFETIME CALCULATION

In this section we will discuss the rigorous theory for tunnelling of a particle from a potential well similar to that shown in Fig. 23.3. We assume that at  $t = 0$ , the particle is described by a wave function which corresponds to the bound state corresponding to Fig. 23.1:

$$\Psi(x, t = 0) = \psi_b(x) \quad (23)$$

where  $\psi_b(x)$  is given by Eq. (8). In order to study its time evolution we must expand it in terms of the (continuum) eigenfunctions corresponding to the potential energy variation shown in Fig. 23.3. Thus we should write

$$\Psi(x, t = 0) = \psi_b(x) = \int \phi(E) \psi_E(x) \, dE \quad (24)$$

For  $t > 0$ , the wave function would be given by

$$\Psi(x, t) = \int_0^\infty \phi(E) \psi_E(x) e^{-iEt/\hbar} dE \quad (25)$$

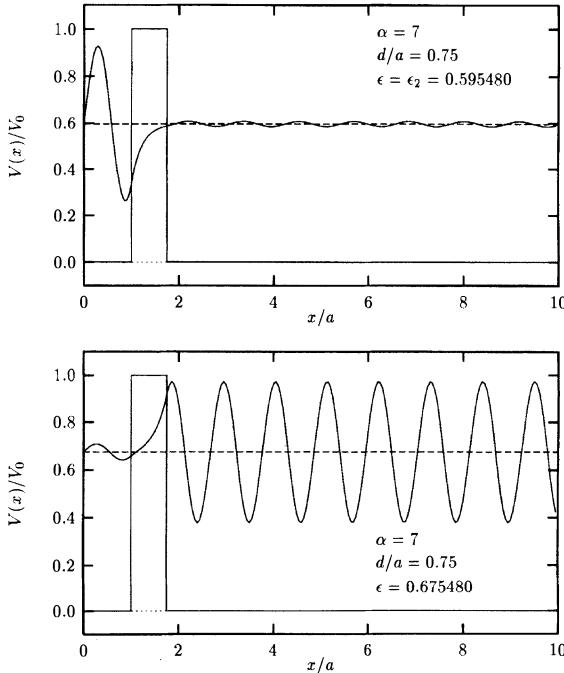


Figure 23.5. (a) The quasi-bound state corresponding to  $\epsilon = \epsilon_2 = 0.595480$   
(b) The eigenfunction corresponding to  $\epsilon = 0.675480$

In order to determine  $\phi(E)$ , we multiply Eq. (24) by  $\psi_{E'}^*(x)$  and integrate over  $x$  to obtain

$$\begin{aligned} \int_0^\infty \psi_{E'}^*(x) \psi_b(x) dx &= \int dE \phi(E) \int dx \psi_{E'}^*(x) \psi_E(x) \\ &= \int dE \phi(E) \delta(E - E') = \phi(E') \end{aligned}$$

where use has been made of Eq. (18). Thus

$$\phi(E) = \int_0^\infty \psi_E^*(x) \psi_b(x) dx \quad (26)$$

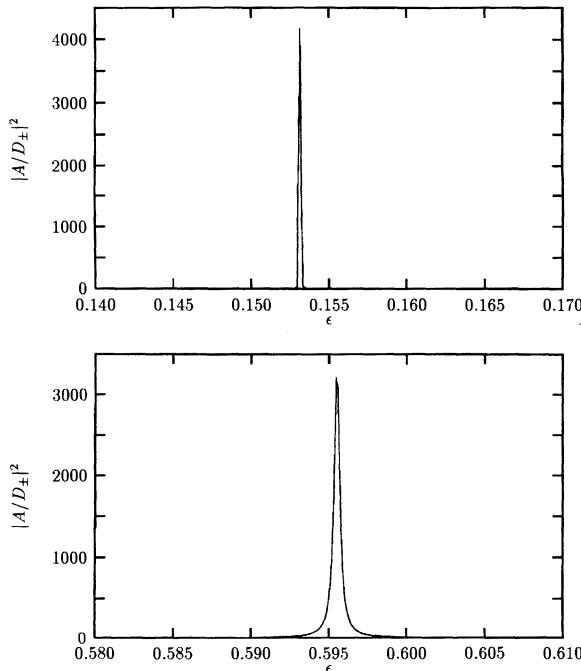


Figure 23.6. A plot of  $|A/D_{\pm}|^2$  which shows two sharply peaked Lorentzians the widths of which are directly related to the lifetime of the quasi-bound states.

Now, it is only around  $E \approx E_b$  that  $\psi_E(x)$  has almost the same spatial dependence as  $\psi_b(x)$  in regions I and II (see Figs 23.4 and 23.5) and therefore in the above equation,  $\phi(E)$  will be appreciable around  $E \approx E_b$ ; this we will explicitly find later. Thus we may write

$$\psi_E(x) \approx \frac{A}{A_b} \psi_b(x) \quad \text{Regions I and II} \quad (27)$$

Since in region III ( $x > a + d$ ),  $\psi_b(x)$  has a negligible value, we may neglect the contribution from region III to the integral in Eq. (26) to write

$$\begin{aligned} \phi(E) &\approx \int_0^{a+d} \psi_E^*(x) \psi_b(x) dx \\ &\approx \frac{A}{A_b} \int_0^{a+d} |\psi_b(x)|^2 dx \end{aligned}$$

$$\approx \frac{A}{A_b} \int_0^\infty |\psi_b(x)|^2 dx = \frac{A}{A_b} \quad (28)$$

In Appendix P we have shown that around  $E \approx E_b$

$$|\phi(E)|^2 \approx \left| \frac{A}{A_b} \right|^2 \approx \frac{\Gamma}{\pi} \frac{1}{(E - E'_b)^2 + \Gamma^2} \quad (29)$$

where

$$\Gamma = \frac{4k_b^3 \kappa_b^3 a^4 \hbar^2}{\mu \alpha^4 (1 + \kappa_b a)} e^{-2\kappa_b d} \quad (30)$$

$$E'_b = E_b - \Delta E_b \quad (31)$$

$$\Delta E_b = \frac{\kappa_b^2 - k_b^2}{2\kappa_b k_b} \Gamma \quad (32)$$

$k_b$  and  $\kappa_b$  are the values of  $k$  and  $\kappa$  at  $E = E_b$ :

$$k_b = \left[ \frac{2\mu E_b}{\hbar^2} \right]^{1/2}; \quad \kappa_b = \left[ \frac{2\mu(V_0 - E_b)}{\hbar^2} \right]^{1/2}$$

The probability that at time  $t$ , the particle is still inside the well is approximately given by the square of the overlap integral

$$P(t) \approx \left| \int_0^\infty \Psi^*(x, 0) \Psi(x, t) dx \right|^2$$

The above integral has been evaluated in Appendix P and has been shown to be given by

$$P(t) \approx \left| \int dE |\phi(E)|^2 e^{-iEt/\hbar} dE \right|^2 \quad (33)$$

where  $|\phi(E)|^2$  has been given by Eq. (29). On substituting the expression for  $|\phi(E)|^2$  and carrying out the integration (see Appendix P), we get

$$P(t) \approx e^{-t/\tau} \quad (34)$$

where

*Tunnelling lifetime of quasi-bound states*

$$\tau = \frac{\hbar}{2\Gamma} = \frac{1}{16} \left[ \frac{2\mu a^2}{\hbar \alpha^2} \right] \frac{\kappa_b \left( a + \frac{1}{\kappa_b} \right)}{[\epsilon_b(1 - \epsilon_b)]^{3/2}} e^{2\kappa_b d} \quad (35)$$

is the mean lifetime of the quasi-bound state and

$$\epsilon_b = \frac{E_b}{V_0} = \frac{(k_b a)^2}{\alpha^2} \quad (36)$$

Equation (35) gives an analytical expression for the tunnelling lifetime of the quasi-bound states. It should be noted that as  $d$  becomes large, the time that the particle spends inside the well becomes large. Equation (35) may be compared with the approximate expression given by Eq. (13). If we replace  $a$  by  $(a + 1/\kappa_b)$  in Eq. (13) we would get Eq. (35). Since  $1/\kappa_b$  represents the perturbation depth of the wave function in the “classically forbidden region” (see Sec. 8.4)  $a + \frac{1}{\kappa_b}$  can be interpreted as the effective width of the well.

Now, in Appendix P we have also shown that [see Eq. (14) of Appendix P]

$$\left| \frac{A}{D_{\pm}} \right|^2 \approx 8 \left( \frac{\hbar^2}{2\mu} \right) \frac{k_b \kappa_b \Gamma}{1 + \kappa_b a} \frac{1}{(E - E'_b)^2 + \Gamma^2} \quad (37)$$

Thus if we are able to calculate  $|A/D_{\pm}|^2$  as a function of  $E$ , we would get a series of Lorentzians, each Lorentzian corresponding to a quasi-bound state of the structure. By fitting each peak to a Lorentzian, we would be able to get  $E'_b$  and  $\Gamma$  and therefore the lifetime. Indeed for an arbitrary potential energy variation one can develop a matrix approach to calculate  $|A/D_{\pm}|^2$  as a function of  $E$  from which the lifetime of a quasi-bound state can be calculated (see, e.g. Ref 2 and 3).

In Appendix P we have also shown that

$$|D_{\pm}| = \frac{1}{4} A \frac{\mu \alpha (1 + \kappa_b a) e^{\kappa_b d}}{a \hbar^2 k_b \kappa_b^2} \left| 1 \pm \frac{\kappa_b}{ik_b} \right| |E - E'_b \mp i\Gamma| \quad (38)$$

Thus if we solve the eigenvalue equation

$$D_{-}(E) = 0 \quad (39)$$

in the complex  $E$  plane, then the imaginary part of the root will give the value of  $\Gamma$  and hence the lifetime of the state.

### 23.3. Perturbation theory for sinusoidally varying potentials

In Sec. 16.5 we had discussed the solution of the Schrödinger equation corresponding to a periodic potential described by a series of delta functions: this was the Krönig-Penney model of the lattice. In this section we present a perturbation approach to solve the Schrödinger equation corresponding to a sinusoidal variation of the potential energy function. The results have been compared with numerical results obtained by solving the Schrödinger equation using the Runge-Kutta method

and the perturbation theory results have been shown to be very accurate for rapid oscillations. In fact if the oscillations are very rapid (this will be quantified later) then the number of bound states are determined not by the number of wells but by the average potential energy variation. The perturbation method can easily be extended to potential energy variations which can be expressed as a sum of sine or cosine functions.

We start with the one-dimensional Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (40)$$

We assume a sinusoidal variation of the potential energy variation given by the following equation (see Fig. 23.7)

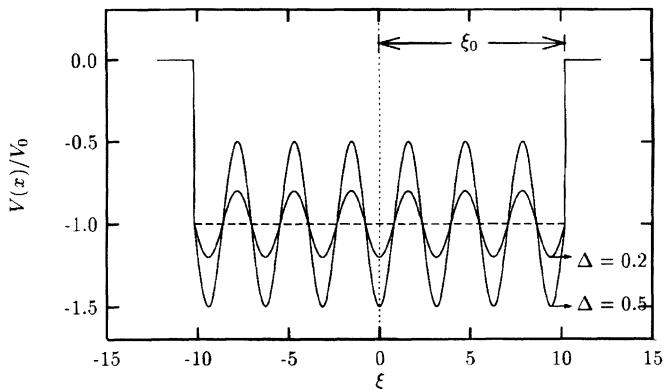


Figure 23.7. The sinusoidal variation of the potential energy function [Eq. (41)]; the average potential energy function [Eq. (51)] has been shown by dashed line.

### *Sinusoidal potential*

$$V(x) = \begin{cases} -V_0 [1 + \Delta \cos(2gx)] & |x| < a/2 \\ 0 & |x| > a/2 \end{cases} \quad (41)$$

We present here a perturbation approach to solve the Schrödinger equation. We assume

$$ga = \left(m + \frac{1}{2}\right)\pi ; \quad m = 0, 1, 2, 3, \dots \quad (42)$$

so that  $V(x) = -V_0$  at  $x = +a/2$ . For the potential energy variation given by Eq. (41), Eq. (40) can be written in the form

$$\left. \begin{aligned} \frac{d^2\psi}{d\xi^2} + [\gamma^2 + 2\epsilon \cos(2\xi)] \psi(\xi) &= 0 \quad |\xi| < \xi_0 \\ \frac{d^2\psi(\xi)}{d\xi^2} - \sigma^2 \psi(\xi) &= 0 \quad |\xi| > \xi_0 \end{aligned} \right\} \quad (43)$$

where we have introduced the following dimensionless variables:

$$\xi = gx; \quad \xi_0 = \frac{1}{2}ga = \left(m + \frac{1}{2}\right) \frac{\pi}{2} \quad (44)$$

and

$$\epsilon = \frac{1}{2} \frac{\alpha^2 \Delta}{[(m + \frac{1}{2}) \frac{\pi}{2}]^2}$$

$$\gamma^2 = 2(1-b) \frac{\epsilon}{\Delta}$$

$$\sigma^2 = 2b \frac{\epsilon}{\Delta}$$

$$\alpha^2 = \frac{2\mu V_0 a^2}{4\hbar^2}$$

$$b = -\frac{E}{V_0} = \frac{|E|}{V_0}$$

For  $\xi < \xi_0$ , Eq. (43) is similar to Mathieu's equation (see, e.g. Chapter 11 of Ref. 4). Following Ref. 4, we write the solution of Eq. (43) in the following form

$$\psi = \psi_0 + \epsilon \psi_1 + \epsilon^2 \psi_2 + \dots \quad (45)$$

If we substitute the above expression in Eq. (43) and equate the coefficients of various powers of  $\epsilon$ , we would get

$$\frac{d^2\psi_0}{d\xi^2} + \gamma^2 \psi_0 = 0 \quad (46)$$

$$\frac{d^2\psi_0}{d\xi^2} + \gamma^2 \psi_1 = -2\psi_0 \cos(2\xi) \quad (47)$$

$$\frac{d^2\psi_0}{d\xi^2} + \gamma^2 \psi_2 = -2\psi_1 \cos(2\xi) \quad (48)$$

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The solution of Eq. (46) is taken to be

$$\psi_0(\xi) = A \cos(\gamma\xi + \phi) \quad (49)$$

where the constant  $\phi$  is determined from the boundary conditions. However, for a symmetric  $V(x)$ , the eigenfunctions are either symmetric ( $\phi = 0$ ) or antisymmetric ( $\phi = \pi/2$ ) functions of  $\xi$ . If we substitute Eq. (49) in Eq. (47) we can solve for the particular integral to obtain  $\psi_1(\xi)$  and similarly solve Eq. (48) to obtain  $\psi_2(\xi)$  ... etc. The final result is

$$\begin{aligned} \psi(x) &= A \cos(\gamma\xi + \phi) + \frac{1}{4}\epsilon A \left\{ \frac{\cos[(2+\gamma)\xi + \phi]}{1+\gamma} \right. \\ &\quad \left. + \frac{\cos[-(2-\gamma)\xi + \phi]}{1-\gamma} \right\} + \frac{1}{32}\epsilon^2 A \left\{ -\frac{8\xi \sin[\gamma\xi + \phi]}{\gamma(1-\gamma^2)} \right. \\ &\quad \left. + \frac{\cos[(4+\gamma)\xi + \phi]}{(1+\gamma)(2+\gamma)} + \frac{\cos[-(4-\gamma)\xi + \phi]}{(1-\gamma)(2-\gamma)} \right\} + \dots \quad \text{for } |\xi| < \xi_0 \\ &= C \exp[-\sigma(|\xi| - \xi_0)] \quad \text{for } |\xi| > \xi_0 \end{aligned} \quad (50)$$

The continuity of  $\psi$  and  $d\psi/d\xi$  at  $\xi = \xi_0$  would lead to the transcendental equation which would determine the energy eigenvalues.

Obviously, the perturbation theory would be accurate for small values of  $\epsilon$ . However, we obtain the general result that for a given value of  $\alpha$ , one can always choose a large enough value of  $m$  to give a large number of oscillations of the potential energy variation in the well and obtain a sufficiently small value of  $\epsilon$  so that the bound states are accurately determined by solving for the average potential energy distribution given by

$$V(x) = \begin{cases} -V_0 & |x| < a/2 \\ 0 & |x| > a/2 \end{cases} \quad (51)$$

We next present some numerical calculations to determine the validity of the perturbation method. We assume

$$\alpha = 7.0 \quad (52)$$

We first consider the average potential energy variation given by Eq. (51). For such a value of  $\alpha$ , the potential well will support 3 symmetric and 2 antisymmetric bound states. Table 23.1 gives the corresponding values of  $b$  (which represent the normalized energy eigenvalues).

Tables 23.2 gives the  $b$  values for the ground state and the 3<sup>rd</sup> excited state for different  $\Delta$  values for a fixed value of  $m (=10)$  and Table 23.3 give the  $b$  values for different  $m$ -values corresponding to  $\Delta = 1$ . The tables give a comparison of the results using perturbation theory with the more accurate results obtained using the Runge-Kutta method.

From the tables we make the following observations:

*Table 23.1.* The normalized energy eigenvalues corresponding to the average potential energy distribution [given by Eq. (51)] for  $\alpha = 7$ .

Mode Number	b-value
0	0.9615098
1	0.8468413
2	0.6588388
3	0.4045254
4	0.1067140

*Table 23.2.* The normalized energy eigenvalues of the ground state and the 3<sup>rd</sup> excited state corresponding to the sinusoidally varying potential energy distribution [given by Eq. (41)] for different values of  $\Delta$  for  $m = 10$  with  $\alpha = 7$ .

$\Delta$	$\epsilon$	b-values			
		Ground State		3 <sup>rd</sup> excited state	
		R-K Method	Pert. Theory	R-K Method	Pert. Theory
1.0	0.090063	0.986268	0.995867	0.460043	0.462060
0.5	0.045032	0.968165	0.968969	0.425971	0.426323
0.25	0.022158	0.963408	0.963489	0.413646	0.413693
0.1	0.009006	0.961928	0.961930	0.407784	0.407787

1. The perturbation method, as expected, becomes more accurate for smaller  $\Delta$  values.
2. For each bound state, the perturbation method becomes more accurate for higher values of  $m$ ; this is to be expected as a large value of  $m$  implies a small value of  $\epsilon$ .
3. As the value of  $m$  increases, i.e. as the number of oscillations in the well increases, the value of  $b$  for each bound state converges to the  $b$  value corresponding to the average potential energy variation which are tabulated in Table 23.1.

Figures 23.8 to 23.10 show the eigenfunctions corresponding to the ground state for various values of  $m$  and  $\Delta$  using the perturbation theory and the (more accurate) Runge-Kutta method. The figures show that the perturbation theory gives an accu-

Table 23.3. The normalized energy eigenvalues of the ground state and the 3<sup>rd</sup> excited state corresponding to the sinusoidally varying potential energy distribution [given by Eq. (41)] for different values of  $m$  for  $\Delta = 1.0$  with  $\alpha = 7$ .

$m$	$\epsilon$	$b$ -values			
		Ground State		3 <sup>rd</sup> excited state	
		R-K Method	Pert. Theory	R-K Method	Pert. Theory
5	0.328247	1.042736	1.046624	0.490174	0.446715
10	0.090063	0.986268	0.995867	0.460043	0.462060
20	0.023628	0.968511	0.969370	0.425882	0.426204
50	0.003893	0.962920	0.962960	0.411655	0.411675

rate description of the eigenfunction for smaller  $\Delta$  values. It may be mentioned that even for maximum perturbation; the eigenfield is very accurate for  $m \geq 20$ . Figures 23.11 shows the eigenfunction of the 3<sup>rd</sup> excited states for  $m = 20$ . Comparison of Figs 23.10 and 23.11 show that the perturbation theory works even better for the excited states. A similar behaviour can be seen for the other excited states also. Thus, we may conclude that the simple perturbation approach can be effectively used to analyse a sinusoidally varying potential energy distribution.

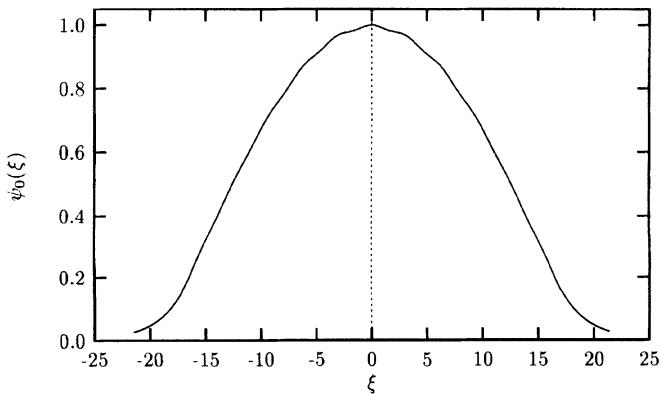


Figure 23.8. Ground state eigenfunction for  $m = 10$  (and  $\Delta = 0.1$ ) using Runge-Kutta method (continuous curve) and perturbation theory (dashed curve); the two curves almost completely overlap each other.

## 23.4. The matrix method

In this section we will describe a versatile matrix method to obtain solutions of the (one-dimensional) Schrödinger equation for a variety of problems. The only

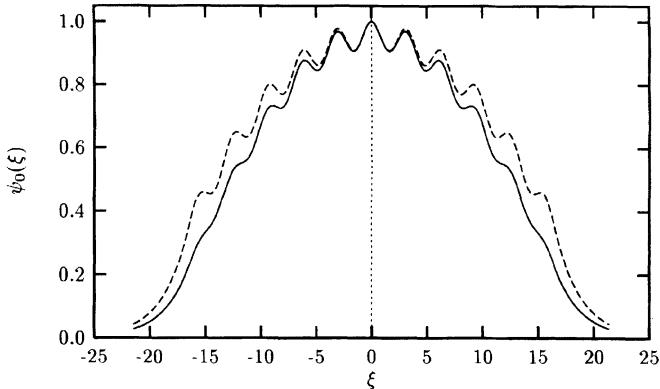


Figure 23.9. Ground state eigenfunction for  $m = 10$  (and  $\Delta = 1.0$ ) using Runge-Kutta method (continuous curve) and perturbation theory (dashed curve).

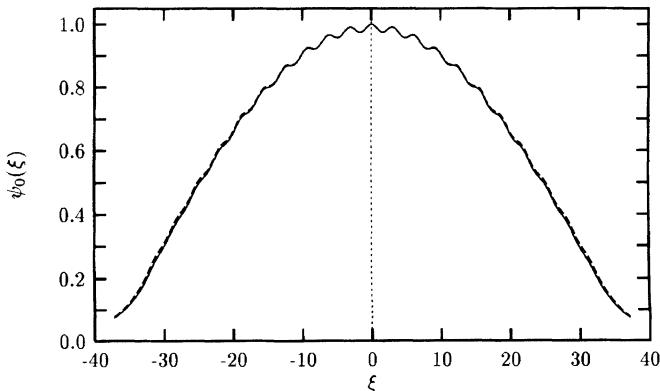


Figure 23.10. Ground state eigenfunction for  $m = 20$  (and  $\Delta = 1.0$ ) using Runge-Kutta method (continuous curve) and perturbation theory (dashed curve).

approximation made would be to replace the actual potential energy variation by a piecewise step variation. Indeed, the method can be used to solve the general scalar wave equation

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi(x) = 0 \quad (53)$$

where, for problems in quantum mechanics

$$k^2(x) = \frac{2\mu}{\hbar^2}[E - V(x)] \quad (54)$$

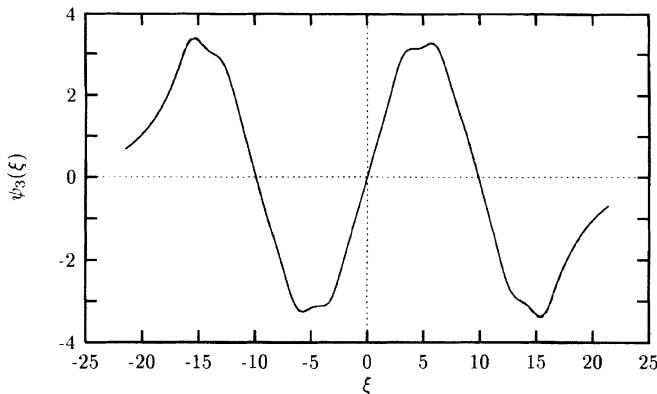


Figure 23.11. 3<sup>rd</sup> excited state eigenfunction for  $m = 20$  (and  $\Delta = 1.0$ ) using Runge-Kutta method (continuous curve) and perturbation theory (dashed curve); the two curves almost completely overlap each other.

We assume piecewise step variation of  $V(x)$ :

$$\left. \begin{aligned} V(x) &= V_1 \quad \text{for } x < d_1 \\ &= V_j \quad \text{for } d_{j-1} < x < d_j; \quad j = 1, 2, \dots, (N-1) \\ &= V_N \quad \text{for } x > d_{N-1} \end{aligned} \right\} \quad (55)$$

(see Fig. 23.12). Indeed an arbitrary variation of  $V(x)$  can always be approximately described by the above equation. The solution of Eq. (53) in the  $j^{\text{th}}$  region can be written in the following form

$$\psi_j(x) = A_j e^{i[k_j(x-d_{j-1})]} + B_j e^{-i[k_j(x-d_{j-1})]} \quad (56)$$

where

$$k_j^2(x) = \frac{2\mu}{\hbar^2} [E - V_j] \quad (57)$$

As shown in Fig. 23.12,  $x = d_j$  represents the position of the right boundary of the  $j^{\text{th}}$  layer. Using the continuity of the wave function and its derivative (at  $x = d_j$ ), it can be readily shown that the coefficients in the adjacent regions are related through the following matrix equation

$$\begin{pmatrix} A_{j+1} \\ B_{j+1} \end{pmatrix} = S^{(j)} \begin{pmatrix} A_j \\ B_j \end{pmatrix} \quad (58)$$

where

$$S^{(j)} = \begin{pmatrix} S_{11}^{(j)} & S_{12}^{(j)} \\ S_{21}^{(j)} & S_{22}^{(j)} \end{pmatrix} \quad (59)$$

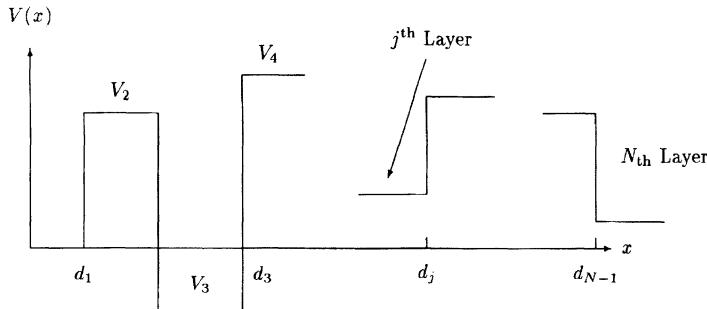


Figure 23.12. Piecewise step variation of the potential energy distribution.

with

$$\begin{aligned} S_{11}^{(j)} &= \frac{1}{2} \left[ 1 + \frac{k_j}{k_{j+1}} \right] e^{i\alpha_j} \\ S_{12}^{(j)} &= \frac{1}{2} \left[ 1 - \frac{k_j}{k_{j+1}} \right] e^{-i\alpha_j} \\ S_{21}^{(j)} &= \frac{1}{2} \left[ 1 - \frac{k_j}{k_{j+1}} \right] e^{i\alpha_j} \\ S_{22}^{(j)} &= \frac{1}{2} \left[ 1 + \frac{k_j}{k_{j+1}} \right] e^{-i\alpha_j} \end{aligned}$$

and

$$\alpha_j = k_j(d_j - d_{j-1}) \quad (60)$$

By successive applications of Eq. (58), the coefficients in any layer can be expressed in terms of the coefficients of the first layer

$$\begin{pmatrix} A_{j+1} \\ B_{j+1} \end{pmatrix} = S^{(j)} S^{(j-1)} \dots S^{(1)} \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} \quad (61)$$

Finally

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} \quad (62)$$

where the  $G$  matrix is given by

$$G = S^{(N-1)} S^{(N-2)} \dots S^{(1)} \quad (63)$$

Thus, for given values of  $A_1$  and  $B_1$  and of energy  $E$  we can obtain the coefficients  $A_N$  and  $B_N$ . We should mention that if  $E > V_j$ ,  $k_j^2$  is positive; however, if  $E < V_j$ ,  $k_j^2$  is negative and  $k_j$  will be replaced by  $(i\kappa_j)$  where

$$\kappa_j^2 = -k_j^2 = \frac{2\mu}{\hbar^2} [V_j - E] \quad (64)$$

Thus, Eq. (56) takes the form

$$\psi_j(x) = A_j e^{-\kappa_j(x-d_{j-1})} + B_j e^{\kappa_j(x-d_{j-1})} \quad (65)$$

We now consider specific cases:

### CASE 1: BOUND STATE CALCULATIONS

For a bound state,  $\psi(x) \rightarrow 0$  as  $x \rightarrow \pm\infty$ . The condition that  $\psi(x) \rightarrow 0$  as  $x \rightarrow -\infty$  gives us

$$A_1 = 0 \quad (66)$$

Without any loss of generality, we may assume  $B_1 = 1$  so that

$$B_N = G_{22} \quad (67)$$

Now,  $B_N$  represents the coefficient of the exponentially amplifying solution; thus the condition that  $\psi(x) \rightarrow 0$  as  $x \rightarrow +\infty$  gives us  $B_N = 0$ . If we therefore plot

$$G_{22}(E)$$

as a function of  $E$ , then the values of  $E$  where  $G_{22}(E)$  becomes zero represent the energy eigenvalues of the system. Thus the roots of the equation

$$G_{22}(E) = 0 \quad (68)$$

would give us the energy eigenvalues (see Problem 23.3).

### CASE 2: SCATTERING PROBLEM

If  $k_1^2$  and  $k_N^2$  are both positive, we will have a scattering problem similar to what we have discussed in Chapter 8. For a wave incident from the left, we must have

$$B_N = 0$$

(see discussion in Sec. 8.3). Thus we would have

$$A_N = G_{11} A_1 + G_{12} B_1 \quad (69)$$

and

$$0 = G_{21} A_1 + G_{22} B_1 \quad (70)$$

Therefore the reflection coefficient would be given by

$$R = \left| \frac{B_1}{A_1} \right|^2 = \left| \frac{G_{21}}{G_{22}} \right|^2 \quad (71)$$

### CASE 3: TUNNELLING STRUCTURE

For a typical tunnelling structure shown in Fig. 23.3,  $A_1 = -B_1$  (so that the wave function vanishes at  $x = 0$ ) and a plot of

$$\left| \frac{A_1}{A_N} \right|^2$$

as a function of  $E$  would give us approximate Lorentzians, the widths of which would enable us to calculate lifetimes of quasi-bound states.

### 23.5. The Thomas-Fermi model of the atom

In an atom consisting of a large number of electrons, the electrons can approximately be assumed to be in a degenerate state (a degenerate electron gas is discussed in Sec. 6.9). The electron gas is in a potential field and in the Thomas-Fermi model, we make two assumptions:

1. The potential function varies very little over a wavelength.
2. Further, the field is assumed to vary slowly enough so that we can consider a volume element  $d\tau$  which contains a large number of electrons and at the same time the field can be assumed to be approximately constant in this volume.

We recall that the maximum kinetic energy for a degenerate electron gas is given by [see Eq. (94) of Chapter 6]

$$(K.E.)_{\max} = E_{F_0} = \frac{\hbar^2}{2\mu} [3\pi^2 n(r)]^{2/3} \quad (72)$$

where  $n(r)$  represents the number of electrons per unit volume. Further,

$$\begin{aligned} \text{Total Energy } E &= \frac{p^2}{2\mu} + V(r) \\ &= \frac{p^2}{2\mu} - q\Phi(r) \end{aligned} \quad (73)$$

where  $\Phi(r)$  represents the potential and  $-q$  represents the charge of the electron. Now, for a bound state, we must have  $E < 0$ ; thus

$$q\Phi(r) = (K.E.)_{\max} = \frac{\hbar^2}{2\mu} [3\pi^2 n(r)]^{2/3} \quad (74)$$

(This is a rather oversimplified model—for a more rigorous analysis one may look up Ref 6 and 7). Thus

$$n(r) = \frac{[2\mu q \Phi(r)]^{3/2}}{3\pi^2 \hbar^3} \quad (75)$$

Now, for the theory to be self-consistent, the potential and the charge density should be related through the Poisson equation

$$\nabla^2 \Phi = -\frac{\rho(r)}{\epsilon_0} \quad (76)$$

where  $\epsilon_0$  is the dielectric permittivity of free space and  $\rho(r) = -qn(r)$  represents the electron charge density. Substituting for  $n(r)$  from Eq. (75) we get

$$\nabla^2 \Phi = \frac{q}{3\pi^2 \hbar^3 \epsilon_0} (2\mu q)^{3/2} \Phi^{3/2} \quad (77)$$

We assume the nucleus (of charge  $Zq$ ) to be at the origin of the coordinate system so that the potential is spherically symmetric and we may write

$$\nabla^2 \Phi = \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d\Phi}{dr} \right] \quad (78)$$

Further, as  $r \rightarrow 0$ , the potential will be essentially due to the nucleus so that (as  $r \rightarrow 0$ ) it will behave as  $Zq/(4\pi \epsilon_0 r)$ . This suggests that we introduce the variable  $\chi(r)$  defined through the following equation

$$\Phi(r) = \frac{Zq}{4\pi \epsilon_0 r} \chi(r) \quad (79)$$

so that we have the boundary condition

$$\chi(0) = 1 \quad (80)$$

Using Eqs (78) and (79), Eq. (77) becomes

$$\frac{d^2 \chi}{dr^2} = \frac{q}{3\pi^2 \hbar^3 \epsilon_0} (2\mu q)^{3/2} \frac{(Zq)^{1/2}}{(4\pi \epsilon_0)^{1/2}} \frac{1}{r^{1/2}} \chi^{3/2} \quad (81)$$

In order to put the above equation in a more convenient form we introduce the dimensionless variable  $x$  defined by the following equation

$$r = \gamma x$$

where the parameter  $\gamma$  is to be defined later. Substituting in Eq. (81) we get

$$\frac{d^2 \chi(x)}{dx^2} = \left[ \gamma^{3/2} \frac{4}{3\pi \hbar^3} Z^{1/2} \left( \frac{2\mu q^2}{4\pi \epsilon_0} \right)^{3/2} \right] \frac{1}{x^{1/2}} \chi(x) \quad (82)$$

We choose  $\gamma$  so that the quantity inside the square brackets is unity:

$$\gamma = \frac{1}{2} \left( \frac{3\pi}{4} \right)^{2/3} \frac{1}{Z^{1/3}} \frac{\hbar^2}{(\mu q^2 / 4\pi\epsilon_0)} \simeq \frac{0.8853 a_0}{Z^{1/3}} \quad (83)$$

where

$$a_0 = \frac{\hbar^2}{(\mu q^2 / 4\pi\epsilon_0)} \simeq 0.53 \times 10^{-10} \text{ m}$$

represents the Bohr radius. Thus Eq.(82) takes the form

$$\frac{d^2\chi}{dx^2} = \frac{1}{x^{1/2}} [\chi(x)]^{3/2} \quad (84)$$

which is known as the dimensionless Thomas-Fermi equation; from now on it will be abbreviated as the TF equation. For an isolated atom, the boundary conditions will be

$$\chi(0) = 1 \quad \text{and} \quad \chi(\infty) = 0 \quad (85)$$

we will denote the solution of the TF equation which satisfies the boundary conditions given by Eq. (85) by  $\chi_i(x)$ . Now, using Eqs (75) and (79), we may write

$$n(r) = \frac{1}{3\pi^2 \hbar^3} \left[ \frac{2\mu Z q^2}{4\pi\epsilon_0 r} \chi_i(r) \right]^{3/2} = \frac{1}{3\pi^2} \left[ \frac{2Z}{a_0} \frac{1}{\gamma x} \chi_i(x) \right]^{3/2} \quad (86)$$

or, using Eq. (83) we get

$$n(r) = \frac{32}{9\pi^3} \frac{Z^2}{a_0^3} \left[ \frac{\chi_i(x)}{x} \right]^{3/2} \quad (87)$$

Thus, if  $\chi_i(x)$  is known, one can determine the charge distribution in the atom. It may be mentioned that Eq. (86) predicts an infinite electron density at the origin: this is one of the basic errors of the TF model—see, e.g., Ref. 8. Indeed, for an atom the TF model is correct only in the domain

$$\frac{a_0}{Z} \lesssim r \lesssim a_0 \quad (88)$$

where  $a_0$  is the Bohr radius. The condition  $a_0/Z < r$  comes from the fact that at distances smaller than  $a_0/Z$  the quasi-classical approximation (which is the basis of the TF model) breaks down. On the other hand, for  $r > a_0$  the de-Broglie wavelength of the electron becomes large. Fortunately, in a complex atom most of the electrons are in the domain

$$\frac{a_0}{Z} \lesssim r \lesssim a_0$$

so that the TF model can be used to describe the complex atom system.

In Problem 23.4 we have shown that a power series solution of the TF equation is given by

$$\chi(x) = 1 + a_2 x + \frac{4}{3} x^{3/2} + \frac{2}{5} a_2 x^{5/2} + \frac{1}{3} x^3 + \dots \quad (89)$$

where  $a_2$  is determined from the initial slope:

$$a_2 = \chi'(0) \quad (90)$$

The power series is convergent for  $x < 1$  and is useful (i.e. rapidly convergent) when  $x \ll 1$ . For  $x \gtrsim 1$ , one normally uses a numerical method to solve the TF equation. Figure 23.13 gives the numerical solution of the TF equation for various values of the initial slope. When

$$a_2 = \chi'(0) = -1.58808 \quad (91)$$

$\chi(x)$  approaches zero asymptotically and the solution corresponds to an isolated atom. Thus [see Eq. (89)]

$$\chi_i(x) = 1 - 1.58808 x + \frac{4}{3} x^{3/2} - 0.635232 x^{5/2} + \frac{1}{3} x^3 + \dots \quad (92)$$

where the subscript  $i$  corresponds to the fact that we are considering an isolated atom. When

$$|\chi'(0)| < 1.58808$$

$\chi(x)$  decreases to a minimum and then starts increasing again (see Fig. 23.13). One of the important advantages of the Thomas-Fermi model is the fact that the curve corresponding to an isolated atom is universal, i.e. for a given value of  $Z$  one has to calculate  $\gamma$  [see Eq. (83)] and simply scale the  $x$ -axis [using the equation  $r = \gamma x$ ] to get  $\chi(r)$  as a function of  $r$ . Once  $\chi(r)$  is known,  $n(r)$  can be determined from Eq. (86). Because of this, detailed tables for the Thomas-Fermi function can be found in many places (see, e.g. References 10 and 11). A convenient formula (corresponding to an isolated atom) is given by (Ref. 12)

$$\chi_i(x) \approx 0.35 e^{-0.3x} + 0.55 e^{-1.2x} + 0.10 e^{-6.0x} \quad (93)$$

The above formula gives an accurate description in the region  $0 < x \lesssim 7$ .

In Fig. 23.14 we have plotted the electron distribution function

$$D(r) = 4\pi r^2 n(r) \quad (94)$$

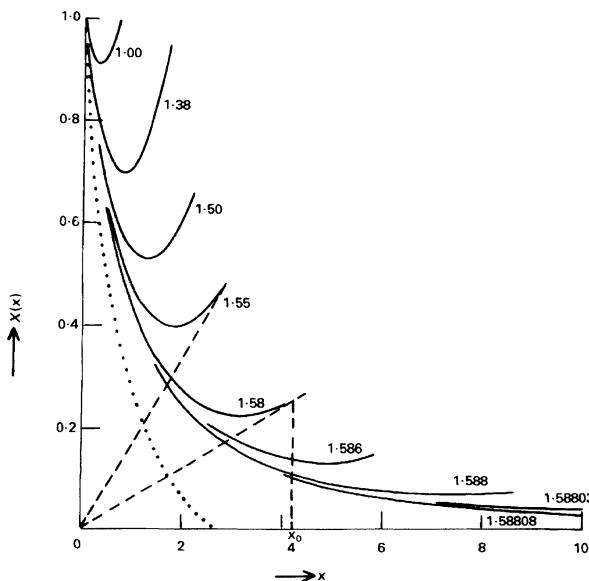


Figure 23.13. The Thomas-Fermi function  $\chi(x)$ , as a function of  $x$ , for various values of the initial slope. The numbers on the curve represent the value of  $-a_2$ . When  $a_2 = -1.58808$ ,  $\chi(x)$  approaches zero asymptotically and the solution corresponds to an isolated atom. The dotted curve represents the qualitative dependence of  $\chi(x)$  on  $x$  when  $|a_2|$  is greater than 1.58808. [Adapted from Ref. 9]

as a function of  $r$  for the mercury atom ( $Z = 80$ ); the quantity  $D(r) dr$  represents the number of electrons in the spherical shell whose inner and outer radii are  $r$  and  $r + dr$  respectively. The solid curve is obtained by using the TF model [e.g. by using the tables given in References 10 and 11—or, may be, the approximate empirical formula given by Eq. (93)] and the dashed curve represents the actual numerical results—the peaks approximately corresponding to the Bohr orbits.

### 23.6. Problems

Note: In Problems 23.1–23.3 all symbols have the same meaning as in Sec. 23.2.

**Problem 23.1** Consider a potential variation corresponding to Fig. 23.3 with  $\alpha = 6.0$  and  $d/a = 1$ . Show that the quasi-modes correspond to

$$\epsilon = \epsilon_1 = 0.19932777$$

and

$$\epsilon = \epsilon_2 = 0.75863041$$

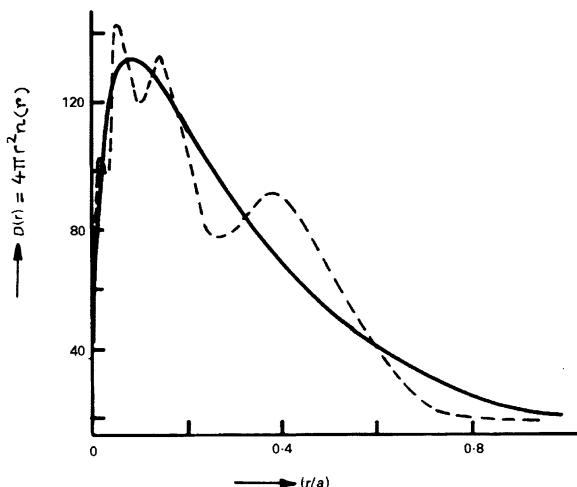


Figure 23.14. The electron distribution function  $D(r)[= 4\pi r^2 n(r)]$  as a function of  $r$  for the Hg atom ( $Z = 80$ ). The solid curve is obtained from the TF model and the dashed curve represents the actual numerical results [adapted from Ref. 12].

Plot the corresponding wave functions and compare with the plots corresponding to

$$\epsilon = \epsilon_1 + 0.0005$$

and

$$\epsilon = \epsilon_2 + 0.0005$$

Also plot  $|A/D|^2$  around  $\epsilon = \epsilon_1$  and  $\epsilon = \epsilon_2$  and find the lifetime of the states.

**Problem 23.2** Consider again the potential variation corresponding to Fig. 23.3 with  $\alpha = 5.0$  and  $d/a = 1$ . Show that the quasi-modes correspond to

$$\epsilon = \epsilon_1 = 0.269514$$

and

$$\epsilon = \epsilon_2 = 0.962869$$

Plot the corresponding wave functions and compare the second plot with the plot corresponding to

$$\epsilon = \epsilon_2 + 0.001$$

Show that the two plots almost overlap with each other (why?).

**Problem 23.3 (a)** Consider the potential energy variation corresponding to Fig. 23.1; we write the solution in the region  $x < a$  as  $\sin(kx)$  and the solution in the region  $x > a$  as

$$\psi(x) = B e^{\kappa(x-a)} + C e^{-\kappa(x-a)}$$

Show that  $B$  (the coefficient of the exponentially amplifying term) is given by

$$B = \sin(\alpha\sqrt{\epsilon}) + \sqrt{\frac{\epsilon}{1-\epsilon}} \cos(\alpha\sqrt{\epsilon})$$

Assume  $\alpha = 5.0$  and plot  $B$  as a function of (in the domain  $0 < \epsilon < 1$ ) and show that the zeroes occur for values of  $\epsilon$  as given in the previous problem.

(b) Repeat the calculations for  $\alpha = 6.0$ .

**Problem 23.4** Substitute the power series solution

$$\begin{aligned}\chi(x) &= \sum_{k=0,1,2,\dots} a_k x^{k/2} \\ &= a_0 + a_1 x^{1/2} + a_2 x + a_3 x^{3/2} + a_4 x^2 + \dots\end{aligned}$$

in the TF equation [Eq. (84)] and assuming  $\chi(0) = 1$ , derive Eq. (89).

**Problem 23.5** Let  $\chi_i(x)$  represent the solution of the TF equation corresponding to an isolated atom; i.e.

$$\chi_i(x) = 1$$

and the slope at  $x = 0$  is -1.58808 so that  $\chi_i(\infty) = 0$ .

- (a) Show that the function  $D(r)$  [as given by Eq. (94)] is proportional to the function

$$F(x) = [x^{1/3} \chi_i(x)]^{3/2}$$

- (b) Using the empirical formula [Eq. (93)] find the value of  $x$  where  $F(x)$  attains its maximum value.
- (c) Using the above result calculate for the Hg atom ( $Z = 80$ ) the value of  $r$  at which  $D(r)$  attains its maximum value and compare with the value that can be approximately obtained from Fig. 23.14.

[Ans: (b)  $\approx 0.39$  (c)  $\approx 0.080 a_0$ ]

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# Chapter 24

## Elementary Theory of Scattering

*Our actual situation in research work in atomic physics is usually this: we wish to understand a certain phenomenon, we wish to recognise how this phenomenon follows from the general laws of nature. Therefore, that part in the phenomenon is the natural ‘object’ in the theoretical treatment and should be separated in this respect from the tools used to study the phenomenon. This again emphasises a subjective element in the description of atomic events, since the measuring device has been constructed by the observer, and we have to remember that what we observe is not nature in itself but nature exposed to our method of questioning.*

— WERNER HEISENBERG in *Physics and Philosophy*,  
Penguin, London (1989).

### 24.1. Introduction

In some of the earlier chapters we had considered solutions of the Schrödinger equation which correspond to bound state problems where the wave function vanished at large distances from the origin; the corresponding energy levels were found to form a discrete set. In this chapter we will consider solutions of the Schrödinger equation where the energy eigenvalues would be continuously distributed; for such a case the wave function would not vanish at large distances from the origin. Such solutions correspond to the scattering of a particle by a force field where the energy is specified in advance and the behaviour of the wave function is found in terms of energy. We should mention here that in Chapter 8 we did consider the scattering by a one-dimensional force field, the corresponding three-dimensional case will be considered here.

Scattering experiments have provided most of the information about interactions among atoms, nuclei and particles. The general technique is to have a collimated beam of projectiles (particles) with well-defined energies and sometimes other properties, such as polarization, as well. The particles are then scattered by a target of atoms and the scattered particles are detected by means of a suitable detector. The measurement could be simply the intensity variation as a function of angle or could involve more detailed information like the change in the

energy or the polarization state, etc. The most commonly used parameter which displays the results of scattering experiments is the cross-section. In Sec. 24.2 we will give the definition of the scattering cross-section according to classical mechanics which will be followed by the corresponding quantum mechanical definition. As mentioned earlier, scattering experiments provide information about interaction among atoms, nuclei and particles. Assuming a certain model for the interaction, one calculates the cross-section which is compared with experimental data. A good agreement between theory and experiment would suggest the validity of the model assumed. However, sometimes a variety of models give good agreement between theory and experiment and it becomes difficult to justify a particular model. In Secs 24.4–24.6 we will develop theoretical methods to calculate the cross-section and wherever possible, comparison will be made with available experimental data.

## 24.2. The classical definition of scattering cross-section

We first give the definition of the scattering cross-section according to classical mechanics. We consider a beam of particles moving along  $z$ -direction with a flux of  $I_0$  particles per unit area per unit time. The particles undergo scattering by a potential and one measures the angular distribution of scattered particles. The scattering cross-section  $\sigma(\theta, \phi)$  is defined by

$$\sigma(\theta, \phi)d\Omega = \frac{\text{Number of particles scattered into solid angle } d\Omega \text{ per unit time}}{\text{Incident Intensity } I_0} \quad (1)$$

where  $d\Omega$  represents an infinitesimal solid angle in the direction  $(\theta, \phi)$ ; the angle  $\theta$  represents the angle of scattering and  $\phi$  represents the azimuthal angle; the origin has been assumed to be at the center of the force (see Fig. 24.1). For a spherically symmetric potential,  $\sigma(\theta, \phi)$  will be independent of  $\phi$ .

The total cross-section is given by

$$\sigma = \iint \sigma(\theta, \phi) d\Omega = \int_0^{\pi} \int_0^{2\pi} \sigma(\theta, \phi) \sin \theta d\theta d\phi \quad (2)$$

Thus  $\sigma I_0$  will represent the number of particles scattered out of the beam per unit time. For a spherically symmetric potential

$$\sigma = 2\pi \int_0^{\pi} \sigma(\theta) \sin \theta d\theta \quad (3)$$

In classical mechanics, each particle has a well-defined trajectory and if we assume that all particles of the incident beam have the same speed  $v_0$ , there is

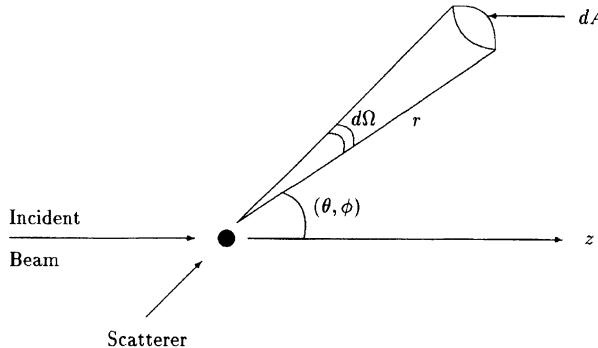


Figure 24.1. The scattering of an incident beam. The particles scattered into the solid angle  $d\Omega$  is received by the detector.

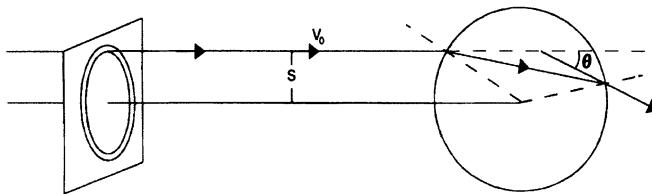


Figure 24.2. The classical trajectory of a particle scattered by a square well potential,  $s$  denotes the impact parameter.

an unique angle of scattering  $\theta$  corresponding to a particular value of the impact parameter  $s$ . For example, for an attractive square well potential defined by

$$\begin{aligned} V(r) &= -V_0 & 0 < r < a \\ &= 0 & r > a \end{aligned} \quad (4)$$

the relation between the impact parameter  $s$  and the scattering angle  $\theta$  is given by (see Fig. 24.2 and Problem 24.20):

$$\begin{aligned} \theta &= -2(i - r) = 2 \left[ \sin^{-1} \left( \frac{s}{na} \right) - \sin^{-1} \left( \frac{s}{a} \right) \right] & \text{for } 0 < s < a \\ &= 0 & \text{for } s > a \end{aligned} \quad (5)$$

where

$$n = \left[ \frac{E + V_0}{E} \right]^{1/2} \text{ and } E = \frac{1}{2}mv_0^2 \quad (6)$$

Now, the number of particles which cross the annular area between  $s$  and  $s + ds$  is  $I2\pi s ds$  and this must represent the number of particles scattered between  $\theta$  and  $\theta + d\theta$  which from Eq. (1) is simply  $\sigma(\theta)I2\pi \sin \theta d\theta$ . Thus

$$I2\pi s ds = -\sigma(\theta) I2\pi \sin \theta d\theta$$

or

$$\sigma(\theta) = -\frac{s}{\sin \theta} \frac{ds}{d\theta} \quad (7)$$

where the negative sign is due to the fact that  $\theta$  decreases with increase in the value of the impact parameter  $s$ . Equation (7) is quite general, if we now use the result given by Eq. (5) we would obtain

$$\sigma(\theta) = \frac{n^2 a^2}{4 \cos \frac{\theta}{2}} \frac{(n \cos \frac{\theta}{2} - 1)(n - \cos \frac{\theta}{2})}{[1 + n^2 - 2n \cos \frac{\theta}{2}]^2} \quad (8)$$

Since no scattering occurs for  $s > a$ , we must have

$$\theta < \left[ \pi - 2 \sin^{-1} \left( \frac{1}{n} \right) \right] \quad (9)$$

In a similar manner one can calculate the scattering cross-section for other forms of  $V(r)$  (see e.g. Chapter 3 of Ref. 1).

#### 24.2.1. PHYSICAL INTERPRETATION OF THE CROSS-SECTION

Let us consider a beam of particles of cross-sectional area  $A$  (and intensity  $I_0$ ) incident normally on a target as shown in Fig. 24.3. Let there be  $N$  scatterers per unit volume inside the target. If  $I(x)$  represents the intensity of the beam after penetrating through a distance  $x$  and if  $dI(x)$  represents the loss of intensity in traversing an additional distance  $dx$  then the total number of interactions (per unit time) in the volume element  $A dx$  will be given by

$$-A dI(x) = \sigma I(x) (N A dx) \quad (10)$$

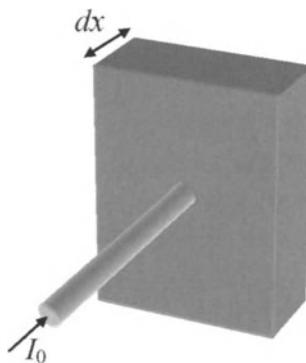


Figure 24.3. A beam of particles of cross-sectional area  $A$  (and intensity  $I_0$ ) incident normally on a target.

where  $\sigma$  represents the total cross-section (see Eq. 3)<sup>1</sup>, the quantity  $(NA dx)$  represents the number of scatterers in the volume element  $A dx$  and the negative sign is due to the fact that  $I(x)$  decreases with  $x$ ; we have neglected multiple scatterings in the volume element  $A dx$ . Simple integration of Eq. (10) gives

$$I(x) = I_0 e^{-\Sigma x} \quad (11)$$

where  $\Sigma = N\sigma$  is known as the macroscopic cross-section and can be interpreted as the inverse of the mean free path. Further, it can be easily seen that the probability that the particle undergoes its first scattering between  $x$  and  $x + dx$  will simply be given by

$$p(x) dx = e^{-\Sigma x} \Sigma dx$$

where the factor  $e^{-\Sigma x}$  represents the probability that it does not undergo scattering in traversing a distance  $x$  and  $\Sigma dx$  represents the probability that it does undergo scattering in traversing the distance  $dx$ . Obviously

$$\int_0^\infty p(x) dx = 1$$

as it indeed should be.

### 24.3. Quantum theory of scattering

In quantum mechanics, strictly speaking, the scattering problem needs a temporal description, namely, how a wave packet representing the incident particle as  $t \rightarrow -\infty$  behaves as it passes through the region of perturbation and proceeds to  $t \rightarrow \infty$  (see Problem 24.19). However, when there is a steady current of particles in the beam, we often dispense with the temporal description. We merely calculate the current of particles at an infinite distance away from the target (as opposed to behaviour at  $t \rightarrow \infty$ ). This is done by looking for asymptotic solutions of the time independent Schrödinger equation. Since in this region the particles are free, we are dealing with the continuous spectrum of positive energies.

We start with the time independent Schrödinger equation

$$\nabla^2 \psi(\mathbf{r}) + \frac{2\mu}{\hbar^2} [E - V(r)] \psi(\mathbf{r}) = 0 \quad (12)$$

---

<sup>1</sup> We are assuming here that the number of particles scattered is simply the sum of the numbers scattered by each atom. In the quantum theory, we will see that if different atoms of the target act coherently, then we cannot simply add scattering-cross sections as above since interference effects are involved. One then has to add the scattering probability *amplitudes* first. An example of this is the scattering of low energy neutrons in crystals (see Problems 24.15 and 25.1).

where, if we are considering a fixed scattering center,  $\mu$  represents the mass of the particle. On the other hand, if we are considering a two body interaction then  $\mu$  represents the reduced mass of the system provided the potential energy function depends only on the magnitude of the distance between the two particles, i.e.  $V = V(|\mathbf{r}_1 - \mathbf{r}_2|)$ ; such potentials are known as spherically symmetric potentials, examples of which are the square well potential [see Eq. (79)], the Coulomb potential (see Sec. 10.3), etc. Then  $E$  (in Eq. (12)) represents the energy in the center of mass system and  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$  represents the relative coordinate (see Secs 10.3 and 24.8). The cross-section is calculated in the center of mass system and the relation which enables one to calculate the cross-section in the laboratory system is discussed in Sec. 24.8.

In order to describe the scattering experiment we will obtain the solution of the Schrödinger equation [Eq. (12)] in the form of an incident plane wave and an outgoing scattered wave. Thus we seek solution of the form:

$$\psi(\mathbf{r}) \xrightarrow[r \rightarrow \infty]{} e^{i\mathbf{k} \cdot \mathbf{r}} + f(\theta) \frac{e^{ikr}}{r} \quad (13)$$

where  $\mathbf{k} = k\hat{\mathbf{z}}$ ,  $\hat{\mathbf{z}}$  representing a vector along the  $z$ -axis. We may mention here that for a short-range force (i.e. when  $\lim_{r \rightarrow \infty} rV(r) = 0$ ) the general form of the asymptotic solution of the Schrödinger equation will be of the form (see Appendix O):

$$f(\theta) \frac{e^{ikr}}{r} + g(\theta) \frac{e^{-ikr}}{r} \quad (14)$$

where the second term corresponds to an incoming wave and hence is neglected in Eq. (13). It may be noted that since the potential is assumed to be spherically symmetric, the amplitude of the scattered wave (i.e. the function  $f$ ) is assumed to be independent of the azimuthal angle  $\phi$ .

If we multiply Eq. (13) by the appropriate time factor  $\exp(-iEt/\hbar)$ , it will be seen that the first term represents a plane wave propagating along the  $z$ -axis. Since  $|e^{ikz}|^2 = 1$  the number of particles crossing an unit time is simply

$$v_\infty = \frac{\hbar k}{m} \quad (15)$$

(see Eqs (38) and (40) of Chapter 4). Corresponding to the second term in Eq. (13) the current density is given by (see Sec. 4.4)

$$\mathbf{J} = \text{Re} \left[ \frac{e^{-ikr}}{r} f^*(\theta) \frac{\hbar}{im} \nabla \left( \frac{e^{ikr}}{r} f(\theta) \right) \right] \quad (16)$$

or

$$\mathbf{J} \simeq v_\infty \frac{|f(\theta)|^2}{r^2} \hat{\mathbf{r}} \quad (17)$$

where we have neglected terms of  $O\left(\frac{1}{r^3}\right)$  which will make a negligible contribution at large values of  $r$ . The  $1/r^2$  dependence of  $\mathbf{J}$  implies that the intensity of the scattered wave falls off according to the inverse square law (see Problem 4.3). The function  $f(\theta)$  describes the angular distribution of the scattered wave and is known as the *scattering amplitude*. It should be pointed out that in our analysis we have calculated the current density due to the two parts of the wave function separately. This is justified because in an actual experiment the incident wave is collimated and does not interfere with the scattered wave.

Now, in Fig. 24.1 the area  $dA$  is given by

$$dA = r^2 d\Omega \quad (18)$$

Therefore, the number of particles scattered in the solid angle  $d\Omega$  will be equal to the number that cross the area  $dA$  and hence equal to

$$\frac{v_\infty}{r^2} |f(\theta)|^2 r^2 d\Omega \quad (19)$$

Thus<sup>2</sup>

$$\sigma(\theta) = \left[ \frac{d\sigma}{d\Omega} \right] = |f(\theta)|^2 \quad (20)$$

Notice that multiplication of the RHS of Eq. (13) by an arbitrary constant would not have changed  $\sigma(\theta)$ .

In order to obtain a solution of Eq. (12) of the form of Eq. (13), we rewrite Eq. (12) in the form

$$(\nabla^2 + k^2) \psi(\mathbf{r}) = F(\mathbf{r}) \quad (21)$$

where

$$k^2 = 2\mu E / \hbar^2 \quad \text{and} \quad F(\mathbf{r}) = \frac{2\mu}{\hbar^2} V(\mathbf{r}) \psi(\mathbf{r})$$

We consider Eq. (21) as an inhomogeneous equation and write the equation in the form

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + v(\mathbf{r}) \quad (22)$$

where  $v(\mathbf{r})$  represents the solution to the inhomogeneous part of Eq. (21) and  $\phi(\mathbf{r})$  is a solution of the homogeneous equation

$$(\nabla^2 + k^2)\phi(\mathbf{r}) = 0 \quad (23)$$

For the scattering problem in which the incident beam travels along  $\mathbf{k}$ , we choose

$$\phi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \quad (24)$$

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<sup>2</sup> In general, the scattering amplitude  $f$  depends on  $\theta$  and  $\phi$ ; but for spherically symmetric potentials, the scattering amplitude and therefore  $\sigma$  is independent of the azimuthal angle.

Now, in order to determine the solution to the inhomogeneous equation, we introduce the Green's function in the next section; an alternative derivation is given in Appendix N.

## 24.4. The Green's function

The Green's function of an operator  $L$  is defined through the following equation

$$LG(\mathbf{r}, \mathbf{r}') = (\delta(\mathbf{r} - \mathbf{r}')) \quad (25)$$

Once the Green's function is known, one can show that the solution of the inhomogeneous equation

$$L\psi = F(\mathbf{r}) \quad (26)$$

is given by

$$\psi = \int G(\mathbf{r}, \mathbf{r}') F(\mathbf{r}') d\mathbf{r}'$$

where the (triple) integral is over the entire 3-dimensional space. We will first determine the Green's function of the operator  $\nabla^2$  and then of the operator  $(\nabla^2 + k^2)$ .

### 24.4.1. THE GREEN'S FUNCTION FOR THE $\nabla^2$ OPERATOR

We will first show that

$$\nabla^2 \left( \frac{1}{r} \right) = -4\pi \delta(\mathbf{r}) = -4\pi \delta(x)\delta(y)\delta(z) \quad (27)$$

Now, for a function  $\psi(r)$  dependent only on the coordinate  $r$ ,

$$\nabla^2 \psi(r) = \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d\psi}{dr} \right]$$

Elementary differentiation shows us that

$$\nabla^2 \left( \frac{1}{r} \right) = \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d}{dr} \left( \frac{1}{r} \right) \right] = 0 \quad \text{for } r \neq 0 \quad (28)$$

At  $r = 0$ , the above expression is not defined because of the factor  $(1/r^2)$ . Now

$$\nabla^2 \left( \frac{1}{r} \right) = \operatorname{div} \mathbf{F}$$

where

$$\mathbf{F}(r) \equiv \operatorname{grad} \left( \frac{1}{r} \right) = -\frac{1}{r^2} \hat{\mathbf{r}}$$

where  $\hat{\mathbf{r}}$  represents a unit vector along  $\mathbf{r}$ . In order to evaluate  $\operatorname{div} \mathbf{F}$  at the origin, we consider a sphere of radius  $R$  surrounding the origin. Then on the spherical surface,  $|\mathbf{F}|$  has a constant value equal to  $(1/R^2)$ . Thus integrating over this spherical surface, we get

$$\begin{aligned}\iint \mathbf{F} \cdot d\mathbf{S} &= -\frac{1}{R^2} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} (\hat{\mathbf{r}} \cdot \hat{\mathbf{r}} R^2 \sin \theta) d\theta d\phi \\ &= -4\pi\end{aligned}$$

(independent of the value of  $R$ ). Using Gauss' theorem,

$$\iiint_V \nabla^2 \left( \frac{1}{r} \right) d\tau = \iiint_V \operatorname{div} \mathbf{F} d\tau = \iint \mathbf{F} \cdot d\mathbf{S}$$

where the volume integration is over a spherical volume of radius  $R$  and the surface integral is over the spherical surface of radius  $R$ . Thus

$$\iiint_V \nabla^2 \left( \frac{1}{r} \right) d\tau = -4\pi$$

Because of Eq.(28),  $V$  can be an *arbitrary* volume surrounding the origin. Thus the above equation would imply

$$\nabla^2 \left( \frac{1}{r} \right) = -4\pi \delta(\mathbf{r}) = -4\pi \delta(x)\delta(y)\delta(z)$$

If we shift the origin of the coordinate system to  $\mathbf{r}'$ , we would obtain

$$\begin{aligned}\nabla^2 \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) &= -4\pi \delta(\mathbf{r} - \mathbf{r}') \\ &= -4\pi \delta(x - x')\delta(y - y')\delta(z - z')\end{aligned}$$

The Green's function  $G(\mathbf{r}, \mathbf{r}')$  for the operator  $\nabla^2$  is defined through the equation [see Eq. (25)]

$$\nabla^2 G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (29)$$

Comparing the above two equations we get

$$G(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|} \quad (30)$$

#### 24.4.2. THE SOLUTION OF THE EQUATION $\nabla^2\psi(r) = F(r)$

We next obtain the solution of the equation

$$\nabla^2\psi(\mathbf{r}) = F(\mathbf{r}) \quad (31)$$

If we multiply Eq.(29) by  $\psi(\mathbf{r}')$  and Eq.(31) by  $G(\mathbf{r}, \mathbf{r}')$ , subtract the resulting equations and then integrate, we obtain

$$\begin{aligned} & \int_V [\psi(\mathbf{r}') \nabla^2 G(\mathbf{r}, \mathbf{r}') - G(\mathbf{r}, \mathbf{r}') \nabla^2 \psi(\mathbf{r}')] d\tau \\ &= \int_V \psi(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') d\tau' - \int_V G(\mathbf{r}, \mathbf{r}') F(\mathbf{r}') d\tau' \end{aligned}$$

Now, the integrand on the left hand side is simply  $\operatorname{div}(\psi \nabla G - G \nabla \psi)$ . Thus if we use the Gauss' theorem, the above equation would become

$$\int_S (\psi \nabla G - G \nabla \psi) \cdot d\mathbf{S} = \psi(\mathbf{r}) - \int_V G(\mathbf{r}, \mathbf{r}') F(\mathbf{r}') d\tau'$$

where  $\mathbf{S}$  represents the surface bounding the volume  $V$ ; if this surface is taken at infinity and if the integrand is assumed to fall off faster than  $1/r^2$ , then the left hand side of the above equation vanishes and we have

$$\psi(\mathbf{r}) = \int_V G(\mathbf{r}, \mathbf{r}') F(\mathbf{r}') d\tau' \quad (32)$$

Using Eq.(30), we get

$$\psi(\mathbf{r}) = - \int \frac{F(\mathbf{r}')}{4\pi \epsilon_0 |\mathbf{r} - \mathbf{r}'|} d\tau' \quad (33)$$

As a simple example we consider the Poisson equation which is given by

$$\nabla^2 \phi = -\frac{\rho(\mathbf{r})}{\epsilon_0}$$

where  $\phi$  is the electrostatic potential,  $\rho(\mathbf{r})$  the charge density and  $\epsilon_0$  the permittivity of free space. Using Eq.(33) we may write the solution of the above equation as

$$\phi(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{4\pi \epsilon_0 |\mathbf{r} - \mathbf{r}'|} d\tau' \quad (34)$$

The above equation is essentially Coulomb's law in electrostatics because due to a point charge  $Q$  at the origin, the electrostatic potential at a distance  $r$  is simply

$$\frac{Q}{4\pi \epsilon_0 r}$$

Thus, since  $\rho(\mathbf{r}')d\tau'$  represents the total charge in the infinitesimal volume element  $d\tau'$ , its contribution to the electric potential at  $\mathbf{r}$  would be

$$\frac{\rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|}d\tau'$$

from which Eq.(34) readily follows.

#### 24.4.3. GREEN'S FUNCTION FOR THE $(\nabla^2 + k^2)$ OPERATOR

Proceeding in a manner similar to that discussed in the previous section, we can show that

$$(\nabla^2 + k^2)\frac{e^{\pm ikr}}{r} = 0 \quad \text{for } r > 0$$

Because of the above equation

$$\int_V \left[ (\nabla^2 + k^2) \frac{e^{ikr}}{r} \right] d\tau = \int_R \left[ (\nabla^2 + k^2) \frac{e^{ikr}}{r} \right] r^2 dr d\Omega$$

where  $V$  is an arbitrary volume surrounding the origin and the second integral is over a sphere of radius  $R$ . Using Gauss's theorem we get

$$\begin{aligned} \text{RHS} &= \iint \nabla \left( \frac{e^{ikr}}{r} \right) \cdot \hat{\mathbf{r}} R^2 d\Omega + k^2 \int_0^R e^{ikr} r dr \iint d\Omega \\ &= [ikRe^{ikR} - e^{ikR}]4\pi + 4\pi k^2 \left[ r \frac{e^{ikr}}{ik} - \frac{e^{ikr}}{(ik)^2} \right]_0^R \\ &= -4\pi \end{aligned}$$

Thus

$$(\nabla^2 + k^2)\frac{e^{\pm ikr}}{r} = -4\pi\delta(\mathbf{r})$$

If we shift the origin, we obtain

$$(\nabla^2 + k^2)\frac{\exp[\pm ik|\mathbf{r} - \mathbf{r}'|]}{-4\pi|\mathbf{r} - \mathbf{r}'|} = \delta(\mathbf{r} - \mathbf{r}')$$

Thus the Green's function of the operator  $(\nabla^2 + k^2)$  is given by

$$G(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \frac{e^{\pm ik|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \quad (35)$$

and the solution of the equation

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = F(\mathbf{r})$$

is given by

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) - \int \frac{e^{\pm ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|} F(\mathbf{r}') d\tau' \quad (36)$$

where  $\phi(\mathbf{r})$  is the solution to the homogeneous part of the equation. If we use Eq. (24) and the fact that

$$F(\mathbf{r}) = \frac{2\mu}{\hbar^2} V(\mathbf{r}) \psi(\mathbf{r})$$

we would get

$$\psi^\pm(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2} \int \frac{\exp(\pm ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}') \psi^\pm(\mathbf{r}') d\tau' \quad (37)$$

[An alternative derivation of the above equation is given in Appendix N].

We make two remarks about these solutions. First, any linear combination of  $\psi^+$  and  $\psi^-$  will also be a solution. Secondly, we really have not solved anything since (37) is an integral equation with the unknown  $\psi^\pm$  appearing on both sides. Actually, we need the asymptotic forms, i.e., the form of  $\psi(\mathbf{r})$  for  $r \rightarrow \infty$ . If we assume that  $V(\mathbf{r}') \neq 0$  only for a finite region, say  $|\mathbf{r}'| < a$  then for  $r \rightarrow \infty$ , the main contribution of the integral in Eq. (37) comes from a region where  $r' \ll r$ ; thus we may write

$$|\mathbf{r}-\mathbf{r}'| = r \left[ 1 - \frac{2\mathbf{r} \cdot \mathbf{r}'}{r^2} + \frac{r'^2}{r^2} \right]^{1/2} \approx r - \hat{\mathbf{r}} \cdot \mathbf{r}'$$

and

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} \approx \frac{1}{r} + \frac{1}{r^2} \hat{\mathbf{r}} \cdot \mathbf{r}' + \dots$$

so that

$$\psi^\pm(\mathbf{r}) \xrightarrow[r \rightarrow \infty]{} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2} \frac{e^{\pm ikr}}{r} \int e^{\pm ikr(r-\hat{\mathbf{r}}\cdot\mathbf{r}')} V(\mathbf{r}') \psi^\pm(\mathbf{r}') d\mathbf{r}'$$

or

$$\psi^\pm(\mathbf{r}) \xrightarrow[r \rightarrow \infty]{} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2} \frac{e^{\pm ikr}}{r} \int e^{\pm i\mathbf{k}' \cdot \mathbf{r}'} V(\mathbf{r}') \psi^\pm(\mathbf{r}') d\mathbf{r}'$$

where  $\mathbf{k}' \equiv kr\hat{\mathbf{r}}$  is a vector along the direction of scattering. The above equation is of the form

$$\psi^\pm(\mathbf{r}) \xrightarrow[r \rightarrow \infty]{} e^{i\mathbf{k}\cdot\mathbf{r}} + f_k(\theta, \phi) \frac{e^{\pm ikr}}{r}$$

where  $\theta, \phi$  are polar angles of the scattered particles. We recall that for the complete solutions we must multiply the above equation by the time part,  $e^{-i\omega t}$ , where  $k$  and  $\omega$  are related by the free particle equation.

$$\frac{\hbar^2 k^2}{2\mu} = \hbar\omega$$

We now recognize that  $\psi^+(\mathbf{r})$  represents a plane wave term plus an outgoing wave while  $\psi^-(\mathbf{r})$  represents a plane wave term plus an incoming wave term. We now restrict ourselves to the solution corresponding to the outgoing wave case  $\psi^+(\mathbf{r})$ . The term

$$f(\theta, \phi) = -\frac{\mu}{2\pi\hbar^2} \int \exp(-i\mathbf{k}' \cdot \mathbf{r}') V(\mathbf{r}') \psi^+(\mathbf{r}') d\mathbf{r}' \quad (38)$$

is called the *scattering amplitude*. Generally in scattering experiments the detector is placed outside the region of the incident beam and counts only the scattered part. It can be seen that the amplitude of the scattered beam is reduced by a factor  $1/r^2$ . Once  $f(\theta, \phi)$  is known, the scattering cross-section can be calculated using the relation

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2$$

## 24.5. The Born approximation

The scattering amplitude [Eq. (38)] cannot be evaluated unless we know  $\psi^+(\mathbf{r}')$  in the first place. However, if the interaction energy  $V$  is treated as a small perturbation, then we can solve for  $\psi^+$  by the method of successive approximations. From Eq. (37) we obtain as the approximation [setting  $\psi^+(\mathbf{r}') \approx e^{i\mathbf{k}' \cdot \mathbf{r}'}$  in the integrand]

$$\psi_1^+(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} - \frac{\mu}{2\pi\hbar^2} \int \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') e^{i\mathbf{k}' \cdot \mathbf{r}'} d\mathbf{r}' \quad (39)$$

The next approximation is obtained by using this value of  $\psi^+$  in the integral in (37), i.e.

$$\begin{aligned} \psi_2^+(\mathbf{r}) &= e^{i\mathbf{k} \cdot \mathbf{r}} - \frac{\mu}{2\pi\hbar^2} \int d\mathbf{r}' \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') e^{i\mathbf{k}' \cdot \mathbf{r}'} d\mathbf{r}' \\ &\quad + \left( \frac{\mu}{2\pi\hbar^2} \right)^2 \iint d\mathbf{r}' d\mathbf{r}'' \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') \frac{\exp(ik|\mathbf{r}' - \mathbf{r}''|)}{|\mathbf{r}' - \mathbf{r}''|} V(\mathbf{r}'') e^{i\mathbf{k} \cdot \mathbf{r}''} \end{aligned}$$

The term  $\psi_n^+(\mathbf{r})$  obtained by this procedure is called the *nth Born Approximation*. Frequently, one uses only the first term and it is referred to as the Born approximation. The first Born approximation for the scattering amplitude is obtained by setting  $\psi^+(\mathbf{r}') = e^{i\mathbf{k}' \cdot \mathbf{r}'}$  in Eq. (38) to obtain

$$f(\theta, \phi) = -\frac{\mu}{2\pi\hbar^2} \int V(\mathbf{r}') e^{-i\mathbf{q} \cdot \mathbf{r}'} d\mathbf{r}' \quad (40)$$

where  $\hbar\mathbf{q} = \hbar(\mathbf{k}' - \mathbf{k})$  is the momentum transfer in scattering. We may also write

$$f(\theta, \phi) = -\frac{\mu}{2\pi\hbar^2} V_{\mathbf{q}}$$

where

$$V_q = \int V(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \quad (41)$$

is the Fourier transform of the potential. For spherically symmetric potentials

$$V(\mathbf{r}') = V(r')$$

and one obtains

$$f(\theta, \phi) = -\frac{\mu}{2\pi\hbar^2} \iiint r'^2 dr' \sin\theta' d\theta' d\phi' V(r') e^{-iqr' \cos\theta'}$$

where we have assumed the  $z'$ -axis to be along  $\mathbf{q}$ , and

$$q = |\mathbf{k}' - \mathbf{k}| = 2k \sin \frac{\theta}{2}$$

$\theta$  being the angle of scattering (the angle between  $\mathbf{k}'$  and  $\mathbf{k}$ ). Carrying out the integrations we get

$$f(\theta) = -\frac{2\mu}{\hbar^2} \int_0^\infty V(r') \frac{\sin qr'}{qr'} r'^2 dr' \quad (42)$$

and

$$\sigma(\theta) = \left( \frac{2\mu}{\hbar^2} \right)^2 \left| \int_0^\infty V(r') \frac{\sin qr'}{qr'} r'^2 dr' \right|^2 \quad (43)$$

Suppose now  $V(\mathbf{r}')$  is a potential which has the same sign everywhere. Then Eq. (42) shows that for large values of  $q$  there will be large phase differences from different regions of the scatterer (i.e. the exponential term oscillates) and effects from different regions will tend to reduce the scattering amplitude. On the other hand for  $q = 0$  (i.e.  $\mathbf{k}'$  parallel to  $\mathbf{k}$ ) the amplitude will be the largest. The scattering amplitude in this case is

$$f(0) = -\frac{\mu}{2\pi\hbar^2} \int V(\mathbf{r}') d\mathbf{r}'$$

The ratio  $f(\mathbf{q})/f(0)$  is called the *form factor*. Another way of looking at the problem is to study the difference between a ‘point’ scatterer and a ‘spread out’ one. It is easy to see that, in general, the effect of a spread is to reduce the scattering.

The Born approximation is useful when the scattered wave is negligible compared to the incident wave. Looking at Eq. (39) this implies that

$$\left| \frac{\mu}{2\pi\hbar^2} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}') e^{i\mathbf{k} \cdot \mathbf{r}'} d\mathbf{r}' \right| \ll 1$$

For short-range central potentials, we can put  $r \approx 0$  and obtain a crude limit

$$\frac{2\mu}{\hbar^2 k} \left| \int_0^\infty e^{ikr'} \sin kr' V(r') dr' \right| \ll 1 \quad (44)$$

a result that is likely to hold for weak potentials and high energies.

#### 24.5.1. APPLICATION OF BORN APPROXIMATION FOR THE SHIELDED COULOMB POTENTIAL

As an example we consider the shielded Coulomb potential for which the potential energy function is given by (see, e.g. Ref. 3, Sec. 14.1)<sup>3</sup>

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \exp\left(-\frac{r}{\lambda}\right) \quad (45)$$

where  $\lambda$  is known as the shielding distance, substituting in Eq. (43) we get

$$\sigma(\theta) = \frac{4\mu^2}{\hbar^4 q^2} (Z_1 Z_2 e^2)^2 \left| \int_0^\infty e^{-r/\lambda} \sin qr dr \right|^2$$

The integral is the imaginary part of  $\int_0^\infty e^{-r/\lambda} e^{iqr} dr$  and gives

$$\frac{q}{q^2 + \frac{1}{\lambda^2}}$$

Thus

$$\sigma(\theta) = \frac{4\mu^2 (Z_1 Z_2 e^2)^2}{\hbar^2 \left(q^2 + \frac{1}{\lambda^2}\right)^2} = \frac{4\mu^2 (Z_1 Z_2 e^2)^2}{\left(4p^2 \sin^2 \frac{\theta}{2} + \frac{\hbar^2}{\lambda^2}\right)^2} \quad (46)$$

If we let  $\lambda \rightarrow \infty$ , we get

$$\sigma = \frac{(Z_1 Z_2 e^2)^2}{16E^2 \sin^4 \frac{\theta}{2}} \quad (47)$$

which is exactly the same as obtained using classical mechanics (see Problem 24.22). Indeed even the exact analysis (see Sec. 24.6) gives the same result.

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<sup>3</sup> We are, for the sake of convenience, using the CGS units. In MKS units  $e^2$  should be replaced by  $q^2/4\pi\epsilon_0$  but then there would be confusion between the charge  $q$  and the momentum transfer vector  $\hbar q$ .

## 24.6. Method of partial waves

In the previous section we have discussed the Born approximation and have also given approximate conditions for its validity. When the Born approximation fails, it is necessary to use other methods; one such method is the method of partial waves which is applicable to the spherically symmetric potentials. For such a potential, the angular momentum of the scattered particle is a constant of motion. It is therefore advantageous to develop solutions in terms of angular momentum eigenfunctions. If the potential is of sufficiently short range (or the energy of the incident particles is low), it will turn out that only a few eigenfunctions with small angular momenta (that is only a few partial waves) will really be affected by the potential. Assuming that the incident momentum is  $\hbar k$ , large angular momenta correspond roughly to large values of the impact parameter<sup>4</sup> and hence the particle is hardly deflected. If the range of the potential is  $a$  it usually suffices to consider angular momenta  $l\hbar$  with

$$l \lesssim k/a$$

Before we give the details of the partial wave analysis, it is necessary to study the properties of spherical Bessel functions.

### 24.6.1. SPHERICAL BESSEL FUNCTIONS

For spherical symmetrically potential, the radial part of the Schrödinger equation is given by [see Sec. 10.2]

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) = 0 \quad (48)$$

For a free particle  $V(r) = 0$ , and the above equation can be written in the form

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR}{d\rho} \right) + \left[ 1 - \frac{l(l+1)}{\rho^2} \right] R(\rho) = 0 \quad (49)$$

where

$$\rho = kr \quad \text{and} \quad k = \left( \frac{2\mu E}{\hbar^2} \right)^{1/2}$$

Equation (49) is known as the spherical Bessel equation and the solutions are denoted by

$$j_l(\rho) \quad \text{and} \quad n_l(\rho)$$

which are known as the spherical Bessel functions. For  $l = 0$ , if we make the transformation

$$R(\rho) = \frac{u(\rho)}{\rho}$$

---

<sup>4</sup> Classically the angular momentum of the particle is  $mv_0s$  (see Fig. 24.2) and clearly for  $s > a$  (where  $a$  is the range of the potential) there is no scattering of the particle.

then

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR}{d\rho} \right) = \frac{1}{\rho^2} \frac{d}{d\rho} \left[ \rho \frac{du}{d\rho} - u(\rho) \right] = \frac{1}{\rho} \frac{d^2 u}{d\rho^2}$$

Thus Eq.(49) [for  $l = 0$ ] simplifies to

$$\frac{d^2 u}{d\rho^2} + u(\rho) = 0$$

the solutions of which are  $\sin \rho$  and  $\cos \rho$ . Thus the 2 independent solutions of Eq.(49) [for  $l = 0$ ] are

$$j_0(\rho) = \frac{1}{\rho} \sin \rho \quad \text{and} \quad n_0(\rho) = \frac{1}{\rho} \cos \rho$$

Obviously,  $n_0(\rho)$  is singular at the origin. The spherical Bessel functions are related to Bessel functions through the following equations (see Appendix J)

$$j_l(\rho) = \sqrt{\frac{\pi}{2\rho}} J_{l+\frac{1}{2}}(\rho) \quad \text{and} \quad n_l(\rho) = (-1)^l \sqrt{\frac{\pi}{2\rho}} J_{-l-\frac{1}{2}}(\rho)$$

Using the expressions for  $j_0(\rho)$  and  $n_0(\eta)$  one can calculate higher order functions using the following recurrence relations

$$j_{l+1}(\rho) = \frac{l}{\rho} j_l(\rho) - j'_l(\rho); \quad n_{l+1}(\rho) = \frac{l}{\rho} n_l(\rho) - n'_l(\rho)$$

Thus

$$\begin{aligned} j_0(\rho) &= \frac{1}{\rho} \sin \rho \\ j_1(\rho) &= \frac{1}{\rho^2} \sin \rho - \frac{1}{\rho} \cos \rho \\ j_2(\rho) &= \left( \frac{3}{\rho^3} - \frac{1}{\rho} \right) \sin \rho - \frac{3}{\rho^2} \cos \rho \end{aligned}$$

etc. Similarly

$$\begin{aligned} n_0(\rho) &= \frac{1}{\rho} \cos \rho \\ n_1(\rho) &= \frac{1}{\rho^2} \cos \rho + \frac{1}{\rho} \sin \rho \\ n_2(\rho) &= \left( \frac{3}{\rho^3} - \frac{1}{\rho} \right) \cos \rho - \frac{3}{\rho^2} \sin \rho \end{aligned}$$

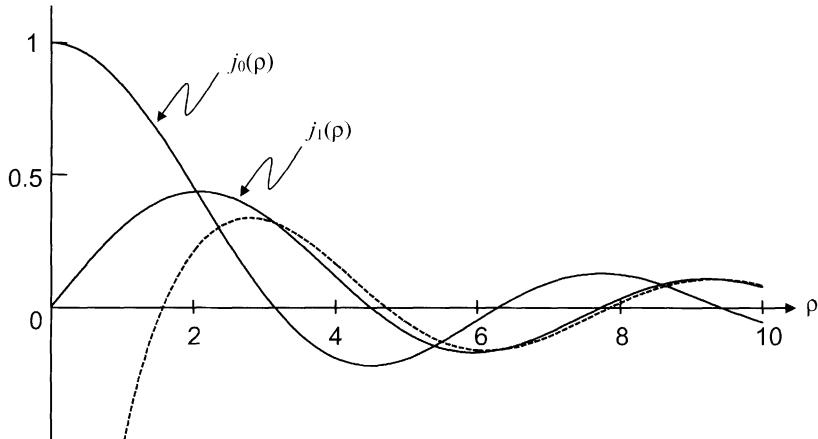


Figure 24.4. The solid curves represent the variations of  $j_0(\rho)$  and  $j_1(\rho)$  with  $\rho$ . The dashed curve represents the asymptotic form of  $j_1(\rho)$ . The asymptotic form of  $j_0(\rho)$  coincides with the exact variation.

etc. One can see that the asymptotic forms are

$$\begin{aligned} j_l(\rho) &\xrightarrow[\rho \rightarrow \infty]{} \frac{1}{\rho} \sin \left( \rho - \frac{l\pi}{2} \right) \\ n_l(\rho) &\xrightarrow[\rho \rightarrow \infty]{} \frac{1}{\rho} \cos \left( \rho - \frac{l\pi}{2} \right) \end{aligned} \quad (50)$$

The variations of  $j_0(\rho)$  and  $j_1(\rho)$ , along with their asymptotic forms are shown in Fig. 24.4.

#### 24.6.2. EXPANSION FORMULA FOR A PLANE WAVE

We assume that particles of momenta are incident along the  $z$ -direction. The plane wave representing the incident particle can be expanded as<sup>5</sup>:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikz} = e^{ikr \cos \theta} = \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos \theta) j_l(\rho) \quad (51)$$

where  $\rho = kr$ ; notice that there is no azimuthal angular dependence in the expansion due to symmetry around the  $z$ -axis. The derivation of Eq. (51) is as follows:

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<sup>5</sup> 4 A more general formula is given by

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-\infty}^{+\infty} i^l Y_{lm}^*(\theta_k, \phi_k) Y_{lm}(\theta_r, \phi_r) j_l(kr)$$

where  $(\theta_k, \phi_k)$  and  $(\theta_r, \phi_r)$  are the polar angles of the vectors  $\mathbf{k}$  and  $\mathbf{r}$  respectively.

We start with the Schrödinger equation for a free particle

$$\nabla^2 \psi + k^2 \psi = 0 \quad (52)$$

where  $k^2 = 2\mu E/\hbar^2$ . The plane wave solution of the above equation is given by

$$\psi = e^{ikz} = e^{ikr \cos \theta}$$

Equation (52) can also be solved in spherical polar co-ordinates. The solution of Eq.(52) with azimuthal symmetry (i.e., independent of  $\phi$ ) must satisfy

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + k^2 \psi = 0 \quad (53)$$

Using the method of separation of variables we write  $\psi(r, \theta) = R(r)\Theta(\theta)$  and the above equation can be written in the form

$$\begin{aligned} \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + k^2 r^2 &= -\frac{1}{\Theta(\theta)} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \\ &= l(l+1) \text{ (say)} \end{aligned} \quad (54)$$

If we define  $\mu = \cos \theta$ ,  $\Theta(\mu)$  can be shown to satisfy the Legendre's equation

$$(1 - \mu^2) \frac{d^2 \Theta}{d\mu^2} - 2\mu \frac{d\Theta}{d\mu} + l(l+1)\Theta(\mu) = 0$$

For the solutions to be bounded at  $\mu = \pm 1$  ( $\theta = 0, \pi$ ),  $l$  must be  $0, 1, 2, \dots$  [see Sec. 9.3] and the well behaved solution of the above equation would be the Legendre's polynomials:

$$\Theta(\mu) = P_l(\mu)$$

Returning to Eq.(54), the function  $R(r)$  satisfies the equation

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR}{d\rho} \right) + \left[ 1 - \frac{l(l+1)}{\rho^2} \right] R(\rho) = 0$$

where  $\rho = kr$ . The above equation is the spherical Bessel equation [Eq. (49)] and the solution which is finite at  $\rho = 0$  will be  $j_l(\rho)$ . Thus any bounded solution of Eq.(53) can be written as a linear combination of  $j_l \rho P_l(\rho)$ . Thus,

$$e^{i\rho\mu} = \sum_{l=0}^{\infty} a_l j_l(\rho) P_l(\mu); \quad \rho = kr$$

If we multiply both sides by  $P_m(\mu)d\mu$ , integrate and use the orthogonality relation of Legendre polynomials, we get

$$a_m \frac{2}{2m+1} j_m(\rho) = \int_{-1}^{+1} e^{i\rho\mu} P_m(\mu) d\mu \quad (55)$$

The above equation must be valid for all values of  $\rho$ ; we take the limit  $\rho \rightarrow \infty$ , then

$$\begin{aligned} \text{LHS} &\sim a_m \frac{2}{2m+1} \frac{1}{\rho} \sin\left(\rho - \frac{m\pi}{2}\right) \\ \text{RHS} &\sim \frac{2i^l}{\rho} \sin\left(\rho - \frac{m\pi}{2}\right) - \frac{1}{i\rho} \int_{-1}^{+1} e^{i\rho\mu} \frac{d}{d\mu} P_m(\mu) d\mu \end{aligned}$$

[integrating by parts]

If we integrate the second term by parts we would obtain terms proportional to  $1/\rho^2$ ; thus in the limit of  $\rho \rightarrow \infty$  we may write

$$\text{RHS} \sim \frac{2i^l}{\rho} \sin\left(\rho - \frac{m\pi}{2}\right)$$

Thus

$$a_m = (2m+1)i^m$$

and we obtain

$$e^{i\rho \cos \theta} = \sum_{l=0,1,\dots}^{\infty} (2l+1)i^l j_l(\rho) P_l(\mu)$$

From Eq.(55), we also get the integral representation of the spherical Bessel functions

$$j_l(\rho) = \frac{1}{2i^l} \int_{-\infty}^{+\infty} e^{i\rho\mu} P_l(\mu) d\mu \quad (56)$$

For any given value of  $l$ , we can substitute the expression for  $P_l(\mu)$  and evaluate the integral to obtain the expression for  $j_l(\rho)$ . Now the asymptotic form of  $j_l(\rho)$  can be written as [see Eq. (50)]:

$$\begin{aligned} j_l(\rho) &\xrightarrow{\rho \rightarrow \infty} \frac{1}{2i\rho} \left[ \exp\left[i\left(\rho - \frac{l\pi}{2}\right)\right] - \exp\left[-i\left(\rho - \frac{l\pi}{2}\right)\right] \right] \\ &\xrightarrow{\rho \rightarrow \infty} \frac{i^{-l}}{2i\rho} [e^{i\rho} - (-1)^l e^{-i\rho}] \end{aligned}$$

Thus the asymptotic form of Eq. (51) will be

$$e^{ikz} = e^{ikr \cos \theta} \rightarrow \sum_l \frac{(2l+1)}{2ikr} [e^{ikr} - (-1)^l e^{-ikr}] P_l(\cos \theta) \quad (57)$$

Now for spherically symmetric potentials, the Schrödinger equation is given by

$$[\nabla^2 + k^2 - U(r)]\psi(\mathbf{r}) = 0$$

where  $U(r) = 2\mu V(r)/\hbar^2$ . The solution of the above equation (with azimuthal symmetry) can be written in the form

$$\psi(r) = \sum_l \frac{(2l+1)}{k} i^l \frac{u_l(r)}{r} P_l(\cos \theta) \quad (58)$$

In writing down (58), we make the following observations:

- (a) Since, in the Schrödinger equation (21), the potential is spherically symmetric, the spherical harmonics  $Y_{lm}(\theta, \phi)$  are solutions (see Sec. 10.2); in this problem  $m = 0$ , because there is no  $\phi$ -dependence. We can, therefore, take the general solution to be linear combination of  $Y_{l0}$  or  $P_l(\cos \theta)$ .
- (b) The factors  $(2l+1)i^l/k$  are introduced for convenience.

Clearly, for (58) to be correct,  $u_l(r)$  must satisfy the Schrödinger equation (21). Substituting (58) into (21) we obtain

$$\frac{d^2 u_l}{dr^2} + \left[ k^2 - U(r) - \frac{l(l+1)}{r^2} \right] u_l(r) = 0 \quad (59)$$

In Appendix O, we have shown that for a short-range force for which

$$\lim_{r \rightarrow \infty} r V(r) = 0 \quad (60)$$

the asymptotic form of  $u_l(r)$  will be  $\exp(\pm ikr)$ ; thus we may write<sup>6</sup>

$$\begin{aligned} u_l(r) &\xrightarrow[r \rightarrow \infty]{} A_l e^{ikr} + B_l e^{-ikr} \\ &= C_l \sin \left( kr - \frac{l\pi}{2} + \delta_l \right) \end{aligned} \quad (61)$$

---

<sup>6</sup> This may be very easily seen for a potential which vanishes beyond a certain distance  $r = a$ ; because then for  $r > a$ ,  $R_l(r) (= u_l(r)/r)$  satisfies the spherical Bessel equation [see Eq. (49)] and therefore

$$u_l(\rho) \xrightarrow[r \rightarrow \infty]{} \rho [a_l j_l(\rho) + b_l n_l(\rho)]$$

Using the asymptotic forms of  $j_l$  and  $n_l$  [see Eq. (50)]:

$$u_l(\rho) \xrightarrow[r \rightarrow \infty]{} \frac{1}{\rho} \left( a_l \sin \left( \rho - \frac{l\pi}{2} \right) + b_l \cos \left( \rho - \frac{l\pi}{2} \right) \right)$$

which is identical in form to Eq. (61) with  $\delta_l = \tan^{-1}(b_l/a_l)$ .

where the factor  $\frac{l\pi}{2}$  has been introduced for the sake of convenience and the quantities  $\delta_l$  are known as phase shifts. We see that when  $V(r) = 0$  everywhere,  $u_l(r)$  is simply  $kr j_l(kr)$  [see Eq. (59)] the asymptotic form of which is  $\sin(kr - l\pi/2)$ . Thus  $\delta_l$  is the “phase shift” introduced by the potential. Equation (61) can be written in the form

$$u_l \sim \frac{1}{2i} C_l (-i)^l [e^{i\delta_l} e^{ikr} - (-1)^l e^{-i\delta_l} e^{-ikr}] \quad (62)$$

Substituting (62) into (58), we obtain

$$\psi(\mathbf{r}) \xrightarrow[r \rightarrow \infty]{} \sum_l \frac{(2l+1)}{2ikr} C_l [e^{i\delta_l} e^{ikr} - (-1)^l e^{-i\delta_l} e^{-ikr}] P_l(\cos \theta) \quad (63)$$

This is to be compared with the form

$$\begin{aligned} \psi(\mathbf{r}) &\longrightarrow e^{ikz} + \frac{e^{ikr}}{r} f(\theta) \\ &= \sum_l \frac{(2l+1)}{2ikr} P_l(\cos \theta) [e^{ikr} - (-1)^l e^{-ikr}] + \frac{e^{ikr}}{r} f(\theta) \end{aligned} \quad (64)$$

where we have used Eq. (57). Equations (63) and (64) represent the same function and hence the coefficients of  $e^{ikr}$  and  $e^{-ikr}$  should be identical; equating the coefficients gives us

$$C_l = e^{i\delta_l}$$

and

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) \frac{\exp(2i\delta_l) - 1}{2ik} P_l(\cos \theta) \quad (65)$$

or

$$f(\theta) = \sum_{l=0}^{\infty} \frac{(2l+1)}{k} \sin \delta_l e^{i\delta_l} P_l(\cos \theta) \quad (66)$$

The total cross-section can be shown to be (see Problem 24.16)

$$\sigma = \int |f(\theta)|^2 d\Omega = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \quad (67)$$

The above expression shows that as far as the total cross-section is concerned, the different partial waves contribute independently, there being no interference. This, however, is not the case for the differential cross-section.

As an application of the method of partial waves, we will consider two examples.

### 24.6.3. SCATTERING BY A HARD SPHERE

We first consider the scattering by a hard sphere for which  $V(r)$  will be given by

$$\begin{aligned} V(r) &= 0 & r > a \\ &= \infty & r < a \end{aligned} \quad (68)$$

Since the region  $r < a$  is impenetrable, the wave function must vanish at  $r = a$ . Now, for  $r > a$  the radial part of the Schrödinger equation is [see Eq. (21)]

$$\frac{d^2 u_l}{dr^2} + \left[ k^2 - \frac{l(l+1)}{r^2} \right] u_l(r) = 0 \quad (69)$$

For  $l = 0$ , the solution (which vanishes at  $r = a$ ) is given by

$$u_0(r) = A \sin k(r - a) \quad (70)$$

Comparing with Eq. (61) we get

$$\delta_0 = -ka \quad (71)$$

which is known as the  $s$ -wave (or  $l = 0$ ) phase shift.

In general, (for arbitrary  $l$ ) the solution is (see Appendix J):

$$u_l(r) = (kr)[A_l j_l(kr) + B_l n_l(kr)] \quad \text{for } r > a \quad (72)$$

Using the boundary condition at  $r = a$  we get

$$\begin{aligned} u_l(r) &= (kr)A_l \left[ j_l(kr) - \frac{j_l(ka)}{n_l(ka)} n_l(kr) \right] \\ &\xrightarrow{r \rightarrow \infty} A_l \left[ \sin \left( kr - \frac{l\pi}{2} \right) - \frac{j_l(ka)}{n_l(ka)} \cos \left( kr - \frac{l\pi}{2} \right) \right] \end{aligned} \quad (73)$$

Comparing with Eq. (61) we immediately get

$$\tan \delta_l = -\frac{j_l(ka)}{n_l(ka)} \quad (74)$$

The above equation is an exact result; for  $l = 0$ , one immediately gets Eq. (71). For  $ka \ll 1$  (i.e. for low energies), if we use Eq. (13) of Appendix J, we would get

$$\tan \delta_l \approx -\frac{(ka)^{2l+1}}{(2l+1)!! (2l-1)!!} \quad (75)$$

Since  $ka \ll 1$ , we get  $\delta_1/\delta_0 \ll 1$ ,  $\delta_2/\delta_1 \ll 1$ , etc. This result is consistent with our earlier statement that at low energies only few of the angular momenta contribute. Thus for sufficiently low energies, only  $\delta_0$  effectively contributes and using Eqs (67) and (71), we get

$$\sigma \approx \frac{4\pi}{k^2} \sin^2 \delta_0 \approx 4\pi a^2 \quad (76)$$

which is 4 times the result obtained by using classical mechanics (see Problem 24.21). At this point it may be worthwhile to discuss the conditions for the validity of the classical theory in describing the scattering process. The classical theory will be valid when one is justified in describing the scattering through the ‘trajectories’ of the classical particle. The situation is analogous to the justification of the ‘ray-picture’ in optics which is valid when the refractive index changes very slowly in distances of the order of wavelength. This is also the condition for the validity of the JWKB approximation (see Chapter 17). When diffraction effects become important it is necessary to have a quantum mechanical description of the scattering process.

For the hard sphere case, when  $ka \gg 1$

$$\tan \delta_l \approx -\tan \left( ka - \frac{l\pi}{2} \right) \quad (77)$$

so that

$$\begin{aligned} \sigma &\approx \frac{4\pi}{k^2} \sum_{l=0}^{l \approx ka} (2l+1) \sin^2 \left( -ka + \frac{l\pi}{2} \right) \\ &\approx \frac{4\pi}{k^2} \int_0^{ka} (2x+1) \sin^2 \left( -ka + \frac{x\pi}{2} \right) dx \\ &\approx 2\pi a^2 \end{aligned} \quad (78)$$

which is still a factor of 2 more than the classical result. This is due to the fact that from the region  $\theta \approx 0$  there is a contribution of  $\pi a^2$ ; this contribution arises from the famous Poisson-diffraction phenomenon according to which when a plane wave is incident normally on an opaque disc, one always obtains a bright spot on the center of the geometric shadow (for further details one may look up Ref. 4, p. 215).

#### 24.6.4. SCATTERING BY A SQUARE WELL AND THE RAMSAUER EFFECT

We next consider the  $s$ -wave scattering by a square well

$$\begin{aligned} V(r) &= -V_0 & 0 < r < a \\ &= 0 & r > a \end{aligned} \quad (79)$$

For  $l = 0$ , the radial part of the Schrödinger equation would be [see Eq. (59)]

$$\frac{d^2 u_0}{dr^2} + K^2 u_0(r) = 0 \quad \text{for } 0 < r < a \quad (80)$$

$$\frac{d^2 u_0}{dr^2} + k^2 u_0(r) = 0 \quad \text{for } r > a \quad (81)$$

where  $K^2 = 2m(E + V_0)/\hbar^2$  and  $k^2 = 2mE/\hbar^2$ . For  $r < a$  we must have  $u_0 = A \sin kr$  (the cosine solution will make  $R_0(r) = u_0(r)/r$  go to infinity at  $r = 0$ ). For  $r > a$  we write the solution in the form  $u_0(r) = B \sin(kr + \delta_0)$ . Continuity of  $u$  and its derivative at  $r = a$  gives

$$\tan(ka + \delta_0) = \frac{k}{K} \tan Ka$$

or

$$\delta_0 = \tan^{-1} \left( \frac{k}{K} \tan Ka \right) - ka \quad (82)$$

Thus

$$\begin{aligned} \sigma &\simeq \frac{4\pi}{k^2} \sin^2 \delta_0 = \frac{4\pi}{k^2} \left[ 1 + \frac{1}{\tan^2 \delta_0} \right]^{-1} \\ &= 4\pi \left[ k^2 + \left( \frac{g + k \tan ka}{1 - g \frac{\tan ka}{k}} \right)^2 \right]^{-1} \end{aligned} \quad (83)$$

where  $g = K \cot Ka$ .

Returning to Eq. (82) we notice that  $\tan \delta_0$  (and hence the scattering cross-section) would vanish if

$$\frac{\tan Ka}{K} = \frac{\tan ka}{k};$$

we are assuming  $ka \ll 1$  so that  $\delta_1, \delta_2$ , etc., are negligible. Although the above equation has been derived for a square well potential, similar vanishing of the cross-section would occur for a ‘localizable’ attractive potential. This effect was first observed by Ramsauer (and hence known as Ramsauer effect) who found that at low energies ( $\sim 0.7$  eV) the scattering cross-section of electrons by noble atoms was extremely small. The effect was later explained by quantum theory.

#### 24.6.5. SCATTERING OF NEUTRONS BY PROTONS

The neutron-proton interaction can be approximately described by the square well interaction [see Eq. (79)]. Thus, we may use the results of Sec. 24.5.2 to

study the scattering of neutrons by protons. For low energies  $ka \rightarrow 0$  and Eq. (83) becomes

$$\sigma \approx \frac{4\pi}{k^2 + \frac{g^2}{(1-ga)^2}} \quad (84)$$

In order to determine the value of  $g (= K \cot Ka)$  we use the data on the binding energy for the ground state of deuteron; this is denoted by  $B$  and its value is  $\approx 2.223$  MeV. Now, for the ground state of deuteron  $E = -B$  and  $l = 0$  so that

$$\begin{aligned} u_0(r) &= A \sin k_1 r \quad \text{for } r < a \\ &= Ce^{-\kappa r} \quad \text{for } r > a \end{aligned}$$

where  $\kappa^2 = 2\mu B / \hbar^2$ ,  $k_1^2 = 2\mu(-B + V_0) / \hbar^2$ ,

$$\mu = \frac{m_n m_p}{m_n + m_p} \approx \frac{1}{2} m_n$$

being the reduced mass of the neutron-proton system. Continuity conditions at  $r = a$  gives us

$$k_1 \cot k_1 a = -\kappa \quad (85)$$

If  $B \ll V_0$  (which is indeed the case because  $V_0 \approx 40$  MeV),

$$k_1 \approx [2\mu V_0 / \hbar^2]^{1/2} \approx K.$$

Thus

$$g = K \cot Ka \approx k_1 \cot k_1 a = -\kappa = -\left(\frac{2\mu}{\hbar^2} B\right)^{1/2} \quad (86)$$

Substituting in Eq. (84) we get

$$\sigma \approx \frac{4\pi}{\frac{2\mu E}{\hbar^2} + \frac{2\mu B}{\hbar^2(1-ga)^2}} \approx \frac{4\pi \hbar^2}{m_n(E+B)} \quad (87)$$

The last step is not very accurate because  $ga \sim 0.3$ , nevertheless the above expression should give a reasonable estimate for  $\sigma$ . However, if we assume  $E \ll B = 2.223$  MeV then the above expression gives  $\sigma \approx 2.4 \times 10^{-24} \text{ cm}^2$  whereas the experimental value is about  $21 \times 10^{-24} \text{ cm}^2$ . This large discrepancy cannot be accounted for by the approximation made in the analysis. In 1935, Wigner made a suggestion which removed this difficulty. He pointed out that the ground state of the deuteron was a triplet; however, there is no reason why the neutron and proton could not interact with their spins antiparallel (i.e. through the singlet state). Let  $E_s$  denote the energy of the neutron-proton system associated with the singlet state then

$$\sigma \approx \frac{4\pi \hbar^2}{m_n} \left[ \frac{3}{4} \frac{1}{E + B} + \frac{1}{4} \frac{1}{E + |E_s|} \right] \quad (88)$$

where  $\frac{3}{4}$  and  $\frac{1}{4}$  are the statistical weights of the triplet and singlet states (see Sec. 22.5). If we assume  $|E_s| \approx 40$  KeV we get the right order of magnitude for  $\sigma$ . However, it is not possible to decide whether the state is real or virtual<sup>7</sup>. For low energies ( $E \lesssim 4 - 5$  MeV) the experimental dependence of  $\sigma$  on  $E$  is in reasonably good agreement with Eq. (88).

#### 24.6.6. APPROXIMATE EXPRESSION FOR PHASE SHIFTS IN THE BORN APPROXIMATION

In this section we will obtain approximate expressions for the phase shifts when they have small values. We start out with the equations satisfied by  $g_l(r)$  [ $= krj_l(kr)$ ] and  $u_l(r)$  [see Eqs (14) and (15) of Appendix J and Eq. (59) of this chapter]:

$$\frac{d^2 g_l}{dr^2} + \left[ k^2 - \frac{l(l+1)}{r^2} \right] g_l(r) = 0 \quad (89)$$

$$\frac{d^2 u_l}{dr^2} + \left[ k^2 - \frac{l(l+1)}{r^2} - U(r) \right] u_l(r) = 0 \quad (90)$$

We multiply Eq. (89) by  $u_l(r)$  and Eq. (90) by  $g_l(r)$ , subtract and integrate to obtain:

$$\left[ g_l(r) \frac{du_l(r)}{dr} - u_l(r) \frac{dg_l}{dr} \right]_0^r = \int_0^r U(r) g_l(r) u_l(r) dr$$

Both  $g_l(r)$  and  $u_l(r)$  vanish at  $r = 0$ , further, we let  $r \rightarrow \infty$ , use the asymptotic forms [see Eq. (12) of Appendix J and Eq. (61)] to obtain for the left-hand side:

$$\begin{aligned} g_l \frac{du_l}{dr} - u_l(r) \frac{dg_l}{dr} &\xrightarrow[r \rightarrow \infty]{} k \sin \left( kr - \frac{l\pi}{2} \right) \cos \left( kr - \frac{l\pi}{2} + \delta_l \right) \\ &\quad - k \sin \left( kr - \frac{l\pi}{2} + \delta_l \right) \cos \left( kr - \frac{l\pi}{2} \right) = -k \sin \delta_l \end{aligned}$$

---

<sup>7</sup> Corresponding to the neutron-proton interaction in the triplet state  $V_0 \approx 21$  MeV and it is possible to have a bound state ( $B \approx 3$  MeV); on the other hand, when the spins are antiparallel  $V_0 \approx 12$  MeV and it is not possible to have a bound state. However, for  $E \simeq 40$  KeV it is possible to have a virtual (or a metastable) state with a finite lifetime (see, e.g. Ref 5, 6 and 7).

Table 24.1. Comparison of exact and approximate values for phases

$ka_0$	Energy (eV)	$\delta_0$	
		Exact	Born
		Approximation	
1.0	13.5	0.905	0.596
2.0	54	0.695	0.602
3.0	122	0.568	0.534
4.0	215	0.490	0.472
5.0	340	0.432	0.422

\* Table adapted from Ref. 7 see also Problem 24.6.

Thus

$$\sin \delta_l = -\frac{1}{k} \frac{2\mu}{\hbar^2} \int_0^\infty V(r) u_l(r) g_l(r) dr \quad (91)$$

The above equation is *exact*. Now, if the phase shifts are small (which is likely to be valid for high energies or weak potentials) then in carrying out the above integration we may assume

$$u_l(r) \approx g_l(r) = kr j_l(kr)$$

Thus

$$\begin{aligned} \sin \delta_l \approx \delta_l &\approx -\frac{2\mu}{k \hbar^2} \int_0^\infty V(r) [kr j_l(kr)]^2 dr \\ &\approx -\frac{\pi \mu}{\hbar^2} \int_0^\infty [J_{l+\frac{1}{2}}(kr)]^2 r dr \end{aligned} \quad (92)$$

where use has been made of Eq. (10) of Appendix J. Since Born approximation is also valid under the same conditions, the calculation of  $\delta_l$  through Eq. (92) is known as the Born approximation. In Table 24.1 we have given the value for  $\delta_0$  (for electron scattering by hydrogen—see Problem 24.6) obtained by using the Born approximation [Eq. (92)] and have compared with the exact values obtained by numerical solution of the differential equation. Notice that higher the values of  $k$  better is the agreement between the two numbers. The agreement with the experimental data is also satisfactory as discussed in Ref. 7.

If we use Eq. (92) for  $\delta_l$ , we should expect  $\sigma(\theta)$  to be given by Eq. (47); this is indeed seen from the following:

$$\begin{aligned}
 f(\theta) &= \frac{1}{2ik} \sum_{l=0,1,2,\dots}^{\infty} (2l+1) P_l(\cos \theta) [e^{2i\delta_l} - 1] \quad [\text{see Eq. (66)}] \\
 &\simeq \frac{1}{k} \sum_l (2l+1) P_l(\cos \theta) \delta_l \\
 &\simeq -\frac{1}{k} \sum_l (2l+1) P_l(\cos \theta) \frac{\pi \mu}{\hbar^2} \int_0^{\infty} V(r) r^2 [j_l(kr)]^2 dr \quad [\text{using Eq. (92)}] \\
 &\simeq -\frac{2\mu}{\hbar^2} \int_0^{\infty} \frac{\sin qr}{qr} V(r) r^2 dr
 \end{aligned} \tag{93}$$

where  $q = 2k \sin \theta / 2$  and use has been made of the identity (see, e.g. Ref. 8),

$$\frac{\sin qr}{qr} = \sum_{l=0,1,2,\dots}^{\infty} (2l+1) P_l(\cos \theta) [j_l(kr)]^2 \tag{94}$$

Equation (93) is identical to Eq. (46).

## 24.7. Coulomb scattering

The Coulomb potential

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \tag{95}$$

is such that

$$\lim_{r \rightarrow \infty} r V(r)$$

does not tend to zero and hence does not describe a short-range force (see Appendix O). Thus the results of the previous sections are not applicable. However, the scattering problem corresponding to the Coulomb potential can be solved directly in parabolic coordinates, the direction of the beam being an axis of symmetry. The coordinate system is

$$x = \sqrt{\xi \eta} \cos \phi; \quad y = \sqrt{\xi \eta} \sin \phi; \quad z = \frac{1}{2}(\xi - \eta) \tag{96}$$

We also have

$$r = \frac{1}{2}(\xi + \eta) \quad (97)$$

In terms of the parabolic coordinates, the Schrödinger equation [Eq. (12)] for the Coulomb potential becomes

$$\begin{aligned} -\frac{\hbar^2}{2\mu} \left[ \frac{4}{\xi + \eta} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial}{\partial \xi} \right) + \frac{4}{\xi + \eta} \frac{\partial}{\partial \eta} \left( \eta \frac{\partial}{\partial \eta} \right) + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \phi^2} \right] \psi \\ + \frac{2Z_1 Z_2 e^2}{(\xi + \eta)} \psi = E\psi \end{aligned} \quad (98)$$

Since we want solutions independent of  $\phi$ , we write

$$\psi = f_1(\xi) f_2(\eta) \quad (99)$$

Substituting from (99) in (98), we obtain

$$\frac{1}{f_1} \frac{d}{d\xi} \left( \xi \frac{df_1}{d\xi} \right) + \frac{1}{f_2} \frac{d}{d\eta} \left( \eta \frac{df_2}{d\eta} \right) - \frac{\mu Z_1 Z_2 e^2}{\hbar^2} + \frac{k^2}{4}(\xi + \eta) = 0$$

so that we can separate the equations

$$\frac{d}{d\xi} \left( \xi \frac{df_1}{d\xi} \right) + \left( \frac{1}{4}k^2\xi - \beta_1 \right) f_1 = 0 \quad (100)$$

and

$$\frac{d}{d\eta} \left( \eta \frac{df_2}{d\eta} \right) + \left( \frac{1}{4}k^2\eta - \beta_2 \right) f_2 = 0 \quad (101)$$

with

$$(\beta_1 + \beta_2) = \frac{\mu Z_1 Z_2 e^2}{\hbar^2} \quad (102)$$

The solution we want must be of the form of a plane wave moving along  $z$ -direction plus an outgoing spherical wave. These are proportional to

$$e^{ikz} = e^{ik(\xi-\eta)/2} \quad (103)$$

and

$$e^{ikr} = e^{ik(\xi+\eta)/2} \quad (104)$$

Both these forms suggest that we look for a solution of the form

$$e^{ik\xi/2} f_2(\eta)$$

In other words, we choose

$$f_1(\xi) = e^{ik\xi/2} \quad (105)$$

Substituting Eq. (105) into Eq. (100), we obtain

$$\left(\frac{ik}{2} - \frac{k^2}{4}\xi\right)e^{ik\xi/2} + \left(\frac{1}{4}k^2\xi - \beta_1\right)e^{ik\xi/2} = 0$$

so that

$$\beta_1 = ik/2$$

Substituting this value of  $\beta_1$  in (101) we obtain, from Eq. (100 b),

$$\frac{d}{d\eta} \left[ \eta \frac{df_2}{d\eta} \right] + \left[ \frac{1}{4}k^2\eta + \left( \frac{ik}{2} - \frac{\mu Z_1 Z_2 e^2}{\hbar^2} \right) \right] f_2 = 0 \quad (106)$$

We try a solution of the form

$$f_2(\eta) = e^{-ik\eta/2} g(\eta)$$

We have

$$\begin{aligned} \frac{df_2}{d\eta} &= \frac{-ik}{2} e^{-ik\eta/2} g + e^{-ik\eta/2} \frac{dg}{d\eta} \\ \frac{d^2 f_2}{d\eta^2} &= -\frac{k^2}{4} e^{-ik\eta/2} g - ik e^{-ik\eta/2} \frac{dg}{d\eta} + e^{-ik\eta/2} \frac{d^2 g}{d\eta^2} \end{aligned}$$

so that Eq. (106) becomes

$$\eta \frac{d^2 g}{d\eta^2} + (1 - ik\eta) \frac{dg}{d\eta} - nkg = 0$$

where we have written

$$n = \frac{\mu Z_1 Z_2 e^2}{\hbar^2 k}$$

We want to reduce it to the equation satisfied by the confluent hypergeometric function,

$$\eta' \frac{d^2 g}{d\eta'^2} + (1 - \eta') \frac{dg}{d\eta'} - ag = 0 \quad (107)$$

We identify  $ik\eta$  with  $\eta'$ ,  $-in$  with  $a$ . Now, the solution of Eq. (107) is (see Appendix F)

$$g = {}_1F_1(a; 1; -\eta') = {}_1F_1(-in; 1; ik\eta) \quad (108)$$

For large values of  $z$ , the confluent hypergeometric function has the following behaviour (see Appendices F, K and L)

$${}_1F_1(a, c, z) = (c - 1)! \left[ \frac{(-z)^{-a}}{\Gamma(c - a)} + \frac{z^{a-c} e^z}{\Gamma(a)} \right] \quad (109)$$

Thus the asymptotic form of  $g$  can be written as

$$g \sim g_1 + g_2$$

where

$$\left. \begin{aligned} g_1 &= \frac{(-ik\eta)^{in}}{\Gamma(1+in)} = \frac{[-ik(r-z)]^{in}}{\Gamma(1+in)} \\ g_2 &= \frac{(ik\eta)^{-in-1}e^{ik\eta}}{\Gamma(-in)} = \frac{[ik(r-z)]^{-in-1}e^{ik(r-z)}}{\Gamma(-in)} \end{aligned} \right\} \quad (110)$$

Writing

$$\begin{aligned} [-ik(r-z)]^{in} &= e^{in \ln[-ik(r-z)]} \\ &= e^{in \ln[k(r-z)]} e^{in \ln(-i)} \end{aligned}$$

Since

$$(-i) = e^{-i\pi/2}$$

we get

$$e^{in \ln(-i)} = e^{in[-i\pi/2]} = e^{n\pi/2}$$

Thus

$$g_1 = \frac{e^{n\pi/2} e^{in \ln[k(r-z)]}}{\Gamma(1+in)} \quad (111)$$

Similarly

$$g_2 = \frac{e^{n\pi/2} e^{-in \ln[k(r-z)]} e^{ik(r-z)}}{ik(r-z)\Gamma(-in)} \quad (112)$$

We recall that the solution required is

$$\psi = e^{ik\xi/2} e^{-ik\eta/2} g(\eta) \longrightarrow e^{ikz} (g_1 + g_2) \quad (113)$$

From Eqs (111)–(113) it is clear that  $e^{ikz} g_1$  gives a modified plane wave and  $e^{ikz} g_2$  gives a spherical wave. We can write

$$\begin{aligned} \psi \longrightarrow & \frac{e^{n\pi/2}}{\Gamma(1+in)} \{ \exp[in \ln[k(r-z)] + ikz] \\ & + \frac{\Gamma(1+in)}{\Gamma(-in)} \frac{\exp[ikr - in \ln[k(r-z)]]}{ik(r-z)} \} \end{aligned}$$

We have

$$\frac{\Gamma(1+in)}{\Gamma(-in)} = \frac{in\Gamma(1+in)}{\Gamma(1-in)}$$

We can write

$$\Gamma(1+in) = |\Gamma(1+in)| \exp(i\sigma_n)$$

Finally

$$\psi \rightarrow \frac{e^{n\pi/2}}{\Gamma(1+in)} \left\{ \exp[in \ln[k(r-z)] + ikz] + \frac{n}{k(r-z)} \exp[ikr - in \ln k(r-z) + i2\sigma_n] \right\} \quad (114)$$

We note that only the phases of the incident and scattered waves are modified. However, the phase of the scattered wave is of the form  $-in \ln[k(r-z)] + 2i\sigma_n$  so that it increases indefinitely for large  $r$ , although only logarithmically. We can still identify (putting  $z = r \cos \theta$ )

$$f(\theta) = \frac{n}{k(1-\cos\theta)} \exp[-in \ln(1-\cos\theta)] \quad (115)$$

as the part containing the angular dependence. This gives the differential cross-section as

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \left( \frac{Z_1 Z_2 e^2}{4 \left( \frac{1}{2} \mu v^2 \right)} \right)^2 \frac{1}{\sin^4 \frac{\theta}{2}} \quad (116)$$

a result that agree with the classical result (see Problem 24.22) as well as with the Born approximation result [see Eq. (53)].

## 24.8. Considerations for identical particles

In this section we will discuss the scattering of identical particles like scattering of protons by protons or of  $\alpha$ -particles by  $\alpha$ -particles. However, in order to point out the peculiarities for identical particles we first consider non-identical particles like scattering of protons by  $\alpha$ -particles. In the center of mass system the two particles approach each other with the same momentum (see Fig. 24.5 and Sec. 24.8) and after scattering they are again moving in opposite directions. If the detector is such that it could detect either the  $\alpha$ -particle or the proton then the detector will register a count if the particle gets scattered along the direction  $(\theta, \phi)$  or along  $(\pi - \theta, \pi + \phi)$  (see Fig. 24.5). Thus the cross-section will be given by

$$\sigma(\theta) = |f(\theta)|^2 + |f(\pi - \theta, \pi + \phi)|^2 \quad (117)$$

However, since most scattering potentials are spherically symmetric, one gets

$$\sigma(\theta) = |f(\theta)|^2 + |f(\pi - \theta)|^2 \quad (118)$$

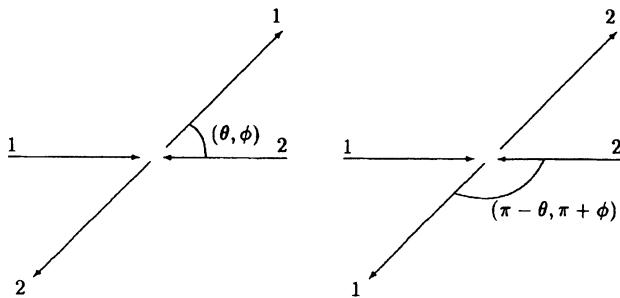


Figure 24.5. Scattering in the centre of mass system.

The above equations gives the correct result for non-identical particles like scattering of  $\alpha$ -particles by protons; however, it gives wrong results for scattering of protons by protons or of alpha particles by alpha particles. This is because of the indistinguishability of identical particles due to which it is impossible to say whether it is the incident particle or the target particle which has reached the detector. Due to this indistinguishability, we must construct appropriate wave functions which are either symmetric or antisymmetric with respect to the interchange of indices (see Sec. 22.5).

We first consider identical Fermions (like protons) for which the total wave function, space and spin, must be antisymmetric. This means that even the asymptotic form of the wave function of a two-particle system must obey this rule. However, the space part of the wave function alone may be either symmetric or antisymmetric, depending on whether the spin part is antisymmetric or symmetric. Thus for the  $p$ - $p$  system, the space wave function must be symmetric for the singlet and antisymmetric for the triplet case. In the center of mass system the collision may be represented as in Fig. 24.5. The asymptotic form of the wave function must therefore be a symmetric or an antisymmetric linear combination of the two cases. If

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta, \phi) \frac{e^{ikr}}{r}$$

describing the form for the first, then

$$\psi(-\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} + f(\pi - \theta, \pi + \phi) \frac{e^{ikr}}{r} \quad (119)$$

describes the second. The combinations are

$$[\psi(\mathbf{r}) \pm \psi(-\mathbf{r})]$$

The scattering cross-section is now

$$\begin{aligned}\sigma(\theta, \phi) &= |f(\theta, \phi) \pm f(\pi - \theta, \phi + \pi)|^2 \\ &= |f(\theta, \phi)|^2 + |f(\pi - \theta, \phi + \pi)|^2 \\ &\quad \pm 2\operatorname{Re}[f(\theta, \phi) f^*(\pi - \theta, \phi + \pi)]\end{aligned}\quad (120)$$

We note that in the absence of interference we get the classical result

$$\sigma(\theta, \phi) = |f(\theta, \phi)|^2 + |f(\pi - \theta, \phi + \pi)|^2 \quad (121)$$

This result merely says that the detector counting the scattered particles will not be able to say whether it is counting particle 1 or 2 so that the number counted at a particular angle is a sum of both probabilities.

However, the complete quantum mechanical result, viz. Eq. (120), is more subtle than just this. It is actually the probability amplitudes that interfere. (This situation is quite similar to electron diffraction by the double slit see Chapter 3).

At  $\theta = \pi/2$ , for a central potential, the results are particularly interesting. We obtain

$$\sigma\left(\theta = \frac{\pi}{2}\right)_{\text{sym}} = 4 \left|f\left(\frac{\pi}{2}\right)\right|^2$$

which is twice the result predicted by the classical equation (121). Moreover,

$$\sigma\left(\theta = \frac{\pi}{2}\right)_{\text{anti}} = 0$$

Thus the  $p - p$  triplet scattering at  $\pi/2$  should be absent. For an unpolarized beam of protons, the cross-section is

$$\sigma(\theta) = \frac{3}{4} \sigma(\theta)|_{\text{triplet}} + \frac{1}{4} \sigma(\theta)|_{\text{singlet}}$$

because the singlet state has statistical weight one and the triplet state three. Using Eq. (120), we obtain

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 + |f(\pi - \theta)|^2 - \operatorname{Re}[f(\theta) f^*(\pi - \theta)]$$

Equation (115) gives

$$\begin{aligned}f(\theta) &= \frac{n}{2k \sin^2 \theta/2} \exp[-in \ln(2 \sin^2 \theta/2)] \\ f(\pi - \theta) &= \frac{n}{2k \cos^2 \theta/2} \exp[-in \ln(2 \cos^2 \theta/2)]\end{aligned}$$

Thus

$$\begin{aligned}\sigma(\theta) &= \frac{n^2}{4k^2} \left\{ \frac{1}{\sin^4 \theta/2} + \frac{1}{\cos^4 \theta/2} - \frac{\operatorname{Re} \exp[-in \ln(\tan^2 \theta/2)]}{\sin^2 \theta/2 \cos^2 \theta/2} \right\} \\ &= \frac{n^2}{4k^2} \left\{ \frac{1}{\sin^4 \theta/2} + \frac{1}{\cos^4 \theta/2} - \frac{\cos[n \ln(\tan^2 \theta/2)]}{\sin^2 \theta/2 \cos^2 \theta/2} \right\}\end{aligned}\quad (122)$$

Here  $n = \mu Z_1 Z_2 e^2 / \hbar^2 k$ . This formula agrees with the experimental data at low energies which are not large enough so as to let the nuclear interaction become effective. For further details see Ref. 9.

It is of interest to mention that for spinless particles ( $\alpha$ - particles) the total wave function must be symmetric and therefore we must have

$$\sigma(\theta) = |f(\theta) + f(\pi - \theta)|^2 \quad (123)$$

The above equation gives

$$\sigma\left(\theta = \frac{\pi}{2}\right) = 4 \left|f\left(\frac{\pi}{2}\right)\right|^2 \quad (124)$$

which is to be compared with the classical result [Eq. (118)] which gives  $\sigma\left(\theta = \frac{\pi}{2}\right) = 2 \left|f\left(\frac{\pi}{2}\right)\right|^2$ . Thus the quantum theory predicts twice as much scattering as we would expect from classical theory; the experimental data confirms the quantum result.

## 24.9. Laboratory and centre of mass coordinate systems

In Sec. 10.3 we had shown that the two body problem can always be reduced to a one body problem provided the potential has spherical symmetry, i.e. the potential energy depended only on the magnitude of the distance between the two particles. It was shown that the Schrödinger equation could be broken up into two one-particle equations, one describing the free motion of the centre of mass and the other describing the relative motion of the two particles (see Sec. 10.3 and Appendix H). Thus the cross-sections calculated in this chapter correspond to the centre of mass system and since all measurements are carried out in the laboratory system we must know how to relate the cross-sections in the two systems<sup>8</sup>. It is the purpose of this section to know the relation between the two systems.

We consider a particle of mass  $m_1$  moving with velocity  $v_1$  towards the target particle of mass  $m_2$  which is initially at rest (see Fig. 24.6 a). The center of mass (shown by  $C$  in the figure) moves with velocity

$$v_c = \frac{m_1 v_1}{m_1 + m_2} \quad (125)$$

After scattering, the incident particle moves in a direction given by the angle  $(\theta_0, \phi_0)$  the target particle also suffers a recoil and moves in a different direction. In the centre of mass system, the centre of mass is at rest and the two particles will approach each other with velocities  $m_2 v_1 / (m_1 + m_2)$  and  $-m_1 v_1 / (m_1 + m_2)$ . It

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<sup>8</sup> It may be mentioned here that while calculating the energies of the bound states in Chapter 5 we could ignore the motion of the center of mass.

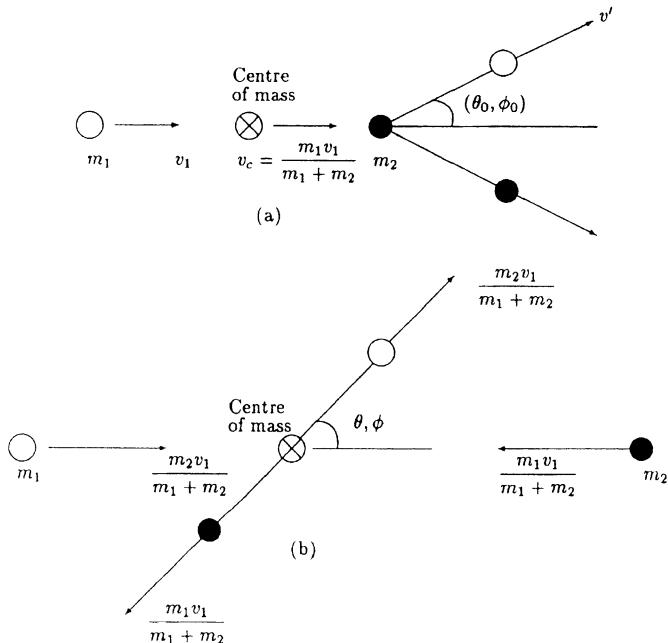


Figure 24.6. (a) The laboratory coordinate system in which the target particle (of mass  $m_2$ ) is initially at rest;  $v_c$  [as given by Eq. (125)] represents the velocity of the centre of mass. After scattering, the two particles fly off in different directions. (b) In the centre of mass system, the two particles approach each other with the same momenta; the centre of mass is at rest.

is easy to see that the total momenta of the two particles before scattering is zero and hence they must fly off in opposite directions after scattering as shown in Fig. 24.6(b). In the centre of mass system, if the scattering angle is denoted by  $(\theta, \phi)$  then for elastic scattering (i.e. when kinetic energies are conserved) the particles should move away with their original speeds as shown in Fig. 24.6(b). In order to get back to the laboratory system we must superpose the velocity of the centre of mass which will readily give

$$\begin{aligned} v' \sin \theta_0 &= \frac{m_2 v_1}{m_2 + m_1} \sin \theta \\ v' \cos \theta_0 &= \frac{m_2 v_1}{m_2 + m_1} \cos \theta + v_c \\ \phi &= \phi_0 \end{aligned} \quad (126)$$

where  $v'$  is the speed of the particle of mass  $m_1$  after scattering. Thus

$$\tan \theta_0 = \frac{\sin \theta}{\frac{m_1}{m_2} + \cos \theta} \quad (127)$$

Notice that when  $m_2 \gg m_1$ , the centre of mass is almost at rest,  $\theta_0 \simeq \theta$  and the two system of coordinates coincide.

Since the laboratory and centre of mass scattering angles are not equal, the angular distribution of the cross-section will be different in the two systems; the relation between the two scattering cross-sections can be obtained by noting that the number of particles scattered in a given element of solid angle must be the same in two systems; thus

$$\sigma(\theta_0, \phi_0) \sin \theta_0 d\theta_0 d\phi_0 = \sigma(\theta, \phi) \sin \theta d\theta d\phi \quad (128)$$

or using Eqs (126) and (127)

$$\sigma(\theta_0, \phi_0) = \frac{(1 + \gamma^2 + 2\gamma \cos \theta)^{3/2}}{|1 + \gamma \cos \theta|} \sigma(\theta, \phi) \quad (129)$$

It is  $\sigma(\theta, \phi)$  which is obtained from the theory, the above equation tells us how to transform it to the laboratory system which should be compared with the experimental data.

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## 24.10. Problems

**Problem 24.1** Calculate the differential cross-section for the following potentials, using the Born approximation:

(a) The square well potential

$$\begin{aligned} V(r) &= -V_0 \quad \text{for } r < a \\ &= 0 \quad \text{for } r > a \end{aligned}$$

(b) The Gaussian potential

$$V(r) = -V_0 \exp \left[ -\frac{1}{2} \left( \frac{r}{a} \right)^2 \right] \quad (130)$$

You may have to use the relation

$$\int_0^\infty e^{-\alpha r^2} \cos(2\beta t) dt = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} e^{-\beta^2/\alpha}$$

**Problem 24.2** The Yukuwa potential is given by

$$V(r) = -g^2 \frac{e^{-\alpha r}}{r} \quad (131)$$

which is of the same form as the shielded Coulomb potential [see Eq. (51)] with  $g^2$  playing the role of  $e^2$  so that the dimensionless parameter  $g^2/\hbar c$  measures the strength of the interaction. Assuming that the neutron-proton interaction can be described by a Yukawa potential (which is, however, not strictly true) and that  $1/\alpha \sim 1.4 \times 10^{-13}$  cm, estimate  $g^2/\hbar c$  from the observed zero energy cross-section of about  $3.6 \times 10^{-24}$  cm<sup>2</sup> (this is the triplet cross-section, see Sec. 24.7).

**Problem 24.3** Assume the charge distribution of a scatterer to be given by

$$Q(\mathbf{r}) = Z_1 e F(\mathbf{r}) \quad (132)$$

where  $\int F(\mathbf{r}) d\mathbf{r} = 1$  implying that the total charge of the scatterer is  $Z_1 e$ . Consider the scattering of a point charge  $Z_2 e$ , calculate  $V_{\mathbf{q}}$  (see Eqs (42) and (43)) by using the Poisson equation and show that

$$f(\theta) = -\frac{\mu}{2\pi \hbar^2} V_{\mathbf{q}} = \left( -\frac{\mu}{2\pi \hbar^2} \right) \frac{4\pi Z_2 e}{q^2} \Lambda(\mathbf{q}) \quad (133)$$

where

$$\Lambda(\mathbf{q}) = \int Q(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \quad (134)$$

**Problem 24.4** Using the results of the previous problem calculate the cross-section for a point charge for which

$$F(\mathbf{r}) = \delta(\mathbf{r})$$

Compare with the result obtained in Sec. 24.4.1.

**Problem 24.5** Use the results of Problem 24.3 to calculate  $\sigma(\theta)$  for the following charge distributions:

(a)

$$\begin{aligned} Q(\mathbf{r}) &= \left( \frac{4\pi}{3} a^3 \right)^{-1} (Z_1 e) \quad \text{for } r < a \\ &= 0 \quad \text{for } r > a \quad (\text{uniformly charged sphere}) \end{aligned} \quad (135)$$

(b)

$$Q(\mathbf{r}) = \frac{Z_1 e}{(2\pi a^2)^{3/2}} e^{-r^2/2a^2} \quad (\text{Gaussian}) \quad (136)$$

(c)

$$Q(\mathbf{r}) = \frac{Z_1 e}{4\pi a^2} \frac{1}{r} e^{-r/a} \quad (\text{Shielded Coulomb}) \quad (137)$$

where  $Z_1 e$  represents the total charge of the scatterer. Notice that all the cases will go over to the result of Problem 24.4 in the limit of  $a \rightarrow 0$ .

**Problem 24.6** The scattering of fast electrons by a complex atom can be, in many cases, represented fairly accurately by assuming the following form for the potential energy distribution:

$$V = -\frac{Ze^2}{r} + Ze^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (138)$$

where the first term is the potential due to the nucleus and the second due to the atomic structure. For the hydrogen atom in the ground state, we may write

$$\rho(r) = |\psi(1s)|^2 = \frac{1}{\pi a_0^3} \exp(-2r/a_0)$$

Use the result of Problem 24.3 to calculate  $\sigma(\theta)$ .

**Problem 24.7** Modify the analysis of the previous problem to study the scattering by helium atom, the ground state function of which can be represented by (see Sec. 21.4)

$$\psi_0 = \frac{Z^3}{\pi a_0^3} \exp[-Z(r_1 + r_2)/a_0], \quad Z = \frac{27}{16}$$

**Problem 24.8** Referring to Fig. 24.6 show that the total energy in the laboratory and centre of mass systems are related by

$$E_c = \frac{m_2}{m_1 + m_2} E_l \quad (139)$$

**Problem 24.9** In the neutron-proton scattering, assuming that the range of the attractive force,  $a$ , to be approximately  $3 \times 10^{-13}$  cm show that the scattering will be almost isotropic (in the centre of mass system) for neutron energy  $\sim 10$  MeV. (This is indeed borne out by experimental data).

**Problem 24.10** Assuming the mass of neutron to be equal to the mass of the proton, prove that there cannot be any back scattering in the scattering of neutron by protons.

**Problem 24.11** For neutron-proton scattering, make an angular distribution for  $l = 0$  (*s*-wave),  $l = 1$  (*p*-wave) and  $l = 2$  (*d*-wave) scattering in the centre of mass and laboratory coordinate systems.

**Problem 24.12** For a short force, use Eq. (92) to prove that

$$\frac{\delta_1}{\delta_0} \sim \frac{(ka)^2}{9}; \quad \frac{\delta_2}{\delta_0} \sim \frac{(ka)^4}{225}, \quad \text{etc.} \quad (140)$$

**Problem 24.13** Consider a repulsive potential given by

$$\begin{aligned} V(r) &= V_0 \quad 0 < r < a \\ &= 0 \quad r > a \end{aligned} \tag{141}$$

Show that

$$\begin{aligned} \delta_0 &= \tan^{-1} \left[ \frac{k}{K} \tanh Ka \right] - ka \quad \text{for } E < V_0 \\ &= \tan^{-1} \left[ \frac{k}{K_1} \tan K_1 a \right] - ka \quad \text{for } E > V_0 \end{aligned}$$

where

$$k^2 = \frac{2mE}{\hbar^2}, \quad K^2 = 2m(V_0 - E)/\hbar^2$$

and

$$K_1^2 = 2m(E - V_0)/\hbar^2$$

**Problem 24.14** For the square well potential discussed in Sec. 24.5.2 show that

$$\tan \delta_l = - \frac{k j'_l(ka) - \alpha_l j_l(ka)}{k n'_l(ka) - \alpha_l n_l(ka)} \tag{142}$$

where

$$\alpha_l = \frac{K j'_l(Ka)}{j_l(Ka)}$$

For  $ka \ll 1$ , using the forms of  $j_l(\rho)$  and  $n_l(\rho)$  for  $\rho \rightarrow 0$ , show

$$\begin{aligned} \delta_0 &\approx \tan^{-1} \left[ - \frac{\alpha_0 k a^2}{1 + \alpha_0 a} \right] \\ \delta_1 &\approx \tan^{-1} \left[ \frac{(ka)^3}{3} \frac{1 - \alpha_1 a}{2 + \alpha_1 a} \right], \text{ etc.} \end{aligned}$$

**Problem 24.15** Obtain an expression for the coherent scattering cross-section for many scattering centres.

**Problem 24.16** Show that the total cross-section, Eq. (67), follows from Eq. (66) on using the orthogonality of Legendre polynomials.

**Problem 24.17** In elastic scattering there is no absorption of the incident particle by the scatterer. Thus the outgoing and incoming intensities must be equal. Equation (63) shows that this implies that  $\delta_l$  must be real. Show that the reaction cross-section, defined as the number of particles removed from the beam per unit flux, is given by

$$\sigma_r = \sum_l \sigma_{r,l} = \sum_l \frac{\pi}{k^2} (2l+1)(1 - |\eta_l|^2) \tag{143}$$

where  $\eta_l = \exp(2i\delta_l)$  and  $\eta_l$  is called the collision amplitude. Show that while there can be scattering without absorption, there can be no absorption without scattering.

**Problem 24.18** Prove the optical theorem

$$\sigma_{\text{total}} = \frac{4\pi}{k} \text{Im}[f(0)] \quad (144)$$

where  $\text{Im}[f(0)]$  is the imaginary part of the forward scattering amplitude.

**Problem 24.19** Consider the scattering of the wave packet

$$\Psi(\mathbf{r}, t_0) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{k} a(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (145)$$

by a fixed short-range potential. The wave packet described by the above equation is assumed to be localized well out of the range of the potential as shown in Fig. 24.7. Assuming that the particle is reasonably well localized in position space and at the same time has a fairly well defined momentum, calculate  $\Psi(\mathbf{r}, t)$  at a time after the particle has been scattered by the target.

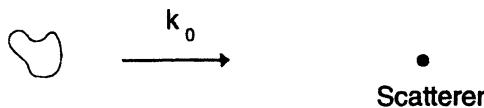


Figure 24.7.

[Hint: Express  $\Psi(\mathbf{r}, t_0)$  in terms of the exact eigen states of the Schrödinger equation; see Ref. 10]

**Problem 24.20** For the square well potential discussed in Sec. 24.2, show that the classical trajectory of the particle is the same as the path of a ray of light incident on a sphere of radius  $a$  with refractive index given by

$$n = \left( \frac{E + V_0}{E} \right)^{1/2} \quad (146)$$

**Problem 24.21** In the classical expression for the scattering cross-section for a square well potential [see Eq. (8)] if we let  $V_0 \rightarrow \infty$  show that  $\sigma(\theta)$  becomes independent of  $\theta$ , i.e. the scattering becomes isotropic. For such a case show that the total cross-section is  $\pi a^2$ .

**Problem 24.22** For a Coulomb potential [see Eq. (95)] show that the relation between the impact parameter and the scattering angle is given by

$$s(\theta) = \frac{Z_1 Z_2 e^2}{2E} \cot \frac{\theta}{2} \quad (147)$$

(see, e.g. Sec. 3.7 of Ref. 1). Hence using Eq. (7) calculate the scattering cross-section.

## 24.11. Solutions

### Solution 24.1

(a)

$$\begin{aligned}\sigma(\theta) &= \frac{4\mu^2 V_0^2}{\hbar^4 q^2} \left| \int_0^a \sin qr r dr \right|^2 \\ &= \frac{4\mu^2 V_0^2}{\hbar^4 q^6} (\sin qa - qa \cos qa)^2\end{aligned}$$

where the symbols have the same meaning as in Sec. 24.4.

(b) Simple integration gives

$$\sigma(\theta) = \left( \frac{\mu}{2\pi \hbar^2} \right)^2 |V_{\mathbf{q}}|^2 = \frac{2\pi \mu^2 a^6 V_0^2}{\hbar^4} e^{-q^2 a^2}$$

**Solution 24.2** Using Eq. (52), we get

$$\sigma = 2\pi \int_0^\pi \sigma(\theta) \sin \theta d\theta = 2\pi \int_0^{2k} \frac{4\mu^2 g^4}{\hbar^4 (q^2 + \alpha^2)^2} \frac{q dq}{k^2}$$

where we have used Eq. (45). On carrying out the integration, we get

$$\sigma = 16\pi \left( \frac{g^2}{\hbar c} \right)^2 \left( \frac{\mu c}{\hbar} \right)^2 \frac{1}{\alpha^4} \frac{1}{(1 + 4k^2/\alpha^2)}$$

or,

$$\sigma \xrightarrow{k \rightarrow 0} 16\pi \left( \frac{g^2}{\hbar c} \right)^2 \left( \frac{\mu c}{\hbar} \right)^2 \frac{1}{\alpha^4}$$

Using the data given in the problem and the fact that

$$\mu \approx \frac{m_n m_p}{m_n + m_p} \approx \frac{1}{2} m_p \approx 0.836 \times 10^{-24} \text{ gm}$$

we get  $g^2/\hbar c \sim 1.3$ . This is very much larger than the ‘strength’ of electromagnetic coupling  $e^2/\hbar c \sim 1/137$ . However, the Yukawa potential is hardly a sufficiently accurate representation of the nuclear interaction and one should treat this value of  $g^2/\hbar c$  as only a rough estimate.

**Solution 24.3** The Poisson equation is given by<sup>9</sup>

$$\nabla^2 V(\mathbf{r}) = -4\pi Z_2 e Q(\mathbf{r}) \quad (148)$$

Now, the Fourier transform of Eq. (43) gives

$$V(\mathbf{r}) = \frac{1}{8\pi^3} \int V_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q} \quad (149)$$

or,

$$\nabla^2 V = \frac{1}{8\pi^3} \int (-q^2) V_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}$$

Thus

$$\frac{1}{8\pi^3} \int (-q^2 V_{\mathbf{q}}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q} = -4\pi Z_2 e Q(\mathbf{r}) = -4\pi Z_2 e \frac{1}{8\pi^3} \int \Lambda(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}$$

where in the last step we have used the Fourier transform of Eq. (134). Thus

$$V_{\mathbf{q}} = \frac{4\pi Z_2 e}{q^2} \Lambda(\mathbf{q}) \quad (150)$$

or

$$\sigma(\theta) = |f(\theta)|^2 = \left( \frac{\mu}{2\pi \hbar^2} \right)^2 \left| \frac{4\pi Z_2 e}{q^2} \Lambda(\mathbf{q}) \right|^2 \quad (151)$$

**Solution 24.5**

(a)

$$\begin{aligned} \Lambda(\mathbf{q}) &= \int Q(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \\ &= \frac{Z_1 e}{\frac{4\pi}{3} a^3} \int_0^{2\pi} \int_0^\pi \int_0^a e^{-iqr \cos\theta} r^2 dr \sin\theta d\theta d\phi \\ &= \frac{3(Z_1 e)}{(qa)^3} [\sin qa - qa \cos qa] \end{aligned} \quad (152)$$

Hence

$$\sigma(\theta) = \left( \frac{2\mu}{\hbar^2} \right)^2 \frac{(Z_1 Z_2 e^2)^2}{q^4} \frac{9}{(qa)^6} [\sin qa - qa \cos qa]^2 \quad (153)$$

<sup>9</sup> Two points ought to be mentioned here: first we are working here in the CGS units (because in MKS units  $e$  should be replaced by  $q$  which would get confused with  $\mathbf{q}$ ) and secondly in MKS units the Poisson equation is

$$\nabla^2 U = -[\text{charge density}] / \epsilon_0$$

where  $U$  is the potential (which is the potential energy per unit charge) and  $\epsilon_0$  is the free space permittivity (see, e.g. Ref. 3). The final result obviously remains unchanged.

(b)

$$\Lambda(\mathbf{q}) = Z_1 e e^{-q^2 a^2 / 2} \quad (154)$$

(c)

$$\Lambda(\mathbf{q}) = \frac{Z_1 e}{(1 + q^2 a^2)} \quad (155)$$

**Solution 24.6** Comparing with the notation of Problem 24.3, we have  $Z_2 = -1$  and for the hydrogen atom  $Q(\mathbf{r}) = e\delta(\mathbf{r}) - e\rho(\mathbf{r})$ ; therefore

$$\therefore \Lambda(\mathbf{q}) = e [1 - F(q)] \quad (156)$$

where

$$\begin{aligned} F(q) &= \int \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \\ &= \frac{1}{\pi a_0^3} \iiint e^{-2r/a_0} e^{-iqr \cos\theta} r^2 dr \sin\theta d\theta d\phi \\ &= \frac{1}{(1 + q^2 a_0^2 / 4)^2} \end{aligned} \quad (157)$$

is sometimes called the atomic form factor. Substituting for  $\Lambda(\mathbf{q})$  in Eq. (133) we get

$$\begin{aligned} \sigma(\theta) &= \left( \frac{2\mu e^2}{\hbar^2 q^2} \right)^2 [1 - F(q)]^2 = \frac{4}{a_0^2 q^4} [1 - F(q)]^2 \\ &= 4a_0^2 \frac{(8 + q^2 a_0^2)^2}{(4 + q^2 a_0^2)^4}, \quad q = 2k \sin \frac{\theta}{2} \end{aligned} \quad (158)$$

The total cross-section will be

$$\begin{aligned} \sigma &= \int_0^\pi \sigma(\theta) 2\pi \sin\theta d\theta = \int_0^{2ka_0} \sigma(q) \frac{2\pi q dq}{k^2} \\ &= \frac{8\pi}{k^2} \int_0^{2ka_0} \frac{(8 + y^2)^2}{(4 + y^2)^4} y dy \end{aligned}$$

where  $y = qa_0$ . Writing

$$(8 + y^2)^2 = [4 + (4 + y^2)]^2 = 16 + 8(4 + y^2) + (4 + y^2)^2$$

we can easily carry out the integration. For  $ka_0 \gg 1$ , we obtain

$$\sigma \simeq \frac{7\pi}{3k^2} \quad (159)$$

**Solution 24.7** For the helium atom we have

$$V(r) = -\frac{2e^2}{r} + e^2 \int \sum_{n=1}^2 \frac{1}{|\mathbf{r} - \mathbf{r}_n|} |\psi_0(\mathbf{r}_1, \mathbf{r}_2)|^2 d\tau_1 d\tau_2 \quad (160)$$

or

$$Q(\mathbf{r}) = 2e\delta(\mathbf{r}) - \frac{2Z^3 e}{\pi a_0^3} \exp[-2Zr/a_0] \quad (161)$$

Proceeding as in the previous problem we get

$$\sigma(\theta) = 16a_0^2 \frac{(8 \times (1.68)^2 + q^2 a_0^2)^2}{(4 \times (1.68)^2 + q^2 a_0^2)^4} \quad (162)$$

Comparison of the theoretical results with experimental data show good agreement at electron energies above 100 eV (for further details, see Ref. 7).

**Solution 24.8** We refer to Fig. 24.6

$$E_{\text{lab}} = \frac{1}{2}m_1 v_1^2$$

and

$$\begin{aligned} E_{\text{cm}} &= \frac{1}{2}m_1 \left( \frac{m_2 v_1}{m_1 + m_2} \right)^2 + \frac{1}{2}m_2 \left( \frac{m_1 v_1}{m_1 + m_2} \right)^2 \\ &= \frac{1}{2}\mu v_1^2 = \frac{m_2}{m_1 + m_2} E_{\text{lab}} \end{aligned} \quad (163)$$

**Solution 24.9** Scattering will be predominantly *s*-wave ( $l = 0$ ) for  $ka \sim 1$

$$E_{\text{lab}} \approx 2E_{\text{cm}} \approx 2 \left( \frac{\hbar^2 k^2}{2\mu} \right) \lesssim \frac{\hbar^2}{\mu a^2}$$

Thus

$$E_{\text{lab}} \lesssim \frac{(10^{-27})^2}{(0.8 \times 10^{-24}) \times (3 \times 10^{-13})^2} \approx 1.6 \times 10^{-5} \text{ erg} \approx 10 \text{ MeV} \quad (164)$$

**Solution 24.10** Equation (127) gives

$$\theta_0 = \theta/2$$

and since  $\theta$  goes from 0 to  $\pi$ ,  $\theta_0$  will be less than  $\pi/2$ .

**Solution 24.12** For a short-range force, only small values of  $r$  will contribute to the integral; therefore

$$\delta_l \approx -\frac{2\mu}{\hbar^2} \frac{(ka)^{2l+1}}{[1.3 \dots (2l+1)]^2} \int_0^a V(r) \left(\frac{r}{a}\right)^{2l+1} r dr \quad (165)$$

where  $a$  denotes the range of the force, and we have made use of the formula

$$j_l(kr) \approx \frac{(kr)^l}{1.3 \dots (2l+1)}$$

Evaluation of  $\delta_l$  requires a knowledge of the potential, but an order of magnitude of the ratios is

$$\frac{\delta_1}{\delta_0} \sim \frac{(ka)^2}{9}; \quad \frac{\delta_2}{\delta_0} \sim \frac{(ka)^4}{225}, \quad \text{etc.}$$

**Solution 24.15** For a single scatterer, the asymptotic wave is given by

$$\psi \sim e^{ikz} - \frac{f}{r} e^{ikr}$$

If the scatterer is located at  $\mathbf{r}_i$  then the distance to the detector is  $|\mathbf{r} - \mathbf{r}_i|$  (see Fig. 24.8). There is, however, an extra phase change suffered by the incident wave by the time it reaches the scatterer so that

$$\psi_{sc}^i = -\frac{f_i}{|\mathbf{r} - \mathbf{r}_i|} e^{ikz_i} e^{ik|\mathbf{r} - \mathbf{r}_i|} \quad (166)$$

The total intensity of the scattered wave is

$$\begin{aligned} |\psi_{sc}|^2 &= \left| \sum_i \psi_{sc}^i \right|^2 = \sum_{ij} f_i f_j^* \frac{\exp[ik(z_i - z_j)]}{\rho_i \rho_j} \exp[ik(\rho_i - \rho_j)] \\ &= \sum_i \frac{|f_i|^2}{\rho_i^2} + \sum_{i \neq j} f_i f_j^* \frac{\exp[ik(z_i - z_j + \rho_i - \rho_j)]}{\rho_i \rho_j} \end{aligned} \quad (167)$$

where  $\rho_i = |\mathbf{r} - \mathbf{r}_i|$ . If we assume that all the scatterers are the same and their spread in much smaller than the distance of the detector, we can write

$$|\psi_{sc}|^2 \approx \frac{N |f|^2}{\rho^2} + \frac{|f|^2}{\rho^2} \sum_i \sum_{j \neq i} \exp[ik(z_i - z_j + \rho_i - \rho_j)] \quad (168)$$

where  $N$  is the number of scatterers. The first sum is the part that gives the incoherent scattering and the second the coherent scattering. Notice that the second term in

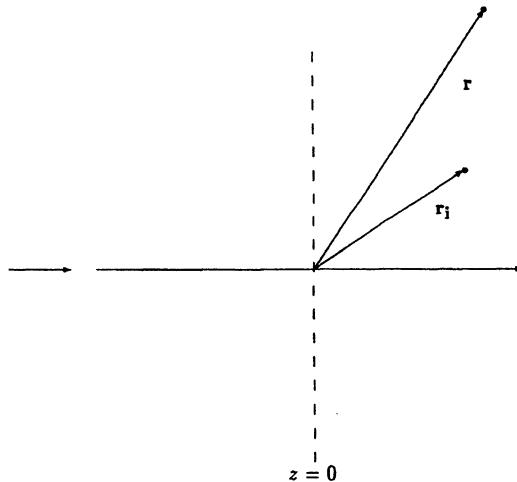


Figure 24.8. If the scatterer is at  $\mathbf{r}_i$ , then the distance to the detector is  $|\mathbf{r} - \mathbf{r}_i|$ .

Eq. (167) is a double sum. The coherent part can give large variations with angle. If the scatterers are all randomly spaced, then the sum will average out to zero, if

$$k\Delta\rho \gg 1$$

where  $\Delta\rho$  is roughly the spread of the scatterers. For  $k\Delta\rho \sim 1$  one can get large values for coherent scattering. In the forward direction,

$$\rho_i = z - z_i \quad \text{so that} \quad \rho_i - \rho_j = z_j - z_i$$

Thus the coherent intensity is

$$|\psi_{\text{sc}}|_{\text{coh}}^2 \approx \frac{|f|^2}{\rho^2} N^2 \quad (169)$$

Again, if there is a regular arrangement of scatterers as in a crystal satisfying the condition

$$k(z_i - z_j + \rho_i - \rho_j) = 2\pi n$$

one gets maxima.

Equation (168) has to be modified for what is called ‘the binding factor’ in crystals. One writes

$$|\psi_{\text{sc}}|_{\text{coh}}^2 \approx \frac{b^2 |f|^2}{\rho^2} \sum_i \sum_{j \neq i} \exp [ik(z_i - z_j + \rho_i - \rho_j)] \quad (170)$$

The cross-section for coherent scattering can be written as

$$\frac{d\sigma}{d\Omega} = b^2 |f|^2 \sum_{i \neq j} \exp [ik(z_i - z_j + \rho_i - \rho_j)]$$

In those directions (Bragg angles) in which coherent scattering is appreciable,  $\sum_{i \neq j} \sim N^2$  (remembering that we have a double sum).

Thus

$$\frac{d\sigma}{d\Omega} \sim N^2 b^2 |f|^2$$

**Solution 24.17** The net flux of particles through a sphere of radius  $R$  is given by [see Eq. (34) of Chapter 4]

$$j_R = \frac{\hbar}{2\mu i} \int \left[ \psi^* \frac{\partial \psi}{\partial r} - \psi \frac{\partial \psi^*}{\partial r} \right]_{r=R} R^2 d\Omega \quad (171)$$

Now

$$\begin{aligned} \frac{\partial \psi}{\partial r} &\xrightarrow{R \rightarrow \infty} \sum_l \frac{(2l+1)}{2ikR} P_l [e^{2i\delta_l} ik e^{ikR} + (-1)^l (ik) e^{-ikR}] \\ &= \sum_l \frac{(2l+1)}{2R} P_l [\eta_l e^{ikR} + (-1)^l e^{-ikR}] \end{aligned}$$

and

$$\psi^* \longrightarrow \sum_l \frac{(2l+1)}{-2ikR} P_l [\eta_l^* e^{-ikR} - (-1)^l e^{ikR}]$$

We now cannot assume that  $\eta_l, \eta_l^*$  to be the same. Thus

$$\left[ \psi^* \frac{\partial \psi}{\partial r} \right]_R = \sum_l \sum_{l'} \frac{(2l+1) P_l (2l'+1) P_{l'} [\eta_l \eta_{l'}^* - 1]}{-4ikR} + \text{terms involving } e^{\pm 2ikR}$$

We can ignore the other two terms which oscillate rapidly and will average to zero. Thus (remembering that we want the net flux inward)

$$j_R = \frac{\hbar}{4\mu k} \sum_l \sum_{l'} \int (2l+1) (2l'+1) P_l P_{l'} [1 - \eta_l \eta_{l'}^*] d\Omega \quad (172)$$

Due to orthogonality relations

$$\int P_l(\cos \theta) P_{l'}(\cos \theta) d(\cos \theta) = \frac{2}{2l+1} \delta_{ll'}$$

we obtain

$$j_R = \frac{4\pi \hbar}{4k\mu} \sum_l (2l+1) [1 - |\eta_l|^2]$$

The current in the  $l$ th partial wave is

$$j_R = \frac{\pi \hbar}{\mu k} (2l + 1) \left[ 1 - |\eta_l|^2 \right] \quad (173)$$

Thus the reaction cross-section is

$$\sigma_r^l = \frac{\pi}{k^2} (2l + 1) \left[ 1 - |\eta_l|^2 \right] \quad (174)$$

In Eq. (174),  $|\eta_l| < 1$ , for otherwise the outgoing current will exceed the incoming one. Since the scattering cross-section is

$$\sigma_{sc}^l = \frac{\pi}{k^2} (2l + 1) |1 - \eta_l|^2$$

and sees that  $\sigma_{sc}^l$  is largest for  $\eta_l = -1$ . In that case  $\sigma_r^l$  vanishes. On the other hand,  $\eta_l = 0$  gives the maximum reaction cross-section for which

$$\sigma_{sc}^l = \sigma_r^l = \frac{(2l + 1) \pi}{k^2}.$$

If there is no scattering ( $\eta_l = 1$ ), there clearly is no reaction either.

**Solution 24.18** The total cross-section (from the previous problem) is

$$\sigma = \sigma_{el} + \sigma_r = \sum_l \sigma^l$$

where

$$\begin{aligned} \sigma^l &= \frac{\pi}{k^2} (2l + 1) [2 - \eta_l - \eta_l^*] \\ &= \frac{2\pi}{k^2} (2l + 1) [1 - \operatorname{Re} \eta_l] \end{aligned}$$

and  $\operatorname{Re} \eta_l$  is the real part of  $\eta_l$ . From Eq. (65) we have for the forward scattering amplitude,

$$\begin{aligned} f(0) &= \sum_l (2l + 1) \frac{\eta_l - 1}{2ik} \\ &= i \sum_l (2l + 1) \frac{(1 - \eta_l)}{2k} \end{aligned}$$

This establishes the optical theorem

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$$\sigma = \frac{4\pi}{k} \operatorname{Im} f(0)$$

## 24.12. References and suggested reading

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# Chapter 25

## Time Dependent Perturbation Theory

... I think I can safely say that nobody understands quantum mechanics.

— RICHARD FEYNMAN.

### 25.1. Time development of states

When a system is isolated and the Hamiltonian is independent of the time, the energy eigenstates are true stationary states. If the system initially is in a particular state  $\Psi_n$  which is an eigenstate of the Hamiltonian  $H_0$ , it will stay there for all time. The time dependence of  $\Psi_n$  is of the form

$$\Psi_n(t) = \Psi_n(0) e^{-i E_n t / \hbar} \quad (1)$$

where  $E_n$  is the energy for the state  $n$ . If, however, the Hamiltonian is time dependent the energy is no longer a constant of motion. Knowledge of the behaviour of the system is obtained by solving the time dependent Schrödinger equation

$$i \hbar \frac{\partial}{\partial t} \Psi = H \Psi \quad (2)$$

Unfortunately the structure of the Hamiltonian  $H$  in most cases does not permit a solution of this equation in closed form.

In many physical problems, the time dependence of the Hamiltonian arises because of what may be thought of an external agency. An atom irradiated by light is an example. The time dependent part in such cases is usually a small perturbation representing the interaction of the system with the external agency. We may then write

$$H = H_0 + V(t) \quad (3)$$

where  $H_0$  may be thought of as the sum of Hamiltonians of two systems in isolation and  $V$ , their interaction. Instead of attempting a direct solution of Eq. (2), we pose

the problem in a slightly different manner. At a particular instant, say  $t = 0$ , the system may be regarded as being approximately in an eigenstate of  $H_0$ , labelled  $i$ . We would like to calculate the probability of finding the system in another state  $f$ , also an eigenstate of  $H_0$  at a later time<sup>1</sup>  $t$ . Under these circumstances, we shall talk of the system being in quasi-stationary states. In most of the physical problems, we only have quasi-stationary states. For example, an excited state of the hydrogen atom *does* decay and is not strictly a stationary state. At the other extreme, we may regard a state that lasts only for  $10^{-20}$  sec. as quasi-stationary; the point is that this lifetime may still be much longer than the natural frequencies of the system.

## 25.2. The transition probability

Let  $\psi_n$  denote the complete set of eigenkets of  $H_0$

$$H_0 \psi_n = E_n \psi_n = \hbar \omega_n \psi_n \quad (4)$$

where  $E_n (= \hbar \omega_n)$  represent the corresponding energy eigenvalues. The wave function representing the actual state  $\Psi(t)$  can be expanded terms of  $\psi_n$ :

$$\Psi(t) = \sum_n b_n(t) \psi_n(\mathbf{r})$$

where  $|b_n(t)|^2$  can be interpreted as the probability of finding the system in the state  $n$  at time  $t$ . For the sake of convenience we write<sup>2</sup>

$$b_n(t) = C_n(t) e^{-i\omega_n t}$$

so that

$$\Psi(t) = \sum_n C_n(t) e^{-i\omega_n t} \psi_n(\mathbf{r}) \quad (5)$$

Obviously,  $|C_n(t)|^2$  will also represent the probability of finding the system in the state  $n$  at time  $t$ . Our objective is to develop a perturbation theory for the calculation of  $C_n(t)$  for a given  $V(t)$ . Now, from Eqs (2), (3) and (5) we have

$$\begin{aligned} i \hbar \frac{\partial}{\partial t} \Psi(t) &= (H_0 + V) \Psi(t) \\ &= (H_0 + V) \sum_n C_n(t) e^{-i\omega_n t} \psi_n \\ &= \sum_n (E_n + V) C_n(t) \psi_n(\mathbf{r}) e^{-i\omega_n t} \end{aligned} \quad (6)$$

---

<sup>1</sup> If  $V(t)$  acts for a finite duration, then the state  $i$  and  $f$  may be exact eigenstates of  $H_0$  provided the perturbation is zero at the initial and final times of observation.

<sup>2</sup> The rapidly varying term in  $b_n(t)$  is the exponential term. Indeed if  $V = 0$ ,  $C_n(t)$  is independent of time.

where in the last step we have used Eq. (4). If we use Eq. (5), the left-hand side of the above equation becomes

$$\begin{aligned} i \hbar \frac{\partial}{\partial t} \Psi(t) &= i \hbar \frac{\partial}{\partial t} \sum_n C_n(t) e^{-i\omega_n t} \psi_n \\ &= i \hbar \sum_n [\dot{C}_n - i\omega_n C_n] e^{-i\omega_n t} \psi_n \end{aligned}$$

Thus we have

$$i \hbar \sum_n [\dot{C}_n - i\omega_n C_n] e^{-i\omega_n t} \psi_n = \sum_n (E_n + V) C_n(t) e^{-i\omega_n t} \psi_n \quad (7)$$

where the second term on the left-hand side cancels the first term on the right-hand side. Multiplying on the left by  $\psi_s^*$  and remembering the orthonormality relation

$$\int \psi_s^* \psi_n d\mathbf{r} = \langle s | n \rangle = \delta_{sn} \quad (8)$$

we get

$$i \hbar \frac{dC_s}{dt} = \sum_n C_n(t) V_{sn}(t) e^{i\omega_{sn} t} \quad (9)$$

where

$$\omega_{sn} = \omega_s - \omega_n = \frac{E_s - E_n}{\hbar} \quad (10)$$

$$V_{sn}(t) = \int \psi_s^* V(t) \psi_n d\tau = \langle s | V | n \rangle \quad (11)$$

The set of equations (corresponding to various values of  $s$ ) represented by Eq. (9) are exact. To solve them, we usually have to resort to perturbation techniques; there are, however, situations where one can obtain exact solutions of the time dependent equations; see, e.g. Sec. 14.6, see also Problem 26.8.

Let us assume that at time  $t$  the amplitudes have not changed very much from their values at  $t = 0$ ; i.e. we replace  $C_n(t)$  by  $C_n(0)$  on the right-hand side of Eq. (9). We can then integrate Eq. (9) to give

$$i \hbar [C_s(t) - C_s(0)] = \sum_n C_n(0) \int_0^t V_{sn} e^{i\omega_{sn} t} dt \quad (12)$$

We can apply this to the case where we know that the system is in a particular state  $i$  at  $t = 0$ . Thus

$$\begin{aligned} C_s(0) &= 1 \text{ for } s = i \\ &= 0 \text{ for } s \neq i \end{aligned} \quad (13)$$

so that

$$C_f(t) = \frac{1}{i\hbar} \int_0^t V_{fi}(t) e^{i\omega_{fi}t} dt, \quad f \neq i \quad (14)$$

Equation (14) gives the probability amplitudes at later times of states other than the initial one.

Suppose now that at  $t = 0$  the perturbation is switched on and for  $t > 0$ , is independent of time<sup>3</sup>. Thus

$$C_f(t) = \frac{1}{i\hbar} V_{fi} \int_0^t e^{i\omega_{fi}t} dt = -V_{fi} \frac{e^{i\omega_{fi}t} - 1}{\hbar\omega_{fi}} \quad (15)$$

Thus the probability for reaching the state  $f$  (at time  $t$ ) is given by

$$P_f(t) = |C_f(t)|^2 = |V_{fi}|^2 \frac{1}{\hbar^2} \frac{\sin^2(\omega_{fi}t/2)}{(\omega_{fi}/2)^2} \quad (16)$$

We rewrite the above equation in terms of  $E_f$  and  $E_i$ :

$$P_f(t) = |V_{fi}|^2 \left[ \frac{\sin((E_f - E_i)t/2\hbar)}{(E_f - E_i)/2} \right]^2 \quad (17)$$

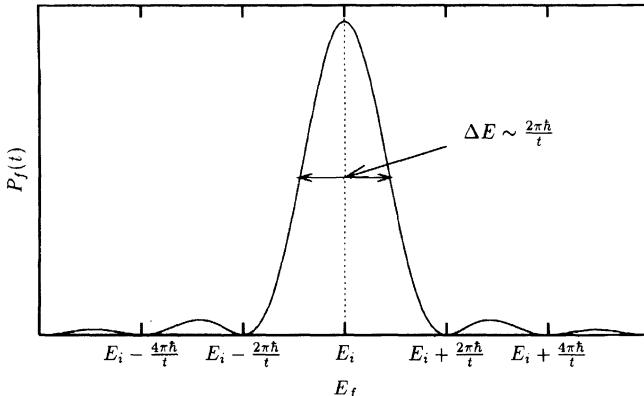


Figure 25.1. The variation of  $P_f(t)$  [as given by Eq. (17)] as a function of  $E_i$ . Notice that the function is peaked at  $E_f = E_i$  with a width  $\Delta E \sim \hbar/t$ .

Figure 25.1 shows the behaviour of  $P_f(t)$  as a function of  $E_f$ . We note the following:

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<sup>3</sup> In the next chapter we will consider harmonic perturbations where  $V(t)$  will vary sinusoidally with time and will describe the atom-field interaction.

- (i) The perturbation theory result, viz., Eq. (17), is valid only when  $P_f(t) \ll 1$ .
- (ii) As long as  $t$  is small enough such that

$$(E_f - E_i) \frac{t}{2\hbar} \ll 1 \quad (18)$$

the quantity  $P_f(t)$  is proportional to  $t^2$  for all values of  $E_f$ , in fact

$$P_f(t) \approx |V_{fi}|^2 \frac{t^2}{\hbar^2} \quad (19)$$

(iii)

$$\underset{E_f \rightarrow E_i}{\text{Lt}} P_f(t) = |V_{fi}|^2 \frac{t^2}{\hbar^2} \quad (20)$$

Equation (17) represents the probability of transition to one particular state  $\psi_f$ . In the applications that we would discuss, we would be interested in transitions to a group of closely spaced states. Thus the probability of transition to any of the states is given by

$$w = \int P_f(t) \rho_f(E_f) dE_f \quad (21)$$

where  $\rho_f(E_f) dE_f$  represents the number of final states in the energy interval  $dE_f$ . The density of states is usually a very smoothly varying function and since  $P_f(t)$  is very sharply peaked around  $E_f \approx E_i$ , we may write

$$w \approx \rho_f(E_i) \int_{\Delta E} P_f(t) dE_f \quad (22)$$

where  $\Delta E$  represents the central peak. We may now replace the limits of integration by  $-\infty$  and  $+\infty$  to obtain

$$\begin{aligned} w &\approx \rho_f(E_i) |V|^2 \int_{-\infty}^{+\infty} \left[ \frac{\sin(E_f - E_i)t/2\hbar}{(E_f - E_i)/2} \right]^2 dE_f \\ &\approx \rho_f(E_i) \frac{2t}{\hbar} |V|^2 \int_{-\infty}^{\infty} \frac{\sin^2 \xi}{\xi^2} d\xi \end{aligned}$$

or

$$w \approx \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f(E_i) t \quad (23)$$

The transition probability per unit time will be given by

$$\Gamma = \frac{dw}{dt} = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f(E_i) \quad (24)$$

which is usually referred to as *Fermi's Golden Rule*. We illustrate the above procedure with a specific example. Suppose a system  $A$  undergoes a transition to two parts  $A \rightarrow a + b$  due to a perturbation. Our question may be framed thus: If at time  $t = 0$  we know that the system is in a specific state  $A$ , what is the probability that at a subsequent time  $t > 0$ , the system has "decayed" into parts  $a$  and  $b$ . According to Eq. (17), there is a finite probability that the final state will have an energy  $E_f \neq E_i$  ( $E_i$  was the energy at  $t = 0$ ) where  $|E_f - E_i| \lesssim \hbar/t$ . Thus we must sum probabilities over a set of states  $f$  within the interval—in fact, we shall sum over all states whatever the value of  $E_f$ . But, Eq. (17) ensures that the contribution from states for which  $|E_f - E_i| \gg \hbar/t$  is negligible. We are, therefore, inevitably interested in the density of states  $f$ , i.e. the more states there are satisfying the relation  $|E_f - E_i| \lesssim \hbar/t$  the more will be the transition probability.

If we assume that the entire system is in a box of volume  $V$ , we shall then have to calculate the number of states of  $a$  and  $b$  within an interval  $dE_f$  of a particular value  $E_f$ , say  $\rho(E_f) dE_f$ , compute the total probability for all these states and then integrate over all values of  $E_f$ . Equation (17) will ensure that we do not have to go far from  $E_f = E_i$ ; i.e. we are essentially interested in the density of states  $\rho(E_f = E_i)$ .

We may mention here that in carrying out the integration in Eq. (23) we have assumed that  $t$  is large enough so that the function  $P_f(t)$  is very sharply peaked around  $E_f = E_i$  (so that  $\rho_f$  can be taken outside the integral); on the other hand, for the validity of perturbation theory,  $P_f(t) \ll 1$  i.e.  $t$  should be small enough so that

$$\frac{|V_{fi}|^2}{\hbar^2} t^2 \ll 1 \quad (25)$$

We digress here to mention that since  $P_f(t)$  is very sharply peaked around  $E_f = E_i$ , it should be possible to express it in the form of a delta function. Indeed, since

$$\lim_{g \rightarrow \infty} \frac{1}{\pi g} \frac{\sin^2 gx}{x^2} = \delta(x) \quad (26)$$

we may write

$$\begin{aligned} \lim_{t \rightarrow \infty} \frac{\sin^2(E_f - E_i)t/2\hbar}{[(E_f - E_i)/2]^2} &= \frac{\pi t}{\hbar} \delta\left(\frac{E_f - E_i}{2}\right) \\ &= \frac{2\pi t}{\hbar} \delta(E_f - E_i) \end{aligned} \quad (27)$$

Thus Eq. (17) gives

$$P_f(t) = \frac{2\pi}{\hbar} t |V_{fi}|^2 \delta(E_f - E_i) \quad (28)$$

a formula which is often used. Equation (28) does appear nonsensical because it is zero for all values of  $E_f \neq E_i$  and  $\infty$  for  $E_f = E_i$  and we know that  $P_f(t)$  should be very small compared to unity. However, Eq. (28) has meaning only when it is multiplied by the smoothly varying function  $\rho_f(E_f)$  and integrated over all energies to give Eq. (24).

### 25.3. Application to the theory of scattering

In Chapter 24 we discussed elastic scattering in which we considered the scattering of a wave packet by a fixed potential  $V(\mathbf{r})$ ; this was done by obtaining a solution of the Schrödinger equation in the form of an incident plane wave and an outgoing scattered wave. Here we will consider another approach to the scattering problem by considering the scattering of a particle as a transition from an initial plane wave state to another plane wave state corresponding to a different direction of propagation. The two approaches will be shown to be equivalent although each approach has its own domain of application.

We consider a particle in a cube of volume  $L^3$  and initially in a plane wave state corresponding to momentum  $\mathbf{p}_i$ . Thus the initial state of the particle is described by the wave function

$$\psi_i = \frac{1}{L^{3/2}} \exp[i\mathbf{k}_i \cdot \mathbf{r}] \quad (29)$$

where

$$\mathbf{k}_i = \frac{1}{\hbar} \mathbf{p}_i \quad (30)$$

It may be mentioned that by confining the particle inside a large box and by imposing the periodic boundary conditions (see Appendix M), the states become discrete; in fact the allowed values of  $k_x$ ,  $k_y$  and  $k_z$  are

$$k_x = \frac{2n_x\pi}{L}, k_y = \frac{2n_y\pi}{L}, k_z = \frac{2n_z\pi}{L} \quad (31)$$

where

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, \pm 3, \dots \quad (32)$$

We now assume that the perturbation  $V(\mathbf{r})$  is switched on at  $t = 0$ . The probability of transition to the final state

$$\psi_f = \frac{1}{L^{3/2}} \exp(i\mathbf{k}_f \cdot \mathbf{r}) \quad (33)$$

is given by [see Eq. (17)]

$$P_f(t) = |C_f(t)|^2 = |V_{fi}|^2 \left[ \frac{\sin(E_f - E_i)t/2\hbar}{(E_f - E_i)/2} \right]^2 \quad (34)$$

where

$$\begin{aligned} V_{fi} &= \int \psi_f^* V \psi_i d\mathbf{r} \\ &= \frac{1}{L^3} \int V(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \end{aligned} \quad (35)$$

and

$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \quad (36)$$

Equation (34) represents the probability of the particle getting scattered to a particular state corresponding to  $\mathbf{k}_f$ . If we wish to get the total probability of the particle getting scattered into the solid angle  $d\Omega$ , which we will denote by  $w d\Omega$ , then we must multiply  $P_f(t)$  by  $\rho_f(E_f) d\Omega$  and integrate over all energies; here  $\rho_f(E_f) dE_f d\Omega$  represents the number of states whose final energy lies between  $E_f$  and  $E_f + dE_f$  and the direction of propagation in the solid angle  $d\Omega$ . Thus, using the method used in the previous section, we get

$$\begin{aligned} w d\Omega &= \int P_f(t) \rho_f(E_f) dE_f d\Omega \\ &\approx \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f(E_i) t d\Omega \end{aligned} \quad (37)$$

Thus the transition probability per unit time into the solid angle  $d\Omega$  is given by

$$\Gamma d\Omega \approx \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f(E_i) d\Omega \quad (38)$$

Now, the density of final states is given by (see Eq. (10) of Appendix M):

$$\rho_f(E) dE d\Omega = \frac{L^3}{16\pi^3 \hbar^3} (2m)^{3/2} E^{1/2} dE d\Omega \quad (39)$$

Further, since there is only one particle in volume  $L^3$ , the number of particles per unit volume will be  $1/L^3$ ; thus the incident intensity,  $I$ , will be  $1/L^3$  multiplied by their velocity  $\hbar k/m$ :

$$I = \frac{1}{L^3} \frac{\hbar k}{m} = \frac{1}{L^3} \frac{(2mE)^{1/2}}{m} \quad (40)$$

From the definition of the cross-section (see Sec. 24.3) the number of particles scattered into the solid angle  $d\Omega$  per unit time =  $I\sigma d\Omega = \Gamma d\Omega$ ; or,

$$\sigma d\Omega = \frac{\Gamma d\Omega}{I} = \frac{1}{(\hbar k/mL^3)} \left[ \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f(E_i) d\Omega \right] \quad (41)$$

or

$$\sigma d\Omega = \left( \frac{mL^3}{2\pi\hbar^2} \right)^2 |V_{fi}|^2 d\Omega \quad (42)$$

Substituting for  $V_{fi}$  from Eq. (37), we get

$$\sigma = \left( \frac{m}{2\pi\hbar^2} \right)^2 \left| \int V(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \right|^2 \quad (43)$$

which is identical to the expression obtained by using the Born approximation [see Eq. (41) of Chapter 24]. This is to be expected because both employ first-order perturbation theory.

## 25.4. Adiabatic approximation

In this section we will consider the case of a perturbation varying slowly with time. For such a case if we can solve the eigenvalue equation

$$H(t) \psi_n(t) = E_n(t) \psi_n(t) \quad (44)$$

then we should expect that if at  $t = 0$  the system is in the (non-degenerate) state  $\psi_m(0)$  then at a later time the system will be in the state  $\psi_m(t)$ . We will show this explicitly in this section and also calculate the probability of transitions to other states.

We assume the potential to be turned on from  $t = -\infty$  so that the initial condition is [cf. Eq. (13)]

$$\begin{aligned} C_s(-\infty) &= 1 \text{ for } s = i \\ &= 0 \text{ for } s \neq i \end{aligned} \quad (45)$$

so that [cf. Eq. (14)]

$$C_f(t) = \frac{1}{i\hbar} \int_{-\infty}^t V_{fi}(t') e^{i\omega_{fi}t'} dt, \quad f \neq i \quad (46)$$

Partial integration of the above equation gives

$$C_f(t) = \left[ -\frac{V_{fi} e^{i\omega_{fi} t}}{\hbar\omega_{fi}} \right]_{-\infty}^t + \int_{-\infty}^t \frac{1}{\hbar\omega_{fi}} \frac{\partial V_{fi}}{\partial t} e^{i\omega_{fi} t} dt$$

If we assume that  $V_{fi}(t) \rightarrow 0$  as  $t \rightarrow -\infty$ , we can write

$$C_f(t) = -\frac{V_{fi}(t)}{\hbar\omega_{fi}} e^{i\omega_{fi} t} + \int_{-\infty}^t \frac{1}{\hbar\omega_{fi}} \frac{\partial V_{fi}}{\partial t} e^{i\omega_{fi} t} dt \quad (47)$$

The state of the system at the time  $t$  is given by (see Eq. (5))

$$\Psi(t) = C_i(t) \psi_i e^{-i\omega_i t} + \sum_{f \neq i} C_f(t) \psi_f e^{-i\omega_f t}$$

Assuming that the initial state has not been depleted very much in time  $t$ , we can put  $C_i(t) \approx 1$ . Substituting the values of  $C_f(t)$  from Eq. (47), we obtain

$$\begin{aligned} \Psi(t) &= \left[ \psi_i - \sum_{f \neq i} \frac{V_{fi}}{\hbar\omega_{fi}} \psi_f \right] e^{-i\omega_i t} \\ &\quad + \sum_{f \neq i} \int_{-\infty}^t \frac{1}{\hbar\omega_{fi}} \frac{\partial V_{fi}}{\partial t} e^{-i\omega_{fi} t} dt \end{aligned} \quad (48)$$

The terms in the parenthesis in Eq. (48) represents the change in the state due to the application of a constant perturbation  $V$  (see Eqs 13, 19 and 20 of Chapter 19) and has nothing to do with transitions. It is therefore the second term in Eq. (48) that gives transitions.

The *adiabatic approximation* is the assumption that the perturbation is turned on slowly, i.e.  $\partial V_{fi}/\partial t$  is small. Equation (47) suggests the transitions to other states are extremely unlikely in this case. Assuming that  $\partial V/\partial t \neq 0$  in an interval  $t_1$  to  $t_2$ , we may write

$$\begin{aligned} C_f(t) &\approx \frac{1}{\hbar\omega_{fi}} \left( \overline{\frac{\partial V_{fi}}{\partial t}} \right) \int_{t_1}^{t_2} e^{i\omega_{fi} t} dt \\ &= \frac{1}{i \hbar\omega_{fi}^2} \left( \overline{\frac{\partial V_{fi}}{\partial t}} \right) [e^{i\omega_{fi} t_2} - e^{i\omega_{fi} t_1}] \end{aligned} \quad (49)$$

The condition that  $|C_f(t)| \ll 1$  gives

$$\frac{1}{\hbar\omega_{fi}^2} \frac{\partial V}{\partial t} \ll 1 \quad (50)$$

Since  $\tau_{fi} = 1/\omega_{fi}$  is the period of the radiation associated with the transition, this statement implies that

$$\frac{1}{\hbar\omega_{fi}} \frac{\partial V}{\partial t} \ll \frac{1}{\tau_{fi}} \quad (51)$$

### 25.5. The sudden approximation

We next consider the case when the potential is turned on very rapidly i.e.

$$\tau \ll \tau_{fi} \sim \frac{1}{\omega_{fi}} \quad (52)$$

which implies that the time in which the perturbation changes appreciably is very small in comparison to the period involved in the transition. As an example, we assume

$$\begin{aligned} H &= H_0 \text{ for } t < 0 \\ &= H_1 \text{ for } t > 0 \end{aligned} \quad (53)$$

where  $H_0$  and  $H_1$  are independent of time. Let  $\psi_n$  and  $\phi_n$  represent the orthonormal set of wave functions of  $H_0$  and  $H_1$  respectively. For  $t < 0$ , let the system be in an eigenstate of  $H_0$  (say  $\psi_m$ ). Since the Schrödinger equation is a first order equation in time, the wave function should be continuous at all times (although its time derivative need not be continuous). Now, at  $t = 0$  we express  $\psi_m$  as a linear combination of  $\phi_n$ :

$$\psi_m = \sum_n a_n \phi_n \quad (54)$$

where

$$a_n = \int \phi_n^* \psi_m \, d\tau \quad (55)$$

represents the probability amplitude for transition to the state  $\phi_n$ .

In general, in the sudden approximation we assume that  $\partial V_{fi}/\partial t$  is essentially finite (and large) for a very small period of time say from  $T$  to  $T + \tau$ . During this time the exponent in the integral in Eq. (47) changes very little so that

$$\begin{aligned} C_f(t) &\simeq \frac{1}{\hbar\omega_{fi}} e^{i\omega_{fi}T} \int_T^{T+\tau} \frac{\partial V_{fi}}{\partial t} \, dt \\ &= \frac{1}{\hbar\omega_{fi}} e^{i\omega_{fi}T} V_{fi} \end{aligned} \quad (56)$$

Thus

$$|C_f(t)|^2 = \frac{1}{\hbar^2\omega_{fi}^2} |V_{fi}|^2 \quad (57)$$

From Eq. (56) we can see that the criterion for validity of sudden approximation is

$$\omega_{fi}\tau \ll 1 \quad (58)$$

The change of the perturbation in the sudden approximation looks somewhat as in Fig. 25.2.

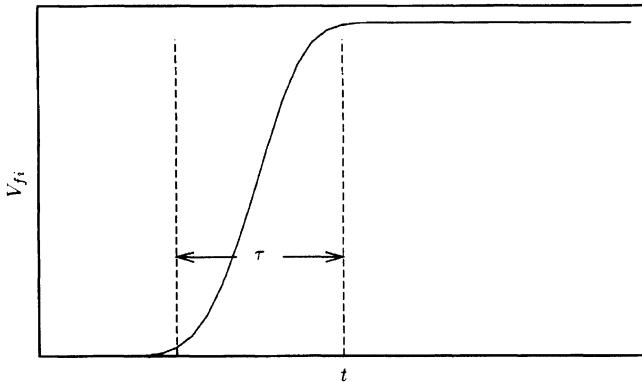


Figure 25.2. A typical variation of the perturbation in the sudden approximation.

## 25.6. Problems

**Problem 25.1** The interaction of the neutron with a lattice can be well represented by the Fermi pseudo-potential

$$H' = \frac{2\pi\hbar^2}{m} \sum_n a_n \delta(\mathbf{r} - \mathbf{r}(n)) \quad (59)$$

where  $m$  is the mass of the neutron,  $a_n$  is known as the bound scattering length of the  $n^{th}$  nucleus,  $\delta(\mathbf{r})$  is the three-dimensional Dirac delta-function,  $\mathbf{r}(n)$  denotes the position of the nucleus and the summation is over all the nuclei in the lattice. Assume all the nuclei to have zero spin and no isotopes so that  $a_n$  is independent of  $n$ . Calculate the elastic scattering cross-section of neutrons by a simple cubic structure of lattice spacing  $d$ . (Neglect lattice vibrations). Show that the condition for non-vanishing scattering is that Bragg law be satisfied.

[Hint: For a simple cubic structure

$$\mathbf{r}(n) = d[n_1\hat{\mathbf{x}} + n_2\hat{\mathbf{y}} + n_3\hat{\mathbf{z}}]$$

where  $n_1, n_2$  and  $n_3$  take integral values.]

**Problem 25.2** In the elementary theory of beta decay, the form of the interaction operator,  $H'$ , is simply assumed to be a constant, which we denote by  $G$ . Thus the matrix element  $H'_{fi}$  of the interaction is defined as

$$H'_{fi} = G \int \psi_{fN}^* \psi_e^* \psi_\nu \psi_{iN} d\tau,$$

where  $\psi_{iN}$  and  $\psi_{fN}$  are the normalized wave functions for the parent and daughter nucleus;  $\psi_e$  and  $\psi_\nu$  are the normalized wave functions for the electron (positron) and the antineutrino (neutrino) respectively. Experiments show that  $G \sim 10^{-48}$  gm cm<sup>5</sup> sec<sup>-2</sup>. Assuming the wavelengths of the leptons being considerably longer than nuclear dimensions, show from phase space considerations that

$$P(p_e) dp_e = \frac{G^2 |M_{fi}|^2}{2\pi^3 \hbar^7 c^3} p_e^2 (E_o - E) [(E_o - E_e)^2 - m_\nu c^2]^{\frac{1}{2}} dp_e,$$

where  $P(p_e) dp_e$  is the probability of emission per unit time of an electron with momentum between  $p_e$  and  $p_e + dp_e$  and

$$M_{fi} = \int \psi_{fN}^* \psi_{iN} d\tau$$

What will be the mean lifetime  $\tau$ ?

(sec, e.g. Ref 1 and 2).

**Problem 25.3** In this problem we will consider the scattering of fast electrons by hydrogen atom; we will neglect exchange collisions. The unperturbed Hamiltonian is given by

$$H_0 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_2} \quad (60)$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  represent the coordinates of the incident electron and the electron bound to the hydrogen atom respectively. The perturbation which causes the scattering will be given by

$$H' = \frac{e^2}{r_{12}} - \frac{e^2}{r_1} \quad (61)$$

where the two terms represent the incident electron-atomic electron interaction and the incident electron-atomic nucleus interaction respectively. Using the theory developed in Sec. 25.3 show that the scattering cross-section corresponding to the excitation of the hydrogen atom from 1s state to the 2s state is given by

$$\sigma(\theta) = \frac{k_1}{k_0} \frac{128a_0^2}{[q^2a_0^2 + \frac{9}{4}]^2} \quad (62)$$

where  $a_0 = \hbar^2/me^2$ ,

$$q^2 = (\mathbf{k}_0 - \mathbf{k}_1)^2 = k_0^2 + k_1^2 - 2k_0 k_1 \cos \theta \quad (63)$$

$\theta$  is the scattering angle,  $\hbar \mathbf{k}_0$  and  $\hbar \mathbf{k}_1$  represent the momenta of the electron before and after the collision. (We may recall here that in Problem 24.6, we had discussed the elastic scattering of electrons by hydrogen atom; the present exercise is an example of inelastic scattering in which the energy of the scattered electron is different from the energy of the incident electron).

**Problem 25.4** A proton is travelling with an energy of 1 MeV in hydrogen gas. Estimate the minimum impact parameter for which there is appreciable energy transfer.

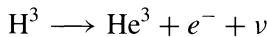
**Problem 25.5** Assuming that a heavy ion (with charge  $Z_1 e$ ) of velocity  $v$  passes undeflected as it suffers a collision with an atom, calculate the probability of transition of the atom from the initial state  $m$  to the final state  $n$  and hence obtain a formula for the rate of energy loss of the heavy charged particle.

**Problem 25.6** The deuteron is a very loosely bound structure, the mean distance between the neutron and the proton being of the order of 4.3 fermi, which is considerably larger than the range of the nuclear forces which is about 1.4 fermi (1 fermi =  $10^{-13}$  cm). It is therefore possible for a deuteron to undergo a grazing collision with a nucleus in such a way that the proton is stripped off the deuteron and is absorbed by the nucleus while the neutron emerges as a free particle. This process is called “stripping”.

- (a) Show that for a deuteron energy of 200 MeV, this process is an example of a sudden transition.
- (b) Calculate the energy distribution of the neutrons.

**Problem 25.7** Show that when perturbation is small (sudden approximation) the probability amplitude given by Eq. (55) reduces to the expression given by Eq. (57).

**Problem 25.8** The radioactive  $H^3$  nucleus decays to  $He^3$ ,



The electron energy is of the order of 10 KeV. (It is actually a continuous spectrum but for most of it the above estimate is reasonable). When a tritium atom decays, the  $He^3$  is a structure with a single atomic electron which has to readjust its motion since the nuclear charge has changed. Show that the sudden approximation holds in this case and calculate the probability that the helium ion is in its ground state.

**Problem 25.9** Calculate the probability of excitation to the 2p state of a hydrogen atom, originally in its ground state, due to a homogeneous electric field with time dependence

$$E = \frac{E_0}{\pi} \frac{\tau}{t^2 + \tau^2}$$

Discuss the limits of small and large values of  $\tau$  and their significance.

**Problem 25.10** Let  $|\psi(t)\rangle$  denote the state of a system at time  $t$ . Let  $|n\rangle$  denote one of a complete set of eigenkets of an observable  $A$ , considered timeindependent. Derive the relation

$$i\hbar \frac{\partial C_n}{\partial t} = \sum_{n'} H_{nn'} C_{n'} \quad (64)$$

where  $C_n(t)$  is the probability amplitude that the system is in the state  $|n\rangle$  at the time  $t$  and  $H_{nn'}$  is the matrix element  $\langle n|H|n'\rangle$  of the Hamiltonian.

**Problem 25.11** The  $K^\circ$  is a meson produced in strong interactions such as



the  $K^\circ$  state being an eigenstate of the strong interaction Hamiltonian. Similarly, the antiparticle  $\bar{K}^\circ$  is also an eigenstate of the strong interaction Hamiltonian. On the other hand, in the absence of strong interactions (i.e. when the  $K^\circ$  is all by itself and has no means of participating in strong interactions), the  $K^\circ$  can decay via a weak interaction, the Hamiltonian for which may be regarded as very much smaller than the strong interaction Hamiltonian,  $H_w \ll H_s$ . As a result of  $H_w$  the  $K^\circ$  and  $\bar{K}^\circ$  are not eigenstates of the full Hamiltonian. As in Sec. 16.4, we choose as the two base states (eigenstates of  $H_s$ )  $|K^\circ\rangle$  and  $|\bar{K}^\circ\rangle$ . It turns out that the proper eigenstates are

$$|K_1^\circ\rangle = \frac{1}{\sqrt{2}} [ |K^\circ\rangle + |\bar{K}^\circ\rangle ] \quad (65)$$

and

$$|K_2^\circ\rangle = \frac{1}{\sqrt{2}} [ |K^\circ\rangle - |\bar{K}^\circ\rangle ] \quad (66)$$

This state  $|K_1^\circ\rangle$  decays into  $\pi^+ + \pi^-$  or  $\pi^0 + \pi^0$  with a lifetime  $\tau_1 \approx 0.9 \times 10^{-10}$  sec. The lifetime of  $|K_2^\circ\rangle$  which we denote by  $\tau_2$  is about  $5.6 \times 10^{-8}$  sec. Thus we may write

$$|\Psi(t)\rangle = [ C_1 |K_1^\circ\rangle e^{-iE_1 t/\hbar} e^{-t/2\tau_1} + C_2 |K_2^\circ\rangle e^{-iE_2 t/\hbar} e^{-t/2\tau_2} ] \quad (67)$$

Since  $\tau_2 \gg \tau_1$ , assume  $\tau_2 = \infty$  and calculate the probability that starting from a  $K^\circ$  particle, we end up with  $\bar{K}^\circ$  particle at time  $t$ .

**Problem 25.12**

- (a) A quantum mechanical system (say a linear oscillator) is in a state  $\psi_i(\mathbf{r})$  at  $t = 0$  when it is subject to a large impulse  $\mathbf{F}(t)$  of the form

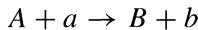
$$\mathbf{F}(t) = \mathbf{P}\delta(t) \quad (68)$$

Show that immediately after the impulse, the wave function of the system is

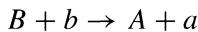
$$\psi_f(\mathbf{r}) = \psi_i(\mathbf{r}) \exp[i\mathbf{P} \cdot \mathbf{r}/\hbar]$$

- (b) Obtain an expression for the probability that, following the impulse, the system is found in the state  $n$ .

**Problem 25.13** Consider the reaction



and the inverse reaction



Show that, for the same center of mass energies

$$\frac{\sigma_{A+a \rightarrow B+b}}{\sigma_{B+b \rightarrow A+a}} = \left( \frac{p_a}{p_b} \right)^2 \frac{(2S_B + 1)(2S_b + 1)}{(2S_A + 1)(2S_a + 1)} \quad (69)$$

where the momenta  $p_a$  and  $p_b$  are measured in the center of mass system (c.m.s).

**Problem 25.14** Consider the nuclear reactions



and



where  $p$ ,  $d$  and  $\pi^+$  represent the proton, deuteron and  $\pi^+$  meson respectively. If  $\sigma_{pp \rightarrow \pi^+ d}$  and  $\sigma_{\pi^+ \rightarrow pp}$  represent the cross-sections for the processes described by Eqs (70) and (71) at the same center of mass energy, then using the results of the previous problem prove that

$$\sigma_{pp \rightarrow \pi^+ d} = \frac{3}{2} \sigma_{\pi^+ d \rightarrow pp} (2s_\pi + 1) \left( \frac{p_{\pi^+}}{p_p} \right)^2 \quad (72)$$

where  $s_\pi$  denotes the spin of the  $\pi$ -meson,  $p_p$  and  $p_{\pi^+}$  are the momenta of the proton and  $\pi^+$  meson respectively.

**Problem 25.15** For an incident proton energy of 340 MeV, the cross-section of the reaction  $pp \rightarrow \pi^+ d$  is found to be  $0.18 \pm 0.06$  mb. In another experiment for an incident deuterium energy of 29 MeV, the cross-section of the reaction  $\pi^+ d \rightarrow pp$  is found to be<sup>4</sup>  $3.1 \pm 0.3$  mb. Show that

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<sup>4</sup> Data quoted from Ref. 3. Experimental results are of Cartwright et al. (Physical Review **91**, 667, 1953) and of Durbin et al. (Physical Review **83**, 646, 1951; **84**, 581, 1951).

- (a) both the reactions correspond approximately to the same center of mass energy, and  
 (b) that the pion spin is 0.

$$(m_{\pi^+} = 139.6 \text{ MeV}/c^2 \\ m_p = 938.3 \text{ MeV}/c^2 \\ m_d = 1875.6 \text{ MeV}/c^2)$$

**Problem 25.16** The  $K^+$  meson has a decay mode

$$K^+ \rightarrow \pi^+ + \pi^+ + \pi^-$$

Assume that the decay rate can be calculated by the Golden Rule and that the matrix element causing the transition depends on the pion energies as

$$M \sim \frac{1}{\sqrt{\epsilon_1 \epsilon_2 \epsilon_3}}$$

where  $\epsilon_1^2 = \sqrt{p_1^2 + m^2}$  is the total energy (including the rest energy) of the first  $\pi$  meson etc. Calculate the energy distribution of the pions (say  $\pi^-$ ) in the *rest system* of  $K$ .

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## 25.7. Solutions

**Solution 25.1** The initial and final states of the neutron are given by

$$\frac{1}{L^{3/2}} \exp[i\mathbf{k}_0 \cdot \mathbf{r}]$$

and

$$\frac{1}{L^{3/2}} \exp[i\mathbf{k}_1 \cdot \mathbf{r}]$$

Since the scattering is elastic, the initial and final states of the crystal are the same and  $|\mathbf{k}_0| = |\mathbf{k}_1|$ . The matrix element of transition is

$$\begin{aligned} H'_{fi} &= \frac{2\pi \hbar^2 a}{m L^3} \int \exp[-i\mathbf{k}_1 \cdot \mathbf{r}] \sum_n \delta(\mathbf{r} - \mathbf{r}_n) \exp(i\mathbf{k}_0 \cdot \mathbf{r}) d\mathbf{r} \\ &= \frac{2\pi \hbar^2 a}{m L^3} \sum_n \int \exp[i\mathbf{k} \cdot \mathbf{r}] \delta(\mathbf{r} - \mathbf{r}_n) d\mathbf{r} \\ &= \frac{2\pi \hbar^2 a}{m L^3} \sum_n \exp[i\mathbf{k} \cdot \mathbf{r}_n] \end{aligned} \quad (73)$$

where

$$\mathbf{k} = \mathbf{k}_0 - \mathbf{k}_1 \quad (74)$$

The differential cross-section for scattering is therefore given by

$$\frac{d\sigma}{d\Omega} = \frac{1}{N} \left[ \frac{1}{\frac{\hbar k_0}{m} \frac{1}{L^3}} \right] \left[ \frac{2\pi}{\hbar} |H'_{fi}|^2 \right] \left[ \frac{m_0 k_1}{8\pi^3 \hbar^2} L^3 \right] \quad (75)$$

where the first bracketed term represents the incident flux and the last bracketed term the density of states. A factor  $1/N$  is introduced to imply that  $d\sigma/d\Omega$  is the differential cross-section per atom ( $N$  is the number of atoms in the crystal). For elastic scattering  $|\mathbf{k}_0| = |\mathbf{k}_1|$  and one obtains

$$\frac{d\sigma}{d\Omega} = \frac{1}{N} a^2 \left| \sum_n \exp[i\mathbf{k} \cdot \mathbf{r}_n] \right|^2 \quad (76)$$

For a simple cubic lattice, the lattice points are given by

$$\mathbf{r}_n = d[n_1 \hat{\mathbf{x}} + n_2 \hat{\mathbf{y}} + n_3 \hat{\mathbf{z}}]$$

where

$$n_\alpha = 0, 1, 2, \dots N_\alpha - 1; \alpha = 1, 2, 3, \dots$$

i.e. the crystal consists of  $N_1$ ,  $N_2$  and  $N_3$  atoms along the  $x$ -,  $y$ - and  $z$ -axes, respectively and  $N = N_1 N_2 N_3$  represents the total number of atoms. The origin is chosen at one of the corners of the crystal. Thus

$$\begin{aligned} \Delta &= \left| \sum_n \exp[i\mathbf{k} \cdot \mathbf{r}_n] \right|^2 \\ &= \left| \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} \exp[id(n_1 k_x + n_2 k_y + n_3 k_z)] \right|^2 \\ &= \Delta_1 \Delta_2 \Delta_3 \end{aligned} \quad (77)$$

where

$$\begin{aligned} \Delta_1 &= \left| \sum_{n_1=0}^{N_1-1} e^{idn_1 k_x} \right|^2 = \left| \frac{1 - e^{iN_1 k_x d}}{1 - e^{ik_x d}} \right|^2 \\ &= \frac{\sin^2 \frac{N_1 k_x d}{2}}{\sin^2 \frac{k_x d}{2}} \end{aligned} \quad (78)$$

For large values of  $N_1$  ( $\approx 10^8$  in a typical crystal) the value of  $\Delta_1$  will be large ( $= N_1^2$ ) if

$$\frac{k_x d}{2} = l\pi$$

$l$  being an integer.

If  $k_x d / 2\pi$  differs from an integer by more than a few times  $1/N_1$  then  $\Delta_1$  will be negligible. Thus, one obtains maximum scattering when

$$\begin{aligned} k_x d &= 2\pi l \\ k_y d &= 2\pi m \\ k_z d &= 2\pi n \end{aligned} \quad (79)$$

where  $l, m$  and  $n$  are integers (these are the Miller indices). Thus

$$k^2 = \frac{4\pi^2}{d^2} (l^2 + m^2 + n^2) \quad (80)$$

Further, using Eq. (74) we get

$$k^2 = k_0^2 - 2k_0 k_1 \cos \theta + k_1^2 = 4k_0^2 \sin^2 \theta \quad (81)$$

where we have used the fact that  $|\mathbf{k}_0| = |\mathbf{k}_1|$  and  $2\theta$  represents the scattering angle (see Fig. 25.3). Equating Eqs (80) and (81) we get

$$2d \sin \theta = [l^2 + m^2 + n^2]^{1/2} \lambda \quad (82)$$

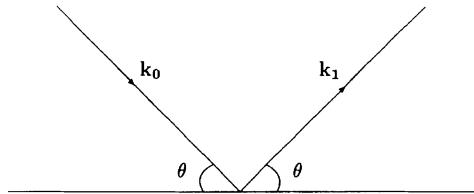


Figure 25.3. Bragg scattering of neutrons by a crystal.

where  $\lambda = 2\pi/k_0$ . The above equation represents the Bragg condition for reflection from a set of planes of spacing  $d/(l^2 + m^2 + n^2)^{1/2}$ . A more detailed theory for elastic (as well as inelastic) scattering of neutrons from a simple Bravais lattice taking into consideration lattice vibrations has been given in Ref. 4.

**Solution 25.2** Since the wavelength of the leptons are much larger than nuclear dimensions ( $\approx 10^{-12}$  cm), we can replace the lepton wave functions with their value at the center of the nucleus<sup>5</sup>. Now

$$\psi_e(r) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_e \cdot \mathbf{r}}$$

<sup>5</sup> We are neglecting the electrostatic distortion of the electron wave function caused by the charge on the nucleus; see Ref. 1, p. 315.

and

$$\psi_v(r) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_v \cdot \mathbf{r}}$$

so that at  $r = 0$

$$\psi_e(0) = \psi_v(0) = \frac{1}{\sqrt{V}}$$

Thus

$$|H'_{fi}|^2 = \frac{G^2}{V^2} |M_{fi}|^2$$

where

$$M_{fi} = \int \psi_{fN}^* \psi_{iN} d\tau$$

Therefore, the probability of emission per unit time  $w$ , is,

$$w = \frac{2\pi}{\hbar} \frac{G^2}{V^2} |M_{fi}|^2 \frac{dn}{dE_0}$$

where

$$E_0 = E_e + E_v$$

$E_e$  and  $E_v$  representing the energies of electron and neutrino respectively. We first calculate the probability for the electron going into the particular state; then  $E_e$  is fixed and

$$\frac{dn}{dE_0} = \frac{dn}{dE_v}$$

Now

$$E_v^2 = m_v^2 c^4 + p_v^2 c^2$$

where  $m_v$  is the rest mass of the neutrino, thus

$$\frac{dn}{dE_v} = \frac{dn}{dp_v} \frac{dp_v}{dE_v} = \frac{E_v}{p_v c^2} \frac{dn}{dp_v}$$

In Appendix M we have shown that the number of states for which the magnitude of the momentum has between  $p_v$  and  $p_v + dp_v$  is given by

$$\frac{V}{(2\pi \hbar)^3} 4\pi p_v^2 dp_v = \frac{V p_v^2 dp_v}{2\pi^2 \hbar^3} \quad (83)$$

Thus

$$\begin{aligned} \frac{dn}{dE_0} &= \frac{dn}{dE_v} = \left( \frac{E_v}{p_v c^2} \right) \frac{V p_v^2}{2\pi^2 \hbar^3} \\ &= \frac{V}{2\pi^2 \hbar^3 c^3} (E_0 - E_e) [(E_0 - E_e)^2 - (m_v c^2)^2]^{1/2} \end{aligned}$$

and

$$w = \frac{G^2 |M_{fi}|^2}{\pi \hbar^4 c^3 V} (E_0 - E_e) [(E_0 - E_e)^2 - (m_v c^2)^2]^{1/2} \quad (84)$$

If  $P(p_e) dp_e$  represent the probability (per unit time) of the momentum of the emitted electron to lie between  $p_e$  and  $p_e + dp_e$ , then in order to obtain  $P(p_e) dp_e$  we must multiply the above expression for  $w$  by the number of electron states whose momenta lie between  $p_e$  and  $p_e + dp_e$ , this is given by [see Eq. (83)]  $V p_e^2 dp_e / 2\pi^2 \hbar^3$ . Thus

$$P(p_e) dp_e = \frac{G^2 |M_{fi}|^2}{2\pi^3 \hbar^7 c^3} p_e^2 (E_0 - E_e) [(E_0 - E_e)^2 - (m_v c^2)^2]^{1/2} dp_e \quad (85)$$

The experimental data on the energy distribution of the emitted electrons show that the plot of  $[P(p_e)/p_e^2]^{1/2}$  as a function of  $E_e$  is very nearly a straight line, which suggests that  $m_v$  is zero or extremely small. A typical plot of  $[P(p_e)/p_e^2]^{1/2}$  as a function of  $E_e$  corresponding to the  $n \rightarrow p + e^- + \bar{\nu}$  process is shown in Fig. 25.4; such a plot is known as the Kurie plot. The departure from the linearity is due to experimental errors and due to the finite velocity of the neutrons which undergo decay. We may mention here that for the  $\beta$  decay from nuclei of large  $Z$  values one should also consider the electrostatic distortion of the electron wave function (see e.g. Ref. 1).

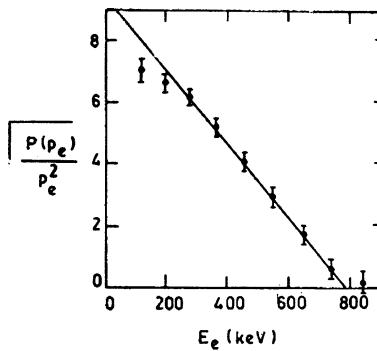


Figure 25.4. The Kurie plot for the  $n \rightarrow p + e^- + \bar{\nu}$  process. The disagreement between theory and experiment at low energies is due to experimental errors and also due to the fact that neutrons form a beam rather than a solid or liquid [Adapted from Ref. 1; the original data is of I.M. Robson, *Phys. Rev.* **83**, 349 (1951)].

The expression for the mean lifetime is obtained by integrating Eq. (85) over all values of  $p$ :

$$\frac{1}{\tau} = \frac{G^2 |M_{fi}|^2}{2\pi^3 \hbar^7 c^3} \int_0^{p_{max}} p^2 [(m^2 c^4 + p_{max}^2 c^2)^{1/2} - (m^2 c^4 + p^2 c^2)^{1/2}]^{1/2} dp$$

where  $p_{max}$  represents the maximum kinetic energy of the emitted electrons and in writing the last equation we have assumed  $m_v = 0$ . Carrying out the integration we obtain

$$\frac{1}{\tau} = \frac{G^2 |M_{fi}|^2}{2\pi^3 \hbar^7 c^3} F(\eta_0) \quad (86)$$

where

$$F(\eta_0) = -\frac{1}{4}\eta_0 - \frac{1}{12}\eta_0^3 + \frac{1}{30}\eta_0^5 + \frac{1}{4}(1 + \eta_0^2)^{1/2} \sinh^{-1} \eta_0 \quad (87)$$

and  $\eta_0 = p_{max}/mc$ . Equation (86) tells us that if  $|M_{fi}|^2$  does not change, the value of  $F\tau$  must be a constant for different  $\beta$ -emitters; this is approximately borne out from experimental data (see, e.g. Ref 1 and 5).

**Solution 25.3** The initial and final states of the system, which are eigenfunctions of  $H_0$ , are given by<sup>6</sup>

$$\psi_i = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_0 \cdot \mathbf{r}_1} \psi_{100}(\mathbf{r}_2)$$

and

$$\psi_f = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} \psi_{200}(\mathbf{r}_2)$$

Energy conservation demands that

$$\frac{\hbar^2 k_0^2}{2m} - \frac{me^4}{2\hbar^2} = \frac{\hbar^2 k_1^2}{2m} - \frac{me^4}{8\hbar^2}$$

or

$$k_1^2 = k_0^2 - \frac{3m^2 e^4}{8\hbar^4}$$

Now, the matrix element for the transition is given by

$$H'_{fi} = \frac{1}{V} \iint e^{-i\mathbf{k}_1 \cdot \mathbf{r}_1} \psi_{200}^*(\mathbf{r}_2) \left[ \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e^2}{r_1} \right] e^{i\mathbf{k}_0 \cdot \mathbf{r}_1} \psi_{100}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Since

$$\int \psi_{200}^*(\mathbf{r}_2) \psi_{100}(\mathbf{r}_2) d\mathbf{r}_2 = 0$$

the integral involving  $e^2/r_1$  would vanish. Thus

$$H'_{fi} = \frac{e^2}{V} \int \psi_{200}^*(\mathbf{r}_2) \psi_{100}(\mathbf{r}_2) I(\mathbf{r}_2) d\mathbf{r}_2 \quad (88)$$

where

$$I(\mathbf{r}_2) = \int \frac{e^{i\mathbf{q} \cdot \mathbf{r}_1}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 = e^{i\mathbf{q} \cdot \mathbf{r}_2} \iiint \frac{e^{iq\rho \cos\theta}}{\rho} \rho^2 d\rho \sin\theta d\theta d\phi$$

---

<sup>6</sup> This solution is adapted from Ref. 6; with kind permission of McGraw-Hill Book Company.

where  $\rho = \mathbf{r}_1 - \mathbf{r}_2$  and in carrying out the integration we have assumed the  $z$ -axis to be along  $\mathbf{q}$ . Carrying out the integrations over  $\theta$  and  $\phi$  we get

$$I(\mathbf{r}_2) = \frac{4\pi}{q} e^{i\mathbf{q}\cdot\mathbf{r}_2} \int_0^\infty \sin q\rho d\rho$$

The above integral does not have a well-defined value. In order to evaluate the integral we introduce an exponentially decaying factor  $e^{-\lambda\rho}$  carry out the integral and take the limit  $\lambda \rightarrow 0$  to obtain <sup>7</sup>

$$\begin{aligned} I(\mathbf{r}_2) &= \frac{4\pi}{q} e^{i\mathbf{q}\cdot\mathbf{r}_2} \lim_{\lambda \rightarrow 0} \int_0^\infty \sin q\rho e^{-\lambda\rho} d\rho \\ &= \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot\mathbf{r}_2} \end{aligned} \quad (89)$$

Substituting the above result and the hydrogen atom wave functions in Eq. (88) we get

$$\begin{aligned} H'_{fi} &= \frac{e^2}{V} \int d\mathbf{r}_2 \left[ \left\{ \left( \frac{1}{32\pi a_0^3} \right)^{\frac{1}{2}} \left( 2 - \frac{r_2}{a_0} \right) e^{-r_2/2a_0} \right\} \right. \\ &\quad \times \left. \left\{ \left( \frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} e^{-r_2/a_0} \right\} \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot\mathbf{r}_2} \right] \end{aligned}$$

where  $a_0 = \hbar^2/me^2$ . Once again we choose the  $z_2$ -axis along  $\mathbf{q}$  and carry out the straightforward integrations to obtain

$$H'_{fi} = \frac{1}{V} \frac{16\sqrt{2}\pi a_0^2 e^2}{(q^2 a_0^2 + \frac{9}{4})^3}$$

The differential cross-section can now be obtained by using the formulae given in Sec. 25.3; however, we must remember that in calculating  $I$  [see Eq. (40)] we should use  $k_0$  and in calculating  $\rho_f$  [see Eq. (39)] we should use  $k_1$ ; consequently

$$\sigma(\theta) = \frac{k_1}{k_0} \left( \frac{m}{2\pi\hbar^2} \right)^2 V^2 |H'_{fi}|^2 \quad (90)$$

---

<sup>7</sup> Such a procedure is justified because when  $\mathbf{r}_1 \gg \mathbf{r}_2$

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \rightarrow \frac{1}{r_1} \left[ 1 + \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2 \frac{r_2}{r_1} \right] = \frac{1}{r_1} + \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2 \frac{r_2}{r_1^2}$$

and therefore, if we first carry out the integration over  $\mathbf{r}_2$  then the result will fall off as  $1/r_1^2$ ; the integral containing the term  $1/r_1$  will vanish because of orthogonality of  $\psi_{100}$  and  $\psi_{200}$ . Thus for large  $r_1$  the integrand will fall off as  $\sin(qr_1)/r_1$  making the integral convergent.

from which one immediately gets Eq. (62). A nice discussion on the total cross-section has been given Sec. 30 of Ref. 6. One can similarly calculate the scattering cross-section for the  $1s \rightarrow 2p$  transition.

**Solution 25.4** Assume that the impact parameter is  $d$  (Fig. 25.5); the collision time, the time for which the potential energy changes appreciably, is of the order of  $2d/v$  where  $v$  is the velocity of the proton. The change in potential energy is of the order  $e^2/d$ . If  $\hbar\omega$  is the energy required for excitation to the  $n = 2$  state of the atom, Eq. (51) suggests that a transition will occur only if

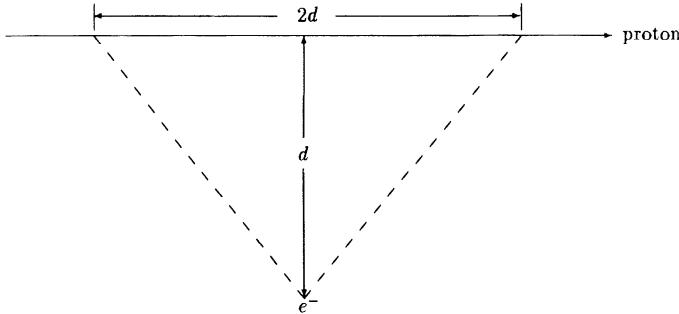


Figure 25.5.

$$\frac{\partial V}{\partial t} \sim \hbar\omega^2$$

or

$$\frac{ve^2}{2d^2} \sim \hbar\omega^2$$

Thus

$$2d^2 \sim \frac{ve^2 \hbar}{(\hbar\omega)^2}$$

Putting  $\hbar\omega \sim 10$  eV, we get the estimate

$$d \sim 2.5 \text{ \AA}$$

**Solution 25.5** We assume that the heavy ion of charge  $Z_1 e$ , velocity  $v$  passes undeflected even as it suffers a collision with an atom (Fig. 25.6). If each atom of the medium (assumed to be of a single element) has  $Z_2$  electrons, the potential energy is

$$V = Z_1 e^2 \sum_{i=1}^{Z_2} \frac{1}{|\mathbf{r}_i - \mathbf{R}|} \quad (91)$$

Assuming  $|\mathbf{r}_i| \ll |\mathbf{R}|$ , we can write

$$V \approx \frac{Z_1 e^2}{R} \sum_i \left( 1 + \frac{r_i}{R} \hat{\mathbf{r}}_i \cdot \hat{\mathbf{R}} \right) \quad (92)$$

In this expression, we treat  $r_i$  as stationary and  $R(t)$  alone as a function of time.

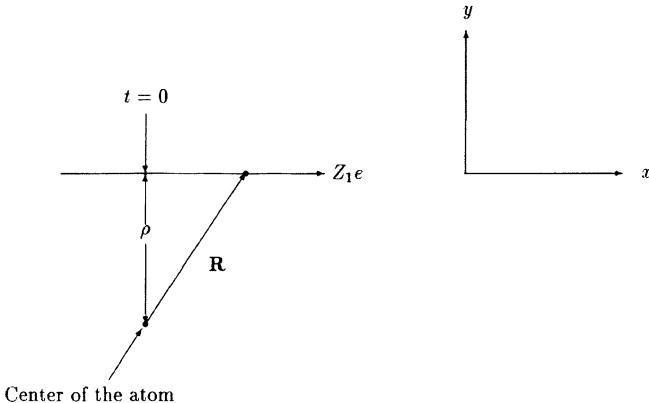


Figure 25.6. Collision of a heavy ion with an atom.

This is in the spirit of the sudden approximation; it can be shown that if the collision is adiabatic there is no loss of energy. We assume that at  $t = 0$ , the ion passes closest to the centre of the atom, the impact parameter being  $\rho$ . We take the coordinates of  $\mathbf{R}$  to be  $(vt, \rho, 0)$ , of  $\mathbf{r}_i$  to be  $(x_i, y_i, z_i)$  so that

$$V = \frac{Z_1 e^2}{R} \sum_i \left[ 1 + \frac{1}{R^2} (x_i vt + \rho y_i) \right] \quad (93)$$

We have to calculate matrix element  $\langle n | V | m \rangle$  where  $m, n$  are the initial and final states of the atom. It is clear that the first term in Eq. (93) contributes nothing. We obtain

$$V_{nm} = \frac{Z_1 e^2}{R^3} \left[ \left( \sum x_i \right)_{nm} vt + \left( \sum y_i \right)_{nm} \rho \right] \quad (94)$$

The transition probability is  $|c_{nm}|^2$  where

$$c_{nm} = -\frac{i}{\hbar} \int_{-\infty}^{\infty} V_{nm} \exp(i\omega_{nm}t) dt \quad (95)$$

For  $\omega_{nm}t \ll 1$ , we can replace the exponential by unity. The first term in Eq. (94) being odd in  $t$ , vanishes and

$$c_{nm} = -\frac{i Z_1 e^2}{\hbar} \int_{-\infty}^{\infty} \frac{\rho \left( \sum y_i \right)_{nm}}{(\rho^2 + v^2 t^2)^{3/2}} dt \quad (96)$$

The integral is easily evaluated by setting  $vt = \rho \tan \theta$ . We get

$$c_{nm} = -\frac{i}{\hbar} Z_1 e^2 \frac{1}{v\rho} 2 y_{nm}$$

where  $y_{nm} = \left( \sum_i y_i \right)_{nm}$  is the  $y$ -component of the dipole matrix element. The transition rate is

$$|c_{nm}|^2 = \frac{4Z_1^2 e^4}{\hbar^2} \frac{1}{v^2 \rho^2} y_{nm}^2$$

The average energy loss by the ion in such excitations of the atom (assuming that  $m$  is always the ground state)

$$\overline{\mathcal{E}} = \sum_n (E_n - E_m) |c_{nm}|^2 = \frac{4Z_1^2 e^4}{\hbar^2} \frac{1}{v^2 \rho^2} \sum_n y_{nm}^2 (E_n - E_m) \quad (97)$$

It is shown in Problem 26.9 that the term

$$\sum_n y_{nm}^2 (E_n - E_m) = \frac{\hbar^2}{2m} Z_2$$

a relation which is called the Thomas-Reiche-Kuhn sum rule;  $Z_2$  is the charge of the target atom. Hence

$$\overline{\mathcal{E}} = \frac{2Z_1^2 Z_2 e^4}{mv^2 \rho^2} \quad (98)$$

We now use this formula for calculating the average energy loss  $-dE$  as the ion transverses a length  $dx$  of the medium. The number of collisions with atoms such that the impact parameter lies between  $\rho$  and  $\rho + d\rho$  is

$$2\pi n \rho \, d\rho \, dx$$

where  $n$  is the number of atoms per unit volume. The energy loss in  $dx$  is

$$-dE = \int_{\rho_{\min}}^{\rho_{\max}} \frac{2Z_1^2 Z_2 e^4}{mv^2 \rho^2} 2\pi n \rho \, d\rho \, dx$$

or

$$-\frac{dE}{dx} = \frac{4\pi Z_1^2 Z_2 e^4 n}{mv^2} \ln \left( \frac{\rho_{\max}}{\rho_{\min}} \right) \quad (99)$$

In order to decide on the limits  $\rho_{\max}$  and  $\rho_{\min}$  we use the following arguments. Referring to Eqs (95) and (96), we can write

$$c_{nm} \sim \int \frac{\exp(i\omega_{nm}t)}{(t^2 + \rho^2/v^2)^{3/2}} dt$$

so that if  $\rho/v \gg 1/\omega_{nm}$ , we can in fact pull out the denominator from the integral and  $c_{nm} \rightarrow 0$  since we shall be averaging over several periods even for small  $t$ . This, in fact, is the adiabatic limit. We therefore set  $\rho$  at this limit.

$$\rho_{\max} = \frac{v}{\omega_{nm}}$$

It can be shown that when relativistic effects are included we should correct this to

$$\rho_{\max} = \frac{v}{\omega_{nm}\sqrt{1-\beta^2}} ; \quad \beta = \frac{v}{c} \quad (100)$$

For  $\rho_{\min}$ , we note that the heavy ion ‘sees’ electrons moving towards it with momenta  $\sim mv$ . The de Broglie wavelength is  $\sim \hbar/mv$ . This must be the minimum value of the impact parameter; when the relativistic expression for momentum is introduced,

$$\rho_{\min} = \frac{\hbar\sqrt{1-\beta^2}}{mv} \quad (101)$$

Inserting Eq. (100) and Eq. (101) in Eq. (99) we get

$$-\frac{dE}{dt} = \frac{4\pi Z_1^2 Z_2 e^4 n}{mv^2} \ln \frac{mv^2}{\hbar\bar{\omega}(1-\beta^2)} \quad (102)$$

where  $\hbar\bar{\omega}$  is an average of the factors  $\hbar\omega_{nm}$ . Formula (102) is a simplified version of Bohr’s treatment of the loss of energy of heavy ions in matter; it has important application in nuclear physics where it is often necessary to know how much energy is deposited by particles as they go through matter<sup>8</sup>.

**Solution 25.6** [Reference: R. Serber, Phys. Rev. **72**, 1008 (1947)] We neglect the effect of Coulomb interaction and assume that the collision time  $\tau = r_0/v$  where  $r_0$  is the range of the nuclear forces and  $v$  the deuteron velocity. The transition here is from the bound deuteron to the continuum, the relevant period being about  $\omega \sim \mathcal{E}_d/\hbar$  where  $\mathcal{E}_d$  is the binding energy of the deuteron. Now  $E_d = \frac{1}{2}(2M)v^2$  so that

$$\omega\tau = \frac{r_0}{v} \frac{\mathcal{E}_d}{\hbar} = r_0 \sqrt{\frac{M}{E_d}} \frac{\mathcal{E}_d}{\hbar}$$

The deuteron binding energy can be expressed in terms of its ‘radius’  $r_d = \hbar/\sqrt{M\mathcal{E}_d}$  so that

$$\omega\tau = \frac{r_0}{r_d} \sqrt{\frac{\mathcal{E}_d}{E_d}} \ll 1 \quad (\text{for } E_d \sim 200 \text{ MeV and } \mathcal{E}_d \sim 2.2 \text{ MeV})$$

which suggests that the collision may be regarded as sudden.

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<sup>8</sup> A more complete treatment was given by H.A. Bethe Ann. Phys. **5**, 325 (1930).

In the center of mass system of the deuteron, the state of the neutron changes from

$$\psi_i = \frac{\alpha}{\sqrt{2\pi}} \frac{e^{-\alpha r}}{r} \quad \text{to} \quad \psi_f \sim A e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \quad (103)$$

where  $\alpha = \sqrt{M\mathcal{E}_d}/\hbar$ ,  $M$  is the mass of the neutron,  $\psi_i$  is the wave function of the deuteron outside the range of the nuclear force. But, as mentioned in the problem, since the deuteron size is much larger than the range, we can treat  $\psi_i$  as valid for the entire space.  $\psi_f$  is the wave function for the free neutron,  $A$  a constant of normalization.

The probability for the transition is

$$\begin{aligned} P(\mathbf{p}) d\mathbf{p} &= \frac{A^2 \alpha^2}{2\pi} \left| \int e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \frac{e^{-\alpha r}}{r} d\mathbf{r} \right|^2 d\mathbf{p} \\ &= \frac{A^2 \alpha^2}{2\pi} \left| \int_0^{\infty} \int_0^{2\pi} e^{-ipr \cos\theta/\hbar} e^{-\alpha r} r dr 2\pi \sin\theta d\theta \right|^2 d\mathbf{p} \\ &= \frac{A^2 \alpha^2}{2\pi} \left| 4\pi \hbar \int_0^{\infty} dr \frac{e^{-\alpha r}}{p} \sin \frac{pr}{\hbar} \right|^2 d\mathbf{p} \end{aligned} \quad (104)$$

Now

$$\int_0^{\infty} \sin kr e^{-\alpha r} dr = \text{Im} \left[ \int_0^{\infty} e^{ikr} e^{-\alpha r} dr \right] = \text{Im} \frac{1}{ik - \alpha} = \frac{k}{k^2 + \alpha^2}$$

Thus

$$P(\mathbf{p}) d\mathbf{p} = B \frac{d\mathbf{p}}{\left( \frac{p^2}{\hbar^2} + \alpha^2 \right)^2} \quad (105)$$

We now wish to transform the expression to the lab system in which the centre of mass of the deuteron moves along the  $z$ -direction with a velocity  $v$  where

$$\frac{1}{2} (2M) v^2 = E_d$$

If we write

$$p^2 = p_z^2 + p_{\perp}^2 \quad (106)$$

then, to the  $z$ -component we have to add the momentum of the centre of mass,

$$p_0 = Mv = \sqrt{ME_d}$$

(we neglect relativistic effects). The distribution in  $p_x$  is [from Eq. (105)]

$$P(p_z) dp_z = B dp_z \int_0^\infty \frac{p_\perp dp_\perp}{\left( \frac{p_\perp^2 + p_z^2}{\hbar^2} + \alpha^2 \right)^2} = \frac{B' dp_z}{(\hbar^2 \alpha^2 + p_z^2)} \quad (107)$$

We can relate  $p_z$  to the neutron and deuteron energies in the laboratory system. If  $\mathbf{p}_n$  is the neutron momentum in the laboratory system, we have

$$\mathbf{p}_n = \mathbf{p} + \mathbf{p}_0 \quad \text{where} \quad p \ll p_0 \quad (108)$$

(The momenta  $p$  are the Fourier components of the deuteron wave function. Since the deuteron is a very loosely bound structure, these momenta are very much smaller than the kinetic energy of the deuteron). From Eq. (108) we get

$$p_n^2 = p^2 + p_0^2 + 2p_0 p_z \approx p_0^2 + 2p_0 p_z$$

In terms of the neutron energy  $E = p_n^2/2M$  deuteron energy  $E_d = p_0^2/M$  this gives

$$E = \frac{E_d}{2} + \sqrt{\frac{E_d}{M}} p_z \quad (109)$$

Thus Eq. (107) gives

$$P(E) dE \propto \frac{dE}{\hbar^2 \alpha^2 + \frac{M}{E_d} \left( E - \frac{1}{2} E_d \right)^2}$$

Writing  $\hbar^2 \alpha^2 = M \varepsilon_d$ , we obtain

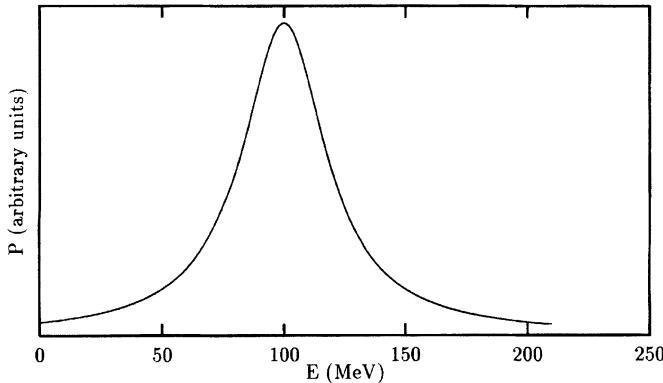
$$P(E) dE = C \frac{dE}{\left( E - \frac{1}{2} E_d \right)^2 + \varepsilon_d E_d} \quad (110)$$

This is a distribution which is peaked around  $E = \frac{1}{2} E_d$  with a width of  $\Delta E = 2\sqrt{\varepsilon_d E_d}$ . Moreover, it goes to a very small value for  $E = 0$  so that we can normalize it by integrating (110) from  $E = -\infty$  to  $+\infty$ . This gives

$$1 = C \frac{\pi}{\sqrt{\varepsilon_d E_d}}$$

so that the normalized distribution is

$$P(E) dE = \frac{\sqrt{\varepsilon_d E_d}}{\pi} \frac{dE}{\left( E - \frac{1}{2} E_d \right)^2 + \varepsilon_d E_d}$$

Figure 25.7. The variation of  $P(E)$  with  $E$ .

The experimental distribution for  $E_d = 200$  MeV agrees very closely with this expression with the peak at 95 MeV and a width of about 45 MeV. The above theory predicts a width of  $2\sqrt{\mathcal{E}_d E_d} \approx 42$  MeV (see Fig. 25.7).

**Solution 25.7** The probability amplitude is

$$\langle \phi_f | \psi_i \rangle = \frac{\langle \phi_f | E_f - E_i | \psi_i \rangle}{E_f - E_i} = \frac{\langle \phi_f | H_1 - H_0 | \psi_i \rangle}{E_f - E_i}$$

If  $V = H_1 - H_0$  is small, we may replace  $\langle \phi_f |$  by  $\langle \psi_f |$  so that

$$|\langle \phi_f | \psi_i \rangle|^2 \approx \frac{|V_{fi}|^2}{\hbar^2 \omega_{fi}^2}$$

**Solution 25.8** That the sudden approximation holds may be seen on comparing the beta energy with the atomic binding energies. The change of the nuclear charge, hence the potential, occurs in approximately the time that the beta particle leaves the atom. This time is of the order of  $10^{-8}/(c/5) \sim 10^{-18}$  sec;  $\omega \sim 10^{17}$  sec $^{-1}$  so that  $\omega\tau \sim 0.1$ . The initial wave function is

$$Y_{00} R_{10} (Z = 1) = \frac{1}{\sqrt{4\pi}} \left(\frac{1}{a_0}\right)^{3/2} 2e^{-r/a_0}$$

The final wave function is

$$Y_{00} R_{10} (Z = 2) = \frac{1}{\sqrt{4\pi}} \left(\frac{2}{a_0}\right)^{3/2} 2e^{-2r/a_0}$$

The probability is

$$P = \left| \int Y_{00}^* R_{10}^* (Z = 2) Y_{00} R_{10} (Z = 1) d\tau \right|^2$$

The integral is

$$\frac{2^{3/2}4}{a_0^3} \int_0^\infty e^{-3r/a_0} r^2 dr = \frac{2^{3/2}4}{a_0^2} \frac{2!}{(3/a_0)^3}$$

or

$$P = \left(\frac{8}{9}\right)^3 \approx 0.703$$

**Solution 25.9** The perturbation is

$$V = -eEz \quad (\text{assuming } E \text{ is along } z)$$

i.e.

$$V = -eEr \cos \theta \quad (111)$$

The transition probability is

$$|C_{n0}|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} \langle n | V | 0 \rangle e^{i\omega t} dt \right|^2 \quad (112)$$

where  $|0\rangle$  is the ground state; from Eq. (111) it is obvious that there are no transitions to the states  $m = \pm 1$  of  $2P$ . The matrix element  $\langle 210 | r \cos \theta | 100 \rangle$  is easily evaluated as  $(2^7 \sqrt{2} a_0 / 3^5)$ . This gives

$$|C|^2 = \frac{1}{\hbar^2} \frac{2^{15}}{3^{10}} e^2 a_0^2 E_0^2 \frac{\tau^2}{\pi^2} \left| \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{\tau^2 + t^2} dt \right|^2$$

The integral can be evaluated by going to the complex  $t$  plane on which poles occur at  $t = \pm i\tau$ . Choosing the contour as the real axis (Fig. 25.8) closed by the upper half semicircle, it is easy to check that the contribution over the semicircle vanishes. Thus

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{\tau^2 + t^2} dt &= 2i\pi \left( \frac{(t - i\tau) e^{i\omega t}}{t^2 + \tau^2} \right)_{t=i\tau} \\ &= \frac{\pi}{\tau} e^{-\omega\tau} \end{aligned}$$

Thus the probability is

$$|C|^2 = \frac{1}{\hbar^2} \frac{2^{15}}{3^{10}} e^2 a_0^2 E_0^2 e^{-2\omega\tau}$$

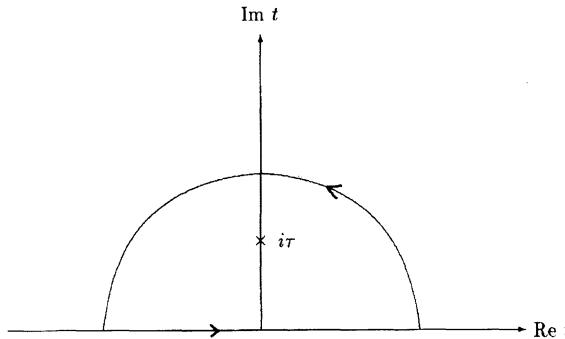


Figure 25.8. The contour of integration.

The limit  $\tau \rightarrow \infty$  corresponds to a turning on the perturbation slowly, i.e.  $\omega\tau \gg 1$ , when the transition probability vanishes. The other limit  $\omega\tau \rightarrow 0$  corresponds to the application of an impulsive perturbation, with

$$\lim_{\tau \rightarrow 0} \frac{\tau}{\pi(t^2 + \tau^2)} = \delta(t)$$

**Solution 25.10** Since  $|n\rangle$  form a complete set, we may write

$$|\Psi(t)\rangle = \sum_n c_n(t) |n\rangle$$

If we substitute the above expression in the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi\rangle$$

and operate by  $\langle m |$ , we would get Eq. (64).

**Solution 25.11** Since  $|\Psi(0)\rangle = |K^\circ\rangle$ ,  $C_1 = C_2 = 1/\sqrt{2}$ , thus

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}} \left[ \frac{1}{\sqrt{2}} (|K^\circ\rangle + |\overline{K}^\circ\rangle) e^{-iE_1 t/\hbar} e^{-t/2\tau_1} + \frac{1}{\sqrt{2}} (|K^\circ\rangle - |\overline{K}^\circ\rangle) e^{-iE_2 t/\hbar} \right] \quad (113)$$

Thus the probability that starting from a  $K^\circ$  particle at  $t = 0$  we end up with  $\overline{K}^\circ$  particle at time  $t$  is given by

$$|C|^2 = |\langle \overline{K}^\circ | \Psi(t)\rangle|^2 = \frac{1}{4} [1 + e^{-t/\tau_1} - 2e^{-t/2\tau_1} \cos(E_2 - E_1)t/\hbar] \quad (114)$$

If the particles are at rest, then  $E_2 - E_1 = c^2 \Delta m$  where  $\Delta m$  is the mass difference of  $K_1^\circ$  and  $K_2^\circ$ . In Eq. (114) if we substitute

$$E_2 - E_1 \approx c^2 \Delta m \quad (115)$$

then the mass difference can be determined from the variation of  $|C|^2$  with time (see Fig. 25.9).

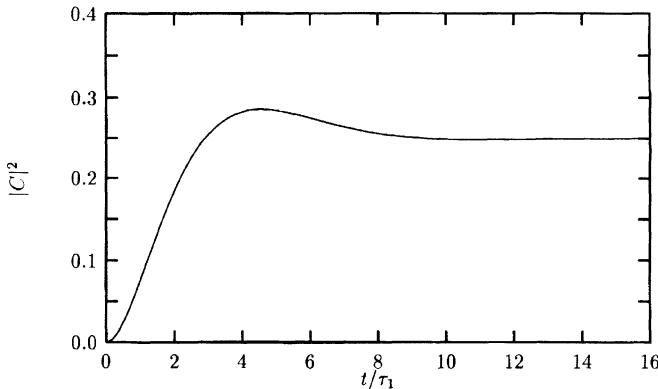


Figure 25.9. The dependence of  $|C|^2$  with time.

The behaviour of the neutral  $K$  is analogous to that of polarized light. To see this, we first summarize the results of this problem. First, at production the neutral  $K$ , produced in strong interactions, is in the state  $K^\circ$ . As time passes by, the  $K^\circ$  which, according to Eqs (65) and (66), is an equal mixture of  $K_1^\circ$  and  $K_2^\circ$  decays; but it is only the  $K_1^\circ$  part that decays—the  $K_2^\circ$  has a long lifetime. The residue, which is practically pure  $K_2^\circ$  is, according to Eqs (65) and (66) again a mixture of  $K^\circ$  and  $\bar{K}^\circ$ . We can detect either component by setting up an appropriate detector. In this case, the difference in the behaviour of  $K^\circ$  and  $\bar{K}^\circ$  is in their strong interactions, and we therefore study a strong reaction induced by the neutral  $K$ .

One can construct an analogy identifying the  $K^\circ$  and  $\bar{K}^\circ$  with the two plane polarized beams of light, one of which is selected by a polarizer. The  $K_1^\circ$  and  $\bar{K}^\circ$  then correspond to right and left circularly polarized light, with an absorber which selectively absorbs only the right circularly polarized light.

Returning to Eq. (114), if we substitute experimental values one finds

$$\frac{E_2 - E_1}{\hbar} \approx \frac{1}{2\tau_1}$$

Thus

$$|C|^2 \approx \frac{1}{4} [1 + e^{-t/\tau_1} - 2e^{-t/2\tau_1} \cos(t/2\tau_1)] \quad (116)$$

The time dependence of  $|C|^2$  is shown in Fig. 25.9 which is in agreement with experimental data. Experimentally, since  $K^\circ$  and  $\bar{K}^\circ$  are both uncharged particles they leave no tracks; they are distinguished from the fact that  $K^\circ$  does not interact

with matter (except elastically) whereas  $\bar{K}^\circ$  can interact with proton to produce  $\Lambda^\circ$  and  $\pi^+$



Now in a hydrogen bubble chamber,  $K^\circ$  is produced through the following reaction



The trajectory of  $\Lambda^\circ$  can be inferred from its subsequent decay to  $\pi^- + p$  because both  $\pi^-$  and proton leave tracks. When  $K^\circ$  is produced in the bubble chamber (see Eq. (118)) both  $K_1^\circ$  and  $K_2^\circ$  are created [see Eqs (65) and (66)]; however,  $K_1^\circ$  decays very quickly (either to  $\pi^+ + \pi^-$  or  $\pi^\circ + \pi^\circ$ ).  $K_2^\circ$  has a large  $\bar{K}^\circ$  component and the  $\bar{K}^\circ$  interacts with hydrogen through the reaction given by Eq. (117). Indeed analysis of the experiment allows one to determine the difference. We conclude this problem by noting that conversion of  $K^\circ$  to  $\bar{K}^\circ$  is a beautiful demonstration of quantum interference effects.

### Solution 25.12

(a) The Schrödinger equation for the particle is

$$i \hbar \frac{\partial \Psi}{\partial t} = (T + V + U) \Psi \quad (119)$$

where  $T$ ,  $V$  are the kinetic and potential energy operators without the impulse and  $U$  represents the energy operator due to the impulse;

$$-\nabla U = \mathbf{F}(t)$$

Integrating, we obtain

$$U = -\mathbf{F} \cdot \mathbf{r} = -\mathbf{P} \cdot \mathbf{r}\delta(t)$$

where we have chosen  $U = 0$  at  $\mathbf{r} = 0$ . During the impulse, we can neglect  $T$ ,  $V$  in comparison to  $U$  in Eq. (119) so that we have

$$i \hbar \frac{\partial \Psi}{\partial t} = U(\mathbf{r}, t) \Psi$$

or

$$i \hbar \frac{\partial}{\partial t} [\ln \Psi] = -\mathbf{P} \cdot \mathbf{r}\delta(t)$$

Integrating,

$$i \hbar \ln \left( \frac{\Psi_f}{\Psi_i} \right) = -\mathbf{P} \cdot \mathbf{r}$$

or

$$\Psi_f(\mathbf{r}) = \Psi_i(\mathbf{r}) \exp \left[ \frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r} \right] \quad (120)$$

(b) The final state given by Eq. (120) is not one of the eigenstates of the system.

We can expand  $\Psi_f$  in terms of these eigenstates  $\Psi_n(\mathbf{r})$

$$\Psi_f = \Psi_i \exp\left[\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r}\right] = \sum_n C_n \Psi_n(\mathbf{r})$$

Since  $\Psi_i, \Psi_n$  are eigenstates, we can use orthonormality to obtain the coefficients

$$C_n = \int \Psi_n^*(\mathbf{r}) \Psi_i(\mathbf{r}) \exp\left[\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r}\right] d\mathbf{r}$$

$|C_n|^2$  is the probability that the system is in the eigenstate  $n$  after the impulse. The above results have a ready application for the so called “Mossbauer effect”. Here, the nucleus of an atom in a crystal lattice emits a  $\gamma$ -ray, thus delivering an impulse to the crystal. If the crystal is originally in the ground state of its vibrational modes, we can calculate, as above, the probability that it remains in the ground state after the  $\gamma$ -emission. In this situation, it is not the atom, which emits the  $\gamma$ , which will vibrate (since this will leave the crystal in a different state) but the crystal as a whole will recoil without changing its internal state. The probability

$$W = |C_i|^2 = \int \Psi_i^* \exp\left[\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r}\right] \Psi_i d\mathbf{r} \quad (121)$$

for such an emission is called the *Debye-Waller factor*. If the system we are considering is, for example, a linear harmonic oscillator, the ground state is

$$\Psi_0(x) = \left(\frac{1}{\sqrt{\pi} a}\right)^{1/2} \exp\left(-\frac{x^2}{2a^2}\right)$$

where  $a$  is the classical amplitude. For this one-dimensional case we have, in place of Eq. (121)

$$W = \exp(-k^2 a^2) \quad (122)$$

where  $\hbar k = P$ . The recoil energy is

$$E_R = \frac{P^2}{2M} = \frac{\hbar^2 k^2}{2M}$$

where  $M$  is the mass of the entire recoiling system. For a crystal,  $M$  is very large and the energy  $E_R$  is negligible. Thus the  $\gamma$ -ray emitted by the excited nucleus appears with the full energy, i.e. the energy difference between the excited and ground states of the nucleus. For a fuller account of Mossbauer effect, the reader is referred to Ref.7.

**Solution 25.13** We have the two reactions



and



We assume that the matrix element for the processes

$$(\mathbf{p}_A, \mathbf{p}_a, \mathbf{s}_A, \mathbf{s}_a) \rightarrow (\mathbf{p}_B, \mathbf{p}_b, \mathbf{s}_B, \mathbf{s}_b)$$

and

$$(-\mathbf{p}_B, -\mathbf{p}_b, -\mathbf{s}_B, -\mathbf{s}_b) \rightarrow (-\mathbf{p}_A, -\mathbf{p}_a, -\mathbf{s}_A, -\mathbf{s}_a)$$

are the same (this is referred to as the invariance under time reversal). We further assume that the initial beams are unpolarized so that in calculating the cross-section we must sum over the final spin states and average over the initial spin states. Thus, for the reaction given by Eq. (123), instead of  $|V|^2$  in Eq. (24) we must have

$$\frac{1}{(2s_A + 1)(2s_a + 1)} \sum |V|^2$$

where the summation is over all the spin states. Similarly, for the reaction given by Eq. (124) we must have

$$\frac{1}{(2s_B + 1)(2s_b + 1)} \sum |V|^2$$

We next calculate the density of states. The number of states with magnitude of momentum lying between  $p$  and  $p + dp$  is given by [see Eq. (8) of Appendix P]

$$dn = \frac{4\pi p^2 dp V}{(2\pi \hbar)^3} \quad (125)$$

or

$$\frac{dn}{dp} = \frac{V p^2}{2\pi^2 \hbar^3}$$

For the reaction given by Eq. (123)  $p = |\mathbf{p}_B| = |\mathbf{p}_b|$  and if  $E_B$  and  $E_b$  represent the total particle energies then<sup>9</sup>

$$\frac{dE}{dp} = \frac{dE_B}{dp} + \frac{dE_b}{dp} = v_{Bb}$$

where  $v_{Bb}$  is the relative velocity in the final state. Thus the density of states is given by

$$\frac{dn}{dE} = \frac{V p^2}{2\pi^2 \hbar^3 v_{Bb}} \quad (126)$$

Substituting in the expression for the cross-section (Eq. (43)) and using Eq. (126) we get

$$\sigma_{A+a \rightarrow B+b} \propto \frac{|p_B|^2 V}{v_{aA} v_{bB}} \frac{1}{(2s_A + 1)(2s_a + 1)} \sum |V|^2 \quad (127)$$

Similarly

$$\sigma_{B+b \rightarrow A+a} \propto \frac{|p_A|^2 V}{v_{bB} v_{aA}} \frac{1}{(2s_B + 1)(2s_b + 1)} \sum |V|^2 \quad (128)$$

(we are assuming the same center of mass energies). Thus

$$\frac{\sigma_{A+a \rightarrow B+b}}{\sigma_{B+b \rightarrow A+a}} = \frac{|p_B|^2}{|p_A|^2} \frac{(2s_B + 1)(2s_b + 1)}{(2s_A + 1)(2s_a + 1)} \quad (129)$$

where  $|\mathbf{p}_A| (= |\mathbf{p}_a|)$  refers to the reaction given by Eq. (129).

**Solution 25.14** Using the results of the previous problem we get (at any scattering angle  $\theta$ )

$$\sigma_{pp \rightarrow \pi^+ d} = \sigma_{\pi^+ d \rightarrow pp} \frac{3}{4} (2s_\pi + 1) \left( \frac{p_\pi}{p_p} \right)^2 \quad (130)$$

where we have used the facts that  $s_d = 1$  and  $s_p = \frac{1}{2}$ . If we integrate over all angles, we must multiply by a factor of 2 to take into account the indistinguishability of

<sup>9</sup>

$$E^2 = c^2 p^2 + m^2 c^4$$

Therefore

$$E \frac{dE}{dp} = c^2 p$$

or

$$\frac{dE}{dp} = \frac{c^2 p}{E} = \frac{c^2 (m_0 v \gamma)}{(m_0 c^2 \gamma)} = v$$

where

$$\gamma = \left( 1 - \frac{v^2}{c^2} \right)^{-1/2}$$

protons in the final state of the  $\pi^+ d \rightarrow pp$  reaction. Then

$$\sigma_{pp \rightarrow \pi^+ d} = \sigma_{\pi^+ d \rightarrow pp} \frac{3}{2} (2s_\pi + 1) \left( \frac{p_\pi}{p_p} \right)^2 \quad (131)$$

**Solution 25.15** In the experiment of Cartwright et al. the incident proton energy of 340 MeV corresponds to a meson energy of 22.3 MeV in the c.m.s. (see Sec. 24.8). On the other hand in the experiment of Durbin et al. the incident meson energy of 29 MeV corresponds to meson energy of 25 MeV in the c.m.s. Thus both the experiments correspond approximately to the same center of mass energies. Further, since the energies involved are small compared to the rest mass energies we may use the non-relativistic expressions giving

$$\frac{p_\pi}{p_p} = \sqrt{\frac{2m_\pi E_\pi}{2m_p E_p}} \approx 0.20$$

Substituting in Eq. (131) we get

$$(0.18 \pm 0.06) = (3.1 \pm 0.3) \times 1.5 \times 0.04 \times (2s_\pi + 1)$$

giving

$$2s_\pi + 1 \approx 1$$

or the spin of the  $\pi$ -meson is zero. For further details on the spin and parity of elementary particles see Ref. 3.

**Solution 25.16** This problem is really an exercise in the calculation of the density of states. Let  $E$  be the rest energy of the  $K^+$ . We then have the constraints:

$$\begin{aligned} E &= \epsilon_1 + \epsilon_2 + \epsilon_3 \\ 0 &= \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 \end{aligned} \quad (132)$$

Let us assume that  $\mathbf{p}_1$  is held fixed. We now calculate the number of final states with this constraint. (Throughout these calculations we shall use the simple rule that the number of states is  $\frac{1}{(2\pi\hbar)^3} \times \text{phase volume}$ ).

We are interested in the number of states  $dN$  such that the energies of two of the pions are fixed, within infinitesimal intervals, and the remaining parameter varied. If we fix  $\mathbf{p}_1$  and  $\mathbf{p}_2$ , it is clear that energy conservation will automatically fix the magnitude of  $\mathbf{p}_3$  (see Fig. 25.10). Looking at the diagram, we see that this also fixes  $\theta_2$ . Now the number  $dN$  is

$$dN = \frac{p_1^2 dp_1 d\Omega_1}{(2\pi\hbar)^3} \frac{p_2^2 dp_2 d\Omega_2}{(2\pi\hbar)^3} V^2 \quad (133)$$

where  $V$  is the volume of the box in which the event takes place and  $d\Omega_1$  and  $d\Omega_2$  are solid angle intervals within which  $\mathbf{p}_1$  and  $\mathbf{p}_2$  lie. Once we consider  $\mathbf{p}_1, \mathbf{p}_2$  fixed,

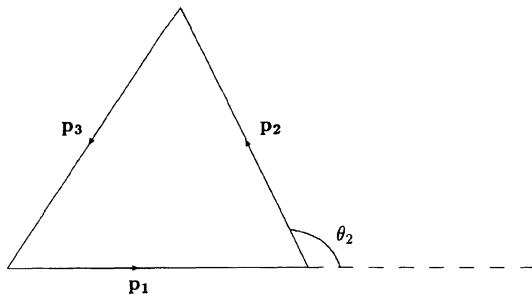


Figure 25.10.

we merely have to count  $dN$  as the number of states within the energy interval  $dE$ , a variation which is related directly to the interval ( $d\Omega_2$ ). To get this relation we use momentum conservation

$$p_1^2 + p_2^2 + 2p_1 p_2 \cos \theta_2 = p_3^2 \quad (134)$$

Since  $p_i^2 + m_i^2 = \epsilon_i^2$  (we have used  $c = 1$ ) we can write Eq. (134) as

$$p_1^2 + p_2^2 + 2p_1 p_2 \cos \theta_2 = \epsilon_3^2 - m_3^2$$

or

$$p_1^2 + p_2^2 + 2p_1 p_2 \cos \theta_2 = (E - \epsilon_1 - \epsilon_2)^2 - m_3^2 \quad (135)$$

Since we keep  $p_1, p_2, \epsilon_1, \epsilon_2$  fixed, we get

$$2p_1 p_2 d(\cos \theta_2) = 2(E - \epsilon_1 - \epsilon_2) dE = 2\epsilon_3 dE$$

or

$$d(\cos \theta_2) = \frac{\epsilon_3 dE}{p_1 p_2} \quad (136)$$

The orientation  $\phi_2$  in  $d\Omega_2$  is irrelevant so we can integrate over it. Moreover, we can now also integrate over  $d\Omega$ , since no further constraint is involved. This gives

$$dN = \frac{4\pi \cdot 2\pi}{(2\pi \hbar)^6} p_1 dp_1 p_2 dp_2 \epsilon_3 dE V^2 \quad (137)$$

Since  $p_i dp_i = \epsilon_i d\epsilon_i$ , we have finally (inserting the factors  $c$  which we had dropped)

$$\rho = \frac{dN}{dE} = \frac{8\pi^2 V^2}{(2\pi \hbar)^6 c^6} \epsilon_1 \epsilon_2 \epsilon_3 d\epsilon_1 d\epsilon_2 \quad (138)$$

The transition probability is, therefore,

$$\Gamma = \frac{2\pi}{\hbar} |M|^2 \rho \sim d\epsilon_1 d\epsilon_2 = dt_1 dt_2 \quad (139)$$

where  $t_1$  and  $t_2$  are kinetic energies of any two pions. The energy distribution of the  $\pi^-$  is obtained by integrating over the energy of the other. But Eq. (139) tells us that there must be an equal number of  $\pi^-$  emitted per unit energy for the entire energy range allowed by energy momentum constraint.

It can be shown that if the pions are emitted in the  $l = 0$  state (low energy) and the interaction of the pions in the final state can be neglected, (which means that they can be represented by plane waves) then the matrix element will have the simple dependence  $M \sim 1/(\epsilon_1 \epsilon_2 \epsilon_3)^{1/2}$  as assumed. This means that any deviation from the prediction Eq. (139), which can be called the “phase space spectrum”, may be attributed to some interaction of the pions in the final state. In the extreme case where two of the pions really are the products of the *decay* of a particle which emerged from the original reaction, there would be a very strong deviation from the phase space spectrum. As an example, we may have

$$\begin{array}{c} \pi^+ + d \rightarrow \omega + p + p \\ \quad \quad \quad \downarrow (\pi^+ + \pi^- + \pi^\circ) \end{array}$$

In a bubble chamber, only the 3 pions are seen but from their energy spectrum one can infer the existence and properties of  $\omega$ . A very short-lived particle such as the  $\omega$  is sometimes referred to as a resonance.

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## 25.8. References and suggested reading

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# Chapter 26

## The Semi-Classical Theory of Radiation and the Einstein Coefficients

*If we have an atom that is in an excited state and so is going to emit a photon, we cannot say when it will emit the photon. It has a certain amplitude to emit the photon at any time, and we can predict only a probability for emission; we cannot predict the future exactly. This has given rise to all kinds of nonsense and questions on the meaning of freedom of will, and of the idea that the world is uncertain..*

— R.P. FEYNMAN in *Feynman Lectures on Physics*, Vol. III,  
p. 1422.

### 26.1. Introduction

In the previous chapter we developed time dependent perturbation theory which we will now use to study the interaction of an atom with electromagnetic field. The theory presented in this chapter is a curious mixture of classical and quantum pictures. Matter, i.e. atoms, are assumed to exist in discrete (quasi-stationary) states. But the electromagnetic radiation with which it interacts, is described classically. This semi-classical theory of atom–field interaction will be discussed in Sec. 26.3 which will enable us to calculate probabilities of absorption and induced emission. It may be mentioned that the semi-classical theory is insufficient to describe the spontaneous emission of radiation because the electromagnetic field is described classically; the fully quantum theory of radiation, which we will discuss in the next chapter, describes the spontaneous emission automatically.

An ingenious idea of Einstein enabled him to obtain a relation which would determine the rate at which spontaneous emissions take place. The idea was based on consideration of matter in equilibrium with radiation assuming that the resultant radiation must obey Planck's law. Einstein introduced coefficients, which are now known as Einstein coefficients, which described induced emission, absorption and spontaneous emission. In Sec. 26.2 we will give the original argument of Einstein (Ref.1) which gave rise to the relation between different coefficients. In Sec. 26.3

we will discuss the atom–field interaction using the semi-classical theory and will derive expressions for stimulated emission rate and stimulated absorption rate. In Sec. 26.4 we will use the Einstein relations to calculate the spontaneous emission rate and hence the lifetime of atomic states. In Sec. 26.5, we will discuss the selection rules governing the transitions.

## 26.2. The Einstein coefficients

Figure 26.1 represents two of the energy levels of an atomic system corresponding

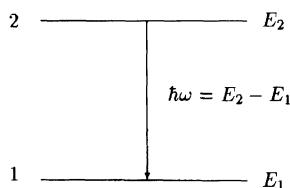


Figure 26.1. The two states of an atomic system. The transition frequency is  $\omega_{21} = (E_2 - E_1)/\hbar$ .

to energies \$E\_1\$ and \$E\_2\$. Let \$N\_1\$ and \$N\_2\$ represent the number of atoms (per unit volume) in levels 1 and 2 respectively. An atom in the lower energy level can absorb radiation and get excited to the level \$E\_2\$. This excitation process can occur only in the presence of radiation. Such a process is known as *stimulated absorption* or simply as absorption. The rate of absorption would depend on the energy density, \$u(\omega)\$, associated with the radiation field corresponding to the frequency

$$\omega = \frac{E_2 - E_1}{\hbar} \quad (1)$$

The energy density \$u(\omega)\$ is defined such that \$u(\omega)d\omega\$ represents the radiation energy per unit volume within the frequency interval \$\omega\$ and \$\omega + d\omega\$. The rate of absorption would be proportional to \$N\_1\$ and also to \$u(\omega)\$. Thus, the number of absorptions per unit time per unit volume can be written as

$$N_1 B_{12} u(\omega) \quad (2)$$

where \$B\_{12}\$ is the coefficient of proportionality and is a characteristic of the energy levels.

On the other hand, when the atom is in an excited state, it can make a transition to a lower energy state through the emission of electromagnetic radiation; however, in contrast to the absorption process, the emission process can occur in two different ways:

- (i) The first is referred to as *spontaneous emission* in which an atom in the excited state emits radiation even in the absence of any incident radiation. It is thus not stimulated by any incident signal but occurs spontaneously. Further, the rate of spontaneous emissions is proportional to the number of atoms in the excited state; thus if we represent the coefficient of proportionality by  $A_{21}$  then

$$N_2 A_{21} \quad (3)$$

would represent the number of spontaneous emissions per unit volume per unit time to the lower energy level.

- (ii) The second is referred to as *stimulated emission* in which an incident signal of appropriate frequency triggers an atom in an excited state to emit radiation. The rate of transition to the lower energy level is directly proportional to the energy density of the radiation at the frequency  $\omega$ . Thus the number of stimulated emissions per unit time per unit volume would be given by

$$N_2 B_{21} u(\omega) \quad (4)$$

The quantities  $A_{21}$ ,  $B_{12}$  and  $B_{21}$  are known as Einstein coefficients and are determined by the atomic system.

At thermal equilibrium, the number of upward transitions must be equal to the number of downward transitions. Thus, we may write

$$N_1 B_{12} u(\omega) = N_2 A_{21} + N_2 B_{21} u(\omega)$$

or

$$u(\omega) = \frac{A_{21}}{\frac{N_1}{N_2} B_{12} - B_{21}} \quad (5)$$

From Boltzmann's law, we have the following expression for the ratio of the populations of two levels at temperature  $T$ :

$$\frac{N_1}{N_2} = \exp \left[ \frac{E_2 - E_1}{k_B T} \right] = \exp \left[ \frac{\hbar\omega}{k_B T} \right] \quad (6)$$

where  $k_B$  represents the Boltzmann constant. Thus, we may write

$$u(\omega) = \frac{A_{21}}{B_{12} \exp(\hbar\omega/k_B T) - B_{21}} \quad (7)$$

Now, according to Planck's law the energy density of radiation (at thermal equilibrium) is given by (see, e.g. Ref 2 and 3):

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\exp(\hbar\omega/k_B T) - 1} \quad (8)$$

Comparing Eqs (7) and (8) we obtain<sup>1</sup>

$$B_{12} = B_{21} = B \text{ (say)} \quad (9)$$

and

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi^2 c^3} \quad (10)$$

Thus, the probabilities of stimulated absorption and stimulated emission are the same and the ratio of the  $A$  and  $B$  coefficients is given by Eq. (10). It is of interest to mention that at thermal equilibrium corresponding to ordinary temperatures ( $T \sim 1000^\circ\text{K}$ ) the spontaneous emission rate for optical sources far exceeds the stimulated emission rate (see Problem 26.1).

### 26.3. The atom–field interaction

In order to calculate the Einstein coefficients we consider an atom in the presence of an oscillating electric field given by<sup>2</sup>

$$\mathcal{E}(t) = \hat{\mathbf{e}}\mathcal{E}_0 \cos \omega t \quad (11)$$

which is switched on at  $t = 0$ ;  $\hat{\mathbf{e}}$  represents the unit vector along the direction of the electric field and the oscillation frequency  $\omega$  is assumed to be close to the resonant frequency  $\omega_{21} [= (E_2 - E_1)/\hbar]$  corresponding to the transition from state 2 to state 1 (see Fig. 26.1). Now, the interaction energy of the electron with the electric field is given by

$$H'(\mathbf{r}, t) = q\mathcal{E} \cdot \mathbf{r} = q\mathcal{E}_0 (\hat{\mathbf{e}} \cdot \mathbf{r}) \cos \omega t \quad (12)$$

<sup>1</sup> If the levels 1 and 2 are  $g_1$ - and  $g_2$ -fold degenerate, then  $N_1/N_2 = (g_1/g_2) \exp(\hbar\omega/k_B T)$ ,  $B_{12} = B_{21} (g_2/g_1)$  and  $A_{21}/B_{21} = \hbar\omega^3/\pi^2 c^3$ .

<sup>2</sup> The electric field associated with an electromagnetic wave will be of the form  $\hat{\mathbf{e}} \cos(\omega t - \mathbf{k} \cdot \mathbf{r})$ ; however, for radiation in the visible region, the wavelength associated ( $\sim 5 \times 10^{-5}$  cm) is much larger than atomic dimensions ( $\sim 10^{-8}$  cm) and we can use the value of  $\mathcal{E}$  at  $\mathbf{r} = 0$ . This is immediately obvious from Eq. (17) where the atomic wave functions are almost zero for  $r \gtrsim 10^{-8}$  cm and since  $k \simeq 10^5 \text{ cm}^{-1}$ , the quantity  $\mathbf{k} \cdot \mathbf{r} \ll 1$  in the domain of integration.

where  $q (> 0)$  represents the magnitude of the electronic charge<sup>3</sup>. Let  $H_0$  represent the Hamiltonian corresponding to the atomic system and let  $\psi_n$  denote the eigenfunctions of  $H_0$  belonging to the energy  $E_n (= \hbar\omega_n)$ :

$$H_0\psi_n = E_n\psi_n = \hbar\omega_n\psi_n \quad (13)$$

Our objective is to solve the equation

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = H\Psi = [H_0 + H'(\mathbf{r},t)]\Psi(\mathbf{r},t) \quad (14)$$

Following the approach developed in Sec. 25.2, we write

$$\Psi(\mathbf{r},t) = \sum_n C_n(t) e^{-i\omega_n t} \psi_n(\mathbf{r}) \quad (15)$$

and obtain [see Eq. (9) of the previous chapter]

$$i\hbar\frac{dC_s}{dt} = \sum_n C_n(t) H'_{sn}(t) e^{i\omega_{sn} t} \quad (16)$$

where

$$\begin{aligned} H'_{sn}(t) &= \int \psi_s^*(\mathbf{r}) H'(\mathbf{r},t) \psi_n(\mathbf{r}) d\tau = \langle s | H' | n \rangle \\ &= \frac{1}{2} q \mathcal{E}_0 \hat{\mathbf{e}} \cdot \langle s | \mathbf{r} | n \rangle [e^{i\omega t} + e^{-i\omega t}] \end{aligned} \quad (17)$$

Substituting for  $H'(\mathbf{r},t)$  from Eq. (12), we get

$$i\hbar\frac{dC_s}{dt} = \frac{1}{2} \mathcal{E}_0 \sum_n D_{sn} C_n(t) [e^{i(\omega_{sn} + \omega)t} + e^{i(\omega_{sn} - \omega)t}] \quad (18)$$

where

$$D_{sn} = \hat{\mathbf{e}} \cdot \mathbf{P}_{sn} \quad (19)$$

and

$$\mathbf{P}_{sn} = q \int \psi_s^*(\mathbf{r}) \mathbf{r} \psi_n(\mathbf{r}) d\tau = q \langle s | \mathbf{r} | n \rangle \quad (20)$$

<sup>3</sup> We are considering here a single electron atom with  $\mathbf{r}$  representing the position vector of the electron with respect to the nucleus. Thus the electric dipole moment of the atom is given by  $\mathbf{p} = -q\mathbf{r}$  because the direction of the dipole moment is from the negative charge to the positive charge. The interaction energy of a dipole placed in an electric field is  $-\mathbf{p} \cdot \mathbf{E}$  which is precisely Eq. (12). It may be mentioned that the interaction term described by Eq. (12) is consistent with the Schrödinger equation for the electron in the dipole approximation (see Sec. 26.4).

is known as the dipole matrix element. We assume that at  $t = 0$  the atom is in the state  $\psi_k$ , i.e.

$$\left. \begin{aligned} C_k(t=0) &= 1 \\ C_n(t=0) &= 0 \text{ for } n \neq k \end{aligned} \right\} \quad (21)$$

Equation (18) represents an infinite set of coupled equations and as a first approximation we replace  $C_n(t)$  by  $C_n(0)$  on the right-hand side of Eq. (18) giving

$$i \hbar \frac{dC_s}{dt} \simeq \frac{1}{2} \mathcal{E}_0 D_{sk} [e^{i(\omega_{sk}+\omega)t} + e^{i(\omega_{sk}-\omega)t}]$$

Integrating, we obtain

$$C_s(t) - C_s(0) = -\frac{i \mathcal{E}_0}{2 \hbar} D_{sk} \left[ \frac{e^{i(\omega_{sk}+\omega)t} - 1}{i(\omega_{sk} + \omega)} + \frac{e^{i(\omega_{sk}-\omega)t} - 1}{i(\omega_{sk} - \omega)} \right]$$

or, for  $s \neq k$

$$\begin{aligned} C_s(t) = & -\frac{i \mathcal{E}_0}{2 \hbar} D_{sk} \left[ e^{i(\omega_{sk}+\omega)t/2} \frac{\sin(\omega_{sk} + \omega)t/2}{(\omega_{sk} + \omega)/2} \right. \\ & \left. + e^{i(\omega_{sk}-\omega)t/2} \frac{\sin(\omega_{sk} - \omega)t/2}{(\omega_{sk} - \omega)/2} \right] \end{aligned} \quad (22)$$

It can be easily seen that for large values of  $t$ , the function

$$\frac{\sin(\omega_{sk} - \omega)t/2}{(\omega_{sk} - \omega)/2} \quad (23)$$

is very sharply peaked around  $\omega \simeq \omega_{sk}$  and negligible everywhere else (see Fig. 26.2). Thus for states for which  $\omega_{sk}$  is significantly different from  $\omega$ ,  $C_s(t)$  would be negligible, and transitions between such states will not be stimulated by the incident field. This implies that in the summation appearing on the right-hand side of Eq. (18) we need only consider those states which correspond closely to the resonance frequency.

In an emission process,  $E_k > E_s$  and hence  $\omega_{sk} (= \frac{E_s - E_k}{\hbar})$  is negative; thus it is the first term on the right-hand side of Eq. (22) which contributes. On the other hand, in an absorption process,  $E_k < E_s$  and hence  $\omega_{sk}$  is positive and consequently it will be the second term on the right-hand side of Eq. (22) which contributes.

Let us consider the emission of radiation and assume that at  $t = 0$  the atom is in state 2 (see Fig. 26.1). We also assume  $\omega$  to be close to  $\omega_{21}$  ( $= [E_2 - E_1]/\hbar$ ). The probability for the transition to state 1 is given by

$$|C_1(t)|^2 = \frac{|D_{12}|^2 \mathcal{E}_0^2}{4 \hbar^2} \left[ \frac{\sin(\frac{-\omega_{21}+\omega}{2})t}{\frac{-\omega_{21}+\omega}{2}} \right]^2 \quad (24)$$

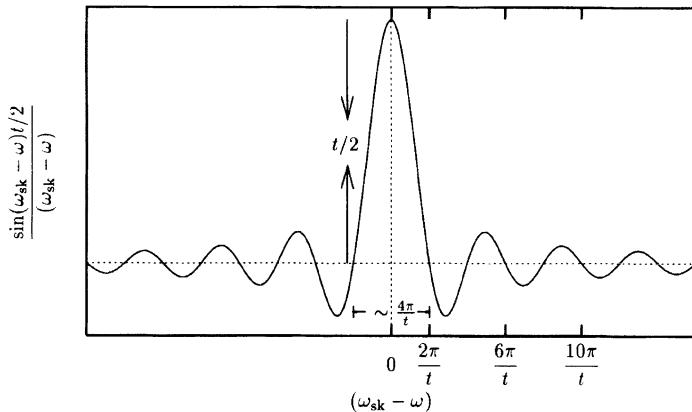


Figure 26.2. For large values of  $t$ , the function given by Eq. (23) is a very sharply peaked function of  $\omega$  about  $\omega = \omega_{sk}$ .

Equation (24) represents the probability for stimulated emission of radiation. In deriving this equation, we have assumed that  $|C_1(t)|^2 \ll 1$ ; thus the result will be valid when either

$$\left(\frac{D_{12}\mathcal{E}_0 t}{\hbar}\right)^2 \ll 1 \quad \text{or} \quad \left(\frac{D_{12}\mathcal{E}_0}{\hbar}\right)^2 / (\omega - \omega_{21})^2 \ll 1 \quad (25)$$

A more accurate result for a two state system will be discussed in Problem 26.8.

Now, the intensity of an electromagnetic wave is related to  $\mathcal{E}$  through the relation (e.g. Ref. 4, Sec. 19.5).

$$I = \frac{1}{2} \epsilon_0 c \mathcal{E}_0^2 \quad (26)$$

where  $\epsilon_0$  is the dielectric permittivity of free space and  $c$  is the speed of light in free space. Thus

$$|C_1(t)|^2 = \frac{1}{2} |D_{12}|^2 \frac{1}{\epsilon_0 c} \left[ \frac{\sin\left(\frac{\omega - \omega_{21}}{2}t\right)}{\frac{\omega - \omega_{21}}{2}} \right]^2 I \quad (27)$$

We apply this formula to the case where there is a continuous spectrum of frequency<sup>4</sup> and there is no correlation between the polarization vectors of different components (as in the case of black body radiation). If  $u(\omega) d\omega$  represents the radiation energy per unit volume in the frequency interval  $\omega$  and  $\omega + d\omega$  then  $I$  should be replaced<sup>5</sup> by  $cu(\omega) d\omega$  and the expression integrated over all frequencies

<sup>4</sup> One could also have an interaction of a near monochromatic wave (as in a laser) with an atom having a broad frequency spectrum. This is discussed in Problem 26.10.

<sup>5</sup> The energy density associated with a monochromatic field is  $I/c$ .

to obtain the following expression for the transition probability

$$\Gamma_{21} = \frac{1}{2\epsilon_0 \hbar^2} \overline{|D_{12}|^2} \int u(\omega) \left[ \frac{\sin(\omega - \omega_{21})t/2}{(\omega - \omega_{21})/2} \right]^2 d\omega \quad (28)$$

where the bar denotes the averaging over different orientations:

$$\begin{aligned} \overline{|D_{12}|^2} &= \overline{q^2 |\langle 1 | \mathbf{r} | 2 \rangle \cdot \hat{\mathbf{e}}|^2} = q^2 |\langle 1 | \mathbf{r} | 2 \rangle|^2 \overline{\cos^2 \theta} \\ &= \frac{q^2}{3} |\langle 1 | \mathbf{r} | 2 \rangle|^2 = \frac{1}{3} |\mathbf{P}_{12}|^2 \end{aligned}$$

because

$$\overline{\cos^2 \theta} = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \cos^2 \theta \sin \theta d\theta d\phi = \frac{1}{3} \quad (29)$$

Assuming that  $u(\omega)$  varies much slowly in comparison to the quantity

$$\left[ \frac{\sin(\omega - \omega_{21})t/2}{(\omega - \omega_{21})/2} \right]^2 \quad (30)$$

we replace  $u(\omega)$  by its value at  $\omega = \omega_{21}$  and take it out of the integral (in Eq. 28) to obtain

$$\Gamma_{21} \simeq \frac{1}{6\epsilon_0 \hbar^2} |\mathbf{P}_{12}|^2 u(\omega_{21}) G \quad (31)$$

where

$$\begin{aligned} G &\simeq \int_{-\infty}^{+\infty} \left[ \frac{\sin(\omega_{21} - \omega)t/2}{(\omega_{21} - \omega)/2} \right]^2 d\omega = 2t \int_{-\infty}^{+\infty} \frac{\sin^2 \xi}{\xi^2} d\xi \\ &= 2\pi t \end{aligned}$$

Thus

$$\Gamma_{21} \simeq \frac{\pi}{3\epsilon_0} \frac{|\mathbf{P}_{12}|^2}{\hbar^2} u(\omega_{21}) t = \beta t \quad (\text{say}) \quad (32)$$

The above expression shows that the probability of transition is proportional to time with  $\beta$  ( $= \frac{\pi}{3\epsilon_0 \hbar^2} |\mathbf{P}_{12}|^2 u(\omega_{21})$ ) representing the proportionality constant. This immediately implies the radioactive decay law, because if there are  $N_2(t)$  atoms (per unit volume) in state 2 at time  $t$  and if  $-dN_2$  represents the number of transitions (per unit volume) in time  $dt$  then according to Eq. (32)

$$-\frac{dN_2}{N_2} = \beta dt \quad (33)$$

the negative sign implying that  $N_2$  will decrease with time. Equation (33) immediately leads to

$$N_2(t) = N_2(0) e^{-\beta t} \quad (34)$$

which is the radioactive decay law with  $1/\beta$  representing the mean lifetime of the state.

It may be noted that Eq. (32) predicts an indefinite increase in the transition probability with time; however, the first-order perturbation theory itself breaks down when  $\Gamma_{21}$  is not appreciably less than unity. Thus, Eq. (32) is valid for times for which

$$\beta t \ll 1 \quad (35)$$

If the lifetime of the state is  $\sim 10^{-9}$  sec, then  $\beta \sim 10^9$  sec $^{-1}$  and we must have

$$t \ll 10^{-9} \text{ sec} \quad (36)$$

However, the large time behaviour<sup>6</sup> is given by Eq. (34).

It should also be noted that in our analysis we have assumed the quantity given by Eq. (30) to be very sharply peaked around  $\omega \approx \omega_{21}$ , for this to happen  $t$  should be large enough so that<sup>7</sup>

$$\frac{1}{t\omega_{21}} \ll 1$$

or

$$t \gg \frac{1}{\omega_{21}} \quad (37)$$

Now in the optical region

$$\omega_{21} \sim 10^{15} \text{ sec}^{-1}$$

then we must have

$$t \gg 10^{-15} \text{ sec}$$

Thus  $t$  in Eq. (32) should satisfy Eq. (37).

Returning to Eq. (32), we get the following expression for the transition probability per unit time (which we denote by  $w_{21}$ ):

$$w_{21} \simeq \frac{\pi}{3\epsilon_0 \hbar^2} |\mathbf{P}_{12}|^2 u(\omega_{21}) \quad (38)$$

If there are  $N_2$  atoms per unit volume in state 2 then the number of stimulated emissions per unit time per unit volume would be given by

$$W_{21} = N_2 w_{21} = N_2 \frac{\pi}{3\epsilon_0 \hbar^2} |\mathbf{P}_{12}|^2 u(\omega_{21}) \quad (39)$$

<sup>6</sup> Equation (32) may, therefore, be interpreted as: If the state has not made a transition upto time  $t$  then the probability that it will make a transition in  $dt$  will be  $\beta dt$  from which Eq. (34) follows.

<sup>7</sup> This follows from the fact that the maximum of (30) occurs at  $\omega = \omega_{21}$  and the first zero at  $\omega = \omega_{21} \pm \frac{\pi}{t}$ .

Comparing the above equation with Eq. (4), we obtain

$$\begin{aligned} B_{21} &= \frac{\pi}{3\epsilon_0} \frac{P^2}{\hbar^2} = \frac{4\pi^2}{3\hbar^2} \left( \frac{q^2}{4\pi\epsilon_0} \right) \left| \int \psi_1^* \mathbf{r} \psi_2 d\mathbf{r} \right|^2 \\ &= \frac{4\pi^2 \alpha c}{3\hbar} |\langle 1 | \mathbf{r} | 2 \rangle|^2 \end{aligned} \quad (40)$$

where

$$\alpha = \frac{q^2}{4\pi\epsilon_0 \hbar c} \simeq \frac{1}{137} \quad (41)$$

represents the fine-structure constant.

The corresponding expression for stimulated absorption is obtained by starting with the first term on the right-hand side of Eq. (22) and proceeding in a similar manner. The final expression is identical to Eq. (40) except for an interchange of indices 1 and 2 and since

$$\left| \int \psi_2^* \mathbf{r} \psi_1 d\mathbf{r} \right|^2 = \left| \int \psi_1^* \mathbf{r} \psi_2 d\mathbf{r} \right|^2 \quad (42)$$

we get

$$B_{12} = B_{21}$$

consistent with Eq. (9).

## 26.4. Spontaneous emission rate

Using Eqs (9), (10) and (40), we get the following expression for the  $A$  coefficient

$$A = \frac{4}{3} \alpha \frac{\omega^3}{c^2} \left| \int \psi_2^* \mathbf{r} \psi_2 d\tau \right|^2 \quad (43)$$

For the  $2P \rightarrow 1S$  transition in the hydrogen atom, i.e. for the transition from any one of the  $(n = 2, l = 1, m = +1, 0, -1)$  states to the  $(n = 1, l = 0, m = 0)$  state, we get (see Problem 26.3)

$$\left| \int \psi_{1S}^* \mathbf{r} \psi_{2P} d\tau \right|^2 = 2^5 \left( \frac{2}{3} \right)^{10} a_0^2 \quad (44)$$

independent of the initial value of  $m$ ; here  $a_0 \left( = \frac{\hbar^2}{me^2} \simeq 0.5 \times 10^{-10} m \right)$  is the Bohr radius. Further, for  $2P \rightarrow 1S$  transition

$$\hbar\omega = \left( -\frac{1}{4} + 1 \right) E_H = \frac{3}{8} \frac{e^2}{a_0}$$

or

$$\omega = \frac{3c}{8a_0}\alpha \quad (45)$$

On substitution in Eq. (43), we get

$$A = \left( \frac{4}{9}\alpha \right)^4 \frac{c}{a_0} \simeq 6 \times 10^8 \text{ sec}^{-1}$$

The coefficient  $A$  gives the probability per unit time for spontaneous emission from state 2 to state 1. Thus if there are  $N_2$  atoms per unit volume in state 2 and if  $-dN_2$  represents the number of atoms undergoing spontaneous transitions in time  $dt$  then

$$dN_2 = -AN_2dt \quad (46)$$

giving once again the radioactive decay law

$$N_2(t) = N_2(0) e^{-At}$$

Thus the mean lifetime of the state is given by

$$\tau = \frac{1}{A} \simeq 1.6 \times 10^{-9} \text{ sec} \quad (47)$$

In Eq. (46),  $dt$  should be small enough so that  $Adt \ll 1$ . Equation (47) tells us that the mean lifetime of the hydrogen atom in the upper level corresponding to the  $2P \rightarrow 1S$  transition is about  $1.6 \times 10^{-9}$  sec. Transitions having such small lifetimes are referred to as strongly allowed transitions<sup>8</sup>. One can similarly calculate lifetimes for other atomic states.

The spontaneous emission rate will give rise to finite widths of the spectral lines which can be estimated from the uncertainty principle

$$\Delta E \sim \frac{\hbar}{\tau} \quad (48)$$

<sup>8</sup> In contrast, levels used in the laser transition are such that the upper level has a very long lifetime ( $\sim 10^{-3}$  to  $10^{-5}$  sec). They are referred to as metastable states. The strength of an atomic transition is usually expressed in terms of the  $f$ -value defined by the equation

$$f = \frac{2m\omega_{21}}{3\hbar} |D_{21}|^2$$

For strongly allowed transitions  $f \sim 1$  and for transitions from metastable states  $f \sim 10^{-3} - 10^{-6}$ .

In practice, the observed widths are much larger because of other factors such as Doppler broadening, collision broadening, etc.

We should also mention here that the  $A$  coefficient for the  $2S \rightarrow 1S$  transition is zero. Such transitions are said to be forbidden transitions.

## 26.5. The selection rules

Whenever the quantity

$$\hat{\mathbf{e}} \cdot \int \psi_f^* \mathbf{r} \psi_i d\tau$$

(also written as  $\hat{\mathbf{e}} \cdot \langle f | \mathbf{r} | i \rangle$ ) vanishes, the transition probability is zero [see Eq. (24)] and the corresponding transition is said to be forbidden (in the dipole approximation)<sup>9</sup>; the subscripts  $i$  and  $f$  refer to initial and final states respectively. If we assume that the electron moves in a central field, then the angular part of the wave function will be of the form  $Y_{lm}(\theta, \phi)$ ; thus, the initial and final states will be given by

$$\left. \begin{aligned} \psi_i &= R_{n_i l_i} Y_{l_i m_i}(\theta, \phi) \\ \psi_f &= R_{n_f l_f} Y_{l_f m_f}(\theta, \phi) \end{aligned} \right\} \quad (49)$$

Now, it can be shown that (see Problem 26.2)

$$\begin{aligned} \int \psi_f^* z \psi_i d\tau &= G \left[ \delta_{l_f, l_i+1} \left( \frac{(l_i + m_i + 1)(l_i - m_i + 1)}{(2l_i + 1)(2l_i + 3)} \right)^{1/2} \right. \\ &\quad \left. + \delta_{l_f, l_i-1} \left( \frac{(l_i + m_i)(l_i - m_i)}{(2l_i + 1)(2l_i + 3)} \right)^{1/2} \right] \delta_{m_f, m_i} \end{aligned} \quad (50)$$

and

$$\begin{aligned} \int \psi_f^* (x \pm iy) \psi_i d\tau &= G \left[ \delta_{l_f, l_i+1} \left( \frac{(l_i + m_i + 1)(l_i + m_i + 2)}{(2l_i + 1)(2l_i + 3)} \right)^{1/2} \right. \\ &\quad \left. \pm \delta_{l_f, l_i-1} \left( \frac{(l_i - m_i)(l_i - m_i - 1)}{(2l_i + 1)(2l_i - 1)} \right)^{1/2} \right] \delta_{m_f, m_i \pm 1} \end{aligned} \quad (51)$$

where

$$G = \int_0^\infty r^3 R_{n_f l_f}(r) R_{n_i l_i}(r) dr \quad (52)$$

---

<sup>9</sup> See Problem 27.1 for higher order transitions.

where  $R_{nl}$  represents the radial part of the wave functions. Equations (50) and (51) tell us that for a transition to occur, we must have

$$\left. \begin{array}{l} \Delta l = l_f - l_i = \pm 1 \\ \Delta m = m_f - m_i = 0 \end{array} \right\} \quad (53)$$

and

$$\left. \begin{array}{l} \Delta l = l_f - l_i = \pm 1 \\ \Delta m = m_f - m_i = \pm 1 \end{array} \right\} \quad (54)$$

which are known as the *selection rules*. Since spin angular momenta are not involved, we have

$$\Delta j = \pm 1 \quad (55)$$

as well.

For the  $\Delta m = 0$  transition, the dipole moment vector

$$\mathbf{P} = q \int \psi_f^* \mathbf{r} \psi_i d\tau \quad (56)$$

is along the  $z$ -direction [because  $P_x = P_y = 0$ —see Eq. (51)].

Now, if we consider an oscillatory dipole in the  $z$ -direction

$$\mathbf{p} = p_0 e^{-i\omega t} \hat{\mathbf{z}}$$

then at large distances from such a dipole, the electric and magnetic fields are of the form (see, e.g. Ref. 5).

$$\mathcal{E} = - \left( \frac{k^2 p_0}{4\pi\epsilon_0} \right) \sin \theta \frac{e^{i(kr - \omega t)}}{r} \hat{\theta} \quad (57)$$

$$\mathcal{H} = - \left( \frac{\omega k p_0}{4\pi} \right) \sin \theta \frac{e^{i(kr - \omega t)}}{r} \hat{\phi} \quad (58)$$

where  $\theta$  represents the polar angle that  $\mathbf{r}$  makes with the  $z$ -axis. Further, the Poynting vector (associated with the emitted radiation field) is given by

$$\mathbf{S} = \frac{\omega k^3 p_0^2}{16\pi^2\epsilon_0} \sin^2 \theta \frac{\cos^2(kr - \omega t)}{r^2} \hat{\mathbf{r}} \quad (59)$$

Thus the electric field associated with the emitted radiation will be linearly polarized with its electric vector oscillating in the plane defined by  $\hat{\mathbf{z}}$  and the direction of the emitted radiation  $\mathbf{k}$  (see Fig. 26.3). Further, the intensity of the radiation will vary as  $\sin^2 \theta$  ( $= |\hat{\mathbf{e}} \cdot \hat{\mathbf{z}}|^2$ ). For  $\theta = \pi/2$  (i.e. for the emitted radiation propagating along any direction which is perpendicular to the  $z$ -axis), the electric field vector will be oscillating in the  $z$ -direction.

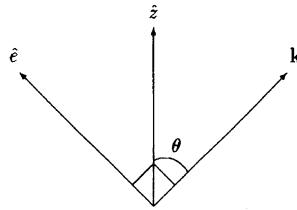


Figure 26.3. The vector  $\mathbf{k}$  represents the direction of propagation of the emitted radiation. The plane of the paper is defined by the vectors  $\mathbf{k}$  and  $\hat{\mathbf{z}}$ . For the  $\Delta m = 0$  transition, the polarization vector of the emitted radiation  $\hat{\mathbf{e}}$  will lie in the  $\mathbf{k} - \hat{\mathbf{z}}$  plane with the intensity of radiation maximum for  $\theta = \pi/2$  and zero for  $\theta = 0$ .

For the

$$m_f = m_i + 1$$

transition

$$P_z = 0 \quad \text{and} \quad P_x - i P_y = 0$$

[see Eqs (50) and (51)]. Thus

$$P_y = -i P_x \quad (60)$$

The above equation implies that the emitted radiation will be superposition of radiation from two dipoles oscillating (with a phase difference of  $\pi/2$ ) in the  $x$ - and  $y$ -directions. Using formulae similar to Eqs (57) and (58) one can easily if  $\mathbf{k}$  is along  $\hat{\mathbf{x}}$  and  $\hat{\mathbf{y}}$ , the emitted radiation is plane polarized along the  $\hat{\mathbf{y}}$ - and  $\hat{\mathbf{x}}$ -directions respectively and if  $\mathbf{k}$  is along  $\hat{\mathbf{z}}$ , the radiation is left circularly polarized. For  $\mathbf{k}$  in any other direction, the polarization is elliptical.

As an example, we consider the  ${}^1D_2 \rightarrow {}^1P_1$  transition (as in the case of the Cd 6438.17 Å line). Since we have neglected spin, we consider only singlet states. If we place the atom in a magnetic field in the  $z$ -direction, the levels will split up as shown in Fig. 26.4 (this is the Zeeman effect). Using the selection rules, we have

Viewed $\perp$ to $\mathbf{B}$ [i.e. $\mathbf{k}$ along $\hat{\mathbf{x}}$ (say)]	$\left\{ \begin{array}{ll} m_f = m_i \text{ (i.e. } \Delta m = 0) & \text{transitions plane} \\ & \text{polarized } \parallel \text{ to } \mathbf{B} \\ & (p\text{-components}) \\ m_f = m_i \pm 1 \text{ (i.e. } \Delta m = \pm 1) & \text{transitions plane} \\ & \text{polarized } \perp \text{ to } \mathbf{B} \\ & (s\text{-components}) \end{array} \right.$
Viewed $\parallel$ to $\mathbf{B}$ [i.e. $\mathbf{k}$ along $\hat{\mathbf{z}}$ (say)]	$\left\{ \begin{array}{ll} m_f = m_i \text{ (i.e. } \Delta m = 0) & \text{transitions not seen} \\ & (p\text{-components}) \\ m_f = m_i \pm 1 \text{ (i.e. } \Delta m = \pm 1) & \text{transitions circularly} \\ & \text{polarized} \\ & (s\text{-components}) \end{array} \right.$

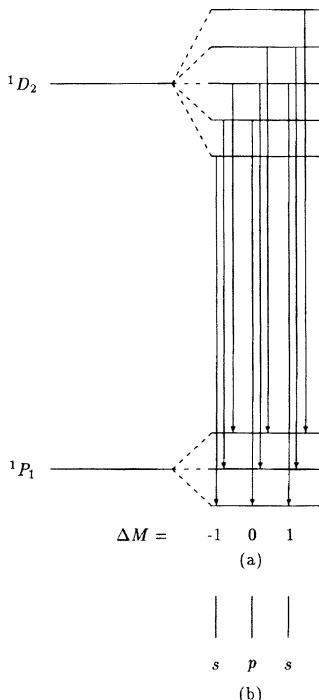


Figure 26.4. (a) The Zeeman pattern for the  $^1D_2 \rightarrow ^1P_1$  transition. (b) If viewed  $\perp$  to  $\mathbf{B}$ , three lines are seen; if light polarized  $\parallel$  to  $\mathbf{B}$  is allowed to reach the film then only the  $p$  components are seen and if light polarized  $\perp$  to  $\mathbf{B}$  is allowed to reach the film then only the  $s$  components are seen.

This is known as the normal Zeeman effect and the lines are known as the Lorentz triplet.

In the presence of spin-orbit interaction of the form  $\xi(r) \mathbf{L} \cdot \mathbf{s}$ , the atomic states are characterized by the quantum numbers  $l, s, j$  and  $m_j$  (see Problem 20.2). The corresponding selection rules are

$$\left. \begin{array}{l} \Delta j = 0, \pm 1 \\ \Delta l = \pm 1 \\ \Delta m_j = 0, \pm 1 \end{array} \right\} \quad (61)$$

However,

$$(m_j)_i = 0 \rightarrow (m_j)_f = 0 \quad \text{transition forbidden if } \Delta j = 0$$

It may be noted that the transition  $\Delta j = 0$  is allowed but  $j_i = j_f = 0$  transition is not allowed. The Zeeman pattern for the  $^2P_{3/2,1/2} \rightarrow ^2S_{1/2}$  transition (as in the case of D lines of Sodium) is shown in Fig. 26.5 (see also Problem 26.7).

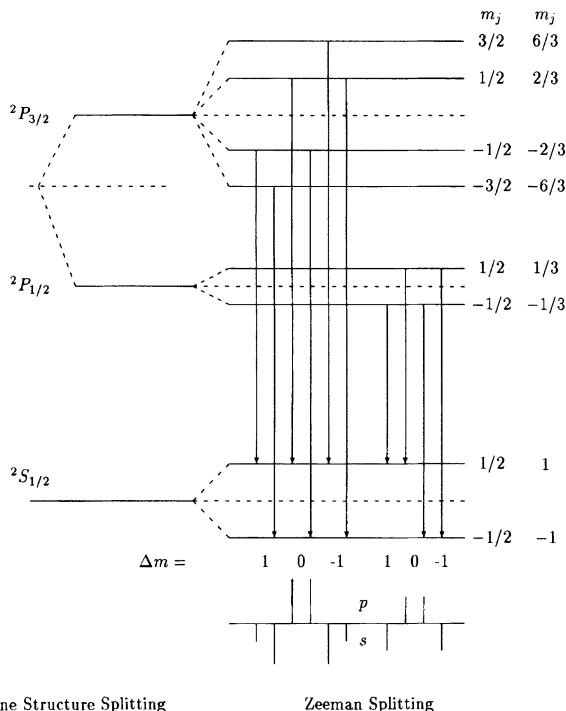


Figure 26.5. The Zeeman pattern for the  $^2P_{3/2,1/2} \rightarrow ^2S_{1/2}$  doublet in sodium. Notice that the Zeeman splitting is different for different levels [the splitting is proportional to  $gm_j$ , see Eq. (66) of Chapter 20]. The lower part of the figure shows that in the transition there are two  $p$  components and four  $s$  components.

## 26.6. Problems

**Problem 26.1** Show that for optical frequencies, at thermal equilibrium (corresponding to  $T \sim 1000^\circ K$ ), the number of spontaneous emissions far exceeds the number of stimulated emissions.

**Problem 26.2** Derive Eqs (50) and (51) and hence the selection rules.

**Problem 26.3** For the  $2P \rightarrow 1S$  transition in hydrogen atom, prove that

$$|\langle 1S | \mathbf{r} | 2P \rangle|^2 = \left| \int \psi_{1S}^* \mathbf{r} \psi_{2P} d\tau \right|^2 = 2^5 \left( \frac{2}{3} \right)^{10} a_0^2$$

independent of the initial value of  $m$ . Using the above result calculate the corresponding lifetime for spontaneous emissions.

**Problem 26.4** Calculate the relative intensities of the two lines corresponding to the transitions  $3P \rightarrow 1S$  and  $2P \rightarrow 1S$  in the hydrogen atom spectrum assuming that equal number of atoms are excited to the  $3P$  and  $2P$  states.

Table 26.1.

Transition	Number of <i>p</i> -components	Number of <i>s</i> -components
$^2D_{5/2} \rightarrow ^2P_{3/2}$	4	8
$^2G_{7/2} \rightarrow ^2F_{5/2}$	6	12
$^3P_2 \rightarrow ^3S_1$	3	6
$^3P_1 \rightarrow ^3S_1$	2	4
$^3P_0 \rightarrow ^3S_1$	1	2

**Problem 26.5** The first line of the Balmer series in hydrogen atom corresponds to the  $n = 3$  to  $n = 2$  transition, this line is known as the  $H_\alpha$  line. What would be the selection rules for the  $n = 3$  to  $n = 2$  transitions and the corresponding lifetimes.

**Problem 26.6** Obtain the angular distribution of the radiation emitted by the  $nP \rightarrow n'S$  transition.

**Problem 26.7** For  $L - S$  coupling the selection rules are

$$\left. \begin{array}{l} \Delta J = 0, \pm 1 \quad (J = 0 \rightarrow J = 0 \text{ transition forbidden}) \\ \Delta L = \pm 1 \\ \Delta S = 0 \\ \Delta M = 0, \pm 1 \quad (M = 0 \rightarrow M = 0 \text{ transition forbidden for } \Delta J = 0) \end{array} \right] \quad (62)$$

Using the above selection rules, show that in the Zeeman splitting of the transitions given in the first column of Table 26.1, the number of *p*- and *s*- components would be as given in the second and third columns.

**Problem 26.8** Assuming that the atom can exist in two possible states characterised by the wave functions  $\psi_1(\mathbf{r})$  and  $\psi_2(\mathbf{r})$  and considering the atom-field interaction to be of the form given by Eq. (12), obtain a solution of the Schrödinger equation in the rotating wave approximation (i.e. neglect terms whose time dependences are of the form  $\exp[\pm i(\omega + \omega_{21})t]$ ).

**Problem 26.9** Using Eqs (100) and (101) of Chapter 19 for  $\psi(n, l, \frac{1}{2}, j, m_j)$  derive the selection rules given by Eq. (61).

**Problem 26.10** In Sec. 26.3 we had considered interaction of an atom with a radiation field having continuous spectrum of frequency. Carry out a similar analysis for a near monochromatic wave interacting with an atom having a broad frequency response.

## 26.7. Solutions

**Solution 26.1** At thermal equilibrium, the ratio of the number of spontaneous to stimulated emissions is given by

$$\frac{A}{Bu(\omega)} = \exp\left(\frac{\hbar\omega}{k_B T}\right) - 1$$

Now

$$\frac{k_B T}{\hbar} \simeq \frac{1.38 \times 10^{-23} (\text{J/s}) \times 10^3 (\text{sec})}{1.054 \times 10^{-34} (\text{J.sec})} \simeq 1.3 \times 10^{14} \text{ sec}^{-1}$$

For the optical region  $\lambda \sim 6000\text{\AA}$  and hence  $\omega \sim 3 \times 10^{14} \text{ sec}^{-1}$ . Thus  $\frac{A}{Bu(\omega)} \gg 1$  and the transitions are mainly due to spontaneous emissions.

**Solution 26.2** The selection rule  $\Delta m = 0, \pm 1$  can be derived easily from the fact that the  $\phi$ -dependence of  $Y_{lm}$  is of the form  $\exp(i m \phi)$  and that

$$z = r \cos \theta, \quad x \pm iy = r \sin \theta e^{\pm i\phi}$$

Since

$$\int_0^{2\pi} e^{i(m'-m)\phi} d\phi = 0 \quad \text{for } m' \neq m$$

the  $\phi$  integration in  $\int \psi_f^* z \psi_i d\tau$  leads to the selection rule  $m_f = m_i$  and the  $\phi$  integration in  $\int \psi_f^*(x \pm iy) \psi_i d\tau$  leads to  $m_f = m_i \pm 1$ .

In order to obtain Eqs (50) and (51), we note that

$$\left. \begin{aligned} z &= r \cos \theta = r \left( \frac{4\pi}{3} \right)^{1/2} Y_{10} \\ x \pm iy &= r \sin \theta e^{\pm i\phi} = \mp r \left( \frac{8\pi}{3} \right)^{1/2} Y_{1,\pm 1} \end{aligned} \right\} \quad (63)$$

Further, if we use the following recurrence relations

$$\left( \frac{8\pi}{3} \right)^{1/2} Y_{1,1} Y_{l,m-1} = \left[ \frac{(l+m)(l+1+m)}{(2l+1)(2l+3)} \right]^{1/2} Y_{l+1,m} - \left[ \frac{(l-m)(l+1-m)}{(2l+1)(2l-1)} \right]^{1/2} Y_{l-1,m} \quad (64)$$

$$\left( \frac{4\pi}{3} \right)^{1/2} Y_{1,0} Y_{l,m} = \left[ \frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)} \right]^{1/2} Y_{l+1,m} - \left[ \frac{(l-m)(l+m)}{(2l+1)(2l-1)} \right]^{1/2} Y_{l-1,m} \quad (65)$$

$$\left(\frac{8\pi}{3}\right)^{1/2} Y_{1,-1} Y_{l,m+1} = \left[ \frac{(l-m)(l+1-m)}{(2l+1)(2l+3)} \right]^{1/2} Y_{l+1,m} - \left[ \frac{(l+m)(l+1+m)}{(2l+1)(2l-1)} \right]^{1/2} Y_{l-1,m} \quad (66)$$

and also the orthonormality condition of spherical harmonics, we immediately get Eqs (50) and (51) from which the selection rules [Eqs (53) and (54)] follow.

**Solution 26.3** We may directly use Eqs (50) and (51); however, in this case, it is possible to calculate the matrix elements without using the recurrence relations [Eqs (64) to (66)]. The eigenfunctions for the  $2P$  and  $1S$  states are

$$\psi_i = \psi_{2P} = R_{21}(r) Y_{1m}(\theta, \phi) \quad (67)$$

and

$$\psi_f = \psi_{1S} = R_{10}(r) Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} R_{10}(r) \quad (68)$$

Substituting for  $R_{21}(r)$  and  $R_{10}(r)$  (see Sec. 10.4) in Eq. (52) and carrying out the integration we get

$$G = 4\sqrt{6} \left(\frac{2}{3}\right)^5 a_0$$

Thus

$$\begin{aligned} z_{fi} &= \int \psi_f^* z \psi_i d\tau = G \iint \frac{1}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}} Y_{10} Y_{1m} \sin \theta d\theta d\phi \\ &= 4\sqrt{2} \left(\frac{2}{3}\right)^5 a_0 \delta_{m,0} \end{aligned} \quad (69)$$

Since

$$Y_{1,-m} = (-1)^m Y_{1,m}^*(\theta, \phi)$$

we have

$$\begin{aligned} (x \pm iy)_{fi} &= G \iint \frac{1}{\sqrt{4\pi}} \left( \pm \sqrt{\frac{8\pi}{3}} Y_{1,\mp 1}^* \right) Y_{1,m} \sin \theta d\theta d\phi \\ &= \pm 8 \left(\frac{2}{3}\right)^5 a_0 \delta_{m,\mp 1} \end{aligned} \quad (70)$$

Thus

$$x_{fi} = 4 \left(\frac{2}{3}\right)^5 a_0 [\delta_{m,-1} - \delta_{m,1}] \quad (71)$$

and

$$y_{fi} = -4i \left(\frac{2}{3}\right)^5 a_0 [\delta_{m,-1} + \delta_{m,1}] \quad (72)$$

It can be easily verified that

$$|\mathbf{r}_{fi}|^2 = |x_{fi}|^2 + |y_{fi}|^2 + |z_{fi}|^2 = 2^5 \left(\frac{2}{3}\right)^{10} a_0^2 \quad (73)$$

for  $m = +1, 0$  and  $-1$  which gives the result as given by Eq. (44). The lifetime calculation is given in Sec. 26.4.

**Solution 26.4** Since the intensity of the emitted line is proportional to the energy emitted per second, the required ratio is given by

$$R = \frac{\hbar\omega_1 A_1}{\hbar\omega_2 A_2} \quad (74)$$

where

$$\begin{aligned} \hbar\omega_1 &= E_{2P} - E_{1S} = \left[-\frac{1}{4} + 1\right] E_H = \frac{3}{4} E_H \\ \hbar\omega_2 &= E_{3P} - E_{1S} = \left[-\frac{1}{9} + 1\right] E_H = \frac{8}{9} E_H \\ A_1 &= A(2P \rightarrow 1S) = \frac{4}{3} \alpha \frac{\omega_1^3}{c^2} \left| \int \psi_{1S}^* \mathbf{r} \psi_{2P} d\tau \right|^2 \end{aligned}$$

and

$$A_2 = A(3P \rightarrow 1S) = \frac{4}{3} \alpha \frac{\omega_2^3}{c^2} \left| \int \psi_{1S}^* \mathbf{r} \psi_{3P} d\tau \right|^2$$

Using the expressions for  $R_{31}(r)$ ,  $R_{21}(r)$  and  $R_{20}(r)$  (given in Sec. 10.4) in Eq. (52) and carrying out the integrations we get

$$G_1 = G(2P \rightarrow 1S) = 4\sqrt{6} \left(\frac{2}{3}\right)^5 a_0 = \frac{256}{81\sqrt{6}} a_0$$

$$G_2 = G(3P \rightarrow 1S) = \frac{1}{4\sqrt{6}} \left(\frac{3}{2}\right)^4 a_0 = \frac{81}{64\sqrt{6}} a_0$$

The angular integrals will be the same for both the transitions and the values will be the same as calculated in the previous solution. Thus

$$R = \left( \frac{\frac{3}{4} E_H}{\frac{8}{9} E_H} \right)^4 \left( \frac{256 \times 64}{81 \times 81} \right)^2 = \frac{256}{81} \simeq 3.16$$

**Solution 26.5** For the  $n = 3$  to  $n = 2$  transition one could have the following possible transitions:  $3S \rightarrow 2P$ ,  $3P \rightarrow 2S$ ,  $3D \rightarrow 2P$ . In order to determine the total transition probability for a given initial state, one must sum over the possible

final states. Thus, for the  $|3, 0, 0\rangle$  state, the final state could be either of the following three states:  $|2, 1, 1\rangle$ ,  $|2, 1, 0\rangle$  and  $|2, 1, -1\rangle$  and the total transition probability (per unit time) would be given by

$$A(3S \rightarrow 2P) = \frac{4}{3} \alpha \frac{\omega^3}{c^2} \sum_{m=1,0,-1} |\langle 2, 1, m | \mathbf{r} | 3, 0, 0 \rangle|^2 \quad (75)$$

where

$$\omega = \frac{E_3 - E_2}{\hbar}$$

Thus, using Eqs (50) and (51)

$$\begin{aligned} A(3S \rightarrow 2P) &= \frac{4}{3} \alpha \frac{\omega^3}{c^2} \left[ |\langle 2, 1, 1 | x | 3, 0, 0 \rangle|^2 + |\langle 2, 1, 1 | y | 3, 0, 0 \rangle|^2 \right. \\ &\quad + |\langle 2, 1, 0 | z | 3, 0, 0 \rangle|^2 \\ &\quad \left. + |\langle 2, 1, -1 | x | 3, 0, 0 \rangle|^2 + |\langle 2, 1, -1 | y | 3, 0, 0 \rangle|^2 \right] \end{aligned} \quad (76)$$

Each of the matrix elements could be calculated easily. For the  $3P \rightarrow 2S$  transition one should consider a particular initial state, say  $|3, 1, 0\rangle$  and calculate the transition probability, which would be

$$\begin{aligned} A(|3, 1, 0\rangle \rightarrow |2, 0, 0\rangle) &= \frac{4}{3} \alpha \frac{\omega^3}{c^2} |\langle 2, 0, 0 | \mathbf{r} | 3, 1, 0 \rangle|^2 \\ &= \frac{4}{3} \alpha \frac{\omega^3}{c^2} |\langle 2, 0, 0 | z | 3, 1, 0 \rangle|^2 \\ &\quad [\text{because } m_f = m_i, \text{ see Eqs (50) and (51)}] \\ &= \frac{4}{9} \alpha \frac{\omega^3}{c^2} |G|^2 \end{aligned} \quad (77)$$

where we have used the relation

$$\iint Y_{00}^* \cos \theta Y_{10} \sin \theta d\theta d\phi = \frac{1}{\sqrt{3}}$$

etc.

**Solution 26.6** Let the direction of propagation of the emitted radiation be denoted by  $\mathbf{k}$  which makes the polar angles  $\Theta, \Phi$  with respect to the  $z$ -axis. Let  $\hat{\mathbf{e}}_1$  represent an unit vector in the  $\mathbf{k}-\hat{\mathbf{z}}$  plane and perpendicular to  $\mathbf{k}$  and let  $\hat{\mathbf{e}}_2$  be the unit vector normal to the  $\mathbf{k}-\hat{\mathbf{z}}$  plane. Thus the Cartesian components of  $\hat{\mathbf{e}}_1$  and  $\hat{\mathbf{e}}_2$  are

$$\begin{aligned} \lambda = 1, \hat{\mathbf{e}}_1 : & -\cos \Theta \cos \Phi \quad -\cos \Theta \sin \Phi \quad \sin \Theta \\ \lambda = 2, \hat{\mathbf{e}}_2 : & \sin \Phi \quad -\cos \Phi \end{aligned}$$

The angular distribution of the emitted radiation is proportional to

$$\left| \int \psi_f^* \hat{\mathbf{e}}_\lambda \cdot \mathbf{r} \psi_i d\tau \right|^2 \sin \Theta d\Theta d\Phi$$

Let us first consider  $\lambda = 1$  for which

$$\begin{aligned} \hat{\mathbf{e}}_\lambda \cdot \mathbf{r} &= r [e_{\lambda x} \sin \theta \cos \phi + e_{\lambda y} \sin \theta \sin \phi + e_{\lambda z} \cos \theta] \\ &= r \left[ \left( \frac{8\pi}{3} \right)^{1/2} \frac{1}{2} (-Y_{1,1} + Y_{1,-1}) (-\cos \Theta \cos \Phi) \right. \\ &\quad + \left( \frac{8\pi}{3} \right)^{1/2} \frac{1}{2i} (-Y_{1,1} - Y_{1,-1}) (-\cos \Theta \sin \Phi) \\ &\quad \left. + \left( \frac{4\pi}{3} \right)^{1/2} Y_{1,0} \sin \Theta \right] \end{aligned}$$

Thus for the  $nP \rightarrow n'S$  transition

$$\begin{aligned} \int \psi_f^* \hat{\mathbf{e}}_1 \cdot \mathbf{r} \psi_i d\tau &= G \iint Y_{00}^* \left( \frac{2\pi}{3} \right)^{1/2} [(Y_{1,1} - Y_{1,-1}) \cos \Theta \cos \Phi \\ &\quad - i(Y_{1,1} + Y_{1,-1}) \cos \Theta \sin \Phi \\ &\quad + \sqrt{2} Y_{1,0} \sin \Theta] Y_{1,m} \sin \theta d\theta d\phi \end{aligned}$$

where  $G$  is given by Eq. (52). Simple integrations give

$$\int \psi_f^* \hat{\mathbf{e}}_1 \cdot \mathbf{r} \psi_i d\tau = \begin{cases} \frac{G}{\sqrt{6}} \cos \Theta e^{i\Phi} & \text{for } m = 1 \\ \frac{G}{\sqrt{3}} \sin \Theta & \text{for } m = 0 \\ -\frac{G}{\sqrt{6}} \cos \Theta e^{-i\Phi} & \text{for } m = -1 \end{cases} \quad (78)$$

Similarly for  $\lambda = 2$

$$\int \psi_f^* \hat{\mathbf{e}}_2 \cdot \mathbf{r} \psi_i d\tau = \begin{cases} \frac{i}{\sqrt{6}} e^{i\Phi} & \text{for } m = 1 \\ 0 & \text{for } m = 0 \\ -\frac{i}{\sqrt{6}} e^{-i\Phi} & \text{for } m = -1 \end{cases} \quad (79)$$

If we write the intensity distribution as

$$I_\lambda d\Omega = I_0 f_\lambda(\Theta, \Phi) \sin \Theta d\Theta d\Phi \quad (80)$$

Table 26.2.

$m$	$\lambda = 1$	$\lambda = 2$
1	$\frac{1}{2} \cos^2 \Theta$	$\frac{1}{2}$
0	$\sin^2 \Theta$	0
-1	$\frac{1}{2} \cos^2 \Theta$	$\frac{1}{2}$

the values of  $f_\lambda$  are given in Table 26.2. Notice that  $\lambda = 2$  case is isotropic.

**Solution 26.8** Assuming that the atom can exist in only two possible states described by the wavefunctions  $\psi_1(\mathbf{r})$  and  $\psi_2(\mathbf{r})$  we get from Eq. (18)

$$i \hbar \frac{dC_1}{dt} = \frac{1}{2} \mathcal{E}_0 D_{12} C_2(t) \left[ e^{-i(\omega' - \omega)t} + e^{-i(\omega' + \omega)t} \right] \quad (81)$$

and

$$i \hbar \frac{dC_2}{dt} = \frac{1}{2} \mathcal{E}_0 D_{21} C_1(t) \left[ e^{i(\omega' + \omega)t} + e^{i(\omega' - \omega)t} \right] \quad (82)$$

where

$$\omega' = \frac{E_2 - E_1}{\hbar} = \omega_{21} = -\omega_{12}$$

and use has been made of the fact that

$$\int \psi_1^* \mathbf{r} \psi_1 d\tau = \int \psi_2^* \mathbf{r} \psi_2 d\tau = 0 \quad (83)$$

and therefore  $D_{11} = D_{22} = 0$ . In the rotating wave approximation<sup>10</sup>, we neglect the terms  $\exp [\pm i (\omega' + \omega) t]$  because of their very rapid oscillations to obtain

$$\frac{dC_1}{dt} = -\frac{i}{2 \hbar} \mathcal{E}_0 D_{12} C_2(t) e^{i(\omega - \omega')t} \quad (84)$$

and

$$\frac{dC_2}{dt} = -\frac{i}{2 \hbar} \mathcal{E}_0 D_{21} C_1(t) e^{-i(\omega - \omega')t} \quad (85)$$

We assume a solution of the type

$$C_1(t) = e^{i\Omega t} \quad (86)$$

<sup>10</sup> Salzman (see Ref. 5) has obtained exact numerical solution of the Schrödinger equation without using the rotating wave approximation. The final result for  $|C_2(t)|^2$  is the same except for the presence of a weak high frequency oscillation superimposed on the solution as shown in Fig. 26.6.

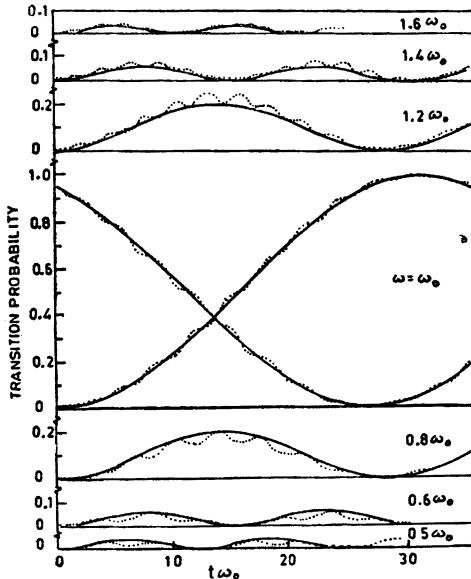


Figure 26.6. Variation of the transition probability for a two level system for different frequencies of the electromagnetic field  $\omega$  as a function of time. The curves correspond to  $\mathcal{D}\mathcal{E}_0/\hbar = 0.1\omega'$ . The solid line corresponds to Eq. (95) and the dotted curve corresponds to an exact numerical computation. Notice the presence of a weak high frequency oscillation present in the exact calculation which is due to the presence of the  $\exp[\pm i(\omega + \omega')t]$  terms in Eqs (81) and (82). The graph for  $\omega = \omega_0$  has been cut at  $t\omega_0 = 36$  and shifted to the origin. [After Ref. 5].

then from Eq. (84)

$$C_2(t) = -\frac{2\hbar\Omega}{\epsilon_0 D_{12}} e^{i(\Omega-\omega+\omega')t} \quad (87)$$

Substituting Eq. (86) and Eq. (87) in Eq. (85) we get

$$\Omega^2 + (\omega' - \omega)\Omega - \frac{1}{4}\Omega_0^2 = 0 \quad (88)$$

where

$$\Omega_0^2 = \frac{D_{12}D_{21}\epsilon_0^2}{\hbar^2} = \frac{D^2\epsilon_0^2}{\hbar^2} \quad (89)$$

and

$$D = D_{12} = D_{21} \quad (90)$$

Equation (88) gives

$$\Omega_{1,2} = \frac{1}{2} \left[ -(\omega' - \omega) \pm \left\{ (\omega' - \omega)^2 + \Omega_0^2 \right\}^{1/2} \right] \quad (91)$$

Thus the general solutions of Eqs (84) and (85) will be

$$C_1(t) = A_1 e^{i\Omega_1 t} + A_2 e^{i\Omega_2 t} \quad (92)$$

and

$$C_2(t) = -\frac{2}{\Omega_0} e^{i(\omega' - \omega)t} [A_1 \Omega_1 e^{i\Omega_1 t} + A_2 \Omega_2 e^{i\Omega_2 t}] \quad (93)$$

$A_1$  and  $A_2$  can be determined from initial conditions. For example, if the atom is initially in the ground state then

$$C_1(0) = 1, \quad C_2(0) = 0 \quad (94)$$

which gives

$$|C_2(t)|^2 = \left[ \frac{\sin(\Omega' t/2)}{\Omega'/2} \right]^2 \left( \frac{\Omega_0}{2} \right)^2 \quad (95)$$

where

$$\Omega' = \left[ (\omega' - \omega)^2 + \Omega_0^2 \right]^{1/2} \quad (96)$$

Equation (95) gives the transition probability for absorption which has been shown in Fig. 26.6.

Now, at resonance,  $\omega = \omega'$  and

$$|C_2(t)|^2 = \sin^2 \frac{\Omega_0 t}{2} \quad (97)$$

which shows that the system flip-flops between states 1 and 2.

**Solution 26.10** We consider a nearly monochromatic field (which is indeed true for a laser) interacting with atoms characterised by the line shape function  $g(\omega)$ . Thus  $N_1 g(\omega) d\omega$  and  $N_2 g(\omega) d\omega$  represent the number of atoms per unit volume in levels 1 and 2 respectively which are capable of interacting with radiation of frequency between  $\omega$  and  $\omega + d\omega$ . Obviously<sup>11</sup>,

$$\int g(\omega) d\omega = 1 \quad (98)$$

Now, for a near monochromatic field, the energy (per unit volume) associated with the field (at frequency  $\omega$ ) is given by

$$u_\omega = \frac{1}{2} \epsilon_0 E_0^2 \quad (99)$$

Thus, for such a case the probability for stimulated emission is given by

$$\begin{aligned} \Gamma_{21} &= \frac{1}{4} |D_{12}|^2 \frac{\epsilon_0^2}{\hbar^2} \int g(\omega') \left[ \frac{\sin \frac{\omega' - \omega}{2} t}{\frac{\omega' - \omega}{2}} \right]^2 d\omega' \\ &\simeq \frac{1}{4} \frac{|D_{12}|^2}{\hbar^2} \epsilon_0^2 g(\omega) 2\pi t \\ &\simeq \frac{\pi P^2}{3 \hbar^2 \epsilon_0} g(\omega) u_\omega t \end{aligned} \quad (100)$$

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<sup>11</sup> Different types of line shape functions have been discussed in Ref. 3—see also Problem 27.3.

where in the last step we have replaced  $|D_{12}|^2$  by its average value. Since

$$B_{21} = \frac{\pi}{3\epsilon_0} \frac{P^2}{\hbar^2} = \frac{\pi^2 c^3}{\hbar \omega^3} A = \frac{\pi^2 c^3}{\hbar \omega^2 \tau} \quad (101)$$

(where  $\tau$  is the spontaneous emission lifetime), we obtain the following expression for the number of stimulated emissions per unit time per unit volume

$$N_1 \frac{\pi^2 c^3}{\hbar \omega^2 \tau} u_\omega g(\omega) \quad (102)$$


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## 26.8. References and suggested reading

1. A. Einstein, *On the Quantum Theory of Radiation*, Physikalische Zeitschrift **18**, 121 (1917); this paper has been reprinted in the book by D. Ter Haar, *The Old Quantum Theory*, Pergamon Press, Oxford (1967).
2. R. Loudon, *The Quantum Theory of Light*, Clarendon Press, Oxford (1973).
3. K. Thyagarajan and A.K. Ghatak, *Lasers: Theory and Applications*, Plenum Press, New York (1981).
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5. W.R. Salzman, *Time evolution of simple quantum mechanical systems:II. Two state system in intense fields*, Phys. Rev. Lett. **26**, 220 (1971).
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## Chapter 27

# The Quantum Theory of Radiation and its Interaction with Matter

*Quantum mechanics is very impressive. But an inner voice tells me that it is not yet the real thing. The theory produces a good deal but hardly brings us closer to the secret of the Old One. I am at all events convinced that He does not play dice.*

— ALBERT EINSTEIN in a letter to Max Born 4 December 1926.

*Neils Bohr's response is somewhat less well known<sup>1</sup>: But still, it cannot be for us to tell God, how he is to run the world.*

### 27.1. Introduction

In the previous chapter we developed the semi-classical theory of interaction of radiation with matter in which matter, i.e. atoms, were assumed to exist in discrete (quasi-stationary states) but the electromagnetic field with which it interacts was described classically. In this chapter we will develop the fully quantum theory of radiation and discuss its interaction with matter.

We will first consider the Hamiltonian of an atomic system in a radiation field (Sec. 27.2). We will next show that the electromagnetic field in a closed cavity can be considered as an infinite set of oscillators, each corresponding to a particular value of the wave vector and particular direction of polarization. By imposing the commutation relations between the canonical variables, it will be shown that the energy of each oscillator can increase or decrease by integral multiples of certain quantum of energy; this quantum of energy is known as the *photon*. In Sec. 27.4 we will use the quantum mechanical description of the radiation field to study its interaction with an atom and thereby obtain explicit expressions for the Einstein *A* and *B* coefficients which will be shown to be identical to the results obtained in the previous chapter. It may be mentioned that the theory developed in Sec. 27.4 automatically leads to spontaneous emissions which in the semi-classical theory

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<sup>1</sup> The authors found this quotation in Jim Baggott's book on *The Meaning of Quantum Theory*, Oxford University Press, Oxford (1992).

had to be introduced in an ad hoc manner through the Einstein coefficients (see Sec. 26.4). In Sec. 27.5 we will discuss the properties of the eigenstates of the Hamiltonian of the radiation field and will show that the state which corresponds to a given number of photons for a particular mode does *not* correspond to the classical plane wave. Indeed, in Sec. 27.6, we will show that the eigenstates of the annihilation operator (which are known as the *coherent states*) resemble the classical plane wave for large intensities. In fact when a laser is operated much beyond the threshold, it generates a coherent state excitation of a cavity mode. Finally, in Sec. 27.7, we will show that it is difficult to give a quantum mechanical description of the phase of the electromagnetic wave.

## 27.2. The Hamiltonian

The Hamiltonian of an atomic system in a radiation field can be written as

$$\begin{aligned} H &= H_0 + H' \\ &= H_a + H_r + H' \end{aligned} \quad (1)$$

where  $H_a$  represents the Hamiltonian of the atom,  $H_r$  the Hamiltonian corresponding to the pure radiation field, which is given by

$$H_r = \frac{1}{2} \int (\epsilon_0 \mathcal{E} \cdot \mathcal{E} + \mu_0 \mathcal{H} \cdot \mathcal{H}) d\tau \quad (2)$$

and  $H'$  represents the interaction between the atom and the radiation field. In Eq. (2)  $\epsilon_0$  and  $\mu_0$  represent the dielectric permittivity and magnetic permeability of free space,  $\mathcal{E}$  and  $\mathcal{H}$  represent the electric and magnetic fields associated with the radiation field. For example, for a non-relativistic electron (of charge  $-q$ ) in a radiation field, we have

$$H = \frac{1}{2m} (\mathbf{p} + q\mathbf{A})^2 + V + H_r \quad (3)$$

since the recipe is to replace the electron momentum operator  $\mathbf{p}$  by  $\mathbf{p}+q\mathbf{A}$  (see Sec. 20.2), where  $\mathbf{A}$  is the vector potential and  $V$  is the potential energy of the electron. We can rewrite Eq. (3) as

$$H = H_0 + H' \quad (4)$$

where

$$\left. \begin{aligned} H_0 &= H_a + H_r \\ H_a &= \frac{p^2}{2m} + V(r) \\ H' &= \frac{q}{2m} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) + \frac{q^2}{2m} A^2 \end{aligned} \right\} \quad (5)$$

and  $H_r$  is given by Eq. (2). In Sec. 27.4 we will treat  $H'$  as a perturbation and study the transitions between eigenstates of  $H_0$ . The term  $\frac{q^2}{2m} A^2$  appearing in the expression for  $H'$  usually represents a very small perturbation and hence will be neglected. Thus the interaction term is given by

$$H' = +\frac{q}{m} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) \quad (6)$$

Now

$$\begin{aligned} \mathbf{p} \cdot \mathbf{A} \Psi &= -i \hbar \nabla \cdot (\mathbf{A} \Psi) \\ &= -i \hbar [(\nabla \cdot \mathbf{A}) \Psi + \mathbf{A} \cdot \nabla \Psi] \\ &= \mathbf{A} \cdot \mathbf{p} \Psi \end{aligned}$$

where we have chosen the Coulomb gauge in which  $\nabla \cdot \mathbf{A} = 0$  (see Sec. 20.3). Thus

$$H' = \frac{q}{m} \mathbf{A} \cdot \mathbf{p} = \frac{q}{m} \mathbf{p} \cdot \mathbf{A} \quad (7)$$

There are now two ways of proceeding further. The first is to treat the electromagnetic field classically; this has indeed been done in the previous chapter. The second and more powerful method is to quantize the radiation field and calculate rates of transition between states of matter and quanta; this will be done in Sections 27.3 and 27.4. However, before we do so, we will first show (in Sec. 27.2.1) that the interaction term given by Eq. (12) of the previous chapter is consistent with Eq. (7) under certain approximation which is known as the dipole approximation.

### 27.2.1. THE INTERACTION TERM IN THE SEMI-CLASSICAL THEORY OF RADIATION

For a plane electromagnetic wave, the vector potential can be written in the form

$$\mathbf{A} = \hat{\mathbf{e}} A_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad (8)$$

where  $\hat{\mathbf{e}}$  represents the unit vector along  $\mathbf{A}$  (denoting the polarization of the wave), and

$$\mathbf{k} = \frac{\omega}{c} \hat{\mathbf{k}} \quad (9)$$

where  $\hat{\mathbf{k}}$  represents the unit vector along the direction of propagation. The condition  $\nabla \cdot \mathbf{A} = 0$  gives

$$\hat{\mathbf{e}} \cdot \mathbf{k} = 0 \quad (10)$$

implying that  $\hat{\mathbf{e}}$  is at right angles to the direction of propagation, i.e. the wave is transverse. The electric field is given by

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} = -\hat{\mathbf{e}} \mathcal{E}_0 \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad (11)$$

where

$$\mathcal{E}_0 = \omega A_0 \quad (12)$$

Now

$$\begin{aligned} H' &= \frac{q}{m} \mathbf{A} \cdot \mathbf{p} \\ &= \frac{q \mathcal{E}_0}{2m\omega} \hat{\mathbf{e}} [e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}] \cdot \mathbf{p} \end{aligned}$$

The matrix element of transition is given by (cf. Eq. 17 of the previous chapter):

$$\begin{aligned} H'_{sn} = \langle s | H' | n \rangle &= \frac{q \mathcal{E}_0}{2m\omega} \hat{\mathbf{e}} \cdot [\langle s | e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{p} | n \rangle e^{-i\omega t} \\ &\quad + \langle s | e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{p} | n \rangle e^{-i\omega t}] \end{aligned} \quad (13)$$

where the kets  $|n\rangle$  and  $|s\rangle$  are eigenstates of the atomic Hamiltonian  $H_a$  and represent the initial and final states. Now

$$e^{\pm i\mathbf{k} \cdot \mathbf{r}} = 1 \pm i\mathbf{k} \cdot \mathbf{r} - \frac{1}{2!} (\mathbf{k} \cdot \mathbf{r})^2 + \dots$$

Since atomic dimensions are  $\sim 10^{-8}$  cm and for optical wavelength

$$k \left( = \frac{2\pi}{\lambda} \right) \sim 10^5 \text{ cm}^{-1}$$

we obtain (in the region of integration)  $kr \ll 1$ . Thus, negligible error will be involved if the exponential is replaced by unity<sup>2</sup> and the transition is said to be an electric dipole transition – a very important case. In this approximation

$$\langle s | e^{\pm i\mathbf{k} \cdot \mathbf{r}} \mathbf{p} | n \rangle \simeq \langle s | \mathbf{p} | n \rangle \quad (14)$$

---

<sup>2</sup> However, if the replacement of  $e^{\pm i\mathbf{k} \cdot \mathbf{r}}$  by unity leads to a vanishing matrix element, one must use higher order terms like  $(\pm i\mathbf{k} \cdot \mathbf{r})^2$ , etc.; these are said to correspond to higher order transitions (see Problem 27.1)

Now the kets  $|n\rangle$  and  $|s\rangle$  are eigenkets<sup>3</sup> of the atomic Hamiltonian  $H_a$ :

$$H_a |n\rangle = E_n |n\rangle = \hbar\omega_n |n\rangle \quad (15)$$

$$H_a |s\rangle = E_s |s\rangle = \hbar\omega_s |s\rangle \quad (16)$$

Further

$$H_a = \frac{p^2}{2m} + V(\mathbf{r})$$

Thus

$$\begin{aligned} [x, H_a] &= \left[ x, \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\mathbf{r}) \right] \\ &= \frac{1}{2m} ([x, p_x] p_x + p_x [x, p_x]) \\ &= \frac{i\hbar}{m} p_x \end{aligned} \quad (17)$$

or,

$$\mathbf{p} = \frac{m}{i\hbar} [\mathbf{r}, H_a] \quad (18)$$

Hence

$$\begin{aligned} \langle s | \mathbf{p} | n \rangle &= \frac{m}{i\hbar} \langle s | \mathbf{r} H_a - H_a \mathbf{r} | n \rangle \\ &= \frac{m}{i\hbar} (E_n - E_s) \langle s | \mathbf{r} | n \rangle \\ &= \frac{m\omega_{ns}}{i} \langle s | \mathbf{r} | n \rangle \end{aligned} \quad (19)$$

where we have used Eq. (15) and conjugate of Eq. (16) and

$$\hbar\omega_{ns} = E_n - E_s$$

On substitution in Eq. (13), we get

$$\langle s | H' | n \rangle = \frac{q\mathcal{E}_0\omega_{ns}}{2\omega} \hat{\mathbf{e}} \cdot \langle s | \mathbf{r} | n \rangle [e^{i\omega t} - e^{-i\omega t}] \quad (20)$$

The above equation is of a form similar (although not identical) to that of Eq. (17) of the previous chapter. However, for  $\omega \approx |\omega_{ns}|$  after one carries out the integration which leads to Eq. (22) of the previous chapter, one obtains identical expressions for probabilities of absorption and of emission [see Eq. (24) of the previous chapter].

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<sup>3</sup> We may warn the reader of some confusion of notation. The initial and final states of the atomic Hamiltonian are also sometimes denoted by  $|i\rangle$  and  $|f\rangle$  and sometimes by  $|a\rangle$  and  $|b\rangle$ .

### 27.3. Quantization of the radiation field

We now develop the second method mentioned in Sec. 27.1. In this method, the electromagnetic field is described in terms of numbers of photons in various states.

We consider first a pure radiation field. In Coulomb gauge, such a field can be derived from the vector potential  $\mathbf{A}$  only, with  $\Phi = 0$  and

$$\nabla \cdot \mathbf{A} = 0 \quad (21)$$

In this gauge, the magnetic and electric fields are given by (see Sec. 20.2)

$$\mathcal{B} = \mu_0 \mathcal{H} = \nabla \times \mathbf{A} \quad (22)$$

and

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} \quad (23)$$

where we have assumed  $\Phi = 0$  since we are considering free space. Substituting for  $\mathcal{H}$  and  $\mathcal{E}$  in the Maxwell equation

$$\nabla \times \mathcal{H} = \frac{\partial \mathbf{D}}{\partial t} = \epsilon_0 \frac{\partial \mathcal{E}}{\partial t} \quad (24)$$

we get

$$\nabla \times (\nabla \times \mathbf{A}) = -\epsilon_0 \mu_0 \frac{\partial^2 \mathbf{A}}{\partial t^2} \quad (25)$$

If we now use the identity<sup>4</sup>

$$\nabla \times (\nabla \times \mathbf{A}) \equiv \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A} = -\nabla^2 \mathbf{A} \quad (26)$$

(because  $\nabla \cdot \mathbf{A} = 0$ ), we finally obtain

$$\nabla^2 \mathbf{A} = \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} \quad (27)$$

where

$$c = (\epsilon_0 \mu_0)^{-1/2} \quad (28)$$

---

<sup>4</sup> It may be worthwhile to point out that the operator  $\nabla^2$  is *defined* by the following equation

$$\nabla^2 \mathbf{A} \equiv \nabla (\nabla \cdot \mathbf{A}) - \nabla \times (\nabla \times \mathbf{A})$$

However,

$$(\nabla^2 \mathbf{A})_x = \nabla \cdot (\nabla A_x)$$

i.e. a Cartesian component of  $\nabla^2 \mathbf{A}$  is div grad of the Cartesian component but

$$(\nabla^2 \mathbf{A})_r \neq \nabla \cdot (\nabla A_r)$$

represents the speed of light in free space. Equation (27) represents the three-dimensional wave equation. In order to solve the wave equation, we use the method of separation of variables:

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}) q(t) \quad (29)$$

Thus

$$q(t) \nabla^2 \mathbf{A}(\mathbf{r}) = \mathbf{A}(\mathbf{r}) \frac{1}{c^2} \frac{d^2 q}{dt^2} \quad (30)$$

We next consider a Cartesian component (say the  $x$ -component) of  $\mathbf{A}(\mathbf{r})$  which we denote by  $A_x(\mathbf{r})$ ; thus

$$\frac{c^2}{A_x(\mathbf{r})} \nabla^2 A_x(\mathbf{r}) = \frac{1}{q(t)} \frac{d^2 q}{dt^2} = -\omega^2 \text{ (say)} \quad (31)$$

Thus

$$q(t) \sim e^{-i\omega t} \quad (32)$$

and

$$\nabla^2 A_x(\mathbf{r}) + k^2 A_x(\mathbf{r}) = 0 \quad (33)$$

where  $k^2 = \omega^2/c^2$ . The solutions of Eq. (33) are plane waves; and similarly if we consider the  $y$ - and  $z$ -components we obtain

$$\mathbf{A}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \hat{\mathbf{e}} \quad (34)$$

where  $\mathbf{k} \cdot \mathbf{k} = k^2$ ,  $\hat{\mathbf{e}}$  is the unit vector along  $\mathbf{A}$ . The condition  $\nabla \cdot \mathbf{A} = 0$  gives us  $\mathbf{k} \cdot \hat{\mathbf{e}} = 0$ , implying the transverse character of the wave [see Eq. (10)].

The allowed values of  $\mathbf{k}$  (and hence of  $\omega$ ) are determined from the boundary conditions. If we assume the radiation to be confined in a cubical cavity of volume  $V (= L^3)$  and use the periodic boundary condition then

$$\mathbf{A}(x = 0, y, z) = \mathbf{A}(x = L, y, z) \quad \text{etc.} \quad (35)$$

giving

$$e^{ik_x L} = 1 = e^{ik_y L} = e^{ik_z L} \quad (36)$$

Thus

$$\left. \begin{aligned} k_x &= \frac{2\pi v_x}{L} \\ k_y &= \frac{2\pi v_y}{L} \\ k_z &= \frac{2\pi v_z}{L} \end{aligned} \right\} v_x, v_y, v_z = 0, \pm 1, \pm 2, \dots \quad (37)$$

The complete solution of Eq. (27) is therefore given by

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\lambda} [q_{\lambda}(t) \mathbf{A}_{\lambda}(\mathbf{r}) + q_{\lambda}^*(t) \mathbf{A}_{\lambda}^*(\mathbf{r})] \quad (38)$$

where

$$\mathbf{A}_\lambda(\mathbf{r}) = e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} \hat{\mathbf{e}}_\lambda \quad (39)$$

$$q_\lambda(t) = |q_\lambda| e^{-i\omega_\lambda t} \quad (40)$$

and the subscript  $\lambda$  signifies the various modes of the field [see Eq. (37)] including the two states of polarization. Thus, a particular value of  $\lambda$  corresponds to a particular set of values of  $v_x, v_y, v_z$  and a particular direction of  $\hat{\mathbf{e}}$ . In Eq. (38) the second term on the RHS is complex conjugate of the first term making  $\mathbf{A}$  necessarily real. Because of the allowed values of  $\mathbf{k}_\lambda$  [see Eq. (37)], we readily obtain

$$\iiint_V \mathbf{A}_\lambda \cdot \mathbf{A}_\mu^* d\tau = \iiint_V \mathbf{A}_\lambda \cdot \mathbf{A}_{-\mu} d\tau = V \delta_{\lambda,\mu} \quad (41)$$

where the integration is over the entire volume of the cavity. Using Eq. (38), we obtain the following expressions for the electric and magnetic fields:

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} = \sum_\lambda \mathcal{E}_\lambda \quad (42)$$

$$\mathcal{H} = \frac{1}{\mu_0} \nabla \times \mathbf{A} = \sum_\lambda \mathcal{H}_\lambda \quad (43)$$

where

$$\mathcal{E}_\lambda = i\omega_\lambda [q_\lambda(t) \mathbf{A}_\lambda(\mathbf{r}) - q_\lambda^*(t) \mathbf{A}_\lambda^*(\mathbf{r})] \quad (44)$$

and

$$\mathcal{H}_\lambda = \frac{i}{\mu_0} \mathbf{k}_\lambda \times [q_\lambda \mathbf{A}_\lambda - q_\lambda^* \mathbf{A}_\lambda^*] \quad (45)$$

The total energy of the radiation field is given by

$$H_r = \frac{1}{2} \int (\epsilon_0 \mathcal{E} \cdot \mathcal{E} + \mu_0 \mathcal{H} \cdot \mathcal{H}) d\tau \quad (46)$$

Now

$$\begin{aligned}
 \frac{1}{2}\epsilon_0 \int_v \mathcal{E} \cdot \mathcal{E} d\tau &= -\frac{1}{2}\epsilon_0 \sum_{\lambda} \sum_{\mu} \omega_{\lambda} \omega_{\mu} \left[ q_{\lambda} q_{\mu} \int \mathbf{A}_{\lambda} \cdot \mathbf{A}_{\mu} d\tau \right. \\
 &\quad - q_{\lambda} q_{\mu}^* \int \mathbf{A}_{\lambda} \cdot \mathbf{A}_{\mu}^* d\tau - q_{\lambda}^* q_{\mu} \int \mathbf{A}_{\lambda}^* \cdot \mathbf{A}_{\mu} d\tau \\
 &\quad \left. + q_{\lambda}^* q_{\mu}^* \int \mathbf{A}_{\lambda}^* \cdot \mathbf{A}_{\mu}^* d\tau \right] \\
 &= -\frac{1}{2}\epsilon_0 V \sum_{\lambda} \sum_{\mu} \omega_{\lambda} \omega_{\mu} [q_{\lambda} q_{\mu} \delta_{\lambda, -\mu} \\
 &\quad - q_{\lambda} q_{\mu}^* \delta_{\lambda, \mu} - q_{\lambda}^* q_{\mu} \delta_{\lambda, \mu} + q_{\lambda}^* q_{\mu}^* \delta_{\lambda, -\mu}] \\
 &= -\frac{1}{2}\epsilon_0 V \sum_{\lambda} \omega_{\lambda}^2 [q_{\lambda} q_{-\lambda} + q_{\lambda}^* q_{-\lambda}^* - 2q_{\lambda} q_{\lambda}^*]
 \end{aligned} \tag{47}$$

Similarly one can evaluate  $\int \mathcal{H} \cdot \mathcal{H} d\tau$ . The final result is

$$\frac{1}{2}\mu_0 \int \mathcal{H} \cdot \mathcal{H} d\tau = \frac{1}{2}\epsilon_0 V \sum_{\lambda} \omega_{\lambda}^2 [q_{\lambda} q_{-\lambda} + q_{\lambda}^* q_{-\lambda}^* + 2q_{\lambda} q_{\lambda}^*] \tag{48}$$

where use has to be made of the vector identity

$$(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d}) = (\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d}) - (\mathbf{b} \cdot \mathbf{c})(\mathbf{a} \cdot \mathbf{d}) \tag{49}$$

and the relation

$$k_{\lambda}^2 = \frac{\omega_{\lambda}^2}{c^2} = \epsilon_0 \mu_0 \omega_{\lambda}^2 \tag{50}$$

Thus

$$H_r = 2\epsilon_0 V \sum_{\lambda} \omega_{\lambda}^2 q_{\lambda}(t) q_{\lambda}^*(t) \tag{51}$$

We next introduce the dimensionless variables  $Q_{\lambda}$  and  $P_{\lambda}$  defined through the equations

$$Q_{\lambda}(t) = (\epsilon_0 V)^{1/2} (q_{\lambda}(t) + q_{\lambda}^*(t)) \tag{52}$$

and

$$P_{\lambda}(t) = \frac{1}{i} (\epsilon_0 V \omega_{\lambda}^2)^{1/2} (q_{\lambda}(t) - q_{\lambda}^*(t)) \tag{53}$$

Thus

$$q_{\lambda}(t) = (4\epsilon_0 V \omega_{\lambda}^2)^{-1/2} (\omega_{\lambda} Q_{\lambda}(t) + i P_{\lambda}(t)) \tag{54}$$

$$q_{\lambda}^*(t) = (4\epsilon_0 V \omega_{\lambda}^2)^{-1/2} (\omega_{\lambda} Q_{\lambda}(t) - i P_{\lambda}(t)) \tag{55}$$

and

$$H_r = \sum_{\lambda} H_{\lambda} \quad (56)$$

where<sup>5</sup>

$$H_{\lambda} = \frac{1}{2} (P_{\lambda}^2 + \omega_{\lambda}^2 Q_{\lambda}^2) \quad (57)$$

The Hamiltonian given by Eq. (57) is identical to that of the linear harmonic oscillator (see Sec. 12.2) which suggests that the electromagnetic field can be regarded as an infinite set of harmonic oscillators, one corresponding to each value of  $\mathbf{k}_{\lambda}$  and to a particular direction of polarization.

### *Quantization of electromagnetic field*

In order to quantize the electromagnetic field we use the same approach as in Sec. 12.2. We consider  $Q_{\lambda}$  and  $P_{\lambda}$  to be real operators satisfying the commutation relations

$$[Q_{\lambda}(t), P_{\lambda}(t)] \equiv Q_{\lambda}(t) P_{\lambda}(t) - P_{\lambda}(t) Q_{\lambda}(t) = i \hbar \quad (58)$$

$$[Q_{\lambda}(t), P_{\lambda'}(t)] = 0; \quad \lambda \neq \lambda' \quad (59)$$

$$[Q_{\lambda}(t), Q_{\mu}(t)] = 0 = [P_{\lambda}(t), P_{\mu}(t)] \quad (60)$$

where all the operators are in the Heisenberg representation (see Sec. 12.9). We next introduce the dimensionless variables

$$a_{\lambda}(t) = \frac{1}{\sqrt{2 \hbar \omega_{\lambda}}} [\omega_{\lambda} Q_{\lambda}(t) + i P_{\lambda}(t)] \quad (61)$$

$$\bar{a}_{\lambda}(t) = \frac{1}{\sqrt{2 \hbar \omega_{\lambda}}} [\omega_{\lambda} Q_{\lambda}(t) - i P_{\lambda}(t)] \quad (62)$$

Since  $[\omega_{\lambda} Q_{\lambda}(t) + i P_{\lambda}(t)]$  is proportional to  $q_{\lambda}(t)$  [see Eq. (54)] which has a time dependence of the form  $e^{-i\omega_{\lambda} t}$ , we may write (see also Sec. 12.8)

$$a_{\lambda}(t) = a_{\lambda} e^{-i\omega_{\lambda} t} \quad (63)$$

Similarly,

$$\bar{a}_{\lambda}(t) = \bar{a}_{\lambda} e^{+i\omega_{\lambda} t} \quad (64)$$

<sup>5</sup> Notice that

$$\frac{\partial H_{\lambda}}{\partial Q_{\lambda}} = \omega_{\lambda}^2 Q_{\lambda} = \omega_{\lambda}^2 (\epsilon_0 V)^{1/2} (q_{\lambda} + q_{\lambda}^*) = i \left( \epsilon_0 V \omega_{\lambda}^2 \right)^{1/2} (\dot{q}_{\lambda} - \dot{q}_{\lambda}^*) = -\dot{P}_{\lambda}$$

Similarly

$$\frac{\partial H_{\lambda}}{\partial P_{\lambda}} = +\dot{Q}_{\lambda}$$

which are nothing but Hamilton's equations of motion [see, Ref. 1]. Thus  $Q_{\lambda}$  and  $P_{\lambda}$  are the canonical coordinates.

where

$$a_\lambda \equiv a_\lambda(0) \quad \text{and} \quad \bar{a}_\lambda \equiv \bar{a}_\lambda(0) \quad (65)$$

Solving Eqs (61) and (62) for  $Q_\lambda(t)$  and  $P_\lambda(t)$  we obtain

$$Q_\lambda(t) = \sqrt{\frac{\hbar}{2\omega_\lambda}} [\bar{a}_\lambda(t) + a_\lambda(t)] \quad (66)$$

$$P_\lambda(t) = i\sqrt{\frac{\hbar\omega_\lambda}{2}} [\bar{a}_\lambda(t) - a_\lambda(t)] \quad (67)$$

Substituting the above expressions for  $Q_\lambda(t)$  and  $P_\lambda(t)$  in Eq. (57), we obtain

$$\begin{aligned} H_r = \sum_\lambda H_\lambda &= \sum_\lambda \frac{1}{2} \hbar\omega_\lambda (\bar{a}_\lambda(t) a_\lambda(t) + a_\lambda(t) \bar{a}_\lambda(t)) \\ &= \sum_\lambda \frac{1}{2} \hbar\omega_\lambda (\bar{a}_\lambda a_\lambda + a_\lambda \bar{a}_\lambda) \end{aligned} \quad (68)$$

If we now carry out an analysis similar to that followed in Sec. 12.2, we obtain

$$\left(n_\lambda + \frac{1}{2}\right) \hbar\omega_\lambda ; \quad n_\lambda = 0, 1, 2, \dots \quad (69)$$

as the eigenvalues of  $H_\lambda$  and

$$\sum_\lambda \left(n_\lambda + \frac{1}{2}\right) \hbar\omega_\lambda \quad (70)$$

as the eigenvalues of the total Hamiltonian  $H_r (= \sum H_\lambda)$ . Thus, quantum mechanically, we can visualize the radiation field as consisting of an infinite number of simple harmonic oscillators; the energy of each oscillator can increase or decrease by integral multiples of  $\hbar\omega_\lambda$ . If we consider  $\hbar\omega_\lambda$  as the energy of a photon, each oscillator can have energy corresponding to  $n_\lambda$  photons.

The eigenkets of the total Hamiltonian would be

$$|n_1\rangle |n_2\rangle |n_3\rangle \dots = |n_1, n_2, n_3, \dots n_\lambda, \dots\rangle \quad (71)$$

where  $n_\lambda$  represents the number of photons in the mode characterized by  $\lambda$ . Thus

$$H_r |n_1, n_2, \dots n_\lambda, \dots\rangle = \left(\sum_\lambda \left(n_\lambda + \frac{1}{2}\right) \hbar\omega_\lambda\right) |n_1, n_2, \dots n_\lambda, \dots\rangle \quad (72)$$

Further [see Eqs (24) and (25) of Chapter 12]:

$$a_\lambda |n_1, n_2, \dots n_\lambda, \dots\rangle = \sqrt{n_\lambda} |n_1, n_2, \dots n_\lambda - 1, \dots\rangle \quad (73)$$

$$\bar{a}_\lambda | n_1, n_2, \dots, n_\lambda, \dots \rangle = \sqrt{n_\lambda + 1} | n_1, n_2, \dots, n_\lambda + 1, \dots \rangle \quad (74)$$

and

$$\langle n'_1, n'_2, \dots, n'_\lambda, \dots | n_1, n_2, \dots, n_\lambda, \dots \rangle = \delta_{n_1, n'_1} \delta_{n_2, n'_2}, \dots, \delta_{n_\lambda, n'_\lambda}, \dots \quad (75)$$

Finally, the state of the radiation field need not be an eigenstate of  $H_r$ , it could be a superposition of the eigenstates like that given by the following equation

$$| \Psi \rangle = \sum_{n_1, \dots} C_{n_1, n_2, \dots, n_\lambda, \dots} | n_1, n_2, \dots, n_\lambda, \dots \rangle \quad (76)$$

Physically  $|C_{n_1, n_2, \dots, n_\lambda, \dots}|^2$  would represent the probability of finding  $n_1$  photons in the first mode,  $n_2$  in the second mode, etc.

## 27.4. Spontaneous and stimulated emissions

We next express the vector potential  $\mathbf{A}$  (and hence the interaction term  $H'$ ) in terms of the operators  $a_\lambda$  and  $\bar{a}_\lambda$ . Now using Eqs (54) and (61), we get

$$q_\lambda(t) = \left( \frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} a_\lambda(t) \quad (77)$$

which is now to be considered as an operator. Using Eq. (38) we get

$$\begin{aligned} \mathbf{A} &= \sum_\lambda \left( \frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} [a_\lambda(t) \mathbf{A}_\lambda(\mathbf{r}) + \bar{a}_\lambda(t) \mathbf{A}_\lambda^*(\mathbf{r})] \\ &= \sum_\lambda \left( \frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} [a_\lambda(t) e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} + \bar{a}_\lambda(t) e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}}] \hat{\mathbf{e}}_\lambda \end{aligned} \quad (78)$$

where all the operators are in the Heisenberg representation (see Sec. 12.9). In the Schrödinger representation, we will have

$$\mathbf{A} = \sum_\lambda \left( \frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} [a_\lambda e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} + \bar{a}_\lambda e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}}] \hat{\mathbf{e}}_\lambda \quad (79)$$

which will be independent of time. The interaction energy is

$$H' = \frac{q}{m} \mathbf{A} \cdot \mathbf{p} \quad (80)$$

or

*Interaction energy*

$$H' = \frac{q}{m} \sum_{\lambda} \left( \frac{\hbar}{2\epsilon_0 V \omega_{\lambda}} \right)^{1/2} [a_{\lambda} e^{i\mathbf{k}_{\lambda} \cdot \mathbf{r}} + \bar{a}_{\lambda} e^{-i\mathbf{k}_{\lambda} \cdot \mathbf{r}}] \hat{\mathbf{e}}_{\lambda} \cdot \mathbf{p} \quad (81)$$

Now, the eigenvalue equations for  $H_a$  and  $H_r$  are

$$H_a |\Psi\rangle = E_i |\Psi_i\rangle \quad (82)$$

and

$$H_r |\psi_1, \psi_2, \dots\rangle = \left[ \sum_{\lambda} \left( n_{\lambda} + \frac{1}{2} \right) \hbar \omega_{\lambda} \right] |\psi_1, \psi_2, \dots, n_{\lambda}, \dots\rangle \quad (83)$$

where  $|\psi_i\rangle$  and  $E_i$  represent respectively the eigenkets and energy eigenvalues of the isolated atom and  $|\psi_1, \psi_2, \dots\rangle$  represent the eigenket of the pure radiation field with  $\sum_{\lambda} (n_{\lambda} + \frac{1}{2}) \hbar \omega_{\lambda}$  representing the corresponding eigenvalue (see Eq. 72).

Thus the eigenvalue equation for  $H_0$  will be

$$H_0 |\psi_n\rangle = W_n |\psi_n\rangle \quad (84)$$

where

$$W_n = E_n + \sum_{\lambda} \left( n_{\lambda} + \frac{1}{2} \right) \hbar \omega_{\lambda} \quad (85)$$

and

$$|\psi_n\rangle = |i\rangle |\psi_1, \psi_2, \dots, n_{\lambda}, \dots\rangle = |i; \psi_1, \psi_2, \dots, n_{\lambda}, \dots\rangle \quad (86)$$

represents the ket corresponding to the atom being in state  $|i\rangle$  and the radiation being in the state  $|\psi_1, \psi_2, \dots, n_{\lambda}, \dots\rangle$ .

Now the Schrödinger equation for the system consisting of the atom and the radiation field is

$$i \hbar \frac{\partial |\Psi\rangle}{\partial t} = (H_0 + H') |\Psi\rangle \quad (87)$$

The solution of the above equation can be written as a linear combination of the eigenkets of  $H_0$  (cf. Eq. 15 of the previous chapter):

$$|\Psi\rangle = \sum_n C_n(t) e^{-iW_n t/\hbar} |\psi_n\rangle \quad (88)$$

Substituting in Eq. (87), we obtain

$$\begin{aligned} i \hbar \sum_n \left[ \frac{dC_n}{dt} - i \frac{W_n}{\hbar} C_n \right] e^{-iW_n t/\hbar} |\psi_n\rangle \\ = \sum_n C_n(t) W_n e^{-iW_n t/\hbar} |\psi_n\rangle + H' \sum_n C_n(t) e^{-iW_n t/\hbar} |\psi_n\rangle \end{aligned}$$

where we have used Eq. (84). Premultiplying by  $\langle u_s |$  we get (cf. Eq. 16 of Chapter 26)

$$i \hbar \frac{dC_s}{dt} = \sum_n \langle u_s | H' | u_n \rangle e^{i(W_m - W_n)t/\hbar} C_n(t) \quad (89)$$

Now using Eq. (81)

$$\begin{aligned} \langle u_s | H' | u_n \rangle &= \frac{q}{m} \sum_{\lambda} \left( \frac{\hbar}{2\epsilon_0 V \omega_{\lambda}} \right)^{1/2} \hat{\mathbf{e}}_{\lambda} \cdot \\ &\quad \langle u_s | (\alpha_{\lambda} e^{i\mathbf{k}_{\lambda} \cdot \mathbf{r}} + \bar{\alpha}_{\lambda} e^{-i\mathbf{k}_{\lambda} \cdot \mathbf{r}}) \mathbf{p} | u_n \rangle \end{aligned} \quad (90)$$

Because of the appearance of  $\alpha_{\lambda}$  and  $\bar{\alpha}_{\lambda}$  in the expression for  $H'$ , the various terms in  $\langle u_s | H' | u_n \rangle$  will be non-zero only if the number of photons in  $| u_s \rangle$  differs by unity from the number of photons in  $| u_n \rangle$ . If we write out completely the right-hand side of Eq. (89) it will lead to a coupled set of an infinite number of equations which would be impossible to solve. We employ the perturbation theory and consider the absorption of one photon (of energy  $\hbar\omega_i$ ) from the  $i^{\text{th}}$  mode. Further, if we assume the frequency  $\omega_i$  to be very close to the resonant frequency corresponding to the transition from the atomic state  $| a \rangle$  to  $| b \rangle$ , then Eq. (89) reduces to the following two coupled equations (see also Solution 27.3):

$$i \hbar \frac{dC_1}{dt} = H'_{12} e^{i(W_1 - W_2)t/\hbar} C_2(t) \quad (91)$$

$$i \hbar \frac{dC_2}{dt} = H'_{21} e^{-i(W_1 - W_2)t/\hbar} C_1(t) \quad (92)$$

where

$$| 1 \rangle = | a; n_1, n_2, \dots, n_{\lambda}, \dots, n_i, \dots \rangle \quad (93)$$

and

$$| 2 \rangle = | b; n_1, n_2, \dots, n_{\lambda}, \dots, n_i - 1, \dots \rangle \quad (94)$$

represent the initial and final states of the system. Obviously, because of relations like Eq. (115),  $H'_{11} = 0 = H'_{22}$ . Further,

$$\left. \begin{aligned} W_1 &= E_a + \sum_{\substack{\lambda \\ \lambda \neq i}} \left( n_\lambda + \frac{1}{2} \right) \hbar \omega_\lambda + \left( n_i + \frac{1}{2} \right) \hbar \omega_i \\ W_2 &= E_b + \sum_{\substack{\lambda \\ \lambda \neq i}} \left( n_\lambda + \frac{1}{2} \right) \hbar \omega_\lambda + \left( n_i - 1 + \frac{1}{2} \right) \hbar \omega_i \end{aligned} \right\} \quad (95)$$

Thus,

$$W_1 - W_2 = (E_a - E_b) + \hbar \omega_i \quad (96)$$

Now

$$\begin{aligned} H'^*_{{21}} &= H'_{{12}} = \frac{q}{m} \sum_{\lambda} \left( \frac{\hbar}{2\epsilon_0 V \omega_{\lambda}} \right)^{1/2} \hat{\mathbf{e}}_{\lambda} \cdot \langle a; n_1, n_2, \dots, n_i, \dots | \\ &\quad (a_{\lambda} e^{i\mathbf{k}_{\lambda} \cdot \mathbf{r}} + \bar{a}_{\lambda} e^{-i\mathbf{k}_{\lambda} \cdot \mathbf{r}}) \mathbf{p} | b; n_1, n_2, \dots, n_i - 1, \dots \rangle \\ &= \frac{q}{m} \left( \frac{\hbar}{2\epsilon_0 V \omega_i} \right)^{1/2} \sqrt{n_i} \hat{\mathbf{e}}_{\lambda} \cdot \langle a | e^{-i\mathbf{k}_{\lambda} \cdot \mathbf{r}} \mathbf{p} | b \rangle \\ &\simeq \frac{q}{m} \left( \frac{\hbar}{2\epsilon_0 V \omega_i} \right)^{1/2} \sqrt{n_i} \hat{\mathbf{e}}_{\lambda} \cdot \langle a | \mathbf{p} | b \rangle \end{aligned} \quad (97)$$

where in the last step we have used the dipole approximation in which we have replaced  $e^{-i\mathbf{k}_{\lambda} \cdot \mathbf{r}}$  by unity (see Eq. 14). If we now use Eq. (19) we get

$$\begin{aligned} \langle a | \mathbf{p} | b \rangle &= \frac{m}{i\hbar} (E_b - E_a) \langle a | \mathbf{r} | b \rangle \\ &= -im\omega_{ba} \langle a | \mathbf{r} | b \rangle \end{aligned}$$

Thus

$$H'^*_{{21}} = H'_{{12}} = -i \left( \frac{\hbar}{2\epsilon_0 V \omega_i} \right)^{1/2} \omega_{ba} \sqrt{n_i} D_{ab} \quad (98)$$

where

$$D_{ab} = q \hat{\mathbf{e}}_{\lambda} \cdot \langle a | \mathbf{r} | b \rangle = \frac{iq}{m\omega_{ba}} \hat{\mathbf{e}}_{\lambda} \cdot \langle a | \mathbf{p} | b \rangle \quad (99)$$

[see Eq. (20) of Chapter 26]. We next try to solve Eqs (91) and (92) by using a method similar to that employed in Problem 26.8. We assume that at  $t = 0$  the system is in the state represented by  $| 1 \rangle$ , i.e.

$$C_1(0) = 1, \quad C_2(0) = 0 \quad (100)$$

On working out the solution one obtains

$$|C_2(t)|^2 \simeq \left( \frac{\Omega_0}{2} \right)^2 \left[ \frac{\sin \Omega' t / 2}{\Omega' / 2} \right]^2 \quad (101)$$

where

$$\Omega_0 = \left[ \frac{2n_i |D_{ab}|^2}{\hbar \epsilon_0 V} \frac{\omega_{ab}^2}{\omega_i} \right]^{1/2} \quad (102)$$

and

$$\Omega' = [(\omega_{ba} - \omega_i)^2 + \Omega_0^2]^{1/2} \quad (103)$$

For  $\Omega_0 t / \hbar \ll 1$ , we obtain

$$|C_2(t)|^2 \simeq \frac{n\omega |D_{ab}|^2}{2\hbar\epsilon_0 V} \left[ \frac{\sin (\omega_{ba} - \omega) t / 2}{(\omega_{ba} - \omega) / 2} \right]^2 \quad (104)$$

where we have dropped the subscript  $i$  and have taken into account the fact that  $|C_2(t)|^2$  is negligible except when  $\omega \approx \omega_{ba}$  and have thus replaced  $\omega_{ba}$  by  $\omega$ . Equation (104) is the same as Eq. (24) of the previous chapter provided we replace<sup>6</sup>  $\mathcal{E}_0^2$  by  $2n\hbar\omega/V\epsilon_0$ . Using Eq. (104) and proceeding as in Sec. 26.4, we would get an expression for the Einstein  $B$  coefficient identical to Eq. (40) of Chapter 26.

In a similar manner, if we consider the emission process, we would obtain

$$|C_2(t)|^2 \simeq \frac{\omega(n+1)}{2\hbar\epsilon_0 V} |D_{ab}|^2 \left[ \frac{\sin (\omega_{ba} - \omega) t / 2}{(\omega_{ba} - \omega) / 2} \right]^2 \quad (105)$$

where the initial and final states  $|1\rangle$  and  $|2\rangle$  are now given by<sup>7</sup>

$$\left. \begin{aligned} |\text{initial}\rangle &= |1\rangle = |b; n_1, n_2, \dots, n_i, \dots\rangle \\ |\text{final}\rangle &= |2\rangle = |a; n_1, n_2, \dots, n_i + 1, \dots\rangle \end{aligned} \right\} \quad (106)$$

Notice the presence of the term<sup>8</sup>  $(n+1)$  in Eq. (105). This implies that even if the number of photons were zero originally, the emission probability is finite. The term proportional to  $n$  in Eq. (105) gives the probability for induced or stimulated

<sup>6</sup> This is justified because the energy density associated with an electromagnetic field is  $\frac{1}{2}\epsilon_0\mathcal{E}_0^2$  and the energy density is also equal to  $n\hbar\omega/V$ .

<sup>7</sup> We would have

$$i\hbar \frac{dC_2}{dt} \simeq H'_{21} e^{-i(W_1 - W_2)t/\hbar} C_1(t) \simeq H'_{21} e^{-i(\omega_{ba} - \omega_i)t}$$

and integration of which would lead to Eq. (105). However, it may be mentioned that the equation for  $C_1(t)$  would be a sum over states as discussed in Solution 27.3.

<sup>8</sup> The appearance of the term  $(n+1)$  is because of the relation  $|\langle n+1 | \bar{a} | n \rangle|^2 = |\sqrt{n+1} \langle n+1 | n+1 \rangle|^2 = (n+1)$ .

emission since the rate at which it occurs is proportional to the intensity of the applied radiation. On the other hand, the second term which is independent of  $n$  gives the spontaneous emission rate into the mode (see also Problem 27.3). It may be noted that the spontaneous emission probability into a particular mode is exactly the same as the stimulated emission probability caused by a single photon into the same mode.

We next calculate the probability per unit time for spontaneous emission of radiation. If we consider the emission to be in the solid angle  $d\Omega$  then the number of modes for which the photon frequency lies between  $\omega$  and  $\omega + d\omega$  is (see Appendix M)

$$N(\omega) d\omega d\Omega = \frac{V\omega^2 d\omega}{8\pi^3 c^3} d\Omega \quad (107)$$

Thus, the total probability of emission in the solid angle  $d\Omega$  would be given by

$$\begin{aligned} \Gamma &= \frac{|D_{ab}|^2}{2\hbar\epsilon_0 V} \int \left[ \frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2} \right]^2 \omega \frac{V}{8\pi^3 c^3} \omega^2 d\omega d\Omega \\ &\simeq \frac{|D_{ab}|^2}{2\hbar\epsilon_0 8\pi^3 c^3} d\Omega \omega_{ba}^3 \int \left[ \frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2} \right]^2 d\omega \end{aligned} \quad (108)$$

where use has been made of the fact that the quantity inside the square brackets is a sharply peaked function around  $\omega = \omega_{ba}$ . Carrying out the integration, using the fact that

$$\int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2} dx = \pi$$

we obtain

$$\Gamma \cong \frac{1}{2\pi} \left[ \frac{q^2}{4\pi\epsilon_0\hbar c} \right] \frac{\omega^3}{c^2} |\langle a | \mathbf{r} | b \rangle \cdot \hat{\mathbf{e}}|^2 d\Omega t$$

Thus the transition rate is given by

$$w_{sp} = \frac{1}{2\pi} \left[ \frac{q^2}{4\pi\epsilon_0\hbar c} \right] \frac{\omega}{m^2 c^2} |\langle a | \mathbf{p} | b \rangle \cdot \hat{\mathbf{e}}|^2 d\Omega \quad (109)$$

$$= \frac{1}{2\pi} \left[ \frac{q^2}{4\pi\epsilon_0\hbar c} \right] \frac{\omega^3}{c^2} |\langle a | \mathbf{r} | b \rangle \cdot \hat{\mathbf{e}}|^2 d\Omega \quad (110)$$

In order to calculate the total probability per unit time for the spontaneous emission to occur (the inverse of which will give the spontaneous lifetime of the state), we must sum over the two independent states of polarization and integrate over the

solid angle. Assuming the direction of  $\mathbf{k}$  to be along the  $z$ -axis, we may choose  $\hat{\mathbf{e}}$  to be along the  $x$ - or  $y$ -axes. Thus, if we sum

$$|\langle a | \mathbf{r} | b \rangle \cdot \hat{\mathbf{e}}|^2$$

over the two independent states of polarization, we obtain

$$\begin{aligned} & |\langle a | \mathbf{r} | b \rangle \cdot \hat{\mathbf{x}}|^2 + |\langle a | \mathbf{r} | b \rangle \cdot \hat{\mathbf{y}}|^2 \\ &= P_x^2 + P_y^2 = P^2 \sin^2 \theta \end{aligned}$$

where  $\mathbf{P} \equiv \langle a | \mathbf{r} | b \rangle$  and  $\theta$  is the angle that  $\mathbf{P}$  makes with the  $z$ -axis. Thus in order to obtain the Einstein  $A$  coefficient (which represents the total probability per unit time for the spontaneous emission to occur), in Eq. (110), we replace  $|\langle a | \mathbf{r} | b \rangle \cdot \hat{\mathbf{e}}|^2$  by  $|\langle a | \mathbf{r} | b \rangle|^2 \sin^2 \theta$  and integrate over the solid angle  $d\Omega$  to obtain

$$\begin{aligned} A &= \frac{1}{2\pi} \left[ \frac{q^2}{4\pi\epsilon_0\hbar c} \right] \frac{\omega^3}{c^2} |\langle a | \mathbf{r} | b \rangle|^2 \iint \sin^2 \theta \sin \theta \, d\theta \, d\phi \\ &= \frac{4}{3} \left[ \frac{q^2}{4\pi\epsilon_0\hbar c} \right] \frac{\omega^3}{c^2} |\langle a | \mathbf{r} | b \rangle|^2 \end{aligned} \quad (111)$$

which is identical to Eq. (43) of the previous chapter.

## 27.5. Properties of the eigenstates of the hamiltonian of the radiation field

If we substitute for  $q_\lambda(t)$  from Eq. (77) in Eq. (44) we would obtain

$$\mathcal{E} = \sum_{\lambda} \mathcal{E}_{\lambda} \quad (112)$$

where

$$\mathcal{E}_{\lambda} = i \left( \frac{\hbar\omega_{\lambda}}{2\epsilon_0 V} \right)^{1/2} [a_{\lambda} e^{i\mathbf{k}_{\lambda} \cdot \mathbf{r}} - \bar{a}_{\lambda} e^{-i\mathbf{k}_{\lambda} \cdot \mathbf{r}}] \hat{\mathbf{e}}_{\lambda} \quad (113)$$

and all operators are in the Schrödinger representation. We consider the state of the radiation field for which there are  $n_{\lambda}$  photons in the  $\lambda^{th}$  state. The expectation value of  $\mathcal{E}_{\lambda}$  in this state would be given by

$$\begin{aligned} & \langle n_1, n_2, \dots, n_{\lambda}, \dots | \mathcal{E}_{\lambda} | n_1, n_2, \dots, n_{\lambda}, \dots \rangle \\ &= \langle n_1 | n_1 \rangle \langle n_2 | n_2 \rangle \dots \langle n_{\lambda} | \mathcal{E}_{\lambda} | n_{\lambda} \rangle \\ &= 0 \end{aligned} \quad (114)$$

because

$$\langle n_\lambda | a_\lambda | n_\lambda \rangle = 0 = \langle n_\lambda | \bar{a}_\lambda | n_\lambda \rangle \quad (115)$$

Similarly

$$\begin{aligned} & \langle n_1, n_2, \dots, n_\lambda, \dots | \mathcal{E}_\lambda^2 | n_1, n_2, \dots, n_\lambda, \dots \rangle \\ &= \langle n_1 | n_1 \rangle \langle n_2 | n_2 \rangle \dots \langle n_\lambda | \mathcal{E}_\lambda^2 | n_\lambda \rangle \dots \\ &= - \left( \frac{\hbar \omega_\lambda}{2\epsilon_0 V} \right) \langle n_\lambda | (a_\lambda e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} - \bar{a}_\lambda e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}}) (a_\lambda e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}} - \bar{a}_\lambda e^{i\mathbf{k}_\lambda \cdot \mathbf{r}}) | n_\lambda \rangle \\ &= \left( \frac{\hbar \omega_\lambda}{\epsilon_0 V} \right) \left( n_\lambda + \frac{1}{2} \right) \end{aligned} \quad (116)$$

where use has been made of relations like (see Sec. 12.2):

$$\langle n_\lambda | a_\lambda \bar{a}_\lambda | n_\lambda \rangle = \sqrt{n_\lambda + 1} \langle n_\lambda | a_\lambda | n_\lambda + 1 \rangle = n_\lambda + 1 \quad (117)$$

$$\langle n_\lambda | \bar{a}_\lambda a_\lambda | n_\lambda \rangle = \sqrt{n_\lambda} \langle n_\lambda | \bar{a}_\lambda | n_\lambda - 1 \rangle = n_\lambda \quad (118)$$

$$\langle n_\lambda | a_\lambda a_\lambda | n_\lambda \rangle = 0 \quad (119)$$

$$\langle n_\lambda | \bar{a}_\lambda \bar{a}_\lambda | n_\lambda \rangle = 0 \quad (120)$$

The uncertainty in  $\mathcal{E}_\lambda$ ,  $\Delta \mathcal{E}_\lambda$ , can be defined through the relation

$$\begin{aligned} (\Delta \mathcal{E}_\lambda)^2 &= \langle \mathcal{E}_\lambda^2 \rangle - \langle \mathcal{E}_\lambda \rangle^2 \\ &= \left( \frac{\hbar \omega_\lambda}{\epsilon_0 V} \right) \left( n_\lambda + \frac{1}{2} \right) \end{aligned} \quad (121)$$

Equation (114) tells us that the expectation value of the electric field in the state  $|n\rangle$  ( $=|n_1, n_2, \dots, n_\lambda, \dots\rangle$ ) is zero. Since the average of sine waves with random phases is zero, we may loosely say that the state  $|n\rangle$  does not specify the phase<sup>9</sup>. Some authors tend to explain this by resorting to the uncertainty principle

$$\Delta E \underset{\sim}{\Delta t} \hbar \quad (122)$$

where  $\Delta E$  is the uncertainty in the energy of the radiation field and  $\Delta t$  is related to the uncertainty in the phase angle through the relation

$$\Delta \phi = \omega \Delta t \quad (123)$$

Since  $E = (n + 1/2) \hbar \omega$ ,  $\Delta E = \hbar \omega \Delta n$  and we obtain

$$\Delta n \underset{\sim}{\Delta \phi} \geq 1 \quad (124)$$

---

<sup>9</sup> We say it loosely because it is not possible to define a phase operator which is real (see Sec. 27.7).

If the number of photons is exactly known, then  $\Delta n = 0$  and consequently there is no knowledge of the phase. However, such arguments are not rigorously correct because it is not possible to give a precise definition of  $\Delta\phi$  (see Sec. 27.7). Nevertheless, we can say that the states described by  $|n\rangle$  do not correspond to the classical electromagnetic wave with a certain phase.

Returning to Eq. (116), we notice that the states  $|n\rangle$  have a definite amplitude  $(2\hbar\omega_\lambda/\epsilon V)^{1/2} (n_\lambda + 1/2)^{1/2}$  for the mode  $\lambda$  which is directly related to the number of photons.

## 27.6. The coherent states

We next consider the radiation field to be in one of the coherent states which are, the eigenkets of the operator  $a_\lambda$  (see Sec. 12.5). We will show that when the radiation field is in a coherent state, the field has properties very similar to that of a classical electromagnetic wave with a certain phase and amplitude. However, before we do so, we would like to discuss some of the properties of the coherent state.

The coherent states satisfy the equation

$$a_\lambda |\alpha_\lambda\rangle = \alpha_\lambda |\alpha_\lambda\rangle \quad (125)$$

where  $\alpha_\lambda$ , which represents the eigenvalues of  $a_\lambda$ , can be an arbitrary complex number. In Sec. 12.5 we had shown that

$$|\alpha_\lambda\rangle = \exp\left[-\frac{1}{2}|\alpha_\lambda|^2\right] \sum_{n_\lambda=0,1,2,\dots} \frac{\alpha_\lambda^{n_\lambda}}{\sqrt{n_\lambda!}} |n_\lambda\rangle$$

For convenience, we drop the subscript  $\lambda$  and write the above equation as

$$|\alpha\rangle = \exp\left[-N/2\right] \sum_n \frac{\alpha^n}{\sqrt{n!}} |n\rangle \quad (126)$$

where  $N (= |\alpha|^2)$  represents the expectation value of the number operator  $N_{op}$  (see Sec. 12.7). Since  $|H\rangle$  are eigenkets of  $H$ , if the field is in the coherent state at  $t = 0$ , then at a later time  $t$ , the state will be given by (see Sec. 12.6)

$$|\Psi(t)\rangle = e^{-N/2} \sum_n \frac{\alpha^n}{\sqrt{n!}} \exp\left[-i\left(n + \frac{1}{2}\right)\omega t\right] |n\rangle \quad (127)$$

It is easy to see that

$$|\Psi(0)\rangle = |\alpha\rangle$$

Further<sup>10</sup>

$$\begin{aligned}\langle \Psi(t) | \bar{a} | \Psi(t) \rangle &= e^{-N} \sum_m \sum_n \frac{\alpha^{*^m} \alpha^n}{\sqrt{m!n!}} e^{i(m-n)\omega t} \sqrt{n+1} \langle m | n+1 \rangle \\ &= e^{i\omega t} e^{-N} \sum_n \frac{\alpha^* |\alpha|^{2n}}{n!} = \alpha^* e^{i\omega t}\end{aligned}\quad (128)$$

Similarly, or taking the complex conjugate of the above equation

$$\langle \Psi(t) | a | \Psi(t) \rangle = \alpha e^{-i\omega t} \quad (129)$$

We now consider the radiation field to be in the coherent state and calculate the expectation value of  $\mathcal{E}$  and  $\mathcal{E}^2$ :

$$\begin{aligned}\langle \Psi(t) | \mathcal{E} | \Psi(t) \rangle &= i \left( \frac{\hbar\omega}{2\epsilon_0 V} \right)^{1/2} \left[ \langle \Psi(t) | a | \Psi(t) \rangle e^{i\mathbf{k} \cdot \mathbf{r}} \right. \\ &\quad \left. - \langle \Psi(t) | \bar{a} | \Psi(t) \rangle e^{-i\mathbf{k} \cdot \mathbf{r}} \right] \hat{\mathbf{e}} \\ &= i \left( \frac{\hbar\omega}{2\epsilon_0 V} \right)^{1/2} [\alpha e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} - \alpha^* e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}] \hat{\mathbf{e}} \\ &= -2 \left( \frac{\hbar\omega}{2\epsilon_0 V} \right)^{1/2} |\alpha| \sin(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi) \hat{\mathbf{e}}\end{aligned}\quad (130)$$

where

$$\alpha = |\alpha| e^{i\phi} \quad (131)$$

Thus the coherent state can be interpreted to represent a harmonic wave with phase  $\phi$ . In a similar manner, we can calculate the expectation value  $\mathcal{E}^2$ . The result is

$$\langle \Psi(t) | \mathcal{E} \cdot \mathcal{E} | \Psi(t) \rangle = \left( \frac{\hbar\omega}{2\epsilon_0 V} \right) [4|\alpha|^2 \sin^2(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi) + 1] \quad (132)$$

Finally, the uncertainty in  $\mathcal{E}$  would be given by (cf. Eq. 121):

$$\begin{aligned}(\Delta \mathcal{E})^2 &= \langle \Psi(t) | \mathcal{E}^2 | \Psi(t) \rangle - \langle \Psi(t) | \mathcal{E} | \Psi(t) \rangle^2 \\ &= \left( \frac{\hbar\omega}{2\epsilon_0 V} \right)\end{aligned}\quad (133)$$

Notice that the uncertainty  $\Delta \mathcal{E}$  is independent of the amplitude  $|\alpha|$ ; thus, greater the intensity of the beam greater will be the proximity of the radiation field (corresponding to the coherent state) to the classical plane wave. Indeed when a laser

<sup>10</sup> In the Heisenberg representation, the expectation value of  $\bar{a}$  would have been

$$\langle \Psi(0) | \bar{a}(t) | \Psi(0) \rangle = \langle \alpha | \bar{a} e^{i\omega t} | \alpha \rangle = \alpha^* e^{i\omega t}$$

which is the same as expressed by Eq. (128).

is operated much beyond the threshold, it generates a coherent state excitation of a cavity mode.

## 27.7. The phase operator

In classical mechanics the displacement and momentum of a linear harmonic oscillator are given by

$$x = A e^{i\phi} + A e^{-i\phi} \quad , \quad \phi = \omega t \quad (134)$$

and

$$p = m\dot{x} = im\omega A [e^{i\phi} - e^{-i\phi}] \quad (135)$$

where  $A$  has been assumed to be real. In quantum mechanics, we have [see Eqs 30 and 31 of chapter 12]:

$$x = \left( \frac{\hbar}{2m\omega} \right)^{1/2} [\bar{a} + a] \quad (136)$$

$$p = im\omega \left( \frac{\hbar}{2m\omega} \right)^{1/2} [\bar{a} - a] \quad (137)$$

The above four equations suggest the phase operator  $\phi$  to be defined through the following equations

$$\bar{a} = R e^{i\phi} \quad (138)$$

and

$$a = e^{-i\phi} R \quad (139)$$

where  $R$  and  $\phi$  are assumed to be Hermitian operators (see, e.g. Ref 2 and 3). However, such a definition will lead to inconsistent results as discussed below. Now, the number operator is given by

$$N_{op} = \bar{a} a = R e^{i\phi} e^{-i\phi} R = R^2$$

or

$$R = N_{op}^{1/2} \quad (140)$$

where the square root of an operator is defined through the relation

$$N_{op} = N_{op}^{1/2} N_{op}^{1/2}$$

Since

$$[a, \bar{a}] = a\bar{a} - \bar{a}a = 1$$

so,

$$e^{-i\phi} R R e^{i\phi} - R e^{i\phi} e^{-i\phi} R = 1$$

or, premultiplying by  $e^{i\phi}$ , we get

$$N_{op}e^{i\phi} - e^{i\phi}N_{op} = e^{i\phi} \quad (141)$$

The above equation is satisfied if  $\phi$  and  $N_{op}$  satisfy the commutation relation<sup>11</sup>

$$[N_{op}, \phi] = N_{op}\phi - \phi N_{op} = -i \quad (142)$$

Thus

$$\langle m | N_{op}\phi - \phi N_{op} | n \rangle = -i \langle m | n \rangle = -i\delta_{mn}$$

or,

$$(m - n) \langle m | \phi | n \rangle = -i\delta_{mn} \quad (143)$$

which is certainly an impossibility! Thus the definition of a Hermitian  $\phi$  through Eq. (138) leads to inconsistent results.

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## 27.8. Problems

**Problem 27.1** Consider the matrix element  $\langle s | e^{-i\mathbf{k} \cdot \mathbf{r}} \hat{\mathbf{e}} \cdot \mathbf{p} | n \rangle$  [see Eq. (13)]. Since in many cases of interest  $kR \ll 1$  (where  $R$  represents the dimension of the system), we may write

$$e^{-i\mathbf{k} \cdot \mathbf{r}} = 1 - i\mathbf{k} \cdot \mathbf{r} - \frac{(\mathbf{k} \cdot \mathbf{r})^2}{2!} + \dots \quad (144)$$

It can be shown that the term  $(\mathbf{k} \cdot \mathbf{r})^n$  gives the electric  $2^{n+1}$  pole and the magnetic  $2^n$  pole transitions. Verify this statement for the case  $n = 1$ .

**Problem 27.2** Obtain the selection rules for allowed transitions of a linear harmonic oscillator. Calculate the lifetime of an oscillator in the first excited state.

**Problem 27.3** Show that the frequency distribution of the emitted radiation from an isolated atom is given by the natural line shape function

$$f(\omega) d\omega = \frac{K d\omega}{(\omega_0 - \omega)^2 + A^2/4} \quad (145)$$

<sup>11</sup> This follows from the repeated application of Eq. (142) which gives

$$N_{op}\phi^m - \phi^m N_{op} = -im\phi^{m-1}$$

Now

$$[N_{op}, e^{i\phi}] = \sum_m \frac{i^m}{m!} [N_{op}, \phi^m] = \sum_m \frac{i^{m-1} \phi^{m-1}}{(m-1)!} = e^{i\phi}$$

where  $A$  represents the Einstein coefficient.

**Problem 27.4** Prove that the average number of photons in a coherent state is  $|\alpha|^2$ , i.e.

$$N \equiv \langle \alpha | N_{op} | \alpha \rangle = |\alpha|^2 \quad (146)$$

**Problem 27.5** Show that the probability of finding  $n$  photons in a coherent state is a Poisson distribution<sup>12</sup> about the mean  $|\alpha|^2$ :

$$|\langle n | \alpha \rangle|^2 = \frac{N^n e^{-N}}{n!} \quad (147)$$

where  $N (= |\alpha|^2)$  is defined in the previous problem.

**Problem 27.6** Prove that the uncertainty in the number of photons in a coherent state is  $\sqrt{N}$ , i.e.

$$\Delta N \equiv \left[ \langle \alpha | N_{op}^2 | \alpha \rangle - \langle \alpha | N_{op} | \alpha \rangle^2 \right]^{1/2} = N^{1/2} \quad (148)$$

Thus the fractional uncertainty in the average number of photons  $\Delta N/N (= 1/\sqrt{N})$  goes to zero with increase in intensity. It may be worthwhile pointing out that even in nuclear counting, the uncertainty in the actual count is  $N^{1/2}$  (see, e.g. Ref. 5).

**Problem 27.7** Show that for  $|\psi(t)\rangle$  given by Eq. (127)

$$\langle \psi(t) | N_{op} | \psi(t) \rangle = N \quad (\text{independent of time})$$

**Problem 27.8** Obtain an expression for the photodisintegration of the deuteron in the electric dipole approximation. Assume that the wave function of the deuteron may be approximated by

$$\psi = \sqrt{\frac{K}{2\pi}} \frac{e^{-Kr}}{r} \quad (149)$$

where  $\hbar K = (2\mu B)^{1/2}$ ,  $\mu = \frac{1}{2}M$  is the reduced mass of the system,  $B = 2.2$  MeV is the binding energy. Neglect the interaction between neutron and proton in the final state [Hint: Use the Golden rule].

**Problem 27.9**

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<sup>12</sup> The photon counting experiment is of considerable importance in determining statistical properties of the light source. In a typical experiment, the light beam is allowed to fall on a phototube for a specific time interval  $T$  by having a shutter open in front of the detector for time  $T$  and one registers the number of photoelectrons so liberated. Then the shutter is again opened for an equal time interval  $T$  after a certain time delay and the experiment is repeated a large number of times. From the experiment one obtains the probability distribution of counting  $n$  photons in time  $T$ . From this one can derive the statistical properties of the sources (see, e.g. Ref. 4).

(a) Derive the Thomas-Reiche-Kuhn sum rule

$$\sum_s (E_s - E_n) |\langle s | x | n \rangle|^2 = \frac{\hbar^2}{2m} \quad (150)$$

(b) Using the above sum rule show that for dipole transitions

$$\int \sigma \, dE = 2\pi^2 \alpha \hbar^2 / m \quad (151)$$

**Problem 27.10** If the quantum energy  $\hbar\omega$  of light falling on an atom is greater than the ionization energy,  $I$ , of the atom the electron is raised into a state of the continuous spectrum. In this case light of all frequencies can be absorbed, and the absorption spectrum is continuous. The kinetic energy  $T$  of the electron after leaving the atom is determined by Einstein's equation

$$T = \hbar\omega - I \quad (152)$$

Show that for the incident radiation polarized with its electric vector along  $\hat{\mathbf{e}}$ , the photoelectric absorption cross-section of an atom, for the ejection of an electron from the  $K$ -shell, is given by

$$\frac{d\sigma}{d\Omega} = \frac{32\hbar k}{m\omega} \left( \frac{q^2}{4\pi\epsilon_0\hbar c} \right) (\hat{\mathbf{e}} \cdot \mathbf{k})^2 \left( \frac{Z}{a_0} \right)^5 \left[ \left( \frac{Z}{a_0} \right)^2 + q^2 \right]^{-4}, \quad (153)$$

where  $\mathbf{k}$  is the wave vector of the ejected electron,  $\mathbf{q}$  is the momentum transferred to the atom in units of  $\hbar$ :

$$\mathbf{q} = \mathbf{k} - \frac{\omega}{c} \hat{\mathbf{n}} \quad (154)$$

$\hat{\mathbf{n}}$  is the unit vector along the direction of propagation. Assume  $\hbar\omega \gg I$ . [Use the Golden rule].

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## 27.9. Solutions

**Solution 27.1** The relevant term in the matrix element is

$$M = \langle s | (i\mathbf{k} \cdot \mathbf{r}) (\hat{\mathbf{e}} \cdot \mathbf{p}) | n \rangle \quad (155)$$

Let us assume that the photon moves along the  $x$ -direction, and the polarization  $\hat{\mathbf{e}}$  is along the  $z$ -direction. Thus

$$M = \langle s | ikxp_z | n \rangle = ik \langle s | xp_z | n \rangle$$

We write  $xp_z$  as

$$xp_z = \frac{1}{2} [xp_z + zp_x] + \frac{1}{2} [xp_z - zp_x]$$

Now, according to Eq. (17)

$$p_z = \frac{m}{i\hbar} [zH_a - H_az]$$

Thus

$$xp_z = \frac{m}{i\hbar} [xzH_a - xH_az]$$

Similarly

$$zp_x = p_xz = \frac{m}{i\hbar} [xH_a - H_ax] z$$

So that

$$\frac{1}{2} (xp_z + zp_x) = \frac{m}{2i\hbar} [xzH_a - H_axz] \quad (156)$$

and

$$\frac{1}{2} (xp_z - zp_x) = -\frac{1}{2} L_y \quad (157)$$

where  $L_y$  is the  $y$ -component of the angular momentum. Thus

$$\begin{aligned} M &= -ik \left\langle s \left| \frac{m}{2i\hbar} (H_axz - xzH_a) + \frac{1}{2} L_y \right| n \right\rangle \\ &= -\frac{m}{2\hbar} (E_s - E_n) \langle s | xz | n \rangle - \frac{1}{2} ik \langle s | L_y | n \rangle \end{aligned} \quad (158)$$

The first term is the electric quadrupole term while the second is the magnetic dipole term (the magnetic moment is related to the angular momentum).

**Solution 27.2** The relevant matrix element for allowed transition is

$$M = \langle m | x | n \rangle$$

The only non-vanishing matrix elements correspond to

$$m = n \pm 1$$

(see Problem 12.3) and the values are given by

$$\left. \begin{aligned} \langle n+1 | x | n \rangle &= \sqrt{\frac{\hbar}{2m\omega}} \sqrt{n+1} \\ \langle n-1 | x | n \rangle &= \sqrt{\frac{\hbar}{2m\omega}} \sqrt{n} \end{aligned} \right\} \quad (159)$$

Thus the selection rule is  $\Delta n = \pm 1$ . The transition rate is given by (see Eq. (109))

$$w_{sp} = \frac{1}{2\pi} \left[ \frac{q^2}{4\pi\epsilon_0\hbar c} \right] \frac{\omega}{m^2c^2} |\langle 0 | p_x | 1 \rangle|^2 d\Omega \quad (160)$$

Now

$$|\langle 0 | p_x | 1 \rangle| = -i\sqrt{\frac{m\hbar\omega}{2}} \quad (161)$$

(see Problem 12.3). Thus the integrated rate over the whole solid angle is

$$\frac{1}{\tau} = \frac{\alpha\hbar\omega^2}{mc^2} \quad (162)$$

which gives the mean life  $\tau$ ; here  $\alpha (\simeq \frac{1}{137})$  is the fine structure constant.

**Solution 27.3** A spontaneous transition from a state  $b$  to  $a$  lower energy state  $a$  does not give radiation at a single frequency  $\omega_{ba}$ . A finite lifetime  $\tau$  of the excited state gives it an energy width of the order  $\hbar/\tau$  so that the emitted radiation has a frequency distribution. This argument may be made more precise by considering the simple case of an atom with only 2 states  $a$  and  $b$  ( $E_b > E_a$ ) undergoing spontaneous transition from  $b$  to  $a$ . We will calculate here the frequency distribution of the emitted radiation from such a spontaneous transition; the analysis is based on the treatment given in Chapter 18 of Ref. 3 and is known as Weisskopf-Wigner theory of the natural line width.

It is assumed that at  $t = 0$ , the atom is in the excited state  $b$  and the radiation field has no photons. We denote this state by

$$| 1 \rangle = | b; 0, 0, 0, \dots \rangle$$

[see Eq. (93)]. The atom makes a transition to the state  $a$  emitting a photon of frequency  $\omega_\lambda$  in the mode characterized by  $\lambda$  [see Eq. (71)]. We denote this state by

$$| a\lambda \rangle = | a; 0, 0, \dots, 1_\lambda, 0, \dots \rangle$$

If we denote the corresponding probability amplitudes by

$$C_1(t) \quad \text{and} \quad C_{a\lambda}(t)$$

then

$$\begin{cases} C_1(0) = 1 \\ C_{a\lambda}(0) = 0 \end{cases} \quad (163)$$

Further [see Eqs (89)–(92)]

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= \sum_{\lambda} \langle 1 | H' | a\lambda \rangle e^{i(W_1 - W_{a\lambda})t/\hbar} C_{a\lambda}(t) \\ &= \sum_{\lambda} \langle 1 | H' | a\lambda \rangle e^{i(\omega_0 - \omega_{a\lambda})t} C_{a\lambda}(t) \end{aligned} \quad (164)$$

and

$$i \hbar \frac{dC_{a\lambda}}{dt} = \langle a\lambda | H' | 1 \rangle e^{-i(\omega_0 - \omega_\lambda)t} C_1(t) \quad (165)$$

where

$$\hbar\omega_0 = E_b - E_a \quad (166)$$

and

$$W_1 - W_{a\lambda} = E_b - (E_a + \hbar\omega_\lambda) = \hbar(\omega_0 - \omega_\lambda) \quad (167)$$

We try to solve Eqs.(164) and (165) by assuming<sup>13</sup>

$$C_1(t) = e^{-\gamma t/2} \quad (168)$$

which satisfies the condition  $C_1(0) = 1$ . It may be noted that since  $|C_1(t)|^2$  represents the probability of finding the atom in the upper state, the quantity  $1/\gamma$  represents the mean lifetime of the state. If we substitute for  $C_1(t)$  in Eq. (165) and carry out the integration we get

$$C_{a\lambda}(t) = \frac{\langle a\lambda | H' | 1 \rangle}{\hbar} \frac{e^{-[i(\omega_0 - \omega_\lambda) + \gamma/2]t} - 1}{(\omega_0 - \omega_\lambda) - i\gamma/2} \quad (169)$$

We substitute Eqs (168) and (169) in (164) to obtain

$$-i \hbar \frac{\gamma}{2} = \sum_{\lambda} \frac{|\langle H' \rangle|^2}{\hbar} \frac{1 - \exp[i(\omega_0 - \omega_\lambda)t + \gamma t/2]}{(\omega_0 - \omega_\lambda) - i\gamma/2} \quad (170)$$

where  $\langle H' \rangle \equiv \langle a\lambda | H' | 1 \rangle$ . The summation on the right-hand side of the above equation is over a number of states  $\lambda$  with very nearly the same frequency. Under these circumstances, the summation can be replaced by an integral

$$\sum_{\lambda} \rightarrow \iint N(\omega) d\omega d\Omega \quad (171)$$

where  $N(\omega)$  represents the density of states [see Eq. (107)]. Equation (170) then becomes

$$\gamma = \frac{2i}{\hbar} \left[ \frac{1}{\hbar} \iint |\langle H' \rangle|^2 N(\omega) J(\omega) d\omega d\Omega \right] \quad (172)$$

where

$$J(\omega) = \frac{1 - \exp[i(\omega_0 - \omega)t + \gamma t/2]}{(\omega_0 - \omega) - i\gamma/2} \quad (173)$$

---

<sup>13</sup> It should be mentioned that the present treatment is consistent with the treatment given in Sec. 27.4. Indeed in Sec. 27.4 we have shown that  $A$  (as given by Eq. (111)) represents the probability for unit time for the spontaneous emission to occur from which the decay given by Eq. (108) follows with  $\gamma = A$ ; this is explicitly shown later [see Eqs (178) and (179)].

We will assume that  $\gamma \ll \omega_0$ ; i.e. the inverse of the lifetime ( $\leq 10^9 \text{ s}^{-1}$ ) is much smaller than the characteristic frequencies ( $\sim 10^{15} \text{ s}^{-1}$ ), this will indeed follow from the final result. Under this assumption  $\gamma$  can be neglected in Eq. (173) to obtain

$$\begin{aligned} J &\simeq \frac{1 - e^{i(\omega_0 - \omega)t}}{\omega_0 - \omega} \\ &\simeq \frac{1 - \cos[(\omega_0 - \omega)t]}{(\omega_0 - \omega)} - i \frac{\sin[(\omega_0 - \omega)t]}{(\omega_0 - \omega)} \end{aligned} \quad (174)$$

The first term has very rapid variation around  $\omega \simeq \omega_0$  and gives negligible contribution to any integral over  $\omega$  except around  $\omega \simeq \omega_0$  where the function itself vanishes. Thus this term will lead to a small imaginary value of  $\gamma$ . We are in any case interested in the real part of  $\gamma$  (which would give the lifetime, etc.) which will be given by

$$\gamma \simeq \frac{2}{\hbar} \left[ \frac{1}{\hbar} \int |\langle H' \rangle|^2 N(\omega_0) d\Omega \int_{-\infty}^{+\infty} \frac{\sin(\omega_0 - \omega)t}{(\omega_0 - \omega)} d\omega \right] \quad (175)$$

We have made two approximations here. First, we have pulled out factors which are essentially constant in the neighborhood of  $\omega \simeq \omega_0$ . Secondly, the limits of the integral have been taken from  $-\infty$  to  $+\infty$  since in any case the contribution vanishes except around  $\omega_0$ . Thus

$$\begin{aligned} \gamma &\simeq \frac{2\pi}{\hbar} \left[ \frac{1}{\hbar} \int |\langle H' \rangle|^2 N(\omega_0) d\Omega \right] \\ &= \frac{2\pi}{\hbar} \frac{1}{\hbar} \frac{V\omega_0^2}{8\pi^3 c^3} \int |\langle H' \rangle|^2 d\Omega \end{aligned} \quad (176)$$

Now

$$\begin{aligned} \langle H' \rangle &= \langle a\lambda | H' | 1 \rangle \\ &= \left\langle a; 0, 0, \dots 1_\lambda, 0, \dots | \frac{q}{m} \sum_\lambda \left( \frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} \right. \\ &\quad \times [a_\lambda e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} + \bar{a}_\lambda e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}}] \hat{\mathbf{e}}_\lambda \cdot \mathbf{p} | b, 0, 0, \dots 0_\lambda \dots \rangle \\ &= iq \left( \frac{\hbar\omega_\lambda}{2\epsilon_0 V} \right)^{1/2} \langle a | \mathbf{r} | b \rangle \cdot \hat{\mathbf{e}}_\lambda \end{aligned} \quad (177)$$

where in the last step we have used the dipole approximation (see the discussion after Eq. (97)). On substitution in Eq. (176), we get

$$\gamma \simeq \frac{1}{2\pi} \left[ \frac{q^2}{4\pi\epsilon_0 \hbar c} \right] \frac{\omega_0^3}{c^2} \int |\hat{\mathbf{e}}_\lambda \cdot \langle a | \mathbf{r} | b \rangle|^2 d\Omega \quad (178)$$

(cf. Eq. (110)). On carrying out the integration and summing over the two states of polarization we get [see Eq. (111)],

$$\gamma = A \quad (179)$$

i.e.  $\gamma$  is simply the Einstein  $A$  coefficient corresponding to spontaneous emissions as it indeed should be!

Now the probability of a photon being emitted in the mode  $\lambda$  is given by [see Eq. (169)]:

$$|C_{a\lambda}(t = \infty)|^2 = \frac{|(H')|^2}{\hbar^2} \frac{1}{(\omega_0 - \omega_\lambda)^2 + \gamma^2/4} \quad (180)$$

If we multiply the above equation by  $N(\omega) d\omega d\Omega$  which gives the number of modes in the frequency interval  $\omega$  to  $\omega + d\omega$  and in the solid angle  $d\Omega$  and carry out the integration over  $d\Omega$  and sum over the two states of polarization, we would get

$$g(\omega) d\omega = \frac{\gamma}{2\pi} \frac{d\omega}{(\omega_0 - \omega)^2 + \gamma^2/4} \quad (181)$$

where we have used Eq. (178). The above equation indeed gives us the probability that the spontaneously emitted photon has its frequency between  $\omega$  and  $\omega + d\omega$ , which is nothing but the Lorenzian line shape. Notice that the above expression is normalized which implies that the probability that the atom makes a spontaneous transition from the upper state to the lower state is unity (as  $t \rightarrow \infty$ ) as it indeed should be.

### Solution 27.6

$$\begin{aligned} \langle \alpha | N_{op} | \alpha \rangle &= e^{-|\alpha|^2} \sum_m \frac{\alpha^{*m}}{\sqrt{m!}} \left\langle m \left| \sum_n \frac{\alpha^n}{\sqrt{n!}} n \right| n \right\rangle \\ &\quad (\text{because } N_{op}|n\rangle = n|n\rangle; \text{ see Sec. 12.7}) \\ &= e^{-|\alpha|^2} \sum_n \frac{|\alpha|^{2n} n}{n!} \\ &= Ne^{-N} \sum_{n=1}^{\infty} \frac{N^{n-1}}{(n-1)!} = N \end{aligned} \quad (182)$$

Similarly

$$\begin{aligned} \langle \alpha | N_{op}^2 | \alpha \rangle &= e^{-N} \sum_n \frac{N^n n^2}{n!} = Ne^{-N} \sum_n \frac{N^{n-1} (n-1+1)}{(n-1)!} \\ &= N^2 + N \end{aligned} \quad (183)$$

from which Eq. (148) follows.

**Solution 27.8** The differential cross-section  $d\sigma$  is given by (see Sec. 25.3)

$$cn \ d\sigma = w \ d\Omega \quad (184)$$

where  $w \ d\Omega$  represents the probability (per unit time) of scattering into the solid angle  $d\Omega$  and  $n$  is the number of photons per unit volume corresponding to one photon in a box of volume,  $V$  i.e.

$$n = \frac{1}{V} \quad (185)$$

Further,  $w \ d\Omega$  is given by the goldenrule (see Eq. (38) of Chapter 25):

$$w \ d\Omega = \frac{2\pi}{\hbar} N(E) \ d\Omega |\langle f | H' | i \rangle|^2 \quad (186)$$

where  $N(E)$  represents the density of states and for the neutron-proton system in a final state of relative momentum  $\mathbf{p}$ , it is given by (see Appendix M).

$$N(E) \ d\Omega = \frac{\mu V}{(2\pi \hbar)^3} p \ d\Omega \quad (187)$$

This  $N(E) \ d\Omega$  represents the number of states (per unit energy interval) such that the direction of  $\mathbf{p}$  lies within a solid angle  $d\Omega$  and  $\mu = M/2$  is the reduced mass of the  $n - p$  system. The kets  $|i\rangle$  and  $|f\rangle$  represent the initial and final states and since the initial state contains one photon and the final state none, we have [cf. Eq. (97)]

$$\langle f | H' | i \rangle \simeq \frac{q}{m} \left( \frac{\hbar}{2\epsilon_0 V \omega} \right)^{1/2} \hat{\mathbf{e}} \cdot \langle a | \mathbf{p} | b \rangle \quad (188)$$

where  $M$  is the proton mass. Thus

$$d\sigma = \frac{V \alpha}{4\pi \hbar^2 \omega M} p |\hat{\mathbf{e}} \cdot \langle a | \mathbf{p} | b \rangle|^2 \ d\Omega \quad (189)$$

where

$$\alpha = \frac{q^2}{4\pi \epsilon_0 \hbar c} \simeq \frac{1}{137}$$

is the fine structure constant and we have used the fact that  $\mu = M/2$ . Integration over all directions gives a factor  $4\pi/3$  thus

$$\sigma = \frac{1}{3} \alpha \frac{p V}{\hbar^2 \omega M} |\langle a | \mathbf{p} | b \rangle|^2 \quad (190)$$

The two states are given by

$$|b\rangle = \sqrt{\frac{K}{2\pi}} \frac{e^{-Kr}}{r} \quad (191)$$

$$|a\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \quad (192)$$

The final state corresponds to a free neutron-proton system. We must remember that in Eq. (190),  $\mathbf{p}$  is the operator  $-i\hbar\nabla$ . The integration, however, poses no problem because<sup>14</sup>

$$\begin{aligned} |\langle a | \mathbf{p} | b \rangle|^2 &= |\langle b | \mathbf{p} | a \rangle|^2 \\ &= p^2 |\langle b | a \rangle| \\ &= p^2 \frac{K}{2\pi V} \left| \int \frac{e^{-Kr}}{r} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} r^2 dr \sin\theta d\theta d\phi \right|^2 \\ &= \frac{Kp^2}{2\pi V} (2\pi)^2 \left| \int_0^\infty \int_0^\pi e^{-Kr} e^{ipr \cos\theta/\hbar} r dr \sin\theta d\theta \right|^2 \end{aligned}$$

where we have chosen the polar axis along  $\mathbf{p}$ . Carrying out the integrations, we get

$$\sigma = \frac{8\pi}{3} \frac{\alpha}{M \hbar^2 \omega} \frac{p^3 K}{(p^2/\hbar^2 + K^2)^2} \quad (193)$$

If  $B$  is the binding energy of the deuteron, then

$$\hbar\omega - B = p^2/M \quad (194)$$

(This relation is slightly incorrect since the incident quantum carries a momentum  $\hbar\omega/c$  which will give the center of mass some energy as well). Also it can be shown that the binding energy is related to the parameter  $K$  though the equation  $\hbar K = (MB)^{1/2}$ . We have finally

$$\sigma \simeq \frac{8\pi}{3} \alpha \frac{\hbar^2}{M} \frac{B^{1/2} (\hbar\omega - B)^{3/2}}{(\hbar\omega)^3} \quad (195)$$

The above equation gives the cross-section for photodisintegration of deuteron corresponding to the electric dipole moment interaction and is in good agreement with the experimental data at high  $\gamma$ -ray energies (see e.g. Ref. 6 for a good discussion on comparison with experimental data).

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<sup>14</sup> Notice that the final state is an eigenstate of  $\mathbf{p}$ , i.e.

$$\mathbf{p} \exp\left(\frac{i\mathbf{p}\cdot\mathbf{r}}{\hbar}\right) = -i\hbar\nabla \exp\left(\frac{i\mathbf{p}\cdot\mathbf{r}}{\hbar}\right) = \mathbf{p} \exp[i\mathbf{p}\cdot\mathbf{r}/\hbar]$$

where on the right-hand side,  $\mathbf{p}$  is simply a number.

**Solution 27.9**

$$\begin{aligned} \sum_s (E_s - E_n) |\langle s | x | n \rangle|^2 &= \sum_s (E_s - E_n) \langle n | x | s \rangle \langle s | x | n \rangle \\ &= \sum_s \langle n | x H_a - H_a x | s \rangle \langle s | x | n \rangle \\ &\quad (\text{see Eqs. 15 and 16}) \end{aligned}$$

$$\begin{aligned} &= \frac{i \hbar}{m} \sum_s \langle n | p_x | s \rangle \langle s | x | n \rangle \quad (\text{using Eq. 17}) \\ &= \frac{i \hbar}{m} \langle n | p_x x | n \rangle \\ &\quad (\text{because } \sum_s |s\rangle \langle s| = 1) \end{aligned} \tag{196}$$

We could also write

$$\begin{aligned} \sum_s (E_s - E_n) |\langle s | x | n \rangle|^2 &= \sum_s \langle n | x | s \rangle \langle s | H_a x - x H_a | n \rangle \\ &= -\frac{i \hbar}{m} \langle n | x p_x | n \rangle \end{aligned} \tag{197}$$

Thus

$$\begin{aligned} \sum_s (E_s - E_n) |\langle s | x | n \rangle|^2 &= -\frac{i \hbar}{2m} \langle n | x p_x - p_x x | n \rangle \\ &= \hbar^2 / 2m \end{aligned}$$

This can be generalized to more than one electron in which case we get

$$\sum_i \sum_s (E_s - E_n) |\langle s | x_i | n \rangle|^2 = \frac{\hbar^2}{2m} Z \tag{198}$$

where  $Z$  is the atomic number. Equation (198) is referred as the dipole sum rule or sometime also as the Thomas–Reiche–Kuhn sum rule. The factors

$$\frac{2m}{\hbar^2} (E_s - E_n) |\langle s | x | n \rangle|^2 = f_{sn} \tag{199}$$

are called oscillator strengths. The reason for this terminology is that classically,  $f_{sn}$  gives the number of electrons moving with oscillator frequency  $\omega_{sn}$ . The quantum mechanical result (199) shows that they need not be integers.

**(b)** We start with the formula for the cross-section in the dipole approximation [see Eq. (184)–(186)]:

$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar} \frac{N(E)}{c/V} |\langle f | H' | i \rangle|^2 \tag{200}$$

or,

$$\frac{d\sigma}{d\Omega} = 4\pi^2\alpha (E_s - E_n) |\hat{\mathbf{e}} \cdot \langle s | \mathbf{r} | n \rangle|^2 N(E) \quad (201)$$

If we integrate this over dE, the right-hand side of Eq. (201) may be regarded as sum over final states to give

$$\int \sigma dE = 4\pi^2\alpha \sum_s (E_s - E_n) |\langle s | \hat{\mathbf{e}} \cdot \mathbf{r} | n \rangle|^2 \quad (202)$$

We consider a beam of photons with a fixed linear polarization, say  $\hat{\mathbf{e}}$  along the  $x$ -direction. We then have

$$\begin{aligned} \int \sigma dE &= 4\pi^2\alpha \sum_s (E_s - E_n) |\langle s | x | n \rangle|^2 \\ &= \frac{2\pi^2\alpha \hbar^2}{m} \end{aligned} \quad (203)$$

**Solution 27.10** For the electron initially in the  $K$  shell (ejection from which is comparatively probable), the initial wave function is given by

$$\psi_i = \left( \frac{1}{\pi a^3} \right)^{1/2} e^{-r/a} \quad (204)$$

where

$$a = \frac{a_0}{Z} = \frac{\hbar^2}{m} \left( \frac{4\pi\epsilon_0}{q^2} \right) \frac{1}{Z} \quad (205)$$

For the evaluation of the matrix element the assumption will be made that  $\hbar\omega$  is much larger than the ionization potential of the atom so that to a good approximation, the final state can be represented by

$$\psi_f = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_1 \cdot \mathbf{r}} \quad (206)$$

where  $\mathbf{k}_1$  represents the electron wave vector; we have put a subscript to  $\mathbf{k}$  so that there is no confusion with the wave vector associated with the electromagnetic wave [see Eq. (208)]. Now the perturbing potential may be taken as [see Eq. (7)]

$$H' = \frac{q}{m} \mathbf{A} \cdot \mathbf{p} \quad (207)$$

where

$$\mathbf{A} = \hat{\mathbf{e}} A_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \text{cc} \quad (208)$$

or

$$\mathbf{A} = 2\hat{\mathbf{e}} |A_0| \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi) \quad (209)$$

In Eq. (208) “cc” denotes the complex conjugate of the first term so that  $\mathbf{A}$  is necessarily real. Now, according to first-order perturbation theory, the amplitude of the final state at time  $t$  is given by [see Eq. (14) of Chapter 25]

$$\begin{aligned} C_f(t) &= \frac{1}{i\hbar} \int_0^t H'_{fi}(t') e^{i\omega_f t'} dt' \\ &= \frac{M_1}{\hbar} \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi} - \omega)} + \frac{M_2}{\hbar} \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi} + \omega)} \end{aligned} \quad (210)$$

where

$$M_1 = -\frac{iqA_0}{m}\hat{\mathbf{e}} \cdot \int \psi_f^* e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{p} \psi_i d\tau$$

and

$$M_1 = -\frac{iqA_0^*}{m}\hat{\mathbf{e}} \cdot \int \psi_f^* e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{p} \psi_i d\tau$$

As discussed in Sec. 25.3, the first term on the RHS of Eq. (210) contributes in an absorption process and the second term contributes in an emission process. Since we are interested in an absorption of a photon, we have [cf. Eq. (16) of Chapter 25]

$$P_f(t) = |C_f(t)|^2 = |M_1|^2 \frac{1}{\hbar^2} \left[ \frac{\sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right]^2 \quad (211)$$

Following a procedure similar to that discussed in Sec. 24.2, we get the following expression for the transition probability to solid angle  $d\Omega$ :

$$W d\Omega = \frac{2\pi}{\hbar} |M_1|^2 N(E) d\Omega \quad (212)$$

where

$$N(E) d\Omega = \frac{mk_1 V}{8\pi^3 \hbar^2} d\Omega \quad (213)$$

represents the density of final states (see Appendix M). Thus

$$W d\Omega = \frac{2\pi}{\hbar} \cdot \frac{mk_1 V}{8\pi^3 \hbar^2} \cdot |M_1|^2 d\Omega \quad (214)$$

Now, the electric field associated with the electromagnetic wave is given by

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} = -2\omega |A_0| \hat{\mathbf{e}} \sin(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi)$$

The time averaged energy density is given by (see Eq. 46)

$$\epsilon_0 4\omega^2 |A_0|^2 \cdot \frac{1}{2}$$

Thus

$$\text{Incident Intensity} = 2\epsilon_0\omega^2 c |A_0|^2$$

and

$$\text{Incident Flux} = \frac{\text{Incident Intensity}}{\hbar\omega} = \frac{2\epsilon_0\omega c}{\hbar} |A_0|^2 \quad (215)$$

Hence

$$d\sigma = \frac{W d\Omega}{\text{Incident Flux}}$$

or

$$\frac{d\sigma}{d\Omega} = \frac{mk_1 V}{8\pi^2 \hbar^2 \epsilon_0 \omega c |A_0|^2} |M_1|^2 \quad (216)$$

Now

$$M_1 = -\frac{iq}{m} A_0 \frac{1}{V^{1/2}} \hat{\mathbf{e}} \cdot \int e^{-i\mathbf{k}_1 \cdot \mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{p} \psi_i d\tau$$

But

$$\begin{aligned} \int \phi p_x \psi d\tau &= -i\hbar \int \phi \frac{\partial \psi}{\partial x} d\tau = i\hbar \int \psi \frac{\partial \phi}{\partial x} d\tau \\ &= - \int \psi p_x \phi d\tau \end{aligned}$$

Thus

$$\int \phi \mathbf{p} \psi d\tau = - \int \psi \mathbf{p} \phi d\tau = i\hbar \int \psi \nabla \phi d\tau \quad (217)$$

This also follows from the Hermitian property of  $\mathbf{p}$  (see Problem 8.14). Using Eq. (217) we get

$$\begin{aligned} M_1 &= \frac{q\hbar}{m} A_0 \frac{1}{V^{1/2}} \hat{\mathbf{e}} \cdot \int \psi_i \nabla e^{i(\mathbf{k}_1 - \mathbf{k}) \cdot \mathbf{r}} d\tau \\ &= -\frac{iq\hbar A_0}{m} (\hat{\mathbf{e}} \cdot \mathbf{k}_1) \frac{1}{V^{1/2}} \int \left[ \frac{1}{\pi a^3} \right]^{1/2} \\ &\quad \times \exp \left[ -i\mathbf{K} \cdot \mathbf{r} - \frac{r}{a} \right] d\tau \end{aligned} \quad (218)$$

where we have used the transverse character of light waves (i.e.  $\hat{\mathbf{e}} \cdot \mathbf{k} = 0$ ) and

$$\mathbf{K} = \mathbf{k}_1 - \mathbf{k} \quad (219)$$

is the momentum transfer in units of  $\hbar$ . In carrying out the integration, we choose the polar axis along  $\mathbf{K}$  to obtain an expression for  $|M_1|^2$  which on substitution in Eq. (216) gives

$$\frac{d\sigma}{d\Omega} = 32\alpha \frac{\hbar k_1}{m\omega} (\hat{\mathbf{e}} \cdot \mathbf{k}_1)^2 \left( \frac{Z}{a_0} \right)^5 \left[ \left( \frac{Z}{a_0} \right)^2 + K^2 \right]^{-4} \quad (220)$$

where  $\alpha$  is the fine structure constant. The above expression is in agreement with the experimental data. For a more thorough treatment of the photoelectric effect, see Ref. 3 p. 21.

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### 27.10. References and suggested reading

1. H. Goldstein, *Classical Mechanics*, Addison-Wesley Publishing Co., Reading, Massachusetts (1950).
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4. F.T. Arecchi, Quantum Optics and Photon Statistics, in *Lasers and Their Applications*, (A. Sona, ed.), p. 497, Gordon and Breach, New York (1976).
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6. H.A. Bethe and P. Morrison, *Elementary Nuclear Theory*, John Wiley, New York (1956).

# Chapter 28

## Relativistic Theory

*The new theories, if one looks apart from their mathematical setting, are built up from physical concepts which cannot be explained in terms of things previously known to the student, which cannot even be explained adequately in words at all.*

— P. A. M. DIRAC in the Preface to the first edition of The Principles of Quantum Mechanics

### 28.1. Introduction

The quantum theory developed so far is non-relativistic. That it is not invariant under Lorentz transformations is obvious if one notes that the time dependent Schrödinger equation contains the first derivative in time and second derivatives in space coordinates. A simple procedure for building a relativistic theory is to follow an approach analogous to the one followed for the non-relativistic theory which is to start with the Hamiltonian formulation, with a relativistically correct Hamiltonian, and to replace the classical observables by operators. This is essentially the procedure we adopt in this chapter. From the point of view of specific predictions, the non-relativistic theory fails in some major features. It fails to explain the spin of an elementary system, such as the electron, and the consequences thereof. Moreover, the theory cannot give a satisfactory account of high energy phenomena such as pair production, bremsstrahlung, etc.

### 28.2. The Klein-Gordon equation

We start with the relativistic Hamiltonian for a free particle

$$H = \sqrt{c^2 p^2 + m^2 c^4} \quad (1)$$

where  $\mathbf{p}$  is the momentum,  $m$  the rest mass. Introducing the operators

$$E \rightarrow i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad \mathbf{p} \rightarrow -i\hbar \nabla$$

and writing  $H\psi = E\psi$  we obtain

$$[-c^2\hbar^2\nabla^2 + m^2c^4]^{1/2}\psi = i\hbar\frac{\partial\psi}{\partial t}$$

an equation beyond which theory can proceed only if we have a consistent scheme for interpreting the square root of the above operator. This can be done but leads to difficulties. (see, e.g., Ref. 1). We avoid them by squaring Eq. (1) and replacing by the operators to obtain

$$(-c^2\hbar^2\nabla^2 + m^2c^4)\psi = -\hbar^2\frac{\partial^2\psi}{\partial t^2}$$

Dividing by  $c^2\hbar^2$  and rearranging the terms, we obtain the Klein-Gordon equation

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right)\psi = 0 \quad (2)$$

The Klein-Gordon equation, it turns out, is the correct one for spinless particles and not for electrons. Although this equation is an important one for further developments of relativistic field theories, we shall not discuss it further here. The reason is that the equation is valid for certain classes of particles such as the  $\pi$ - and  $K$ -mesons which are strongly interacting. The approximation methods of elementary quantum mechanics, such as the perturbation theory, are usually inadequate for these anyway.

### 28.3. The Dirac equation

In this section we will discuss the Dirac equation and in subsequent sections of this chapter we will give some simple consequences of the Dirac equation; for more thorough treatments we refer the reader to References 1–8. The original argument of Dirac, in search of a relativistic equation was that it must be a first-order differential equation in time because knowledge of the wave-function alone at an initial time  $t_0$  should suffice to predict its value at a later time. Since in relativity, time and space coordinates are treated symmetrically, the equation (he argued) must be a first-order differential equation in space coordinates as well. Dirac started with a Hamiltonian of the form

$$H = c(\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z) + \beta mc^2 \quad (3)$$

where the coefficients  $\alpha_1, \alpha_2, \alpha_3$  and  $\beta$  are not mere numbers but (square) matrices. For brevity, we shall often write Eq.(3) as

$$H = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2$$

It must be clear that  $\alpha$  is not to be thought of as a vector;  $\alpha \cdot \mathbf{p}$  is defined to be equal to  $\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z$ . The wave equation corresponding to this Hamiltonian is

$$i\hbar \frac{\partial \psi}{\partial t} = -i\hbar c(\alpha \cdot \nabla \psi) + \beta mc^2 \psi \quad (4)$$

Since  $\alpha$  and  $\beta$  are allowed to be matrices of numbers, it follows that the wavefunction  $\psi$  must have more than one component; i.e., at each point the state of the particle will be described by more than one wavefunction. It follows that Eq.(4) will be capable of describing a particle with additional intrinsic degrees of freedom. The Hamiltonian given by Eq. (3) must still satisfy the energy-momentum relation

$$E^2 = H^2 = c^2 p^2 + m^2 c^4 \quad (5)$$

We introduce the notation

$$p_1 = p_x, \quad p_2 = p_y, \quad p_3 = p_z, \quad p_4 = iE/c$$

$$x_1 = x, \quad x_2 = y, \quad x_3 = z, \quad \text{and} \quad x_4 = +ict.$$

Thus Eq.(3) becomes

$$H = c \sum_{j=1}^3 \alpha_j p_j + \beta mc^2$$

and

$$\begin{aligned} H^2 &= c^2 \left\{ \sum_j \sum_k (\alpha_j \alpha_k + \alpha_k \alpha_j) p_j p_k + \sum_{j=3}^3 \alpha_j^2 p_j^2 \right. \\ &\quad \left. + mc^3 \sum_{j=1}^3 (\alpha_j \beta + \beta \alpha_j) p_i + m^2 c^4 \beta^2 \right\} \end{aligned} \quad (6)$$

Equations (5) and (6) are consistent if

$$\alpha_j \alpha_k + \alpha_k \alpha_j = 0 \quad (\text{for } j \neq k) \quad (7)$$

$$\alpha_j \beta + \beta \alpha_j = 0 \quad (8)$$

$$\alpha_j^2 = 1 \quad (9)$$

and

$$\beta^2 = 1 \quad (10)$$

Since Eqs.(7)-(10) are to be matrix relations, the symbols 0 and 1 on the right ought to be regarded as the null matrix and the unit matrix respectively.

We first show that these matrices must be of even dimension. We have for example,

$$\alpha_1 \beta = -\beta \alpha_1$$

Multiplying by  $\alpha_1$  on the left, setting  $\alpha_1^2 = 1$  and taking the trace, we obtain

$$\text{Trace } \beta = -\text{Trace}(\alpha_1 \beta \alpha_1) = -\text{Trace}(\alpha_1^2 \beta) = -\text{Trace } \beta$$

where we have used the result  $\text{Trace}(ABC) = \text{Trace}(CAB)$ . We therefore have  $\text{Trace } \beta = 0$ , a result which applies to each of the  $\alpha$  matrices as well. Equations (9) and (10) also tell us that the eigenvalues of the matrices must be  $\pm 1$ . Since the trace is just the sum of all eigenvalues, it follows that the  $+1$  and  $-1$  eigenvalues must occur the same number of times. Hence each of the matrices must be of even dimension  $N$ . Now  $N$  cannot be 2, since we can only have three  $2 \times 2$  independent non-commuting matrices. We shall see that  $4 \times 4$  matrices satisfy all the conditions.

We may mention here that the Pauli spin matrices are given by (see Sec. 13.4)

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (11)$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (12)$$

and

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (13)$$

We can readily see that

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \quad (14)$$

where the RHS represents the unit matrix. Further, the spin matrices satisfy the anticommutative relation [cf. Eqs. (8) and (9)]

$$\left. \begin{array}{l} \sigma_x \sigma_y + \sigma_y \sigma_x = 0 \\ \sigma_y \sigma_z + \sigma_z \sigma_y = 0 \\ \sigma_z \sigma_x + \sigma_x \sigma_z = 0 \end{array} \right\} \quad (15)$$

Comparing Eqs. (14) and (15) with Eqs. (7)–(10), we may choose the following representation for the  $\alpha$  and  $\beta$  matrices:

$$\alpha_1 = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad (16)$$

$$\alpha_2 = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix} \quad (17)$$

$$\alpha_3 = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \quad (18)$$

and

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad (19)$$

Obviously, each element of the  $2 \times 2$  matrices shown above is itself a  $2 \times 2$  matrix. One can immediately see that the above matrices satisfy Eqs.(7)–(10). For example,

$$\alpha_1\alpha_3 + \alpha_3\alpha_1 = \begin{pmatrix} 0 & \sigma_x\sigma_z + \sigma_z\sigma_x \\ \sigma_x\sigma_z + \sigma_z\sigma_x & 0 \end{pmatrix}$$

where the RHS is indeed a  $4 \times 4$  null matrix. Equations (16)–(18) can be written as

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\alpha} \\ \boldsymbol{\alpha} & 0 \end{pmatrix} \quad (20)$$

We note that all these matrices are Hermitian, i.e.,

$$\alpha_j^\dagger = \alpha_j, \quad \beta^\dagger = \beta$$

Now, Eq. (4) can be written as

$$-\frac{\partial \psi}{\partial x_4} = -i\alpha \cdot \nabla \psi + \beta \frac{mc}{\hbar} \psi$$

Multiplying by  $\beta$  on the left side, we have

$$-i\beta\alpha \cdot \nabla \psi + \beta \frac{\partial \psi}{\partial x_4} + \frac{mc}{\hbar} \psi = 0$$

We define the following four  $\gamma$  matrices.

$$\gamma_j = -i\beta\alpha_j; \quad j = 1, 2, 3$$

and

$$\gamma_4 = \beta$$

Note that these  $\gamma$  matrices are also Hermitian, i.e.,  $\gamma_\mu^\dagger = \gamma_\mu$ . The Dirac equation now takes the form

$$\left( \sum_{\mu=1}^4 \gamma_\mu \frac{\partial}{\partial x_\mu} + \kappa \right) \psi = 0 \quad (21)$$

where  $\kappa = mc/\hbar$ . It is usual to drop the summation over the repeated index  $\mu$  and write simply

$$\gamma_\mu \frac{\partial \psi}{\partial x_\mu} + \kappa \psi = 0$$

(A convention we shall adopt is to use Greek indices  $\lambda, \mu, \nu$ , etc., when their values range 1 to 4 and Roman ones  $i, j, k$ , etc for values ranging from 1 to 3). In terms of the momentum operator, we can write

$$(\gamma_\mu p_\mu - imc)\psi = 0 \quad (22)$$

Equations (21) and (22) are the covariant forms of Dirac equation; they do not appear to single out the space and time parts. However, writing them in those forms does not automatically guarantee that the equation is covariant under Lorentz transformations.

We may mention here that the above equations are meaningful only if we interpret  $\psi$  as a 4-row, 1-column matrix (i.e., a spinor with 4 components). Equation (22) is a shorthand for the four equations ( $\lambda = 1, 2, 3, 4$ )

$$\sum_{\mu=1}^4 \sum_{\sigma=1}^4 \{(\gamma_\mu)_{\lambda\sigma} p_\mu - imc\delta_{\lambda\sigma}\} \psi_\sigma = 0 \quad (23)$$

where  $(\gamma_\mu)_{\lambda\sigma}$  is the  $\lambda\sigma$ th component of the matrix  $\gamma_\mu$  and  $\delta_{\lambda\sigma}$  is the  $\lambda\sigma$ th component of the unit matrix. The summation over  $\mu$  runs over 4-terms because these are 4 space-time components. On the other hand,  $\lambda$  and  $\sigma$  takes values 1 to 4 because the Dirac matrices happen to be 4-dimensional. Thus, if one is not alert, there can be some confusion in the algebraic work. It is never really necessary to write the equation in this elaborate form, but if ever in doubt, the reader is advised to write it out in full.

## 28.4. Probability and current density

We introduce the Hermitian conjugate (adjoint) matrix  $\psi^\dagger = (\psi_1^* \psi_2^* \psi_3^* \psi_4^*)$  which is a 1-row 4-column matrix. Multiplying Eq. (4) on the left by  $\psi^\dagger$ , we have

$$i\hbar\psi^\dagger(\partial\psi/\partial t) = -i\hbar c\psi^\dagger\boldsymbol{\alpha} \cdot \nabla\psi + mc^2\psi^\dagger\beta\psi \quad (24)$$

Similarly, starting with the adjoint of Eq. (4),

$$-i\hbar(\partial\psi^\dagger/\partial t) = i\hbar c\nabla\psi^\dagger \cdot \boldsymbol{\alpha} + mc^2\psi^\dagger\beta \quad (25)$$

(recall that  $\alpha, \beta$  are Hermitian) and after multiplying by  $\psi$ , we obtain

$$-i\hbar(\partial\psi^\dagger/\partial t)\psi = i\hbar c\nabla\psi^\dagger \cdot \boldsymbol{\alpha}\psi + mc^2\psi^\dagger\beta\psi \quad (26)$$

Subtracting (26) from (24), we can obtain the following:

$$\partial(\psi^\dagger\psi)/\partial t + c\nabla \cdot (\psi^\dagger\alpha\psi) = 0 \quad (27)$$

The above equation can be written in the form of the continuity equation

$$\frac{\partial\rho}{\partial t} + \nabla \cdot \mathbf{j} = \mathbf{0} \quad (28)$$

provided we make the identification

$$\rho = \psi^\dagger\psi = \sum_{\lambda=1}^4 \psi_\lambda^*\psi_\lambda \quad (29)$$

and

$$\mathbf{j} = c\psi^\dagger\alpha\psi = c \sum_{\lambda,\sigma=1}^4 \psi_\lambda^*(\alpha)_{\lambda\sigma}\psi_\sigma \quad (30)$$

## 28.5. An identity

In this section we will prove the identity

$$(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) \quad (31)$$

which will be extensively used in this chapter. In the above equation  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$  represent the Pauli spin matrices and components of  $\mathbf{A}$  and  $\mathbf{B}$  are assumed to commute with components of  $\boldsymbol{\sigma}$ ; however, components of  $\mathbf{A}$  need not commute with components of  $\mathbf{B}$ . Now

$$\begin{aligned} (\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) &= (\sigma_x A_x + \sigma_y A_y + \sigma_z A_z)(\sigma_x B_x + \sigma_y B_y + \sigma_z B_z) \\ &= (A_x B_x + A_y B_y + A_z B_z) + i\sigma_x(A_y B_z - A_z B_y) + \dots + \dots \end{aligned}$$

where we have used the relations

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$$

and

$$\sigma_x\sigma_y = -\sigma_y\sigma_x = i\sigma_z \text{ etc.}$$

Thus

$$\begin{aligned} (\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) &= \mathbf{A} \cdot \mathbf{B} + i[\sigma_x(\mathbf{A} \times \mathbf{B})_x + \sigma_y(\mathbf{A} \times \mathbf{B})_y + \dots] \\ &= \mathbf{A} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) \end{aligned}$$

proving the identity.

## 28.6. Plane wave solutions

We start with the free particle Dirac equation:

$$(c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2)\psi(\mathbf{r}, t) = \hat{E}(\mathbf{r}, t)\psi(\mathbf{r}, t) \quad (32)$$

where we have explicitly indicated that  $\hat{\mathbf{p}}$  and  $\hat{E}$  are the operators. We try plane wave solutions

$$\psi(\mathbf{r}, t) = \chi \exp\left[\frac{i}{\hbar}(\mathbf{p} \cdot \mathbf{r} - Et)\right] \quad (33)$$

where  $\mathbf{p}$  and  $E$  are now numbers, not operators and the  $\chi$  are spinors. Clearly Eq.(32) is satisfied if  $\chi$  obeys the equation

$$(c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2)\chi = E\chi \quad (34)$$

Again in Eq. (34),  $\mathbf{p}$  and  $E$  are now numbers. Since  $\alpha$  and  $\beta$  can be conveniently expressed in terms of  $2 \times 2$  matrices, we start by writing

$$\chi = \begin{pmatrix} u \\ v \end{pmatrix}$$

where  $u, v$  are themselves 2-component spinors. Using Eqs. (19) and (20), we obtain

$$\left( c \begin{pmatrix} 0 & \boldsymbol{\sigma} \cdot \mathbf{p} \\ \boldsymbol{\sigma} \cdot \mathbf{p} & \mathbf{0} \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 \right) \begin{pmatrix} u \\ v \end{pmatrix} = E \begin{pmatrix} u \\ v \end{pmatrix} \quad (35)$$

We can recover the four equations, if we want, by writing

$$u = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}, \quad v = \begin{pmatrix} u_3 \\ u_4 \end{pmatrix}$$

after solving for  $u$  and  $v$ . Equation (35) gives

$$c\boldsymbol{\sigma} \cdot \mathbf{p}v = (E - mc^2)u \quad (36)$$

$$c\boldsymbol{\sigma} \cdot \mathbf{p}u = (E - mc^2)v \quad (37)$$

We can decouple  $u, v$  by solving (say) for  $v$  from (37) and substituting in (36). This gives us

$$v = \frac{c\boldsymbol{\sigma} \cdot \mathbf{p}}{E + mc^2}u \quad (38)$$

and

$$\frac{c^2(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p})}{E + mc^2}u = (E - mc^2)u$$

Since

$$\sigma \cdot \mathbf{p} \sigma \cdot \mathbf{p} = p^2 \quad (\text{a number})$$

[see Eq. (31)], we have

$$c^2 p^2 u = (E^2 - m^2 c^4) u \quad (39)$$

Apart from the trivial solution  $u = 0$  (and hence  $v = 0$ ) we have the result

$$E = \pm \sqrt{c^2 p^2 + m^2 c^4} = E_{\pm} \quad (40)$$

We note that for small momenta [see Eqs. (36) and (37)]

$$|v| \sim \frac{cp}{2mc^2} |u| \sim \frac{V}{2c} |u| \quad (\text{for } E = E_+)$$

and

$$|u| \sim \frac{V}{2c} |v| \quad (\text{for } E = E_-)$$

where  $V$  is the velocity of the particle. Thus, for positive energies,  $u$  are large components and for negative energies,  $v$  are large components. For  $E = E_+$ , we express  $v$  in terms of  $u$

$$v = \frac{c\sigma \cdot \mathbf{p}}{E_+ + mc^2} u \quad (41)$$

Similarly for  $E = E_-$ , we express  $u$  in terms of  $v$

$$u = \frac{c\sigma \cdot \mathbf{p}}{E_- - mc^2} v \quad (42)$$

We can obtain 4 linearly independent solutions from Eqs. (41) and (42) as follows. Writing

$$u = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{or} \quad u = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and substituting in (41), in turn, we obtain two solutions. For example,  $u = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  gives

$$\begin{aligned} v &= \begin{pmatrix} u_3 \\ u_4 \end{pmatrix} = \left( \frac{c}{E_+ + mc^2} \right) \begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_x \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \left( \frac{c}{E_+ + mc^2} \right) \begin{pmatrix} p_z \\ p_x + ip_y \end{pmatrix} \end{aligned}$$

This solution is therefore,

$$\chi_{\uparrow}^{+} = N \begin{pmatrix} u \\ v \end{pmatrix} = N \begin{pmatrix} 1 \\ 0 \\ cp_z/(E_+ + mc^2) \\ cp_+/ (E_+ + mc^2) \end{pmatrix} \quad (43)$$

The other solution for  $E = E_+$  can be constructed in the same way.

$$\chi_{\downarrow}^{+} = N \begin{pmatrix} 0 \\ 1 \\ cp_{-}/(E_{+} + mc^2) \\ -cp_z/(E_{+} + mc^2) \end{pmatrix} \quad (44)$$

Similarly, for  $E = E_-$ , we choose  $v = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$  in turn and substitute in (42) to obtain

$$\chi_{\uparrow}^{-} = N \begin{pmatrix} cp_z/(E_{-} - mc^2) \\ cp_{+}/(E_{-} - mc^2) \\ 1 \\ 0 \end{pmatrix}, \quad \chi_{\downarrow}^{-} = N \begin{pmatrix} cp_{-}/(E_{-} - mc^2) \\ -cp_z/(E_{-} - mc^2) \\ 0 \\ 1 \end{pmatrix}, \quad (45)$$

In these equations we have used the symbols

$$p_{\pm} = p_x \pm ip_y$$

and the normalization  $N$  is chosen to satisfy

$$\chi^{\dagger} \chi = 1$$

for each of the solutions. It is easily shown that

$$N = \left[ 1 + \frac{c^2 p^2}{(|E| + mc^2)^2} \right]^{1/2} \quad (46)$$

and the different solutions (34) are orthogonal,

$$\chi_a^{\dagger} \chi_b = 0$$

The complete plane wave solutions take the form

$$\psi_{p\sigma}(r, t) = \chi_{p\sigma} \exp \left[ \frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - Et) \right] \quad (47)$$

The suffix  $p$  is to tell us that we are dealing with plane waves of momentum  $p$  and the suffix  $\sigma$ .

## 28.7. The electron in an electromagnetic field

We modify the Dirac equation simply by replacing the operators

$$\mathbf{p} \text{ by } \mathbf{p} - Q\mathbf{A}$$

and

$$E \text{ by } E - Q\phi$$

where  $\mathbf{A}$  and  $\phi$  are the vector and scalar potentials (see Sections 20.2 and 20.3). The solutions will no longer be of the plane wave form. However, we still write

$$\psi(\mathbf{r}, t) = \begin{pmatrix} u(\mathbf{r}, t) \\ v(\mathbf{r}, t) \end{pmatrix}$$

and remember that the spinors  $u$  and  $v$  now incorporate the space-time dependence. Thus the Dirac equation can be written in the form

$$(c\boldsymbol{\alpha} \cdot (\mathbf{p} - Q\mathbf{A}) + \beta mc^2)\psi(\mathbf{r}, t) = (E - Q\phi)\psi(\mathbf{r}, t) \quad (48)$$

Using Eqs. (19) and (20), the above equation can be written in the form

$$c \begin{pmatrix} 0 & \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \\ \boldsymbol{\sigma} \cdot \boldsymbol{\pi} & 0 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} E - Q\phi - mc^2 & 0 \\ 0 & E - Q\phi + mc^2 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix}$$

where

$$\boldsymbol{\pi} \equiv \mathbf{p} - Q\mathbf{A} \quad (49)$$

Thus

$$c\boldsymbol{\sigma} \cdot \boldsymbol{\pi}v = (E - Q\phi - mc^2)u \quad (50)$$

and

$$c\boldsymbol{\sigma} \cdot \boldsymbol{\pi}u = (E - Q\phi + mc^2)v \quad (51)$$

We are interested in positive energy solutions and write

$$E = mc^2 + E' \quad (52)$$

where  $E'$  is the energy that appears in the (non-relativistic) Schrödinger equation. For small values of  $E'$  and  $Q\phi$  ( $\ll mc^2$ ), we may write

$$E - Q\phi + mc^2 \approx 2mc^2 \quad (53)$$

Thus Eq. (51) would give

$$v \approx \frac{1}{2mc}\boldsymbol{\sigma} \cdot \boldsymbol{\pi}u \quad (54)$$

Substituting in Eq. (50) we obtain for the large component

$$\frac{1}{2m}(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})u = (E' - Q\phi)u \quad (55)$$

If we now use the identity given by Eq. (31), we would get

$$(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) = \boldsymbol{\pi} \cdot \boldsymbol{\pi} + i\boldsymbol{\sigma} \cdot (\boldsymbol{\pi} \times \boldsymbol{\pi}) \quad (56)$$

Now

$$\begin{aligned}(\boldsymbol{\pi} \times \boldsymbol{\pi}) &= (\mathbf{p} - Q\mathbf{A}) \times (\mathbf{p} - Q\mathbf{A}) \\&= -Q(\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p})\end{aligned}$$

where we have used the fact that the components  $p_x$ ,  $p_y$  and  $p_z$  commute with each other; however, since  $\mathbf{p}$  is an operator,  $\mathbf{p} \times \mathbf{A} \neq -\mathbf{A} \times \mathbf{p}$ . Indeed

$$\begin{aligned}(\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p})_x \psi &= (p_y A_z - p_z A_y + A_y p_z - A_z p_y) \psi \\&= -i\hbar \left[ \frac{\partial}{\partial y}(A_z \psi) - \frac{\partial}{\partial z}(A_y \psi) + A_y \frac{\partial \psi}{\partial z} - A_z \frac{\partial \psi}{\partial y} \right] \\&= -i\hbar \left[ \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right] \psi \\&= -i\hbar(\nabla \times \mathbf{A})_x \psi \\&= -i\hbar B_x \psi\end{aligned}$$

Thus

$$\boldsymbol{\pi} \times \boldsymbol{\pi} = i\hbar Q\mathbf{B} \quad (57)$$

Substituting in Eq. (56) we get

$$(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) = (\mathbf{p} - Q\mathbf{A})^2 - Q\hbar\boldsymbol{\sigma} \cdot \mathbf{B}$$

Equation (55) therefore becomes

$$\left[ \frac{1}{2m}(\mathbf{p} - Q\mathbf{A})^2 - \frac{Q\hbar}{2m}\boldsymbol{\sigma} \cdot \mathbf{B} + Q\phi \right] u = E'u \quad (58)$$

If we compare the above equation with the corresponding non relativistic Schrödinger equation, we find that we now have an important extra term. This term suggests that the electron in a magnetic field, acquires an extra energy

$$-\boldsymbol{\mu} \cdot \mathbf{B} = -\frac{Q\hbar}{2m}\boldsymbol{\sigma} \cdot \mathbf{B}$$

so that it behaves as if it has a moment  $\boldsymbol{\mu}$  associated with its spin, namely

$$\boldsymbol{\mu} = \frac{Q\hbar}{2m}\boldsymbol{\sigma} = -\frac{q\hbar}{2m}\boldsymbol{\sigma} \quad (59)$$

where  $Q = -q$  represents the actual charge of the electron;  $q \approx +1.6 \times 10^{-19} C$  represents the magnitude of the electronic charge. Thus the Dirac equation predicts that for a spin  $\frac{1}{2}$  particle, the magnetic moment is always given by the relation (59). While this prediction is in very good agreement with experiment it fails badly

for the proton and the neutron. It is possible to modify the equation keeping it relativistically invariantly introducing, *ad hoc*, an extra term that accounts for the anomalous magnetic moment of these particles (see, e.g., Ref. 6).

## 28.8. The spin-orbit interaction

Another new feature that may be expected is the interaction between the spin and orbital motions. We examine the higher order corrections to the Pauli equation in an electrostatic field.<sup>1</sup> Writing  $\mathbf{A} = 0$  we obtain from Eqs. (50) and (51)

$$c(\boldsymbol{\sigma} \cdot \mathbf{p})v = (E' - Q\phi)u \quad (60)$$

$$c(\boldsymbol{\sigma} \cdot \mathbf{p})u = (2mc^2 + E' - Q\phi)v \quad (61)$$

The charge density is

$$\rho = \psi^\dagger \psi = u^\dagger u + v^\dagger v$$

From Eq. (61), we have

$$v \approx \frac{1}{2mc} \boldsymbol{\sigma} \cdot \mathbf{p} u \quad (62)$$

so that

$$v^\dagger v \approx u^\dagger \frac{p^2}{4m^2 c^2} u$$

This gives  $\rho = u^\dagger (1 + p^2/4m^2 c^2) u$  (to order  $v^2/c^2$ ) which suggests that to this order we *cannot* regard  $u$  as the wavefunction in the non-relativistic approximation. Instead, if we take

$$u' = \left( 1 + \frac{p^2}{8m^2 c^2} \right) u$$

and

$$u = \left( 1 - \frac{p^2}{8m^2 c^2} \right) u' \quad (63)$$

then  $\rho = (u')^\dagger u'$  to order  $v^2/c^2$  so that it is  $u'$  that we want for the wavefunction. Our aim is to obtain an equation for  $u'$ , taking care to retain terms up to order  $1/c^2$ . From Eq. (61), we have

$$c\boldsymbol{\sigma} \cdot \mathbf{p} u = (2mc^2)v + (E' - Q\phi)\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc}u$$

where in the term multiplying  $(E' - Q\phi)$ , which is small in comparison to  $2mc^2$ , we have used the lower approximation (62) for  $v$ . Thus

$$v = \frac{1}{2mc} \left[ 1 - \frac{(E' - Q\phi)}{2mc^2} \right] \boldsymbol{\sigma} \cdot \mathbf{p} u \quad (64)$$

---

<sup>1</sup> We follow the analysis given in Ref. 7.

Substituting this into Eq. (60), we obtain

$$\begin{aligned}(E' - Q\phi)u &= \frac{1}{2m}(\boldsymbol{\sigma} \cdot \mathbf{p}) \left( 1 - \frac{E' - Q\phi}{2mc^2} \right) \boldsymbol{\sigma} \cdot \mathbf{p} u \\ &= \frac{1}{2m} \left[ p^2 - \frac{E'}{2mc} p^2 + \frac{Q}{2mc^2} (\boldsymbol{\sigma} \cdot \mathbf{p})\phi(\boldsymbol{\sigma} \cdot \mathbf{p}) \right] u\end{aligned}$$

Rearranging terms, we get

$$E' \left( 1 + \frac{p^2}{4m^2c^2} \right) u = \left[ Q\phi + \frac{1}{2m} \left\{ p^2 + \frac{Q}{2mc} (\boldsymbol{\sigma} \cdot \mathbf{p})\phi(\boldsymbol{\sigma} \cdot \mathbf{p}) \right\} u \right]$$

We multiply this on the left by  $1 - p^2/8m^2c^2$ , retain the terms up to  $1/c^2$  and use Eq. (63)

$$E'u' = \left( 1 - \frac{p^2}{8m^2c^2} \right) \left[ Q\phi + \frac{p^2}{2m} + \frac{Q}{4m^2c^2} (\boldsymbol{\sigma} \cdot \mathbf{p})\phi(\boldsymbol{\sigma} \cdot \mathbf{p}) \right] \left( 1 - \frac{p^2}{8m^2c^2} \right) u' \quad (65)$$

The above equation gives us the required eigenvalue relation

$$E'u' = Hu'$$

Retaining terms up to the order  $1/c^2$ , we have

$$H = Q\phi + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} - \frac{Q}{8m^2c^2} (p^2\phi + \phi p^2) + \frac{Q}{4m^2c^2} (\boldsymbol{\sigma} \cdot \mathbf{p})\phi(\boldsymbol{\sigma} \cdot \mathbf{p})$$

Now

$$\begin{aligned}(\boldsymbol{\sigma} \cdot \mathbf{p})\phi(\boldsymbol{\sigma} \cdot \mathbf{p}) &= \phi(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p}) + (\boldsymbol{\sigma} \cdot \mathbf{p}\phi)(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ &= \phi p^2 + i\hbar(\boldsymbol{\sigma} \cdot \mathbf{E})(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ &= \phi p^2 + i\hbar(\mathbf{E} \cdot \mathbf{p} + i\boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}))\end{aligned} \quad (66)$$

where

$$\mathbf{E} = -\nabla\phi \text{ is the electric field}$$

We also have

$$\begin{aligned}(p^2\phi - \phi p^2)u' &= -\hbar^2[\nabla^2(\phi u') - \phi\nabla^2u'] \\ &= -\hbar^2[\nabla \cdot (u'\nabla\phi + \phi\nabla u') - \phi\nabla^2u'] \\ &= -\hbar^2[2\nabla\phi \cdot \nabla u' + (\nabla^2\phi)u']\end{aligned}$$

Writing this in terms of  $\mathbf{E}$  and  $\mathbf{p}$ , we obtain

$$p^2\phi - \phi p^2 = 2i\hbar\mathbf{E} \cdot \mathbf{p} + \hbar^2\nabla \cdot \mathbf{E} \quad (67)$$

Substituting (66) and (67) into expression of  $H$ , we obtain

$$H = V + \frac{p^2}{2m} - \frac{p^4}{8m^3c^3} - \frac{Q\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot \mathbf{E} \times \mathbf{p} - \frac{Q\hbar^2}{8m^2c^2}\nabla \cdot \mathbf{E} \quad (68)$$

where

$$V = Q\phi \quad (69)$$

represents the potential energy function. Now, the first two terms on the RHS of Eq. (68) represent the usual non relativistic terms. The third term is the kinetic energy correction up to order  $1/c^2$  as may be seen by expanding

$$mc^2 \left[ 1 + \frac{p^2}{m^2c^2} \right]^{\frac{1}{2}} - mc^2 \approx \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

(see Sec. 19.5.1). The fourth term represents spin-orbit interaction; this can be seen by noting that for a spherically symmetric potential  $V(r)$

$$Q\mathbf{E} = -\nabla V = -\frac{1}{r} \frac{dV}{dr} \mathbf{r} \quad (70)$$

Thus the spin-orbit interaction energy is given by

$$\begin{aligned} H_{s-o} &= -\frac{Q\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot \mathbf{E} \times \mathbf{p} \\ &= \frac{1}{2mc^2c^2r} \frac{dV}{dr} \mathbf{s} \cdot \mathbf{r} \times \mathbf{p} \end{aligned}$$

where

$$\mathbf{s} = \frac{1}{2}\hbar\boldsymbol{\sigma}$$

represents the spin angular momentum (see Sec. 14.3). Thus

$$H_{s-o} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{s} \cdot \mathbf{L} \quad (71)$$

For a hydrogen like atom problem,  $V(r)$  is given by the Coulomb potential

$$V(r) = -\frac{Ze^2}{r} \quad (72)$$

where, to be consistent with our notations in Sec. 19.5, we have used cgs units. Thus

$$H_{s-o} = \frac{Z\alpha\hbar}{2m^2c} \frac{1}{r^3} \mathbf{s} \cdot \mathbf{L} \quad (73)$$

where

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \quad (74)$$

is the fine structure constant. Equation (73) is the perturbation due to spin-orbit interaction that we had used in Sec. 19.5.2.

The last term in Eq. (68) is a correction to the potential energy  $V$ , and is known as the Darwin term (see, e.g., Ref. 1 for more details). We may mention here that for the Coulomb potential [see Eq. (72)] the Darwin term is given by

$$\begin{aligned} H_D &= \frac{\hbar^2}{8m^2c^2} \nabla^2 V \\ &= \frac{\pi\hbar^3 Z\alpha}{2m^2c} \delta(\mathbf{r}) \end{aligned} \quad (75)$$

where we have used the relation [see Sec. 24.3.1]:

$$\nabla^2 \left( \frac{1}{r} \right) = -4\pi \delta(\mathbf{r}) \quad (76)$$

Since  $R_{nl}(r = 0) = 0$  for  $l = 1, 2, 3, \dots$  (see Sec. 10.4.2); the Darwin term contributes only for  $s(l = 0)$  states. Indeed for the ground state of the hydrogen like atom, the perturbation due to the Darwin term is given by

$$\begin{aligned} (\Delta E)_D &= \frac{\pi\hbar^3 Z\alpha}{2m^2c} |\psi_{n00}(r = 0)|^2 \\ &= \frac{\pi\hbar^3 Z\alpha}{2m^2c} \frac{Z^3}{n^3 \pi a_0^3} = \frac{1}{2} \frac{mc^2 Z^4 \alpha^4}{n^3} \end{aligned} \quad (77)$$

## 28.9. Central potential

Let us now consider the solution of the Dirac equation for a particle in a central potential  $V(r)$ ; we follow the general method described in Ref. 8. The Hamiltonian is

$$H = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V(r) = H_0 + V(r) \quad (78)$$

It can be shown that the free particle Hamiltonian  $H_0$  does not commute with the orbital angular momentum  $\mathbf{L}$  (see Problem 28.2). However, it does commute with  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ . Here

$$\hbar\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\Sigma} = \frac{1}{2}\hbar \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix} \quad (79)$$

For the central potential the Hamiltonian still commutes with  $\mathbf{J}$  and  $J^2$  so that eigenfunctions can be conveniently chosen so that they belong to definite states of  $J^2$  and  $J_z$ . We label these states by  $j$  and  $m$ , the eigenvalue of  $\mathbf{J}^2$  is  $j(j+1)\hbar^2$  and of  $J_z$  is  $m\hbar$  for the particular state.

We shall proceed by separating the variables in spherical polar coordinates, the appropriate coordinates in view of the spherical symmetry of  $V(r)$ . To do this, it is convenient to introduce the operators (see Problem 28.5)

$$\begin{aligned} p_r &= \frac{1}{r}[xp_x + yp_y + zp_z - i\hbar] \\ &= \frac{1}{r}[\mathbf{r} \cdot \mathbf{p} - i\hbar] = -i\hbar \left[ \frac{\partial}{\partial r} + \frac{1}{r} \right] \end{aligned} \quad (80)$$

and

$$\alpha_r = \frac{1}{r}(\boldsymbol{\alpha} \cdot \mathbf{r}) \quad (81)$$

Note that

$$\alpha_r^2 = 1$$

Using the relation

$$(\boldsymbol{\alpha} \cdot \mathbf{B})(\boldsymbol{\alpha} \cdot \mathbf{C}) = \mathbf{B} \cdot \mathbf{C} + i\boldsymbol{\Sigma} \cdot (\mathbf{B} \times \mathbf{C}) \quad (82)$$

and putting  $\mathbf{B} = \mathbf{r}$ ,  $\mathbf{C} = \mathbf{p}$ , we obtain

$$\begin{aligned} (\boldsymbol{\alpha} \cdot \mathbf{r})(\boldsymbol{\alpha} \cdot \mathbf{p}) &= rp_r + i\hbar + i\boldsymbol{\Sigma} \cdot (\mathbf{r} \times \mathbf{p}) \\ &= rp_r + i\hbar(\boldsymbol{\Sigma} \cdot \mathbf{L} + 1) \end{aligned} \quad (83)$$

where we have used the definition  $\mathbf{L} = (\mathbf{r} \times \mathbf{p})/\hbar$ . Thus

$$r\alpha_r \boldsymbol{\alpha} \cdot \mathbf{p} = rp_r + i\hbar(\boldsymbol{\Sigma} \cdot \mathbf{L} + 1)$$

Multiplying by  $\alpha_r/r$  on the left, we obtain

$$\boldsymbol{\alpha} \cdot \mathbf{p} = \alpha_r p_r + i\hbar \frac{\alpha_r}{r}(\boldsymbol{\Sigma} \cdot \mathbf{L} + 1) \quad (84)$$

It is convenient to introduce the operator

$$K = \beta(\boldsymbol{\Sigma} \cdot \mathbf{L} + 1) \quad (85)$$

It is easily shown that this commutes with the Hamiltonian. (This is the reason for the  $\beta$  in the definition of  $K$ )

$$\begin{aligned} K^2 &= [\beta(\boldsymbol{\Sigma} \cdot \mathbf{L} + 1)]^2 = (\boldsymbol{\Sigma} \cdot \mathbf{L} + 1)^2 \\ &= (\boldsymbol{\Sigma} \cdot \mathbf{L})^2 + 2\boldsymbol{\Sigma} \cdot \mathbf{L} + 1 \quad (\text{since } \beta \text{ commutes with } \boldsymbol{\Sigma}) \end{aligned}$$

Now

$$(\boldsymbol{\Sigma} \cdot \mathbf{L})^2 = L^2 - \boldsymbol{\Sigma} \cdot \mathbf{L}$$

using Eq. (82) and

$$\boldsymbol{\Sigma} \times \boldsymbol{\Sigma} = i \boldsymbol{\Sigma}$$

Thus

$$\begin{aligned} K^2 &= L^2 + \boldsymbol{\Sigma} \cdot \mathbf{L} + 1 \\ &= \left( \mathbf{L} + \frac{\boldsymbol{\Sigma}}{2} \right)^2 + \frac{1}{4} = J^2 + \frac{1}{4} \end{aligned} \quad (86)$$

since the eigenvalue of  $\boldsymbol{\Sigma}^2$  is 3. The eigenvalues of  $K^2$  are, therefore,

$$j(j+1) + \frac{1}{4} = \left( j + \frac{1}{2} \right)^2$$

Since  $K$  commutes with the Hamiltonian, we can set up a representation in which  $K$  and  $H$  are diagonal. Now

$$H = c\alpha_r p_r + \frac{i\hbar c}{r}\alpha_r \beta K + \beta mc^2 + V(r) \quad (87)$$

We can now choose (matrix) representations of  $\alpha_r$  and  $\beta$  which satisfy the conditions

$$\alpha_r^2 = \beta^2 = 1 \quad \text{and} \quad [\alpha_r, \beta_r] = 0 \quad (88)$$

A simple one is  $\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$  and  $\alpha_r = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ . Writing  $\psi = \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$ , the relation  $H\psi = E\psi$  gives the two coupled equations

$$(E - mc^2 - V)\psi_a + \left( icp_r + \frac{\hbar c}{r}K \right) \psi_b = 0 \quad (89)$$

and

$$(E + mc^2 - V)\psi_b - \left( icp_r - \frac{\hbar c}{r}K \right) \psi_a = 0 \quad (90)$$

The angle and spin dependent parts are included in  $K$ . If we choose  $\psi_a, \psi_b$  to be eigenfunctions of  $K$  (with eigenvalue denoted by the same symbol  $K$ ), then in Eqs. (89) and (90), we need only concern ourselves with the radial parts of  $\psi_a$  and  $\psi_b$ . We set

$$\psi_a = \frac{F}{r}, \quad \psi_b = \frac{G}{r} \quad (91)$$

Noting that

$$p_r \left( \frac{F}{r} \right) = -\frac{i\hbar}{r} \left( r \frac{\partial}{\partial r} + 1 \right) \left( \frac{F}{r} \right) = -\frac{i\hbar}{r} \frac{dF}{dr}, \quad \text{etc.}$$

we obtain

$$(E - mc^2 - V)F + \hbar c \left( \frac{dG}{dr} + \frac{KG}{r} \right) = 0 \quad (92)$$

and

$$(E + mc^2 - V)G + \hbar c \left( \frac{dF}{dr} - \frac{KF}{r} \right) = 0 \quad (93)$$

## 28.10. Energy levels of the Hydrogen atom

For the hydrogen like atom, we set  $V(r) = -Ze^2/r$ . Before trying a series solutions of Eqs. (92) and (93) let us look at the asymptotic behaviour of  $F$  and  $G$ . We may write (as  $r \rightarrow \infty$ ),

$$(E - mc^2)F + \hbar c \frac{dG}{dr} = 0$$

$$(E + mc^2)G - \hbar c \frac{dF}{dr} = 0$$

whence

$$\frac{d^2F}{dr^2} - \frac{m^2c^4 - E^2}{(\hbar c)^2} F = 0 \quad (94)$$

Since we expect, for the bound state,  $F \rightarrow 0$  as  $r \rightarrow \infty$ , we must have  $mc^2 > |E|$ —otherwise, the solution to Eq. (94) will be oscillatory. For positive energies, this merely states that we expect the total energy of the atom to be somewhat less than the rest energy of the electron; one must not forget that we have not included the rest energy of the proton in the Hamiltonian in the first place. Thus, the asymptotic behaviour is

$$F, G \sim e^{-\rho} \quad (95)$$

where

$$\rho = \frac{\sqrt{m^2c^4 - E^2}}{\hbar c} r \quad (96)$$

is an obviously convenient dimensionless variable. Eqs. (92) and (93) become

$$\left( -\nu + Z \frac{\alpha}{\rho} \right) F + \frac{dG}{d\rho} + \frac{KG}{\rho} = 0 \quad (97)$$

$$\left( \frac{1}{\nu} + V \frac{\alpha}{\rho} \right) G - \frac{dF}{d\rho} + \frac{KG}{\rho} = 0 \quad (98)$$

where we have put

$$\sqrt{\frac{mc^2 - E}{mc^2 + E}} = \nu, \quad \frac{e^2}{\hbar c} = \alpha \quad (99)$$

The asymptotic forms (95) suggest a solution of the following form

$$F(\rho) = f(\rho)e^{-\rho}, \quad G(\rho) = g(\rho)e^{-\rho} \quad (100)$$

so that we have

$$\left(-\nu + Z \frac{\alpha}{\rho}\right) f + \left(\frac{d}{d\rho} + \frac{K}{\rho} - 1\right) g = 0 \quad (101)$$

$$\left(\frac{1}{\nu} + Z \frac{\alpha}{\rho}\right) g - \left(\frac{d}{d\rho} - \frac{K}{\rho} - 1\right) f = 0 \quad (102)$$

Substituting

$$f(\rho) = \rho^s \sum_{j=0}^{\infty} a_j p^j, \quad g(\rho) = \rho^s \sum_{j=0}^{\infty} b_j p^j \quad (103)$$

and comparing the coefficients of  $\rho^{s+j-1}$ , we shall get the following indicial equations:

$$-\nu a_{j-1} + Z\alpha a_j + (j+s)b_j + Kb_j - b_{j-1} = 0 \quad (104)$$

$$\frac{1}{\nu} b_{j-1} + Z\alpha b_j - (j+s)a_j + Ka_j + a_{j-1} = 0 \quad (105)$$

From the coefficients of the lowest term  $\rho^{s-1}$ , we obtain

$$Z\alpha a_0 + (s+K)b_0 = 0 \quad \text{and} \quad Z\alpha b_0 - (s-K)a_0 = 0 \quad (106)$$

Since  $a_0$  and  $b_0$  are not zero, we must have

$$s^2 = K^2 - Z^2\alpha^2$$

or

$$s = \sqrt{K^2 - Z^2\alpha^2} \quad (107)$$

where the positive root is chosen to keep the functions  $F$  and  $G$  regular at the origin. Multiplying Eq. (105) by  $\nu$  and adding it to Eq. (104) we obtain

$$a_j[(j+s-K) - Z\alpha] = b_j[(j+s+K) + Z\alpha] \quad (108)$$

It can be shown, as was done for the Schrödinger equation solution of the hydrogen atom, that if we let the series go to an infinite number of terms, the functions  $f(\rho)$  and  $g(\rho)$  will behave like  $e^{2\rho}$  so that the solutions  $F(\rho)$  and  $G(\rho)$  will diverge. We must, therefore, assume that  $j = n'$ , where  $n'$  is a fixed integer, the series terminates and  $a_{n'+1} = 0$  [and hence  $b_{n'+1} = 0$ , according to Eq. (108)]. Setting  $j = n' + 1$  in Eqs. (104) and (105), we obtain

$$-\nu a_{n'} - b_{n'} = 0 \quad \text{or} \quad b_{n'} = -\nu a_{n'} \quad (109)$$

Using Eq. (108), with  $j = n'$ , we obtain

$$(n' + s - K) - Z\alpha = -\nu[(n' + s + K) + Z\alpha] \quad (110)$$

or

$$\begin{aligned} 2v(n' + s) &= Z\alpha(1 - v^2) \\ &= \frac{Z\alpha^2 E}{mc^2 + E} \end{aligned}$$

remembering that  $v^2 = (mc^2 - E)/(mc^2 + E)$ . Squaring, we have  $(m^2c^4 - E^2)(n' + s)^2 = Z^2\alpha^2 E^2$ . This gives

$$E = mc^2 \left[ 1 + \frac{Z^2\alpha^2}{(n' + s)^2} \right]^{-1/2} \quad (111)$$

$\alpha$  here, it may be recalled, is the fine structure constant,

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

Now, the eigenvalues of  $K^2$  are  $(j + \frac{1}{2})^2$  so that  $s = \sqrt{(j + \frac{1}{2})^2 - Z^2\alpha^2}$ . To appreciate the change from the non-relativistic theory, let us introduce the small number

$$\varepsilon_j = \left( j + \frac{1}{2} \right) - \sqrt{\left( j + \frac{1}{2} \right)^2 - Z^2\alpha^2}$$

so that  $s = j + \frac{1}{2} - \varepsilon_j$ . We also introduce the principal quantum number

$$n = j + \frac{1}{2} + n' \begin{pmatrix} n = 1, 2, 3, \dots \\ j = \frac{1}{2}, \frac{3}{2}, \dots, n - \frac{1}{2} \end{pmatrix}$$

Thus  $n' + s = n - \varepsilon_j$ , so that

$$E = mc^2 \left[ 1 + \frac{Z^2\alpha^2}{(n - \varepsilon_j)^2} \right]^{-1/2} \quad (112)$$

Remembering that  $\varepsilon_j$  is also a function of  $Z^2\alpha^2$ , one can expand  $E$  as a power series in  $Z^2\alpha^2$  to obtain

$$E_{n,j} = mc^2 \left[ 1 - \frac{Z^2\alpha^2}{2n^2} - \frac{Z^4\alpha^4}{2n^4} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right] \quad (113)$$

Apart from the constant mass term, the second term in Eq. (113) is identical to the non-relativistic expression while the third gives the relativistic corrections. We

label the energy levels as

$$2S_{1/2} \text{ (for } n = 2, j = 1/2 \text{ and } l = 0\text{)}$$

$$2P_{1/2} \text{ (for } n = 2, j = 1/2 \text{ and } l = 1\text{)}$$

$$2P_{3/2} \text{ (for } n = 2, j = 3/2 \text{ and } l = 1\text{)}$$

We note that, while non-relativistic theory predicts that these three states are all degenerate, Eq. (113) predicts that only  $2S_{1/2}$  and  $2P_{1/2}$  are degenerate while  $2P_{3/2}$  lies lower by about  $10^{-4}$  eV; for detailed calculations see Sec. 19.5. In 1947, a crucial experiment by Lamb and Rutherford established that  $2S_{1/2}$  lies about 1058 MHz below  $2P_{1/2}$  (the frequency corresponds to the energy difference  $\sim 4.4 \times 10^{-9}$  eV). Although this might appear a very small discrepancy, this experiment initiated very important developments which led to a consistent theory of quantum electrodynamics.<sup>2</sup>

## 28.11. Covariance of Dirac equation

Let us first see what covariance demands. Assume that there are two observers in Lorentz frames  $\Sigma$  and  $\Sigma'$ . We require that scalar quantities remain the same in the two systems while four vectors must transform like the space-time coordinates. Finally, although the wavefunctions for the two observers need not be the same, the recipe for writing down Dirac equation must be the same for both observers. The equation in  $\Sigma$  and  $\Sigma'$  are to be

$$\left( \gamma_\mu \frac{\partial}{\partial x_\mu} + \kappa \right) \psi(x_\mu) = 0 \quad (114)$$

$$\left( \gamma_\mu \frac{\partial}{\partial x'_\mu} + \kappa \right) \psi'(x'_\mu) = 0 \quad (115)$$

Notice that the  $\gamma_\mu$  are the same in both frames; they define the recipe and ought not to be changed. The coordinates  $x$  and  $x'$  are related through

$$x'_\nu = \alpha_{\nu\mu} x_\mu \quad (116)$$

and the inverse transformation

$$x_\mu = a_{\nu\mu} x'_\nu \quad (117)$$

with the restrictions

$$a_{\lambda\mu} a_{\mu\nu} = \delta_{\lambda\nu} \quad (118)$$

---

<sup>2</sup> For a simple picture of the origin of the Lamb Shift see Chapter 4 of Ref. 4.

We have

$$\frac{\partial \psi}{\partial x_\mu} = \frac{\partial \psi}{\partial x'_v} \frac{\partial x'_v}{\partial x_\mu} = a_{v\mu} \frac{\partial \psi}{\partial x'_v} \quad (119)$$

Writing

$$\psi'(x'_\mu) = S\psi(x_\mu) \quad (120)$$

and the inverse relation

$$\psi(x_v) = S^{-1}\psi'(x'_v) \quad (121)$$

we can rewrite Eq. (114) as

$$\left( \gamma_\mu a_{v\mu} \frac{\partial}{\partial x'_v} + \kappa \right) S^{-1}\psi'(x'_\mu) = 0$$

Multiplying on the left by  $S$ , we have

$$\left( a_{v\mu} S \gamma_\mu S^{-1} \frac{\partial}{\partial x'_v} + \kappa \right) \psi'(x'_\mu) = 0 \quad (122)$$

This is identical with Eq. (115) provided we can find an  $S$  which satisfies

$$a_{\mu\nu} S \gamma_\mu S^{-1} = \gamma_\nu$$

Multiplying by  $a_{\lambda\nu}$ , summing over  $\nu$  and using relation (118), we obtain

$$S \gamma_\lambda S^{-1} = a_{\lambda\nu} \gamma_\nu \quad (123)$$

For the complete proof of covariance one has to show that such an  $S$  exists. Here we merely assert that this is true and refer the interested reader to other works for explicit construction of  $S$  for every type of Lorentz transformation [see, e.g., Ref. 4 and 5]. Equation (123) suggests that a set of matrices  $\gamma'_\lambda = a_{\lambda\nu} \gamma_\nu$  will obey all the commutation properties of  $\gamma_\nu$  and would serve just as well. One could, therefore, have written down the equation in  $\Sigma'$  frame as

$$\left( \gamma'_\lambda \frac{\partial}{\partial x'_\lambda} + \kappa \right) \psi'(x'_\lambda) = 0 \quad (124)$$

and  $\gamma'_\lambda$  and  $\gamma_\nu$  are related exactly as four vectors are in the two frames. Nevertheless, one must remember that the four  $\gamma_\lambda$  are matrices and cannot be regarded as a physical vector.

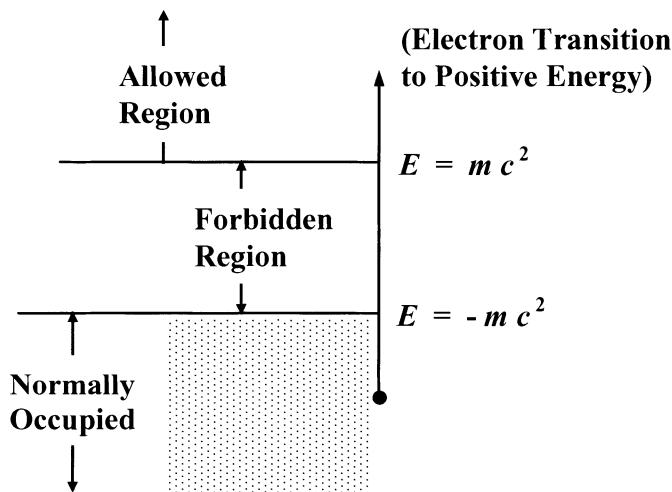


Figure 28.1. The positive and negative energy states of the electron.

## 28.12. The hole theory and positrons

We have seen that the Dirac equation admits both positive and negative energy solutions. In the presence of a field one would expect the electron to make radiative transitions to a negative energy state in fact, to  $E = -\infty$ . There are other difficulties with negative energies. An electron at rest in a negative energy state has a negative rest mass. Clearly, such electrons would move opposite to an applied force. The theory presented so far, is thus an incomplete *physical* theory.

Dirac made a remarkable suggestion to avoid these difficulties. He assumed that all the negative energy states are normally occupied by electrons; i.e., vacuum is the state of fully occupied negative energy states and empty positive ones. An electron with positive energy now introduced into this system is prevented from making a transition to a negative energy state because of the exclusion principle. In vacuum, one therefore has this negative energy ‘sea’ of electrons giving an infinite charge density. Dirac, therefore, made a further assumption, namely, that electrons filling up negative energy states do not contribute to the external field, the total energy and momentum of the system. Only *departures* from the distribution in a vacuum will contribute to observable quantities.

To see how this works, suppose a negative energy electron with an energy  $-|E_i|$  and momentum  $\mathbf{p}$  is removed from the negative energy sea, under the action of an external field, to a positive energy state (see Fig. 28.1).

The system (the sea) is now *deficient in energy*  $-|E_i|$  and momentum  $\mathbf{p}$ . This means that the residual sea behaves as though it has a *hole* with energy  $|E_i|$  and momentum  $-\mathbf{p}$ . (Notice that the hole has a positive energy  $|E_i|$ .) Also, with the removal of charge  $-e$ , the net effect of the hole is that of a positive charge  $+e$ .

This hole therefore, behaves like a particle with the electronic mass  $m$  and charge  $e$  and is interpreted as a positron.<sup>3,4</sup>

If the external field removes an electron of momentum  $\mathbf{p}_i$  from a negative energy state  $-|E_i|$  to a state of momentum  $\mathbf{p}_f$  and positive energy  $+|E_f|$ , then the hole will have an energy  $+|E_i|$  and momentum  $-\mathbf{p}_i$ . In other words, the final system now consists of an electron of energy  $|E_f|$  and momentum  $\mathbf{p}_f$  and a positron of energy  $|E_i|$  and momentum  $-\mathbf{p}_i$ . Clearly, the total energy  $|E_i| + |E_f|$  and the total momentum  $\mathbf{p}_f - \mathbf{p}_i$  of the two particles in the final states must have been supplied by the external field. Moreover, since

$$|E_i| + |E_f| > 2mc^2$$

this is the minimum required energy for this process, called *pair production*. Thus, the hole theory provides a simple explanation for the positron and phenomena such as the creation or annihilation of pairs.

However what has been gained in interpretation has made the theory far more complicated. Electron-electron scattering, for example is no longer to be thought of a simple two body process. The vacuum,<sup>5</sup> with its infinite number of particles can participate in the phenomenon making the theory a many-body one. While it is true that for low energies generally the situation is not as drastic, nevertheless one should expect new phenomena to manifest themselves.

### 28.13. Problems

**Problem 28.1** Show that the four spinors described by Eqs. (43)–(45) are orthonormal, i.e.,

$$\chi_a^\dagger \chi_b = \delta_{ab}$$

where  $\chi_a^\dagger, \chi_b$  are any two of them.

**Problem 28.2** Show that  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$  does not commute with the free particle Dirac Hamiltonian, while  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  does and hence  $\mathbf{J}$  is a constant of the motion. Here  $\mathbf{S} = \frac{1}{2}\hbar\Sigma$ , where

$$\Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}$$

<sup>3</sup> All observed states are states of positive energy. When making calculations for physical quantities it is necessary to select out final states of positive energy.

<sup>4</sup> The hole theory treats the positron on a different footing (at least in the physical interpretation) from the electron. Modern theories of quantum electrodynamics have avoided this distinction.

<sup>5</sup> Dirac's original idea of the particle as an excitation of the strange 'vacuum' has been very fruitful and the idea is exploited in the theory of condensed states (see Kaempffer, *Concepts in Quantum Mechanics*, Academic Press, New York, 1965).

**Problem 28.3** Prove

$$(\boldsymbol{\alpha} \cdot \mathbf{B})(\boldsymbol{\alpha} \cdot \mathbf{C}) = \mathbf{B} \cdot \mathbf{C} + i \boldsymbol{\Sigma}(\mathbf{B} \times \mathbf{C}) \quad (125)$$

**Problem 28.4** Verify that the rate of change of position operator (in the Heisenberg picture) is given by

$$\frac{d\mathbf{r}}{dt} = c\boldsymbol{\alpha} \quad (126)$$

Discuss this result.

**Problem 28.5 (a)** Use the operator representations of  $p_x$ ,  $p_y$  and  $p_z$  to show that

$$\frac{1}{r}[xp_x + yp_y + zp_z - i\hbar]\psi = -i\hbar \left[ \frac{\partial \psi}{\partial r} + \frac{1}{r} \right]$$

**(b)** Show that

$$[r, p_r] = i\hbar$$

**Problem 28.6** Assume that the frame  $\Sigma'$  introduced in Sec. 28.11 is obtained by a simple rotation of  $\Sigma$  about the  $z$ -axis by an angle  $\varphi$ . Show that the following matrix  $S$  satisfies Eq. (123).

$$S = \exp \left[ \frac{i\varphi}{2} \sigma_{12} \right] \quad (127)$$

where

$$\sigma_{12} = \frac{i}{2}[\gamma_1, \gamma_2] = i\gamma_1\gamma_2 \quad (128)$$

**Problem 28.7** Suppose  $\Sigma'$  moves along the  $x$ -axis with respect to  $\Sigma$  with a velocity  $\beta c$ . Show that the matrix  $S$  is given by

$$S = \exp \left[ \frac{i\varphi}{2} \sigma_{14} \right], \quad \sigma_{14} = i\gamma_1\gamma_4 \quad (129)$$

Writing

$$\varphi = i\theta, \text{ show that } \tanh \theta = \beta$$

## 28.14. Solutions

**Solution 28.2** We consider first  $[L_x, H]$ . This is

$$\begin{aligned} c\boldsymbol{\alpha} \cdot [(yp_z - zp_y)\mathbf{p} - \mathbf{p}(yp_z - zp_y)] \\ &= c\alpha_2(yp_y - p_yy)p_z + c\alpha_3(-zp_z + p_zz)p_y \\ &= ic\hbar(\alpha_2 p_z - \alpha_3 p_y) \end{aligned}$$

To calculate  $[\Sigma_x, H]$ , we note that

$$\Sigma_x = \begin{pmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{pmatrix} \quad \text{and} \quad \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$$

so that

$$\begin{aligned}\Sigma_x \alpha_2 - \alpha_2 \Sigma_x &= 2i\alpha_3 \\ \Sigma_x \alpha_3 - \alpha_3 \Sigma_x &= -2i\alpha_2\end{aligned}$$

This gives

$$\begin{aligned}[\Sigma_x, H] &= ic(\alpha \cdot \mathbf{p} \Sigma_x - \Sigma_x \alpha \cdot \mathbf{p}) \\ &= 2ic(\alpha_3 p_y - \alpha_2 p_z)\end{aligned}$$

Thus  $J_x = L_x + \frac{1}{2}\hbar\Sigma_x$  (and similarly other components) commutes with  $H$ .

**Solution 28.3** From Heisenberg's equation, we have

$$\frac{d\mathbf{r}}{dt} = \frac{i}{\hbar}[\mathbf{H}, \mathbf{r}]$$

We have

$$\frac{dx}{dt} = \frac{i}{\hbar}c[\alpha \cdot \mathbf{p}x - x\alpha \cdot \mathbf{p}]$$

We need only consider  $\alpha_x p_x$  in  $\alpha \cdot \mathbf{p}$ , the rest commute. Thus

$$\frac{dx}{dt} = \frac{ic}{\hbar}\alpha_x(p_x x - x p_x) = c\alpha_x$$

Since the eigenvalues of  $\alpha_x$  are  $\pm 1$ ,  $\pm c$  are the only possible eigenvalues of each of the operators  $d\mathbf{r}/dt$ .

A precise velocity measurement requires the precise measurement of position at two different times which means the uncertainties in momenta approach infinity. In relativity, these correspond to the speed of light.

**Solution 28.6** We have

$$S = 1 + \left(\frac{i\phi}{2}\right)\sigma_{12} + \frac{1}{2!} \left(\frac{i\phi}{2}\right)^2 \sigma_{12}^2 + \dots$$

Now

$$\begin{aligned}\sigma_{12}^2 &= (i)^2 \gamma_1 \gamma_2 \gamma_1 \gamma_2 = -(-\gamma_1 \gamma_2 \gamma_2 \gamma_1) = +1 \\ \sigma_{12}^3 &= \sigma_{12} \sigma_{12}^2 = \sigma_{12} \text{ etc.}\end{aligned}$$

It is easily shown that

$$S = \cos \frac{\phi}{2} - \gamma_1 \gamma_2 \sin \frac{\phi}{2} \quad (130)$$

We now have to show that

$$S \gamma_\lambda S^{-1} = a_{\lambda\nu} \gamma_\nu \quad (131)$$

or

$$S \gamma_\lambda = a_{\lambda\nu} \gamma_\nu S \quad (132)$$

Here

$$a_{\lambda\nu} = \begin{pmatrix} \cos \phi & \sin \phi & 0 & 0 \\ -\sin \phi & \cos \phi & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

as may be seen from working out the coordinate transformations under the desired rotation

$$x' = ax$$

For  $\lambda = 3$  and  $4$ , Eq. (132) merely says that  $S$  and  $\gamma_i$  commute. For example, the second term in  $S$  [see Eq. (130)] gives a term proportional to  $\gamma_1 \gamma_2 \gamma_3 = -\gamma_1 \gamma_3 \gamma_2 = \gamma_3 \gamma_1 \gamma_2$ . We, therefore, merely have to prove the result for  $\lambda = 1, 2$ . We have (for  $\lambda = 1$ )

$$S \gamma_1 = \gamma_1 \cos \frac{\phi}{2} + \gamma_2 \sin \frac{\phi}{2}$$

and

$$\begin{aligned} a_{1\nu} \gamma_\nu S &= (\gamma_1 \cos \phi + \gamma_2 \sin \phi) S \\ &= \gamma_1 \cos \phi \cos \frac{\phi}{2} - \gamma_2 \cos \phi \sin \frac{\phi}{2} \\ &\quad + \gamma_2 \sin \phi \cos \frac{\phi}{2} + \gamma_1 \sin \phi \sin \frac{\phi}{2} \\ &= \gamma_1 \cos \frac{\phi}{2} + \gamma_2 \sin \frac{\phi}{2} \end{aligned}$$

Similarly, we can establish the result for  $\lambda = 2$ .

**Solution 28.7** The Lorentz transformation is defined by

$$a_{\lambda\nu} = \begin{pmatrix} \gamma & 0 & 0 & i\beta\gamma \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -i\beta\gamma & 0 & 0 & \gamma \end{pmatrix} \quad (133)$$

where  $\gamma = (1 - \beta^2)^{-1/2}$ , not to be confused with the  $\gamma$  matrices. Proceeding as in the previous problem, we have

$$S\gamma_1 = \gamma_1 \cos \frac{\phi}{2} + \gamma_4 \sin \frac{\phi}{2}$$

and

$$\begin{aligned} a_{1v}\gamma_v S &= (\gamma\gamma_1 + i\beta\gamma\gamma_4)S \\ &= \gamma_1 \left( \gamma \cos \frac{\phi}{2} + i\beta\gamma \sin \frac{\phi}{2} \right) + \gamma_4 \left( i\beta\gamma \cos \frac{\phi}{2} - \gamma \sin \frac{\phi}{2} \right) \end{aligned}$$

from which we obtain (equating the two expressions)

$$\begin{aligned} \cos \phi &= \cos \theta = \gamma \\ \sin \phi &= i \sinh \theta = i\beta\gamma \quad (\text{where } \phi = i\theta) \end{aligned}$$

Thus

$$\tanh \theta = \beta$$

and

$$S = \cosh \frac{\theta}{2} - i\gamma_1\gamma_4 \sin \frac{\theta}{2} \tag{134}$$

## 28.15. References

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## Appendices

### Appendix A: Gamma functions and integrals involving Gaussian functions

We will first show that

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2 + \beta x} dx = \sqrt{\frac{\pi}{\alpha}} \exp\left[\frac{\beta^2}{4\alpha}\right] \quad \text{Re } \alpha > 0 \quad (1)$$

We consider the integral

$$I = \int_{-\infty}^{+\infty} e^{-x^2} dx \quad (2)$$

Thus

$$\begin{aligned} I^2 &= \int_{-\infty}^{+\infty} e^{-x^2} dx \int_{-\infty}^{+\infty} e^{-y^2} dy \\ &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-(x^2+y^2)} dx dy \end{aligned}$$

Transforming to polar coordinates we get

$$\begin{aligned} I^2 &= \int_0^{\infty} e^{-r^2} r dr \int_0^{\pi} d\theta \\ &= \left[ -\frac{1}{2} e^{-r^2} \right]_0^{\infty} 2\pi \\ &= \pi \end{aligned}$$

Thus

$$I = \int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\pi} \quad (3)$$

Now

$$\begin{aligned} \int_{-\infty}^{+\infty} e^{-\alpha x^2 + \beta x} dx &= \exp \left[ \frac{\beta^2}{4\alpha} \right] \int_{-\infty}^{+\infty} \exp \left[ -\alpha \left( x - \frac{\beta}{2\alpha} \right)^2 \right] dx \\ &= \exp \left[ \frac{\beta^2}{4\alpha} \right] \int_{-\infty}^{+\infty} e^{-\alpha z^2} dz \end{aligned}$$

where  $z = x - \frac{\beta}{2\alpha}$ . Using Eq. (3) we get

$$\int_{-\infty}^{+\infty} e^{-\alpha z^2} dz = \sqrt{\frac{\pi}{\alpha}} \quad (4)$$

using which we obtain Eq. (1). We also get

$$\begin{aligned} \sqrt{\pi} &= 2 \int_0^{\infty} e^{-x^2} dx \\ &= \int_0^{\infty} y^{-1/2} e^{-y} dy \end{aligned}$$

Thus

$$\Gamma \left( \frac{1}{2} \right) = \sqrt{\pi} \quad (5)$$

where  $\Gamma(z)$  is defined through the equation

$$\Gamma(z) = \int_0^{\infty} x^{z-1} e^{-x} dx \quad \text{Re } z > 0 \quad (6)$$

For  $\text{Re } z > 1$ , if we integrate by parts we would obtain

$$\Gamma(z) = (z-1) \Gamma(z-1) \quad (7)$$

Since

$$\Gamma(1) = \int_0^{\infty} e^{-x} dx = 1$$

we obtain

$$\Gamma(n+1) = n! ; \quad n = 0, 1, 2, \dots \quad (8)$$

Further since  $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$ , we obtain

$$\left. \begin{aligned} \Gamma\left(\frac{3}{2}\right) &= \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{1}{2}\sqrt{\pi} \\ \Gamma\left(\frac{5}{2}\right) &= \frac{3}{2}\Gamma\left(\frac{3}{2}\right) = \frac{3}{2} \cdot \frac{1}{2}\sqrt{\pi} \\ \Gamma\left(\frac{7}{2}\right) &= \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2}\sqrt{\pi} \end{aligned} \right\} \quad (9)$$

etc. Finally for  $n = 0, 1, 2, \dots$

$$\int_{-\infty}^{+\infty} x^{2n} e^{-x^2} dx = \Gamma\left(n + \frac{1}{2}\right) = \frac{1 \cdot 3 \cdot 5 \dots (2n - 1) \sqrt{\pi}}{2^n} \quad (10)$$

and

$$\int_{-\infty}^{+\infty} x^{2n+1} e^{-x^2} dx = 0 \quad (11)$$

## Appendix B: Equation of continuity

According to Gauss's theorem,

$$\int_{\Omega} \operatorname{div} \mathbf{J} d\tau = \int_S \mathbf{J} \cdot \hat{\mathbf{n}} dS \quad (12)$$

where  $\Omega$  represents an arbitrary volume bounded by the surface  $S$  with  $\hat{\mathbf{n}}$  representing the outward unit normal on the surface. Now, if  $\mathbf{J}$  is assumed to represent the current density then

$$\mathbf{J} \cdot \hat{\mathbf{n}} dS$$

would represent the number of particles going *out* of the area  $dS$  (per unit time). Thus the right-hand side of Eq. (1) would represent the total number of particles going out of the volume per unit time. This is nothing but

$$-\frac{\partial}{\partial t} \int_{\Omega} \rho d\tau$$

where  $\rho$  represents the number of particles per unit volume. Thus

$$-\frac{\partial}{\partial t} \int_{\Omega} \rho d\tau = \int_{\Omega} \operatorname{div} \mathbf{J} d\tau \quad (13)$$

Since the above equation holds for an arbitrary volume, we get

$$\operatorname{div} \mathbf{J} + \frac{\partial \rho}{\partial t} = 0 \quad (14)$$

which represents the equation of continuity.

## Appendix C: The Fresnel integrals

If we substitute Eq. (90) [of Chapter 5] in Eq. (76) [of Chapter 5] we would obtain

$$\Psi(x, y, t) = \Psi(x, t) \Psi(y, t) \quad (15)$$

where  $\Psi(x, t)$  is given by Eq. (35) [of Chapter 5] and

$$\Psi(y, t) = \sqrt{\frac{m}{2\pi i \hbar t}} \frac{1}{\sqrt{b}} \int_{-b/2}^{+b/2} \exp \left[ i \frac{(y' - y)^2 m}{2 \hbar t} \right] dy' \quad (16)$$

We would like to express the right-hand side of the above equation in terms of the Fresnel integrals

$$C(v) = \int_0^v \cos \left( \frac{\pi x^2}{2} \right) dx \quad (17)$$

and

$$S(v) = \int_0^v \sin \left( \frac{\pi x^2}{2} \right) dx \quad (18)$$

Thus we define the variable

$$u = (y' - y) \sqrt{\frac{m}{\pi \hbar t}} \quad (19)$$

to obtain

$$\Psi(y, t) = \frac{1}{\sqrt{2ib}} \int_{-\mu-\nu}^{-\mu+\nu} \exp \left[ i \frac{\pi u^2}{2} \right] du \quad (20)$$

where

$$\mu = y \sqrt{\frac{m}{\pi \hbar t}} = \frac{1}{\tau \sqrt{\pi}} \left( \frac{y}{\sigma_{x0}} \right) \quad (21)$$

and

$$\nu = \frac{b}{2} \sqrt{\frac{m}{\pi \hbar t}} = \frac{1}{\tau \sqrt{\pi}} \left( \frac{b}{2\sigma_{x0}} \right) \quad (22)$$

where  $\tau$  is given by Eq. (36) [of Chapter 5] with  $\sigma_0$  replaced by  $\sigma_{x0}$ . Straightforward algebra gives

$$\begin{aligned} |\Psi(y, t)|^2 &= \frac{1}{2b} \left\{ [C(-\mu + \nu) - C(-\mu - \nu)]^2 \right. \\ &\quad \left. + [S(-\mu + \nu) - S(-\mu - \nu)]^2 \right\} \end{aligned} \quad (23)$$

Obviously, the probability distribution will be symmetric about the  $y$ -axis and therefore we may replace  $\mu$  by  $-\mu$  to obtain

$$|\Psi(y, t)|^2 = \frac{1}{2b} \left\{ [C(\mu + \nu) - C(\mu - \nu)]^2 + [S(\mu + \nu) - S(\mu - \nu)]^2 \right\} \quad (24)$$

For a given value of  $\nu$ , the probability distribution (as a function of  $\mu$ ) is a universal curve. The total probability distribution is therefore given by

$$\begin{aligned} |\Psi(x, y, t)|^2 &= \left[ \frac{1}{\sqrt{\pi}\sigma(t)} \exp \left[ -\frac{(x - \frac{p_0}{m}t)^2}{\sigma^2(t)} \right] \right] \\ &\times \left[ \frac{1}{2b} \left\{ [C(\mu + \nu) - C(\mu - \nu)]^2 \right. \right. \\ &\quad \left. \left. + [S(\mu + \nu) - S(\mu - \nu)]^2 \right\} \right] \end{aligned} \quad (25)$$

where

$$\sigma(t) = \sigma_{x0} \left[ 1 + \frac{\hbar^2}{m^2 \sigma_{x0}^4} t^2 \right]^{1/2} \quad (26)$$

The analysis (and the corresponding intensity plots) are very similar to the calculation of the Fresnel diffraction pattern for a long narrow slit in wave optics (see, e.g. Sec. 5.10 of Ref. 1).

## Reference

1. A.K. Ghatak and K. Thyagarajan, *Optical Electronics*, Cambridge University Press, Cambridge (1989); Reprinted by Foundation Books, New Delhi (1991).

## Appendix D: Airy functions

noindent Airy functions are the two independent solutions of the differential equation

$$\frac{d^2y}{dx^2} - x y(x) = 0 \quad (27)$$

The above equation is usually referred to as the Airy equation (after the well-

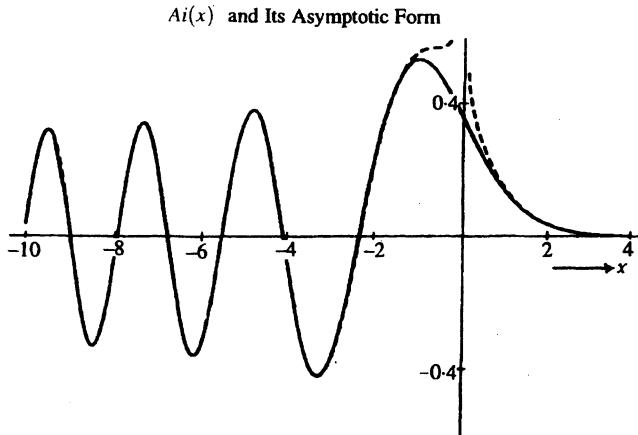


Figure D.1. The solid curve represents the Airy function  $Ai(x)$ . The dashed curves on the left and on the right side of the origin represent the asymptotic forms as given by Eqs (21) and (20) respectively.

known British astronomer G.B. Airy). In order to solve Eq. (1) we try out a power series solution

$$y(x) = a_0 + a_1 x + a_2 x^2 + \dots \quad (28)$$

Substituting in Eq. (1), we get

$$\begin{aligned} 2a_2 + 3 \cdot 2a_3 x + 4 \cdot 3a_4 x^2 + \dots + n(n-1)a_n x^{n-2} + \dots \\ = a_0 + a_1 x + a_2 x^2 + \dots + a_{n-3} x^{n-2} + \dots \end{aligned}$$

Thus

$$a_2 = 0, \quad a_3 = \frac{a_0}{2 \cdot 3}, \quad a_4 = \frac{a_1}{3 \cdot 4}, \quad \dots, \quad a_n = \frac{a_{n-3}}{n(n-1)}, \quad \dots$$

and

$$\begin{aligned} y(x) = a_0 \left[ 1 + \frac{x^3}{3 \cdot 2} + \frac{x^6}{2 \cdot 3 \cdot 5 \cdot 6} + \dots \right] \\ + a_1 \left[ x + \frac{x^4}{3 \cdot 4} + \frac{x^7}{3 \cdot 4 \cdot 6 \cdot 7} + \dots \right] \end{aligned} \quad (29)$$

where  $a_0$  and  $a_1$  are arbitrary constants. Thus we may write

$$y(x) = a_0 f(x) + a_1 g(x) \quad (30)$$

where

$$f(x) = 1 + \frac{1}{3!}x^3 + \frac{1 \cdot 4}{6!}x^6 + \frac{1 \cdot 4 \cdot 7}{9!}x^9 + \dots \quad (31)$$

$$g(x) = x + \frac{2}{4!}x^4 + \frac{2 \cdot 5}{7!}x^7 + \frac{2 \cdot 5 \cdot 8}{10!}x^{10} + \dots \quad (32)$$

The Airy functions  $Ai(x)$  and  $Bi(x)$  are defined as

$$Ai(x) = c_1 f(x) - c_2 g(x) \quad (33)$$

$$Bi(x) = \sqrt{3}[c_1 f(x) + c_2 g(x)] \quad (34)$$

where

$$c_1 = Ai(0) = \left[ 3^{2/3} \Gamma\left(\frac{2}{3}\right) \right]^{-1} = 0.35503 \quad (35)$$

$$c_2 = -Ai'(0) = \left[ 3^{1/3} \Gamma\left(\frac{1}{3}\right) \right]^{-1} = 0.25882 \quad (36)$$

Further,

$$Bi(0) = \sqrt{3} c_1 = 0.61493 \quad (37)$$

and

$$Bi'(0) = \sqrt{3} c_2 = 0.44829 \quad (38)$$

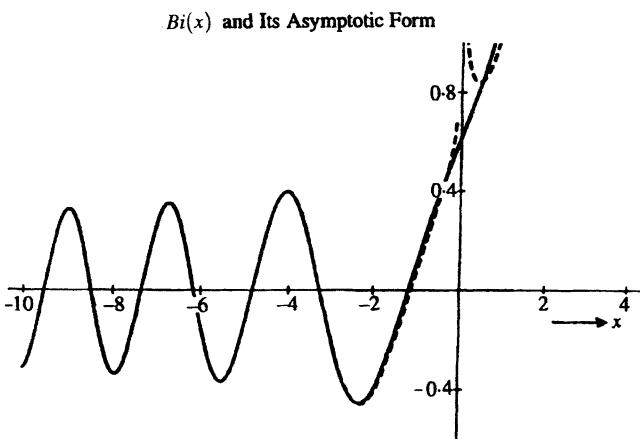


Figure D.2. The solid curve represents the Airy function  $Bi(x)$ . The dashed curves on the left and on the right side of the origin represent the asymptotic forms as given by Eqs (23) and (22) respectively.

The two functions  $Ai(x)$  and  $Bi(x)$  represent the two independent solutions of Eq. (1). Actually, originally,  $Ai(x)$  and  $Bi(x)$  were defined through the following

integrals:

$$\begin{aligned} Ai(x) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp \left[ i \left( \eta x + \frac{1}{3} \eta^3 \right) \right] d\eta = \frac{1}{\pi} \int_0^{\infty} \cos \left[ \eta x + \frac{1}{3} \eta^3 \right] d\eta \\ &= \left[ 3^{2/3} \Gamma \left( \frac{2}{3} \right) \right]^{-1} \left[ 1 + \frac{1}{3!} x^3 + \frac{1 \cdot 4}{6!} x^6 + \frac{1 \cdot 4 \cdot 7}{9!} x^9 + \dots \right] \\ &\quad - \left[ 3^{1/3} \Gamma \left( \frac{1}{3} \right) \right]^{-1} \left[ x + \frac{2}{4!} x^4 + \frac{2 \cdot 5}{7!} x^7 + \frac{2 \cdot 5 \cdot 8}{10!} x^{10} + \dots \right] \end{aligned} \quad (39)$$

$$\begin{aligned} Bi(x) &= \frac{1}{\pi} \int_0^{\infty} \left[ \exp \left( -\frac{1}{3} \eta^3 + x\eta \right) + \sin \left( \frac{1}{3} \eta^3 + x\eta \right) \right] d\eta \\ &= \sqrt{3} \left[ 3^{2/3} \Gamma \left( \frac{2}{3} \right) \right]^{-1} \left[ 1 + \frac{1}{3!} x^3 + \frac{1 \cdot 4}{6!} x^6 + \dots \right] \\ &\quad + \sqrt{3} \left[ 3^{1/3} \Gamma \left( \frac{1}{3} \right) \right]^{-1} \left[ x + \frac{2}{4!} x^4 + \frac{2 \cdot 5}{7!} x^7 + \dots \right] \end{aligned} \quad (40)$$

The Airy functions (and their derivatives) are related to Bessel functions through the following equations

$$\zeta = \frac{2}{3} x^{3/2}, \quad x > 0 \quad (41)$$

$$Ai(-x) = \frac{1}{3} \sqrt{x} [J_{-1/3}(\zeta) + J_{+1/3}(\zeta)] \quad (42)$$

$$Bi(-x) = \sqrt{\frac{x}{3}} [J_{-1/3}(\zeta) - J_{+1/3}(\zeta)] \quad (43)$$

$$Ai(x) = \frac{1}{3} \sqrt{x} [I_{-1/3}(\zeta) - I_{+1/3}(\zeta)] = \frac{1}{\pi} \left( \frac{x}{3} \right)^{1/2} K_{1/3}(\zeta) \quad (44)$$

$$Bi(x) = \sqrt{\frac{x}{3}} [I_{-1/3}(\zeta) + I_{+1/3}(\zeta)] \quad (45)$$

Using the asymptotic forms of Bessel functions, we have the following asymptotic (i.e. large  $|x|$ ) behaviour of the Airy functions:

$$Ai(x) \xrightarrow{x \rightarrow \infty} \frac{1}{2\sqrt{\pi} x^{1/4}} e^{-\zeta} \quad (46)$$

$$Ai(-x) \xrightarrow{x \rightarrow \infty} \frac{1}{\sqrt{\pi} x^{1/4}} \sin \left( \zeta + \frac{\pi}{4} \right) \quad (47)$$

$$Bi(x) \xrightarrow{x \rightarrow \infty} \frac{1}{\sqrt{\pi} x^{1/4}} e^{\zeta} \quad (48)$$

$$Bi(-x) \underset{x \rightarrow \infty}{\longrightarrow} \frac{1}{\sqrt{\pi}x^{1/4}} \cos\left(\zeta + \frac{\pi}{4}\right) \quad (49)$$

The Airy functions along with their asymptotic forms are plotted in Figs 1 and 2. The asymptotic forms were used in Chapter 17 to determine the JWKB connection formulae. Zeros of Airy functions and their first derivatives are given in Table 1.

Table 1. Zeros of airy functions and their first derivatives\*.

	$Ai(a_s)=0$	$Bi(b_s)=0$	$Ai'(a'_s)=0$	$Bi'(b'_s)=0$
$S$	$a_s$	$b_s$	$a'_s$	$b'_s$
1.	-2.33811	-1.17371	-1.01879	-2.29444
2.	-4.08795	-3.27109	-3.24820	-4.07316
3.	-5.52056	-4.83074	-4.82010	-5.51240
4.	-6.78671	-6.16985	-6.16331	-6.78129 <sup>1</sup>
5.	-7.94413	-7.37676	-7.37218	-7.94018
6.	-9.02265	-8.49195	-8.48849	-9.01958
7.	-10.04017	-9.53819	-9.53545	-10.03770
8.	-11.00852	-10.52991	-10.52766	-11.00646
9.	-11.93602	-11.47695	-11.47506	-11.93426
10.	-12.82878	-12.38642	-12.38479	-12.82726

<sup>1</sup>\* Adapted from Reference 2.

## References

1. H. Jeffreys and B. Jeffreys, *Methods of Mathematical Physics*, Cambridge University Press, Cambridge (1972).
2. M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions*, National Bureau of Standards, United States Department of Commerce, Washington, D.C. (1964).
3. A.K. Ghatak, I.C. Goyal and S.J. Chua, *Mathematical Physics*, Macmillan India Limited, New Delhi (1995).

## Appendix E: Integral and summation involving Hermite-Gauss functions

We first write the generating function associated with Hermite polynomials

$$e^{-s^2+2s\xi} = \sum_{m=0,1,2,\dots}^{\infty} \frac{s^m}{m!} H_m(\xi) \quad (50)$$

Thus

$$e^{-s^2+2s\xi} e^{-t^2+2t\xi} = \sum_n \sum_m \frac{s^m t^n}{m! n!} H_m(\xi) H_n(\xi)$$

If we multiply both sides by  $e^{-\xi^2}$  and integrate we would obtain

$$\text{RHS} = \sum_n \sum_m \frac{s^m t^n}{m! n!} \int_{-\infty}^{+\infty} H_m(\xi) H_n(\xi) e^{-\xi^2} d\xi \quad (51)$$

and

$$\begin{aligned} \text{LHS} &= e^{-s^2-t^2} \int_{-\infty}^{+\infty} e^{-\xi^2-2(s+t)\xi} d\xi \\ &= e^{-s^2-t^2} \sqrt{\pi} e^{(s+t)^2} \end{aligned}$$

where we have used Eq. (1) of Appendix A. Thus

$$\begin{aligned} \text{LHS} &= \sqrt{\pi} e^{2st} \\ &= \sqrt{\pi} \sum_{n=0,1,\dots}^{\infty} \frac{2^n s^n t^n}{n!} \end{aligned} \quad (52)$$

If we use Eqs (2) and (3) we would obtain

$$\frac{1}{n! m!} \int_{-\infty}^{+\infty} H_m(\xi) H_n(\xi) e^{-\xi^2} d\xi = \sqrt{\pi} \frac{2^n}{n!} \delta_{mn}$$

or,

$$\int_{-\infty}^{+\infty} u_m(\xi) u_n(\xi) d\xi = \delta_{mn} \quad (53)$$

where

$$u_n(\xi) = \left[ \frac{1}{2^n n! \sqrt{\pi}} \right]^{1/2} H_n(\xi) e^{-\frac{1}{2}\xi^2} \quad (54)$$

Equation (4) represents the orthonormality condition of Hermite-Gauss functions.

We next evaluate the integral

$$I_n = \int_{-\infty}^{+\infty} H_n(\xi) e^{-[\xi^2 - \xi \xi_0 + \frac{1}{2} \xi_0^2]} d\xi \quad (55)$$

We multiply both sides of Eq. (1) by the exponential factor in the integrand of Eq. (1) and carrying out the integration we get

$$\begin{aligned} \sum_{n=0,1,2,\dots}^{\infty} \frac{s^n}{n!} I_n &= \int_{-\infty}^{+\infty} e^{-s^2 + 2s\xi} e^{-[\xi^2 - \xi \xi_0 + \frac{1}{2} \xi_0^2]} d\xi \\ &= e^{-s^2 - \frac{1}{2} \xi_0^2} \int_{-\infty}^{+\infty} e^{-\xi^2} e^{(2s + \xi_0)\xi} d\xi \\ &= e^{-s^2 - \frac{1}{2} \xi_0^2} \sqrt{\pi} \exp \left[ \frac{(2s + \xi_0)^2}{4} \right] \end{aligned}$$

where we have used Eq. (1) of Appendix A. Thus

$$\begin{aligned} \sum_{n=0,1,2,\dots}^{\infty} \frac{s^n}{n!} I_n &= \sqrt{\pi} e^{-\frac{1}{4} \xi_0^2} e^{s\xi_0} \\ &= \sqrt{\pi} e^{-\frac{1}{4} \xi_0^2} \sum_{n=0,1,2,\dots}^{\infty} \frac{s^n}{n!} \xi_0^n \end{aligned}$$

Comparing coefficients of  $s^n$  on both sides we get

$$I_n = \sqrt{\pi} \xi_0^n e^{-\frac{1}{4} \xi_0^2}$$

using which we would readily get Eq. (57) of Chapter 7.

We next consider the summation [see Eq. (58) of Chapter 7]

$$\begin{aligned} \Psi(x, t) &= \sum_{n=0,1,2,\dots}^{\infty} \left[ \frac{1}{\sqrt{n!}} \left( \frac{1}{2} \xi_0^2 \right)^{n/2} \exp \left( -\frac{1}{4} \xi_0^2 \right) \right] \\ &\times \left[ \frac{\gamma}{2^n n! \sqrt{\pi}} \right]^{1/2} H_n(\xi) e^{-\frac{1}{2} \xi^2} e^{-i(n+\frac{1}{2})\omega t} \end{aligned}$$

$$\begin{aligned}
&= \left( \frac{\gamma}{\sqrt{\pi}} \right)^{1/2} \exp \left[ -\frac{1}{4} \xi_0^2 - \frac{1}{2} \xi^2 - \frac{i}{2} \omega t \right] \\
&\quad \times \sum_{n=0,1,\dots}^{\infty} \frac{1}{n!} \left[ \frac{1}{2} \xi_0 e^{-i\omega t} \right]^n H_n(\xi) \\
&= \left( \frac{\gamma}{\sqrt{\pi}} \right)^{1/2} \exp \left[ -\frac{1}{4} \xi_0^2 - \frac{1}{2} \xi^2 - \frac{i}{2} \omega t \right] \\
&\quad \times \exp \left[ -\frac{1}{4} \xi_0^2 e^{-2i\omega t} + \xi \xi_0 e^{-i\omega t} \right] \\
&= \left( \frac{\gamma}{\sqrt{\pi}} \right)^{1/2} \exp \left[ -\frac{1}{2} (\xi - \xi_0 \cos \omega t)^2 \right. \\
&\quad \left. - i \left( \frac{1}{2} \omega t + \xi \xi_0 \sin \omega t - \frac{1}{4} \xi_0^2 \sin 2\omega t \right) \right]
\end{aligned}$$

## Appendix F: The confluent hypergeometric equation

The confluent hypergeometric equation is given by

$$x \frac{d^2y}{dx^2} + (c - x) \frac{dy}{dx} - ay(x) = 0 \quad (56)$$

where  $a$  and  $c$  are constants. If we substitute a power series solution

$$y(x) = \sum_{r=0}^{\infty} d_r x^{p+r}, \quad d_0 \neq 0 \quad (57)$$

in Eq. (1) we would obtain (see, e.g. Ref. 1)

$$p = 0 \text{ or } p = 1 - c \quad \text{Roots of indicial equation} \quad (58)$$

$$d_r = \frac{p + r + a - 1}{(p + r + c - 1)(p + r)} d_{r-1} \quad \text{for } r \geq 1 \quad \text{Recurrence relation} \quad (59)$$

CASE 1:  $c \neq 0, \pm 1, \pm 2, \pm 3, \dots$

For  $c \neq 0, \pm 1, \pm 2, \pm 3, \dots$ , the two roots of the indicial equation will yield linearly independent solutions of Eq. (1); these are

$$y_1(x) = {}_1F_1(a, c, x) = 1 + \frac{a}{c} \frac{x}{1!} + \frac{a(a+1)}{c(c+1)} \frac{x^2}{2!} + \dots \quad (60)$$

and

$$y_2(x) = x^{1-c} {}_1F_1(a - c + 1, 2 - c, x) \quad (61)$$

The function  ${}_1F_1(a, c, x)$  as defined by Eq. (5) is known as the confluent hypergeometric function. Thus for  $c \neq 0, \pm 1, \pm 2, \pm 3, \dots$  the general solution of Eq. (1) is given by

$$y(x) = C_1 {}_1F_1(a, c, x) + C_2 x^{1-c} {}_1F_1(a - c + 1, 2 - c, x) \quad (62)$$

CASE 2:  $c = 1$

This is the case of repeated roots of the indicial equation. In this case, we write the solution of Eq. (1) as

$$y(x, p) = x^p \left[ 1 + \frac{p+a}{(p+1)^2} x + \frac{(p+a)(p+a+1)}{(p+1)^2(p+2)^2} x^2 + \dots \right] \quad (63)$$

The two independent solutions are given by [see, e.g. Ref.1, Chapter 8]

$$\begin{aligned} y_1(x) &= [y(x, p)]_{p=0} = 1 + \frac{a}{(1!)^2} x + \frac{a(a+1)}{(2!)^2} x^2 + \dots \\ &= {}_1F_1(a, 1, x) \end{aligned} \quad (64)$$

and

$$\begin{aligned} y_2(x) &= \left( \frac{\partial y}{\partial p} \right)_{p=0} = y_1(x) \ln x + \left[ (1-2a)x + \left( \frac{1}{a} + \frac{1}{a+1} - \frac{2}{1} - \frac{2}{2} \right) \right. \\ &\quad \times \left. \frac{a(a+1)}{(2!)^2} x^2 + \left( \frac{1}{a} + \frac{1}{a+1} - \frac{2}{1} - \frac{2}{2} - \frac{2}{3} \right) \frac{a(a+1)(a+2)}{(3!)^2} x^3 + \dots \right] \end{aligned} \quad (65)$$

CASE 3:  $c = 0, -1, \pm 2, \pm 3, \dots$

It can be seen that in this case the coefficients of one of the series [Eq. (5) or (6)] become infinite. Let us assume  $c = 0$  which gives  $p = 0$  and 1. Equation (4) can now be written as

$$d_r = \frac{(p+r+a-1)}{(p+r-1)(p+r)} d_{r-1}; \quad r \geq 1 \quad (66)$$

Thus

$$y(x, p) = d_0 x^p \left( 1 + \frac{p+a}{p(p+1)} x + \frac{(p+a)(p+a+1)}{p(p+1)^2(p+2)} x^2 + \dots \right) \quad (67)$$

which we rewrite as

$$y(x, p) = b_0 x^p \left( p + \frac{p+a}{(p+1)} x + \frac{(p+a)(p+a+1)}{(p+1)^2(p+2)} x^2 + \dots \right) \quad (68)$$

The two linearly independent solutions are :

$$\begin{aligned} y_1(x) &= y(x, p)|_{p=0} = a \left( x + \frac{a+1}{1^2 \cdot 2} x + \frac{(a+1)(a+2)}{1^2 \cdot 2^2 \cdot 3} x^3 + \dots \right) \\ &= a x {}_1F_1(a+1, 2, x) \end{aligned} \quad (69)$$

and

$$\begin{aligned} y_2(x) &= \left. \frac{\partial y}{\partial p} \right|_{p=0} = y_1(x) \ln x + \left[ 1 + (1-a)x + \left( \frac{1}{a} + \frac{1}{a+1} - \frac{2}{1} - \frac{1}{2} \right) \right. \\ &\quad \times \left. \frac{a(a+1)}{1^2 \cdot 2} x^2 + \dots \right] \end{aligned} \quad (70)$$

Similarly, for  $c = -2$ , the two roots of the indicial equation are

$$p = 0 \quad \text{and} \quad 3$$

with

$$y(x, p) \quad (71)$$

$$= b_0 p x^p \left( 1 + \frac{(p+a)}{(p-2)(p+1)} x + \frac{(p+a)(p+a+1)}{(p-2)(p-1)(p+1)(p+2)} x^2 + \dots \right)$$

Since  $p = 0$  represents the lower root, the two independent solutions would be

$$y(x, p) \Big|_{p=0} \quad \text{and} \quad \frac{\partial y(x, p)}{\partial p} \Big|_{p=0}$$

Obviously

$$y(x, p) \Big|_{p=0} = b_0 \frac{a(a+1)(a+2)}{2.1 \cdot (3!)} x^3 \left[ 1 + \frac{(a+3)}{1.4} x + \frac{(a+3)(a+4)}{1.2 \cdot 4.5} x^2 + \dots \right] \quad (72)$$

which is proportional to the second solution on the right-hand side of Eq. (7). On the other hand, for  $c = +2$ , the two roots of the indicial equation are

$$p = 0 \quad \text{and} \quad -1$$

and the two independent solutions would be

$$y(x, p) \Big|_{p=-1} \quad \text{and} \quad \frac{\partial y(x, p)}{\partial p} \Big|_{p=-1}$$

where

$$y(x, p) = b_0 (p+1) x^p \left[ 1 + \frac{(p+a)}{(p+2)(p+1)} x + \frac{(p+a)(p+a+1)}{(p+2)(p+1)(p+1)(p+2)} x^2 + \dots \right] \quad (73)$$

We may mention that the associated Laguerre polynomials and the Hermite polynomials can be expressed in terms of the confluent hypergeometric functions and are given by

$$L_{n+l}^{2l+1}(x) = -\frac{[(n+l)!]^2}{(n-l-1)!(2l+1)!} {}_1F_1(l+1-n, 2l+2, x) \quad (74)$$

$$H_n(x) = \begin{cases} (-1)^{n/2} \frac{n!}{\frac{n}{2}!} {}_1F_1\left(-\frac{n}{2}, \frac{1}{2}, x^2\right) & \text{for } n = 0, 2, 4, \dots \\ (-1)^{(n-1)/2} \frac{n!}{\frac{n-1}{2}!} 2x {}_1F_1\left(-\frac{n-1}{2}, \frac{3}{2}, x^2\right) & \text{for } n = 1, 3, 5, \dots \end{cases} \quad (75)$$

As mentioned in Sec. 10.6, many eigenvalue equations can be transformed to an equation of the following form

$$\frac{d^2u}{dx^2} + \left[ -\frac{1}{4} + \frac{\lambda}{x} + \frac{\frac{1}{4} - \mu^2}{x^2} \right] u(x) = 0 \quad (76)$$

Making the transformation

$$u(x) = x^{\mu+\frac{1}{2}} e^{-x/2} y(x) \quad (77)$$

we readily obtain

$$x \frac{d^2y}{dx^2} + (2\mu + 1 - x) \frac{dy}{dx} - \left( \mu + \frac{1}{2} - \lambda \right) y(x) = 0 \quad (78)$$

which is the confluent hypergeometric equation with

$$a = \mu + \frac{1}{2} - \lambda \quad \text{and} \quad c = 2\mu + 1 \quad (79)$$

Thus, for  $c \neq 0, \pm 1, \pm 2, \dots$  the two independent solutions are

$$u_1(x) = x^{\mu+\frac{1}{2}} e^{-x/2} {}_1F_1\left(\mu + \frac{1}{2} - \lambda, 2\mu + 1, x\right) \quad (80)$$

and

$$u_2(x) = x^{-\mu+\frac{1}{2}} e^{-x/2} {}_1F_1\left(\frac{1}{2} - \mu - \lambda, -2\mu + 1, x\right) \quad (81)$$

For  $c = 0, \pm 1, \pm 2, \dots$  one has to proceed as detailed earlier.

## References

1. A.K. Ghatak, I.C. Goyal and S.J. Chua, *Mathematical Physics*, Macmillan India Limited, New Delhi (1995).
2. J. Irving and N. Mullineux, *Mathematical Physics and Engineering*, Academic Press, New York (1959).

## Appendix G: Associated Legendre polynomials

We first consider positive values of  $m$ . Now in order to obtain the solution of Eq. (35) (of Chapter 9) for  $m > 0$ , we differentiate it  $m$  times to obtain

$$(1 - \mu^2) \frac{d^2 P^{(m)}}{d\mu^2} - 2(m+1) \frac{dP^{(m)}}{d\mu} + [\lambda - m(m+1)] P^{(m)}(\mu) = 0 \quad (82)$$

where

$$P^{(m)}(\mu) = \frac{d^m P}{d\mu^m} \quad (83)$$

Further, in Eq. (35) [of Chapter 9], if we make the substitution

$$F(\mu) = (1 - \mu^2)^{m/2} G(\mu) \quad (84)$$

then  $G(\mu)$  will be found to satisfy the same equation as satisfied by  $P^{(m)}$  [i.e. Eq. (1)]. Thus, for  $m = 1, 2, 3, \dots$  the solution of Eq. (35) [of Chapter 9] is the associated Legendre polynomial

$$P_l^m(\mu) = (1 - \mu^2)^{m/2} \frac{d^m P_l(\mu)}{d\mu^m} \quad (85)$$

defined only for non-negative integers. Since  $P_l(\mu)$  is a polynomial of degree  $l$ , we must have  $m \leq l$ . Obviously,

$$P_l^0(\mu) = P_l(\mu) \quad (86)$$

Thus, the well-behaved solutions of Eq. (28) (of Chapter 9)

$$Y_{lm}(\theta, \phi) = (-1)^m \left[ \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi}; \quad m \geq 0 \quad (87)$$

For negative values of  $m$ , Eq. (35) (of Chapter 9) and therefore the part dependent on  $\theta$  remains the same, only the  $\phi$  dependent part changes. Thus, for  $m < 0$ , we may define the solution as

$$Y_{lm}(\theta, \phi) \equiv (-1)^m Y_{l,-m}^*(\theta, \phi); \quad m < 0 \quad (88)$$

Further,

$$l = 0, 1, 2, \dots; \quad m = -l, -l+1, \dots, l-1, l \quad (89)$$

## Appendix H: Schrödinger equation in centre of mass and relative coordinates

The  $x$ -components of Eqs (26) and (27) of Chapter 10 are

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \quad (90)$$

and

$$x = x_1 - x_2 \quad (91)$$

Thus

$$\begin{aligned} \frac{\partial \Psi}{\partial x_1} &= \frac{\partial \Psi}{\partial x} \cdot \frac{\partial x}{\partial x_1} + \frac{\partial \Psi}{\partial X} \cdot \frac{\partial X}{\partial x_1} \\ &= \frac{\partial \Psi}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial \Psi}{\partial X} \end{aligned} \quad (92)$$

and

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial x_1^2} &= \frac{\partial}{\partial x} \left[ \frac{\partial \Psi}{\partial x} \right] \frac{\partial x}{\partial x_1} + \frac{\partial}{\partial X} \left[ \frac{\partial \Psi}{\partial x} \right] \frac{\partial X}{\partial x_1} \\ &\quad + \frac{m_1}{m_1 + m_2} \left[ \frac{\partial}{\partial x} \left( \frac{\partial \Psi}{\partial X} \right) \frac{\partial x}{\partial x_1} + \frac{\partial}{\partial X} \left( \frac{\partial \Psi}{\partial X} \right) \frac{\partial X}{\partial x_1} \right] \end{aligned}$$

or

$$\frac{\partial^2 \Psi}{\partial x_1^2} = \frac{\partial^2 \Psi}{\partial x^2} + \frac{2m_1}{(m_1 + m_2)} \frac{\partial^2 \Psi}{\partial X \partial x} + \left( \frac{m_1}{m_1 + m_2} \right)^2 \frac{\partial^2 \Psi}{\partial X^2}$$

Similarly

$$\frac{\partial^2 \Psi}{\partial x_2^2} = \frac{\partial^2 \Psi}{\partial x^2} - \frac{2m_2}{(m_1 + m_2)} \frac{\partial^2 \Psi}{\partial X \partial x} + \left( \frac{m_2}{m_1 + m_2} \right)^2 \frac{\partial^2 \Psi}{\partial X^2}$$

Thus

$$\begin{aligned} &-\frac{\hbar^2}{2m_1} \frac{\partial^2 \Psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2 \Psi}{\partial x_2^2} \\ &= -\frac{\hbar^2}{2\mu} \frac{\partial^2 \Psi}{\partial x^2} - \frac{\hbar^2}{2M} \frac{\partial^2 \Psi}{\partial X^2} \end{aligned} \quad (93)$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (94)$$

represents the reduced mass and

$$M = m_1 + m_2 \quad (95)$$

We therefore finally obtain

$$\begin{aligned} & -\frac{\hbar^2}{2m_1}\nabla_1^2\Psi-\frac{\hbar^2}{2m_2}\nabla^2\Psi \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)\Psi \end{aligned} \quad (96)$$

## Appendix I: Hydrogen atom wave functions

For the hydrogen-like atom  $V = -Ze^2/r$  (see Sec. 10.4) and the eigenfunctions are

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad (97)$$

where

$$\begin{aligned} n &= 1, 2, 3, \dots \\ l &= 0, 1, 2, \dots n \\ m &= -l, -l + 1, \dots +l \end{aligned} \quad (98)$$

and  $Y_{lm}(\theta, \phi)$  are the spherical harmonics which have been discussed in Secs 9.3 and 15.3 and in Appendix G. The normalized radial functions are given by

$$\begin{aligned} R_{nl}(r) &= - \left\{ \left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{-(\rho/2)} \rho^l L_{n+l}^{2l+1}(\rho) \right. \\ &= \frac{1}{(2l+1)!} \left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{(n+l)!}{2n(n-l-1)!} \right\}^{\frac{1}{2}} e^{-\rho/2} \rho^l {}_1F_1(l+1-n, 2l+2, \rho) \end{aligned} \quad (99)$$

where

$$a_0 = \frac{\hbar^2}{\mu e^2}, \quad \rho = \frac{2Z}{na_0} r \quad (100)$$

and

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+2l+1} \frac{[(n+l)!]^2 \rho^k}{(n-l-1-k)! (2l+1+k)! k!} \quad (101)$$

are known as the associated Laguerre polynomials. It may be noted that  $\rho$  depends on  $n$ . The orthonormality condition is

$$\int_0^\infty R_{n'l'}(r) R_{nl}(r) r^2 dr = \delta_{nn'} \delta_{ll'} \quad (102)$$

and first few  $R_{nl}(r)$  are given by

$$R_{10} = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-\xi} \quad (103)$$

$$\left. \begin{aligned} R_{20} &= \frac{1}{\sqrt{2}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\xi/2} \left( 1 - \frac{\xi}{2} \right) \\ R_{21} &= \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\xi/2} \xi \end{aligned} \right\} \quad (104)$$

$$\left. \begin{aligned} R_{30} &= \frac{2}{3\sqrt{3}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\xi/3} \left( 1 - \frac{2\xi}{3} + \frac{2\xi^2}{27} \right) \\ R_{31} &= \frac{8}{27\sqrt{6}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\xi/3} \left( \xi - \frac{\xi^2}{6} \right) \\ R_{32} &= \frac{4}{81\sqrt{30}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\xi/3} \xi^2, \text{ etc.} \end{aligned} \right\} \quad (105)$$

where  $\xi = Zr/a_0$ . Further

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \frac{1}{n^2} \left( \frac{Z}{a_0} \right) \\ \left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{n^3 (l + \frac{1}{2})} \left( \frac{Z}{a_0} \right)^2 \\ \left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{n^3 l (l + \frac{1}{2}) (l + 1)} \left( \frac{Z}{a_0} \right)^3 \\ \langle r \rangle &= n^2 \left[ 1 + \frac{1}{2} \left\{ 1 - \frac{l(l+1)}{n^2} \right\} \right] \frac{a_0}{Z} \end{aligned} \quad (106)$$

where

$$\langle r^m \rangle = \int_0^\infty r^m [R_{nl}(r)]^2 r^2 dr \quad (107)$$

In general, for  $p > -2l - 3$

$$\begin{aligned} &\frac{p+1}{n^2} \langle r^p \rangle - (2p+1) \frac{a_0}{Z} \langle r^{p-1} \rangle \\ &+ \frac{p}{4} [(2l+1)^2 - p^2] \left( \frac{a_0}{Z} \right)^2 \langle r^{p-2} \rangle = 0 \end{aligned} \quad (108)$$

The above relation has been derived in Chapter III of Ref. 1.

## Reference

1. F. Constantinescu and E. Magyari, *Problems in Quantum Mechanics*, Pergamon Press, Oxford (1971).

## Appendix J: Bessel functions and spherical Bessel functions

The differential equation

$$x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} + (x^2 - n^2) y(x) = 0 \quad (109)$$

is known as the Bessel equation. For  $n \neq 0, 1, 2, \dots$  the two linearly independent solutions are

$$J_n(x) \quad \text{and} \quad J_{-n}(x)$$

where

$$J_n(x) = \sum_{r=0}^{\infty} (-1)^r \frac{1}{r! \Gamma(n+r+1)} \left(\frac{x}{2}\right)^{n+2r} \quad (110)$$

For  $n = 0, 1, 2, \dots$   $J_{-n}(x)$  is a multiple of  $J_n(x)$ ; indeed

$$J_{-n}(x) = (-1)^n J_n(x); \quad n = 0, 1, 2, \dots \quad (111)$$

For  $n = 0, 1, 2, \dots$  the other independent solution is

$$Y_n(x) = \lim_{v \rightarrow n} \frac{\cos v\pi J_v(x) - J_{-v}(x)}{\sin v\pi} \quad (112)$$

In fact  $Y_n(x)$  always represents an independent solution<sup>1</sup>.

For  $n = \pm \frac{1}{2}, \pm \frac{3}{2}, \dots$  the infinite series given by Eq. (2) can be summed<sup>2</sup> and one has

$$\left. \begin{aligned} J_{1/2}(x) &= \left(\frac{2}{\pi x}\right)^{1/2} \sin x, \quad J_{-1/2}(x) = \left(\frac{2}{\pi x}\right)^{1/2} \cos x \\ J_{3/2}(x) &= \left(\frac{2}{\pi x}\right)^{1/2} \left(\frac{\sin x}{x} - \cos x\right), \\ J_{-3/2}(x) &= \left(\frac{2}{\pi x}\right)^{1/2} \left(\frac{-\cos x}{x} - \sin x\right) \end{aligned} \right\} \quad (113)$$

---

<sup>1</sup> The series representing  $Y_n(x)$  is never really needed but is given below for the sake of completeness

$$Y_n(x) = \frac{2}{\pi} \left[ \left( \ln \frac{x}{2} + \gamma \right) J_n(x) - \frac{1}{2} \sum_{r=0}^{\infty} \frac{(n-r-1)!}{r!} \left(\frac{x}{2}\right)^{-n+2r} \right. \\ \left. - \frac{1}{2} \sum_{r=0}^{\infty} (-1)^r \frac{(x/2)^{n+2r}}{r!(r+n)!} \{\phi(r) + \phi(r+n)\} \right]$$

where  $\gamma = \lim_{n \rightarrow \infty} \left[ 1 + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{n} - \ln n \right] \approx 0.5772$ ,  $\phi(r) = 1 + \frac{1}{2} + \dots + \frac{1}{r}$  with  $\phi(0) = 0$ .

<sup>2</sup> This can also be seen by using the transformation  $w = x^{1/2} y(x)$  in Eq. (1), the resulting equation for  $n = \frac{1}{2}$  is  $w'' + w(x) = 0$ , the solutions of which are  $\sin x$  and  $\cos x$ .

$J_{\pm 5/2}(x)$ ,  $J_{\pm 7/2}(x)$ , etc. can be found from the recurrence relation

$$J_{n+1}(x) = \frac{2n}{x} J_n(x) - J_{n-1}(x) \quad (114)$$

The asymptotic forms are

$$\left. \begin{aligned} J_n(x) &\xrightarrow{x \rightarrow \infty} \left( \frac{2}{\pi x} \right)^{1/2} \cos \left( x - \frac{n\pi}{2} - \frac{\pi}{4} \right) \\ Y_n(x) &\xrightarrow{x \rightarrow \infty} \left( \frac{2}{\pi x} \right)^{1/2} \sin \left( x - \frac{n\pi}{2} - \frac{\pi}{4} \right) \end{aligned} \right\} \quad (115)$$

We would like to introduce the Hankel functions which are often used (as independent solutions of Eq. (1)) for their convenient asymptotic forms:

$$\begin{aligned} H_n^{(1)}(x) &= J_n(x) + i Y_n(x) \xrightarrow{x \rightarrow \infty} \left( \frac{2}{\pi x} \right)^{1/2} e^{i(x - \frac{n\pi}{2} - \frac{\pi}{4})} \\ H_n^{(2)}(x) &= J_n(x) - i Y_n(x) \xrightarrow{x \rightarrow \infty} \left( \frac{2}{\pi x} \right)^{1/2} e^{-i(x - \frac{n\pi}{2} - \frac{\pi}{4})} \end{aligned} \quad (116)$$

## Spherical Bessel functions

In the Bessel equation Eq. (1) corresponding to  $n = l + 1/2$  ( $l = 0, 1, 2, \dots$ ) if we make the transformation  $f(x) = \frac{1}{\sqrt{x}} y(x)$ , we would obtain

$$\frac{d^2 f}{dx^2} + \frac{2}{x} \frac{df}{dx} + \left[ 1 - \frac{l(l+1)}{x^2} \right] f(x) = 0 \quad (117)$$

which is known as the spherical Bessel equation. Equation (9) is of the same form as the radial part of the Schrödinger equation (Eq. (15) of Chapter 10) with  $V(r) = 0$  and  $x = \left( \frac{2mE}{\hbar^2} \right)^{1/2} r$ . For  $l = 0, 1, 2, \dots$  the two independent solutions are known as the spherical Bessel functions and are defined through the following equations

$$\left. \begin{aligned} j_l(x) &= \left( \frac{\pi}{2x} \right)^{1/2} J_{l+1/2}(x) \\ n_l(x) &= (-1)^l \left( \frac{\pi}{2x} \right)^{1/2} J_{-l-1/2}(x) \end{aligned} \right\} \quad (118)$$

Using the results given in the previous section it is easy to show that

$$\begin{aligned} j_0(x) &= \frac{\sin x}{x}, \quad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \\ n_0(x) &= \frac{\cos x}{x}, \quad n_1(x) = \frac{\cos x}{x^2} - \frac{\sin x}{x}, \quad \text{etc.} \end{aligned} \quad (119)$$

$j_2(x)$ ,  $n_2(x)$ , etc. can be obtained from the recurrence relation [see Eq. (6)]. Further, the asymptotic forms are

$$\begin{aligned} j_l(x) &\xrightarrow{x \rightarrow \infty} \frac{1}{x} \sin\left(x - \frac{l\pi}{2}\right) \\ n_l(x) &\xrightarrow{x \rightarrow \infty} \frac{1}{x} \cos\left(x - \frac{l\pi}{2}\right) \end{aligned} \quad (120)$$

and

$$\begin{aligned} j_l(x) &\xrightarrow{x \rightarrow 0} \frac{x^l}{(2l+1)!!} \\ n_l(x) &\xrightarrow{x \rightarrow 0} \frac{(2l+1)!!}{(2l+1)} \frac{1}{x^{l+1}} \end{aligned} \quad (121)$$

where  $(2l+1)!! = 1 \cdot 3 \cdot 5 \dots (2l+1)$ . Finally, the function  $u(x) = xf(x)$  satisfies the equation

$$\frac{d^2u}{dx^2} + \left[1 - \frac{l(l+1)}{x^2}\right] u(x) = 0 \quad (122)$$

which is of the same form as Eq. (17) of Chapter 10 and Eq. (59) of Chapter 24 with  $V(r) = 0$  and  $x = \left(\frac{2mE}{\hbar^2}\right)^{1/2} r$ . Obviously, the solution of Eq. (14) is given by

$$u(x) = A[xj_l(x)] + B[xn_l(x)] \quad (123)$$

## Modified Bessel functions

In the Bessel equation [Eq. (1)] if we make the transformation  $\xi = -ix$ , we would obtain

$$\xi^2 \frac{d^2y}{d\xi^2} + \xi \frac{dy}{d\xi} - (\xi^2 + n^2)y(\xi) = 0 \quad (124)$$

The solutions are  $J_n(i\xi)$  and  $Y_n(i\xi)$ . For  $n \neq 0, 1, 2, \dots$  the two independent solutions are written as  $I_{\pm n}(\xi)$  where

$$I_n(\xi) = i^{-n} J_n(i\xi) = \sum_{r=0}^{\infty} \frac{(\xi/2)^{n+2r}}{r! \Gamma(n+r+1)} \quad (125)$$

The functions  $I_n(\xi)$  are known as modified Bessel functions with the asymptotic form

$$I_n(\xi) \xrightarrow{x \rightarrow \infty} \frac{1}{(2\pi\xi)^{1/2}} e^{\xi} \quad (126)$$

These functions are not oscillatory in character [cf. Eq. (7)]. Often it is more convenient to choose

$$K_n(x) = \frac{\pi}{2} \frac{I_{-n}(x) - I_n(x)}{\sin n\pi} \xrightarrow{x \rightarrow \infty} \left(\frac{\pi}{2x}\right)^{1/2} e^{-x} \quad (127)$$

as an independent solution. The functions  $K_n(x)$  are known as modified Bessel function of the second kind.

## Appendix K: Asymptotic series

In order to study the behaviour of various functions for large values of  $x$ , it is often convenient to expand them in inverse powers of  $x$ :

$$f(x) = \phi(x) \left[ a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \dots \right] \quad (128)$$

where  $\phi(x)$  is a known function whose behaviour for large  $x$  is known. The series, which is often divergent, is usually of great practical importance not only for a qualitative understanding of a function, but even in its computation for large values of  $x$ .

### Definition

The series  $a_0 + (a_1/x) + (a_2/x^2) + \dots$  is said to represent  $f(x)/\phi(x)$  asymptotically, if

$$\lim_{x \rightarrow \pm\infty} \left\{ x^N \left[ \frac{f(x)}{\phi(x)} - \sum_{n=0}^N \frac{a_n}{x^n} \right] \right\} \rightarrow 0 \quad (129)$$

i.e. for a given value of  $N$ , the first  $N$  terms of the series can be made as close as may be desired to the ratio  $f(x)/\phi(x)$  by making  $x$  large enough. When the series diverges, there will be an optimal number of terms of the series to be used to represent  $f(x)/\phi(x)$  for a given  $x$ ; and therefore, there will be an *unavoidable error*. This *unavoidable error* would decrease as  $|x|$  increases. We will now consider a few examples:

**Example 1** Consider the exponential integral

$$f(x) = \int_x^\infty \frac{e^{-y}}{y} dy$$

Integrating by parts

$$\begin{aligned} f(x) &= \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-y}}{y^2} dy \\ &= \frac{e^{-x}}{x} - \frac{e^{-z}}{x^2} + 2 \int_x^\infty \frac{e^{-y}}{y^3} dy \end{aligned}$$

Continuing this procedure, we get

$$f(x) = \frac{e^{-x}}{x} \left[ 1 - \frac{1}{x} + \frac{2!}{x^2} - \frac{3!}{x^3} + \dots + \frac{(-1)^n n!}{x^n} \right] \\ + (-1)^{n+1} (n+1)! \int_x^\infty \frac{e^{-y}}{y^{n+2}} dy$$

Thus, in this problem  $\phi(x) = e^{-x}/x$ ;  $a_0 = 1, a_1 = -1, \dots a_n = (-1)^n n!$ . The limit of the ratio of two successive terms of the series is given by

$$\lim_{n \rightarrow \infty} \left| \frac{T_{n+1}}{T_n} \right| = \lim_{n \rightarrow \infty} \frac{n}{x} \rightarrow \infty$$

Thus, the series diverges. Further, the two successive terms become equal in magnitude for  $n = x$ , indicating that the optimum number of terms for a given  $x$  is roughly the integer closest to  $x$ . Typically, for  $x = 4$ , the exact value of  $xe^{+x} f(x)|_{x=4} = 0.82533$ .

However, the sum of the series including the 1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 8th and 9th term in the series are 1.00000, 0.75000, 0.87500, 0.78125, 0.87500, 0.75781, 0.93360, 0.62347 and 1.24373 respectively. Thus the optimal value is 0.78125 which occurs at  $N = 3$  and  $0.82533 - 0.78125$  is the unavoidable error. Further, by taking a large number of terms the accuracy becomes poorer.

**Example 2** In a similar manner, one may discuss the asymptotic series of the error function,

$$\text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-y^2} dy \\ = \frac{1}{\sqrt{\pi}} e^{-x^2} \left( \frac{1}{x} - \frac{1}{2x^3} + \frac{1.3}{2^2 x^5} - \frac{1.3.5}{2^3 x^7} + \dots \right)$$

**Example 3** Finally, we will consider the asymptotic form of the solutions of the confluent hypergeometric equation: (see also Appendix L)

$$x \frac{d^2 y}{dx^2} + (c-x) \frac{dy}{dx} - ay = 0$$

We substitute the series

$$y = e^{mx} \sum_{r=0}^{\infty} a_r x^{-s-r}$$

On substitution and equating the highest power of  $x$  we obtain

$$m = 0 \text{ or } m = 1$$

(i) For  $m = 0$ ,  $s = a$ ,  $a_1 = -a(a - c + 1)a_0$ , etc. giving

$$y = a_0 x^{-a} \left[ 1 - \frac{a(a - c + 1)}{1!x} + \frac{a(a + 1)(a - c + 1)(a - c + 2)}{2!x^2} \dots \right]$$

(ii) For  $m = 1$ ,  $s = c - a$ ,  $a_1 = (c - a)(1 - a)a_0$ , etc. giving

$$y = a_0 e^x x^{a-c} \left[ 1 + \frac{(c - a)(1 - a)}{1!x} + \frac{(c - a)(c - a + 1)(1 - a)(2 - a)}{2!x^2} \dots \right]$$

The asymptotic form of  ${}_1F_1(a, c, x)$  is a linear combination of the above solutions.

## Appendix L: Complex variable

### Complex integration

In the theory of functions of a complex variable there is a famous theorem due to Cauchy which states that, if  $f(z)$  is an analytic function of  $z$  in a certain region around a point  $z = a$ , then

$$\int_C f(z) dz = 0 \quad (130)$$

and

$$\frac{1}{2\pi i} \int_C \frac{f(z)}{z - a} dz = f(a) \quad (131)$$

where  $C$  is a closed contour taken around  $z = a$  in a contour-clockwise direction (Fig. 1). If  $f(z)$  can be expanded around  $z = z_0$  in the form

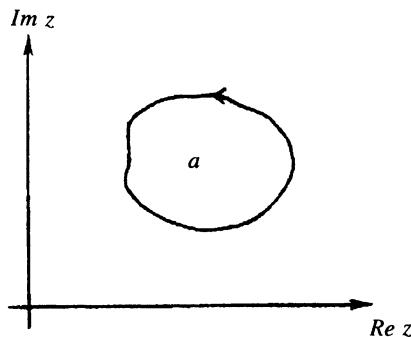


Figure L.1.

$$f(z) = \frac{a_{-m}}{(z - z_0)^m} + \frac{a_{-m+1}}{(z - z_0)^{m-1}} + \cdots + \frac{a_{-1}}{z - z_0} + a_0 + a_1(z - z_0) + \cdots \quad (132)$$

where  $m$  is a *finite* integer, then it can be shown that

$$\frac{1}{2\pi i} \int_C f(z) dz = a_{-1} \quad (133)$$

where  $C$  is a contour around  $z = z_0$  in the counter-clockwise direction. Note that in Eqs (3) and (4),  $f(z)$  is *not* analytic at  $z = z_0$ ;  $f(z)$  has a pole of order  $m$ . If  $m = 1$ , the pole is said to be a simple pole.

The coefficient  $a_{-1}$  in the expansion (3) is called the residue of the function  $f(z)$ . If the pole at  $z = z_0$  is a simple pole, then

$$[(z - z_0) f(z)]_{z=z_0} = a_{-1} \quad (134)$$

Eq. (5) is the recipe for evaluating at simple poles. When there are  $n$  poles within a contour  $C$ , we can generalize (4) to

$$\frac{1}{2\pi i} \int_C f(z) dz = \sum_{r=1}^n \alpha_r \quad (135)$$

where  $\alpha_r$  is the residue at the  $r$ th pole.

Eq. (6) remains unaltered, no matter how we distort the counter  $C$  as *long as we do not cross any new poles*. This technique is exploited frequently in mathematical manipulations.

A remarkable property of an analytic function  $f(z)$  is that all its derivatives are also analytic in the same region. It can be shown that Eq. (2) can be generalized to

$$f^n(a) = \frac{n!}{2\pi i} \int_C \frac{f(z)}{(z - a)^{n+1}} dz \quad (136)$$

## Singularities

A function  $f(z)$  which can be expanded with  $m \leq -1$  but finite is said to have a singularity at  $z = z_0$ .

It may turn out that an expansion of the form (3) is not possible for finite  $m$ . For example

$$f(z) = e^{1/z} = \sum_{m=0}^{\infty} \frac{z^{-m}}{m!}$$

In this case the function  $f(z)$  is said to have an *essential singularity* at  $z = 0$ .

One should not get the idea that a singularity is merely a point at which the function goes to infinity. For example,  $f(z) = z^{1/2}$  cannot be expanded near  $z = 0$  in the form (3). Such singularities arise when we have multivalued functions and are called branch points.

## Multivalued functions

We discuss the example

$$f(z) = z^{1/2}$$

Writing

$$z = re^{i\phi} \quad (137)$$

and

$$f(z) = Re^{i\theta}$$

we see that  $R = r^{1/2}$  and  $\theta = \phi/2$ . As  $\phi$  goes from  $-\pi + \epsilon$  to  $\pi - \epsilon$  where  $\epsilon$  is a small positive quantity,  $\theta$  goes from  $-\pi/2 + \epsilon/2$  to  $\pi/2 - \epsilon/2$ . As  $\epsilon \rightarrow 0$ ,  $\phi$  goes from  $-\pi$  to  $+\pi$  and  $z$  returns to its original value. However  $f$  does not. To describe this situation, one draws a *double line* such as  $I$  (Fig. 2), around the

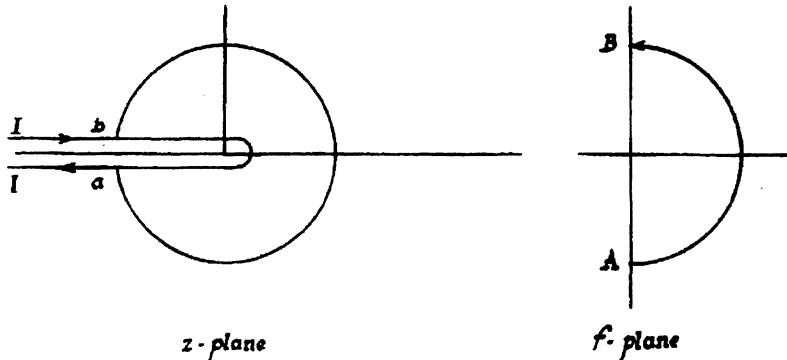


Figure L.2.

branch point ( $z = 0$  in this case). Whenever, one crosses this line (called *branch line*) on the  $z$ -plane, the function  $f(z)$  will not return to its original value.

It can be shown that branch points, occur in pairs and a branch line joins a pair of branch points. In the above example,  $z = \infty$  is the other branch point.

## Application to solution of confluent hypergeometric equation

We apply the methods of contour integrals to solve the confluent hypergeometric equation

$$zF'' + (c - z)F' - aF = 0 \quad (138)$$

This equation is of great importance in quantum mechanical problems, since many equation such as Hermite's equation, Legendre and associated Legendre equation and Bessel's equation can be converted to this form (see Appendix F). We write

tentatively, its solution as  $F(a, c, z)$ . The method employed is to take the Laplace transform

$$F = \int_C e^{zt} v(t) dt \quad (139)$$

where  $C$  is a contour in the complex  $t$  plane and  $v(t)$  a function to be chosen so as to give a solution of Eq. (9) with the desired behaviour. We note that

$$\begin{aligned} F'(z) &= \int_C t e^{zt} v(t) dt \\ &= \left[ \frac{e^{zt}}{z} t v(t) \right]_C - \int_C \frac{e^{zt}}{z} \frac{d}{dt} [t v(t)] dt \end{aligned}$$

and

$$\begin{aligned} F''(z) &= \int_C t^2 e^{zt} v(t) dt \\ &= \left[ \frac{e^{zt}}{z} t^2 v(t) \right]_C - \int_C \frac{e^{zt}}{z} \frac{d}{dt} [t^2 v(t)] dt \end{aligned}$$

This permits us to write

$$\begin{aligned} zF'' &= \left[ e^{zt} t^2 v \right]_C - \int_C e^{zt} \frac{d}{dt} [t^2 v] dt \\ zF' &= \left[ e^{zt} t v \right]_C - \int_C e^{zt} \frac{d}{dt} [t v] dt \end{aligned}$$

and

$$cF' = \int_C ct v e^{zt} dt$$

so that Eq.(9) becomes

$$\left[ e^{zt} t(t-1)v(t) \right]_C - \int_C e^{zt} \left[ t^2 \frac{dv}{dt} + 2tv - t \frac{dv}{dt} - v - ct v + av \right] dt = 0 \quad (140)$$

We now make the restriction that the contour  $C$  will be so chosen that

$$[e^{zt} t(t-1)v(t)]_C = 0 \quad (141)$$

and the function  $v(t)$  will be chosen so that the integrand in (11) vanishes; i.e.

$$\frac{dv}{dt} t(t-1) = v[1 - a + (c-2)t] \quad (142)$$

Eq. (13) is readily integrated<sup>3</sup> to give

$$v \sim t^{a-1}(t-1)^{c-a-1}$$

and the condition for the contour, Eq. (12), becomes

$$[\phi(t)]_C = [e^{zt} t^a (t-1)^{c-a}]_C = 0 \quad (143)$$

The solution is [from Eq. (10)]

$$F = \int_C e^{zt} t^{a-1} (t-1)^{c-a-1} dt \quad (144)$$

Before we proceed further, we note that if one substitutes

$$F = z^{1-c} F_1 \quad (145)$$

into Eq. (9), we obtain

$$zF''_1 + (2 - c - z)F'_1 - (a - c + 1)F_1 = 0 \quad (146)$$

which is of the same form as (9). Thus, if we write the solution of (9) in the form

$$F = F(a, c, z)$$

then  $z^{1-c} F(a - c + 1, 2 - c, z)$  is another independent solution of the confluent hypergeometric equation. Thus this solution is

$$z^{1-c} \int e^{zt} t^{a-c} (t-1)^c dt \quad (147)$$

Now the contour  $C$  need not be a closed one; all that is necessary is that Eq. (14) is obeyed so that the value of the function  $\phi(t) [= e^{zt} t^a (t-1)^{a-c}]$  must be the same at the two ends of the curve  $C$ . For  $\operatorname{Re} z > 0$ , any contour which starts and ends at  $t = -\infty$  clearly satisfies this. However, we shall consider the case  $\operatorname{Re} c > \operatorname{Re} a > 0$  so that  $\phi(t)$  vanishes at  $t = 0$  and  $t = 1$ . Hence we choose, for our contour, the portion of the real axis extending from 0 to 1. Thus,

$$\begin{aligned} F &= \int_0^1 e^{zt} t^{a-1} (t-1)^{c-a-1} dt \\ &= (-1)^{c-a-1} \sum_{n=0}^{\infty} \frac{z^n}{n!} \int_0^1 t^{n+a-1} (1-t)^{c-a-1} dt \end{aligned} \quad (148)$$

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<sup>3</sup> This is the point of the whole exercise; the equation in  $v$  is a simpler than the original one in  $F$ .

This series can be expressed in terms of  $\Gamma$  functions by using the relation

$$\int_0^1 t^{\alpha-1} (1-t)^{\beta-1} dt = \frac{\Gamma(\alpha)\Gamma(\beta)}{\Gamma(\alpha+\beta)} \quad (149)$$

Thus

$$F = (-1)^{c-a-1} \sum_n \frac{z^n}{n!} \frac{\Gamma(n+a)\Gamma(c-a)}{\Gamma(c+n)}$$

The series<sup>4</sup>

$${}_1F_1(a, c, z) = \frac{\Gamma(c)}{\Gamma(a)} \sum_{n=0}^{\infty} \frac{\Gamma(a+n)}{\Gamma(c+n)} \frac{z^n}{n!} \quad (150)$$

is called the **confluent hypergeometric** series. Further

$$F = (-1)^{a-c-1} \frac{\Gamma(c-a)\Gamma(a)}{\Gamma(c)} {}_1F_1(a, c, z) \quad (151)$$

A general solution of the hypergeometric equation can, therefore, be expressed as a linear combination of

$${}_1F_1(a, c, z) \quad \text{and} \quad z^{1-c} {}_1F_1(a-c+1, 2-c, z)$$

## Asymptotic behaviour

The function (21), written out in a series as

$${}_1F_1(a, c, z) = 1 + \frac{a}{c} z + \frac{a(a+1)}{c(c+1)} \frac{z^2}{2!} + \dots \quad (152)$$

is convergent for all finite values of  $|z|$ ; the only restriction is that  $c$  is not a negative integer. We now study the behaviour of this series for large values of  $|z|$  when  $a$  and  $c$  are integers. In this series, the term containing  $z^n$  is

$$\frac{(a+n)!}{(a-1)!} \frac{(c-1)!}{(c+n)!} \frac{z^n}{n!}$$

For large  $n \gg a, c$  we have

$$\frac{(a+n)!}{(a-1)!} \sim n^{a-c} \sim n(n-1)\dots(n-a+c+1)$$

---

<sup>4</sup> The peculiar notation  ${}_1F_1$  is because this is a special form of generalized hypergeometric function  ${}_nF_m(a, c, z)$ .

This gives, for the term with  $z^n$ ,

$$\frac{(c-1)!}{(a-1)!} \frac{n^{a-c}}{n!} z^n \approx \frac{(c-1)!}{(a-1)!} \frac{z^n}{(n-a+c)!}$$

Thus, for  $z \rightarrow \infty$ , we have

$${}_1F_1 \sim \frac{(c-1)!}{(a-1)!} \sum_n \frac{z^n}{(n-a+c)!} = \frac{(c-1)!}{(a-1)!} z^{a-c} e^z$$

Thus

$${}_1F_1(a, c, z) \rightarrow \frac{\Gamma(c)}{\Gamma(a)} z^{a-c} e^z \quad (153)$$

We have put the results in terms of the  $\Gamma$  functions because the result it turns out, is valid for non-integral values of  $a$  and  $c$  as well. While (24) gives the right asymptotic behaviour for  $\operatorname{Re} z \rightarrow \infty$ , it can be seen that for  $\operatorname{Re} z \rightarrow -\infty$ , the limit goes to zero exponentially. In this case the limit given by (24) is not valid; however, the following result may be established

$${}_1F_1(a, c, z) = e^z {}_1F_1(c-a, c, -z) \quad (154)$$

so that, for  $z \rightarrow -\infty$ , we substitute the asymptotic form (24) on the RHS of Eq. (25), to obtain

$${}_1F_1(a, c, z) \longrightarrow \frac{\Gamma(c)}{\Gamma(c-a)} (-z)^{-a} \quad (155)$$

## Connection with other functions

It can be easily shown that the Hermite polynomials and the associated Laguerre polynomials are related to the confluent hypergeometric function (see Appendix F). Further, the Bessel functions are given by

$$J_\nu(z) = \frac{z^\nu e^{-iz}}{2^\nu \Gamma(1+\nu)} {}_1F_1\left(\nu + \frac{1}{2}, 2\nu + 1, 2iz\right) \quad (156)$$

For  $\operatorname{Re}(\nu + \frac{1}{2}) > 0$ , the following integral representation can be established by the methods discussed:

$$J_\nu(z) = \frac{1}{\sqrt{\pi} \Gamma(\nu + \frac{1}{2})} \left(\frac{z}{2}\right)^\nu \int_{-1}^1 e^{izt} (1-t^2)^{\nu-1/2} dt \quad (157)$$

## Appendix M: The periodic boundary conditions and the density of states

In developing the scattering theory, we consider the particle inside a cube of volume  $L^3$  and initially in a plane wave state corresponding to momentum  $\mathbf{p}$  (see Sec. 25.3). Thus the particle is described by the wave function

$$\psi = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (158)$$

where

$$\mathbf{k} = \frac{1}{\hbar} \mathbf{p} \quad (159)$$

and the factor  $L^{-3/2}$  normalizes the wave function

$$\int_0^L \int_0^L \int_0^L |\psi|^2 dx dy dz = 1$$

The allowed values of  $\mathbf{k}$  are determinated from the boundary conditions. It is convenient to use the periodic boundary conditions (see also Sec. 27.3):

$$\begin{aligned} \psi(x=0, y, z) &= \psi(x=L, y, z) \\ \psi(x, y=0, z) &= \psi(x, y=L, z) \end{aligned} \quad (160)$$

and

$$\psi(x, y, z=0) = \psi(x, y, z=L)$$

giving

$$\exp[ik_x L] = 1 = \exp[ik_y L] = \exp[ik_z L] \quad (161)$$

Thus the allowed values of  $k_x$ ,  $k_y$  and  $k_z$  are given by [cf. Eq. (37) of Chapter 27]:

$$k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L} \quad (162)$$

where

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots \quad (163)$$

Now, the number of states whose  $x$ - component of  $\mathbf{k}$  lies between  $k_x$  and  $k_x + dk_x$  would simply be the number of integers lying between  $Lk_x/2\pi$  and  $L(k_x + dk_x)/2\pi$ ; this number would be approximately equal to  $Ldk_x/2\pi$ . Similarly, the number of states whose  $y$ - and  $z$ - components of  $\mathbf{k}$  lie between  $k_y$  and  $k_y + dk_y$  and  $k_z$  and  $k_z + dk_z$  would, respectively, be

$$\frac{L}{2\pi} dk_y \text{ and } \frac{L}{2\pi} dk_z$$

Thus there will be

$$\frac{L^3}{8\pi^3} dk_x dk_y dk_z \quad (164)$$

states in the range  $dk_x dk_y dk_z$  of  $\mathbf{k}$ . Obviously, the number of states in the range  $dp_x dp_y dp_z$  of  $\mathbf{p}$  will be

$$\frac{L^3}{8\pi^3 \hbar^3} dp_x dp_y dp_z \quad (165)$$

Now if  $\rho(k) dk d\Omega$  represents the number of states whose  $|\mathbf{k}|$  lies between  $k$  and  $k + dk$  and the direction of  $\mathbf{k}$  lies in the solid angle  $d\Omega (= \sin \theta d\theta d\phi)$  then

$$\rho(k) dk d\Omega = \frac{L^3}{8\pi^3} k^2 dk d\Omega \quad (166)$$

For a non-relativistic particle of mass  $m$  we have  $E = \hbar^2 k^2 / 2m$  giving

$$\rho(E) dE d\Omega = \frac{L^3}{16\pi^3 \hbar^3} (2m)^{3/2} E^{1/2} dE d\Omega \quad (167)$$

If we integrate over  $d\Omega$  we would get the total number of states whose energies lie between  $E$  and  $E + dE$

$$g(E) dE = \frac{L^3}{4\pi^2 \hbar^3} (2m)^{3/2} E^{1/2} dE \quad (168)$$

which is identical to the expression for  $g(E)$  derived in Sec. 6.8.1 (except for the additional factor of 2 introduced there) where we had assumed end point boundary conditions, i.e.  $\psi$  was assumed to vanish on the surface of the cube. Thus the expression for density of states is independent of the boundary conditions used.

Returning to Eq. (9) we note that for an electromagnetic field inside a cube (see Sec. 27.3)  $\omega = ck$  and one has

$$\rho(\omega) d\omega d\Omega = \frac{L^3}{8\pi^3 c^3} \omega^2 d\omega d\Omega \quad (169)$$

If we sum over two independent modes of polarization and integrate over the solid angle we would get

$$\rho(\omega) d\omega = \frac{L^3}{\pi^2 c^3} \omega^2 d\omega \quad (170)$$

## Appendix N: Alternative derivation of the Green's function for the $(\nabla^2 + k^2)$ operator

The free particle Green's function is defined through the equation

$$(\nabla^2 + k^2)G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (171)$$

We Fourier analyze  $G$  and  $\delta$ :

$$G(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int g(\mathbf{k}') \exp[i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')] d\mathbf{k}' \quad (172)$$

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int \exp[i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')] d\mathbf{k}' \quad (173)$$

where we have used Eq. (46) of Chapter 1. Substituting these in Eq. (171) we get

$$(-k'^2 + k^2)g(\mathbf{k}') = 1$$

or

$$g(\mathbf{k}') = -\frac{1}{k'^2 - k^2} \quad (174)$$

Thus

$$G(\mathbf{r} - \mathbf{r}') = -\frac{1}{8\pi^3} \int \frac{1}{(k'^2 - k^2)} \exp[i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')] d\mathbf{k}' \quad (175)$$

which is the Green's function for the operator  $(\nabla^2 + k^2)$ . We may mention that the integrals in Eqs. (172), (173) and (175) are 3 dimensional integrals. We define a new variable  $\rho = \mathbf{r} - \mathbf{r}'$  and choose the direction of the polar axis (i.e., the direction of  $k'_z$ ) along  $\rho$  to get

$$\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}') = \mathbf{k}' \cdot \rho = k' \rho \cos \theta \quad (176)$$

so that

$$\begin{aligned} G(\rho) &= -\frac{1}{8\pi^3} \int_0^\infty \frac{k'^2 dk'}{k'^2 - k^2} \int_0^\pi e^{ik' \rho \cos \theta} \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= -\frac{1}{8\pi^3} \cdot 2\pi \int_0^\infty \frac{k'^2 dk'}{k'^2 - k^2} \left[ \frac{e^{ik' \rho} - e^{-ik' \rho}}{ik' \rho} \right] \end{aligned}$$

or

$$G(\rho) = -\frac{1}{4\pi^2 i \rho} \int_{-\infty}^{+\infty} dk' \left[ \frac{k' e^{ik' \rho}}{(k' + k)(k' - k)} \right] \quad (177)$$

We integrate this by going over to the complex  $k'$ -plane. The integrand has poles on the real axis at  $k' = \pm k$ . For the contour we shall choose the real axis closed by

the infinitely far upper half semicircle (see Fig. N.1) since the factor  $e^{ik'\rho}$  ensures that the integral vanishes on the upper half semicircle; this follows from Jordan's lemma (see, for example, Ref. 1). There, however, remains the important question of how to go around the two poles. We shall choose the two contours shown in Figs D.1(a) and (b). In case (a), the result is

$$G(\rho) = -\frac{1}{4\pi^2\rho i} 2\pi i \left[ \frac{k' e^{ik'\rho}}{k' + k} \right]_{k'=k}$$

This gives

$$G_+(\rho) = -\frac{e^{ik\rho}}{4\pi\rho} \quad (178)$$

Similarly case (b) gives

$$G_-(\rho) = -\frac{e^{-ik\rho}}{4\pi\rho} \quad (179)$$

Another way of formulating the rules for evaluating  $G_\pm$  is that for  $G_+$  we replace  $k$  in the denominator in the integral by  $k + i\varepsilon$  and for  $G_-$  we replace  $k$  by  $k - i\varepsilon$  always remembering that  $\varepsilon$  is positive and letting  $\varepsilon \rightarrow 0$ .

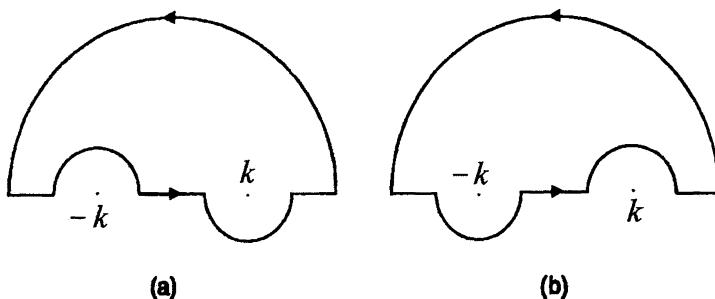


Figure N.1. The two contours of integration chosen

## Reference

1. J. Irving and N. Mullineux, *Mathematics in Physics and Engineering*, Academic Press, New York (1959).

## Appendix O: Asymptotic form of the radial part of the Schrödinger equation for a short-range force

For a spherically symmetric potential, the radial part of the Schrodinger equation can be put in the form [see Eq. (59) of Chapter 24]:

$$\frac{d^2 u_l(r)}{dr^2} + \left[ k^2 - U(r) - \frac{l(l+1)}{r^2} \right] u_l(r) = 0 \quad (180)$$

where  $u_l(r) = r R_l(r)$ ,  $k^2 = 2mE/\hbar^2$ ,  $U(r) = 2mV(r)/\hbar^2$ . In this appendix we will show that for a short-range force for which

$$\lim_{r \rightarrow \infty} r V(r) = 0 \quad (181)$$

the asymptotic form of  $u_l(r)$  is  $\exp(\pm ikr)$ .

We first assume that at large values of  $r$ , the terms  $U(r)$  and  $l(l+1)/r^2$  in Eq. (1) can be neglected. Then the solution will be  $u_l \sim \exp(\pm ikr)$ , this suggests that we try a solution of the form

$$u_l(r) = A \exp \left[ \int_a^r f(r') dr' \right] \exp[\pm ikr] \quad (182)$$

If we substitute in Eq. (1), we would obtain

$$\frac{df}{dr} + f^2 \pm 2ik f(r) = U(r) + \frac{l(l+1)}{r^2} \equiv W(r) \quad (183)$$

If  $W(r)$  behaves as  $e^{-\alpha r}$  for  $r \rightarrow \infty$  (then  $l$  is necessarily zero),  $f(r)$  will also behave as  $e^{-\alpha r}$  as can be seen by substitution (the term  $f^2$  will be negligible). Consequently the integral  $\int_a^r f(r') dr'$  will tend to a constant value and  $u_l(r)$  will behave as  $\exp(\pm ikr)$ . On the other hand if  $W(r) \sim A'/r^\alpha$  ( $\alpha > 0$ ) then  $f(r) \sim \mp(A'/2ik)(1/r^\alpha)$  (the terms involving  $df/dr$  and  $f^2$  would be negligible). However, only for  $\alpha > 1$ , the integral  $\int_a^r f(r') dr'$  would tend to a constant value. Indeed for  $\alpha = 1$  (i.e. for the Coulomb potential) we will have

$$u_l(r) \xrightarrow[r \rightarrow \infty]{} \exp \left( \pm ikr \pm \frac{A'}{2ik} \ln r \right) \quad (184)$$

Thus the form of  $u_l(r)$  for  $r \rightarrow \infty$  does not approach a definite phase; however, we can still obtain an expression for the scattering cross-section (see Sec. 24.6). Thus, if  $\alpha > 1$ , the asymptotic form of  $u_l(r)$  is indeed of the form of  $\exp(\pm ikr)$ .

## Appendix P: Tunnelling calculations

The probability that at time  $t$ , the particle is still inside the well is approximately given by the overlap integral

$$P(t) \approx \left| \int_0^\infty \Psi^*(x, 0) \Psi(x, t) dx \right|^2 \quad (185)$$

Now

$$\Psi(x, t) = \int_0^\infty dE \phi(E) \psi_E(x) e^{-iEt/\hbar} \quad (186)$$

[see Eq. (25) of Chapter 23]. Thus

$$\begin{aligned} P(t) &\approx \left| \int dx \left[ \int dE' \phi^*(E') \psi_{E'}^*(x) \right] \left[ \int dE \phi(E) \psi_E(x) e^{-iEt/\hbar} \right] \right|^2 \\ &\approx \left| \int dE' \phi^*(E') \int dE \phi(E) e^{-iEt/\hbar} \int dx \psi_{E'}^*(x) \psi_E(x) \right|^2 \end{aligned}$$

Since the last integral is  $\delta(E - E')$ , we readily get

$$P(t) \approx \left| \int dE |\phi(E)|^2 e^{-iEt/\hbar} dE \right|^2 \quad (187)$$

In order to evaluate the above integral, we must evaluate  $|\phi(E)|^2$  which is given by [see Eq. (28) of Chapter 23]:

$$|\phi(E)|^2 \approx \left| \frac{A}{A_b} \right|^2 \quad (188)$$

Now,  $A_b$  is given by [see Eq. (9) of Chapter 23]

$$A_b = \left[ \frac{2\kappa_b}{1 + \kappa_b a} \right]^{1/2} \quad (189)$$

In order to evaluate  $A$ , we express it in terms of  $D$  and then use Eq. (19) of Chapter 23. Since the wave packet is a superposition of states around the *quasi-bound state*,  $|\phi(E)|^2$  is very sharply peaked around  $E \approx E_b$  and therefore all calculations will be carried out around  $E \approx E_b$ . We begin with calculation of  $C$  around  $E = E_b$ ; we first note that at resonance

$$-k_b a \cot k_b a = \kappa_b a \quad (190)$$

[see Eq. (2) of Chapter 23]. Thus

$$\sin k_b a = \pm \frac{k_b a}{\alpha}, \quad \cos k_b a = \mp \frac{\kappa_b a}{\alpha} \quad (191)$$

where

$$\alpha^2 = \frac{2\mu V_0 a^2}{\hbar^2} \quad (192)$$

[see Eq. (5) of Chapter 23]. Now,

$$\begin{aligned} C &= \frac{1}{2} A \left[ \sin ka - \frac{k}{\kappa} \cos ka \right] \quad k \approx k_b \\ &\approx \frac{1}{2} A \left[ \sin k_b a - \frac{k_b}{\kappa_b} \cos k_b a \right] \\ &\approx \pm \frac{1}{2} A \left[ \frac{k_b a}{\alpha} + \frac{k_b \kappa_b a}{\alpha} \right] \\ &\approx \pm A \frac{k_b a}{\alpha} \end{aligned} \quad (193)$$

Since

$$B|_{E=E_b} = 0$$

we must make a Taylor series expansion of  $B$  around  $E = E_b$ :

$$\begin{aligned} B &\approx \left. \frac{dB}{dE} \right|_{E=E_b} (E - E_b) \\ &\approx \frac{1}{2} A \left[ \left( a \cos ka + \frac{1}{\kappa} \cos ka - \frac{ka}{\kappa} \sin ka \right) \frac{dk}{dE} \right. \\ &\quad \left. - \frac{k}{\kappa^2} \cos ka \frac{d\kappa}{dE} \right]_{E=E_b} (E - E_b) \end{aligned}$$

Since

$$k^2 = \frac{2\mu E}{\hbar^2} \quad \text{and} \quad \kappa^2 = \frac{2\mu}{\hbar^2} (V_0 - E) \quad (194)$$

we get

$$\frac{dk}{dE} = \frac{\mu}{\hbar^2 k} \quad \text{and} \quad \frac{d\kappa}{dE} = -\frac{\mu}{\hbar^2 \kappa} \quad (195)$$

Using the above equations [and Eq. (7)] we readily obtain

$$B \approx -\frac{1}{2} A \frac{\mu \alpha}{a \hbar^2 k_b \kappa_b^2} (1 + \kappa_b a) (E - E_b) \quad (196)$$

where we have used the fact that

$$k^2 + \kappa^2 = \frac{2\mu V_0}{\hbar^2} = \frac{\alpha^2}{a^2} \quad (197)$$

Substituting for  $B$  and  $C$  from Eqs (12) and (9) in the expression for  $D_{\pm}$  [see Eq. (17) of Chapter 23], we get

$$|D_{\pm}| = \frac{1}{4} A \frac{\mu\alpha(1 + \kappa_b a) e^{\kappa_b d}}{a \hbar^2 k_b \kappa_b^2} \left| 1 \pm \frac{\kappa_b}{ik_b} \right| |E - E'_b \mp i\Gamma| \quad (198)$$

where

$$\Gamma = \frac{4k_b^3 \kappa_b^3 a^4 \hbar^2}{\mu\alpha^4(1 + \kappa_b a)} e^{-2\kappa_b d} \quad (199)$$

$$E'_b = E_b - \frac{\kappa_b^2 - k_b^2}{2\kappa_b k_b} \Gamma \quad (200)$$

Since

$$|D_{+}| = \frac{1}{\hbar} \left[ \frac{\mu}{2\pi k} \right]^{1/2} \quad \text{and} \quad A_b = \left[ \frac{2\kappa_b}{1 + \kappa_b a} \right]^{1/2} \quad (201)$$

[see Eqs (19) and (9) of Chapter 23], we may write

$$|\phi(E)|^2 \approx \left| \frac{A}{A_b} \right|^2 \approx \frac{\Gamma}{\pi} \frac{1}{(E - E'_b)^2 + \Gamma^2} \quad (202)$$

Thus Eq. (3) becomes

$$P(t) \approx \left| \int \frac{\Gamma}{\pi} \frac{e^{-iEt/\hbar}}{(E - E'_b)^2 + \Gamma^2} dE \right|^2 \quad (203)$$

We may evaluate the integral from  $-\infty$  to  $+\infty$  since most of the contribution will come from the region near resonance ( $E \approx E'_b$ ). We introduce the variable

$$\eta = \frac{(E - E'_b)}{\hbar} \quad (204)$$

to write

$$P(t) \approx \left| \frac{\Gamma}{\pi \hbar} \int_{-\infty}^{+\infty} \frac{e^{-i\eta t}}{\left(\eta + i\frac{\Gamma}{\hbar}\right)\left(\eta - i\frac{\Gamma}{\hbar}\right)} d\eta \right|^2 \quad (205)$$

For  $t > 0$ , the integral may be evaluated by using complex variable techniques and Jordan's lemma. In the complex  $\eta$ -plane we choose a contour which consists of the

real axis and a semicircle in the lower-half plane where the integral vanishes. There is a simple pole within the contour at

$$\eta = -\frac{i\Gamma}{\hbar}$$

so that

$$\begin{aligned} P(t) &\approx \left| \frac{\Gamma}{\pi \hbar} \cdot 2\pi i \frac{e^{-\Gamma t/\hbar}}{-\frac{2i\Gamma}{\hbar}} \right|^2 \\ &\approx e^{-t/\tau} \end{aligned} \quad (206)$$

where

$$\tau = \frac{\hbar}{2\Gamma} \quad (207)$$

represents the mean lifetime of the particle.

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