

PH3102

QUANTUM MECHANICS

LECTURE NOTES

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Foreword

These are notes partly based on lectures I have been giving at the Department of Physical Sciences (DPS), IISER-Kolkata for the course on introductory Quantum Mechanics (PH2201) over the years. The rest of the matter covers topics in the next course (PH3012). I am very thankful to Ms. Mounica Mahankali, Mr. Abhirup Mukherjee and Mr. Som Dev Bishoyi for kindly typing up the first version of the lectures notes (along with drawing and including several figures) so meticulously. Any errors, typographical or otherwise, can be laid at my door. Please do email me with corrections.

The intention of the lectures is to provide a (hopefully gentle!) introduction to the theoretical machinery of quantum mechanics. Even as attention has been given towards covering the phenomenology of quantum mechanics, an effort has also been made to provide adequately the mathematical underpinnings of the subject. Given their venerable status, almost all the topics covered within these areas are well-known and covered in detail in several places. I have tried to bring things together in my own way. The material has been separated into first covering the basics and leads to a presentation of some advanced topics. The classification of topics into basic and advanced is certainly subjective, and I trust that upon strengthening her/his fundamentals, the reader will find passage through some of the advanced topics easier as well as informative.

The topics covered are in keeping with the syllabus that has evolved at IISER Kolkata over the years. Certainly, there are many interesting topics that I have not been able to cover in the lectures, primarily as they are the ambit of more advanced courses in Quantum Mechanics that are taught at IISER Kolkata. I do not expect that advanced students and researchers in theoretical physics will find the lectures particularly enlightening. However, I hope that my lecture notes will prove to be a good companion to the existing excellent textbooks in Quantum Mechanics (of which there are more than stars in the night sky!) for study by undergraduates (and perhaps even early graduate students) keen to strengthen their foundations by learning some of the material I have covered. In this sense, I hope that these lecture notes can act as a springboard on which students can launch deeper explorations of the fascinating world of Quantum Mechanics.

A word on prerequisites. Even though these lectures are introductory in nature, the reader will need a sound grasp of the basics of vectors, matrices, determinants and ordinary differential equations in making quick progress through the material covered. For readers unfamiliar with these prerequisites, there are several excellent textbooks that impart the basics of these topics in mathematical physics. I would like to acknowledge many discussions with my grad-

uate students Santanu Pal, Anirban Mukherjee, Siddhartha Patra and Abhirup Mukherjee as well as many colleagues and former students at IISER-Kolkata whose insight into the subject I have benefited from greatly. Thanks are also due to the students who attended the lectures, and offered valuable feedback. Unless mentioned specifically, no claims of originality are being made in either the content or presentation of material covered in these lectures. Indeed, they were prepared from a thorough consultation of a selection of excellent textbooks already available on the topics I covered, including:

- Robert Scherrer, “Quantum Mechanics: an accessible introduction”, Pearson Addison-Wesley, 2006
- D. J. Griffiths, “Introduction to Quantum Mechanics”, 2nd Edition, Pearson Prentice Hall, 2005
- R. Shankar, “Principles of Quantum Mechanics”, 2nd Edition, Springer, 1994
- E. Merzbacher, “Quantum Mechanics”, 3rd Edition, Wiley, 2004
- R. P. Feynman, R. B. Leighton and M. Sands, “The Feynman Lectures on Physics Vol. III”, Addison-Wesley, 1965
- F. Schwabl, “Quantum Mechanics”, 4th Edition, Springer, 2007
- J.J. Sakurai, “Modern Quantum Mechanics”, Revised Edition, Addison-Wesley, 1999
- L. E. Ballentine, “Quantum Mechanics: a modern development”, 2nd Edition, World Scientific, 2015
- Y. B. Band and Y. Avishai, “Quantum Mechanics with Applications to Nanotechnology and Information Science”, 1st Edition, Academic Press, 2013 .

Several pictures have been taken from various sources on the internet, and I am deeply grateful to colleagues from all over the world for such excellent figures! I offer my sincere apologies for not citing them specifically in every instance.

Finally, I invite you to begin your journey into these lectures with a quote from a favourite fictional character of mine:

To ∞ and beyond!

Siddhartha Lal
Mohanpur, West Bengal, India
January, 2020



To ∞ and Beyond! (Source: The internet.)

Chapter 1

Introduction

Through the course of our journey through these lectures, we are going to depart from our familiar classical world and learn about the fascinating world of quantum phenomena. This is not an easy passage, as the world around us does not easily show us quantum phenomena. Our intuition is, instead, built from our observations of the “classical world” around us. I will, therefore, try to introduce you here to some surprising differences between the classical and quantum worlds.

1.1 Getting started

Features of the Classical World

1. Our everyday observations tell us that the physical universe is deterministic.

By this we mean that with enough information about a given system, we can predict its evolution in time precisely!

2. Light consists of waves, while matter consists of particles.

Our understanding of Maxwell’s theory for classical electromagnetism, together with the field of classical optics, confirms that light is made of waves. On the other hand, the view of the ancient Hindu and Greek philosophers that all matter is constructed from some indivisible units — the atomistic view of matter — is confirmed by experiments starting with the Brownian motion of particles. All of chemistry is contingent on this view.

3. Physical quantities are continuous variables.

Consider examples of quantities you have measured in the laboratory thus far: energy, linear momentum, angular momentum, position etc.

4. There exists an objective reality independent of any observer.

In making an observation of a classical system, we never affect the system in the process of making the measurement.

NONE OF THESE ARE COMPLETELY ACCURATE IN THE WORLD OF

QUANTUM PHYSICS!

Features of the Quantum World

1. The physical universe is not deterministic!
 - (a) In the quantum world, the various outcomes of any process have probabilities associated with them: we cannot predict the exact result with certainty.
 - (b) Uncertainty is an intrinsic property of the quantum world, and has nothing to do with our ability to make accurate observations of the world around us.

1.2 The Schrödinger's Cat gedanken

For an illustration of both these (seemingly mysterious) concepts, consider the famous example of the Schrödinger's Cat *gedanken* (or “thought experiment” in the German language).

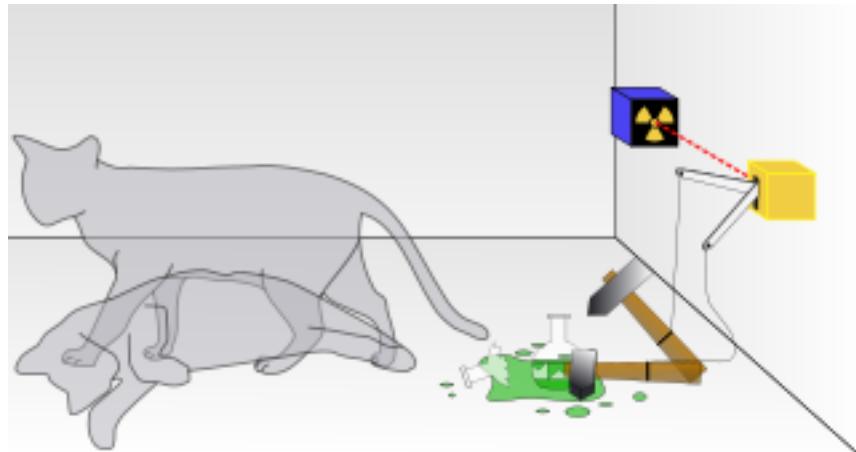


Figure 1.1: A schematic diagram of the Schrödinger's Cat thought experiment. See discussion in text. Disclaimer: No such experiment has ever been carried out with a real cat! Source: The internet.

The gedanken is straight-forward. A cat is placed in an opaque box together with a radioactive source, a Geiger counter that can detect the radioactivity and a vial of poison gas. Any radioactive source has a well-defined lifetime, i.e., a definite fraction of the population of the atoms will have undergone radioactive decay within the lifetime. The decay process is, however, probabilistic; this means that at any given time, we can associate a probability that a given atom will have undergone radioactive decay. Now, if during the time the cat is kept in the box, the radioactive source undergoes decay, the Geiger counter will sense this and break the vial of poison gas, killing the cat. Thus, upon opening the lid of the box, we

will find the cat to be dead. On the other hand, if the source does not decay, the cat will be alive upon observation.

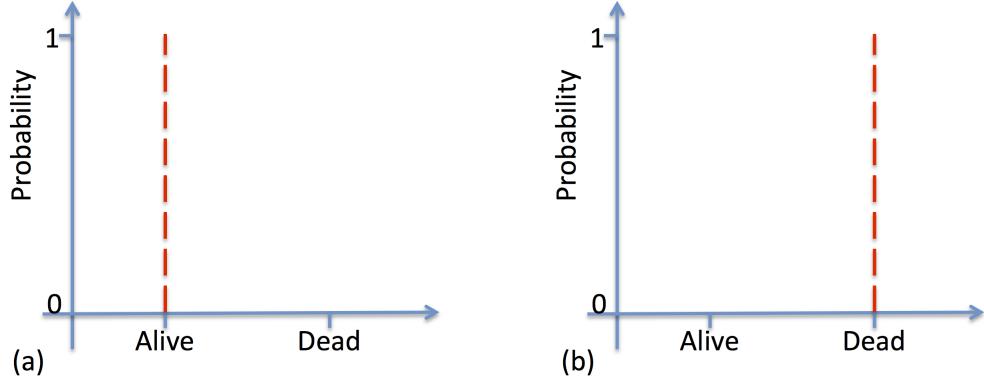


Figure 1.2: A schematic diagram of the probability for observations of the “Dead” and “Alive” states in the Schrödinger’s Cat thought experiment by continuous classical observations. See discussion in text.

Now this is where things become strange. While in the classical world, the cat would have been either Dead or Alive with perfect precision, it exists in a strange admixture of both possibilities within the quantum world (i.e., with the box closed!). For instance, if we carry out the gedanken with a large number (say, a million) of identical set-ups, each of which is being continuously observed by a classical observer for a time T (i.e., with the lid of the box open) and the distribution of all million outcomes then plotted in a histogram, we should either find a histogram of the kind shown in Fig.1.2(a) or Fig.1.2(b) depending on whether the class is alive or dead at time T . This is completely consistent with our knowledge of the classical states of the cat.



Figure 1.3: A schematic diagram of the probability for observations of the “Dead” and “Alive” states in the Schrödinger’s Cat thought experiment by a classical observer who only observes the state of the cat after a certain time interval T . See discussion in text.

However, as mentioned above, the cat can exist in a linear superposition of the two classical probabilities in the quantum world. For instance, for an equal probability admixture of the

classical states of “Alive” and “Dead”, we can think of the “Quantum Mechanical State” of the cat within the closed box as being:

$$|\psi_{\text{Quantum Cat}}\rangle = \frac{1}{\sqrt{2}}(|\text{Alive}\rangle + |\text{Dead}\rangle) , \quad (1.1)$$

$$P_{\text{Alive}} = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2} = P_{\text{Dead}} , \quad (1.2)$$

where the P s are the probabilities for the classical states of “Alive” and “Dead” (see Fig.1.3). Such an admixture tells us that (i) the cat is dead or alive with well-defined probabilities. As with the gedanken protocol set out above, these probabilities will be revealed if we were to carry out similar measurements on a large number of identical setups of the gedanken, and only if the observations are taken after a time interval T has elapsed with the lid of the box closed (allowing for the quantum state of the cat to be realised). Further, the uncertainty in our knowledge of the state of the cat (i.e., whether it is alive or dead) arises from its state being an admixture of the two, and has nothing to do with our ability to observe it once we open the box. Thus, the passage from the quantum to the classical world can be charted when the probability for a certain outcome becomes perfect (i.e., 1).

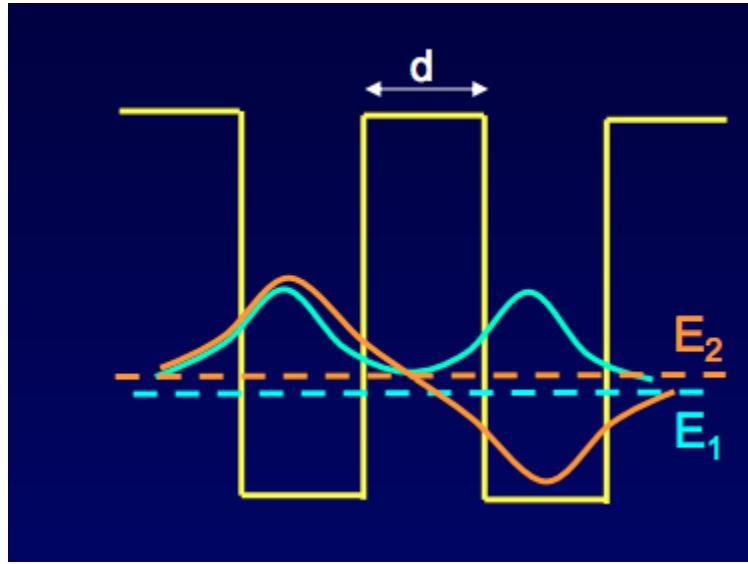


Figure 1.4: The wavefunctions for the symmetric and anti-symmetric states of a quantum particle placed in a double well potential. The symmetric state is lower in energy than the anti-symmetric one due to quantum tunneling. Source: The internet.

A disclaimer: this gedanken has never been implemented in the laboratory with cats (and hopefully, never will be!). Further, as my 11 year old daughter pointed out, a real cat would have died of suffocation (or even boredom!) first. (Yes, we physicists often miss the obvious truths!) However, versions of this experiment with atoms in a superposition of two classical states have been conducted, e.g., quantum particle in a double well potential.

2. Both light and matter displays properties of waves as well as particles!

This is called “wave-particle duality”. For instance, the Schrödinger’s Cat gedanken gives a “wave-like” linear superposition of possible classical states to the quantum state of a creature clearly composed of particles. It is important to note, however, that any given experiment shows either a wave-like property or a particle-like property, but never both simultaneously. Nevertheless, it is amazing to consider the fact that different experiments show very different features of the same system!

3. Physical quantities can have discrete values, i.e., they may be quantised.

The word “quanta” comes from the ancient Greek word for a discrete unit. The phenomenon of quantisation is at the heart of all quantum phenomena: it helps us understand blackbody radiation, the photoelectric effect, the stability of the atom and so much more!

4. A System and its Observer are entangled with one another in the quantum world:

the observer affects the system through the process of measurement. Words like “entanglement” and “measurement” need careful explanation, and I will dwell on this in more detail in one of the final chapters.

1.3 A historical background

If all of this has left you confused, worried and/or excited, then that’s fine. Everything that I mentioned above is not only counter-intuitive, it is plain outrageous! Then why believe it? Because it works! And it has taken us around 120 years to come to terms with the intrinsic “strangeness” of quantum mechanics.

Indeed, around 1900, most physicists were convinced that almost everything could be understood using the conceptual pillars of classical mechanics, electromagnetism and thermodynamics. Very few experimental puzzles remained to be understood, e.g., Blackbody radiation, the Michelson-Morley experiment, the photoelectric effect, Brownian motion and diffusion etc. It is quite sobering to consider that it was these same experiments that went on to shake the very foundations of physics, and gave birth to the fields of quantum mechanics and statistical mechanics.

Quantum mechanics took roughly three decades to be formalised, with a lot of the action in the 1920s. Some of the greats involved in this effort are shown below from the famous Solvay Conference in 1927. Please note that among all the Nobel prize-winning luminaries in that photograph, none is more distinguished than Madame Curie (who happens to be the only double Nobel prize winner among them all!). While the epicentre of the action was in Europe (and mostly Germany and France), people from all over the world contributed to this effort. Noteworthy contributors from India included Prof. Satyendranath Bose and Prof. C. V. Raman. While the latter won the Nobel prize for his contribution (the “Raman effect”), the former richly deserved one (but was never awarded it) for the particles (“bosons”) that bear his name. Some small comfort can perhaps be taken from the fact that since all “force” particles are classified as bosons, his legacy extends far beyond the narrow purview of any award.

Importantly, Quantum mechanics led to the discovery of new fields of study in atomic,



SOLVAY CONFERENCE 1927

colourised by pastincolour.com

A. PICARD	E. HENRIOT	P. EHRENFEST	Ed. HERSEN	Th. DE DONDER	E. SCHRÖDINGER	E. VERSCHAFFELT	W. PAULI	W. HEISENBERG	R.H FOWLER	L. BRILLOUIN
P. DEBYE	M. KNUDSEN	W.L. BRAGG	H.A. KRAMERS	P.A.M. DIRAC	A.H. COMPTON	L. de BROGLIE	M. BORN		N. BOHR	
I. LANGMUIR	M. PLANCK	Mme CURIE	H.A. LORENTZ	A. EINSTEIN	P. LANGEVIN	Ch.E. GUYE	C.T.R. WILSON	O.W. RICHARDSON		

Absents : Sir W.H. BRAGG, H. DESLANDRES et E. VAN AUBEL

Figure 1.5: A photograph of the participants at the famous Solvay Conference in 1927. Many of the founding greats of quantum mechanics were present. Source: The internet.

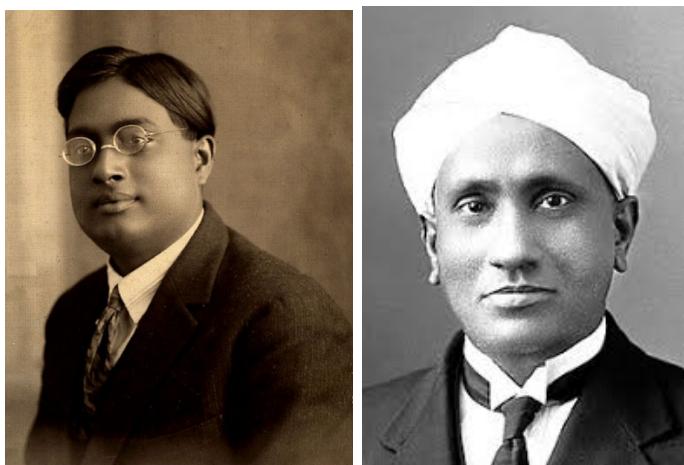


Figure 1.6: Left: Prof. Satyendranath Bose. Right: Prof. C. V. Raman Source: The internet.

nuclear, particle and condensed matter physics! This journey has revolutionised not only our view of the universe around us, but also led to a surge in technological progress over the past century. In a photo below, representative examples of our progress involve the creation of a quantum computer by Google in 2019, and the experimental finding of a single-sheet of Carbon atoms, Graphene, in 2005 by Novoselov and Geim. Also, marvel at the picture given below of a superconducting sample “floating” above a magnet due to the Meissner-Ochsenfeld effect (and the sumo wrestler standing on such a levitating superconducting slab in the accompanying picture) at very low temperatures. Superconductivity is an excellent example of quantum mechanics at the macroscale. A challenge would be to obtain a superconductor at room temperatures! Even more importantly, physics is at its heart an empirical science:

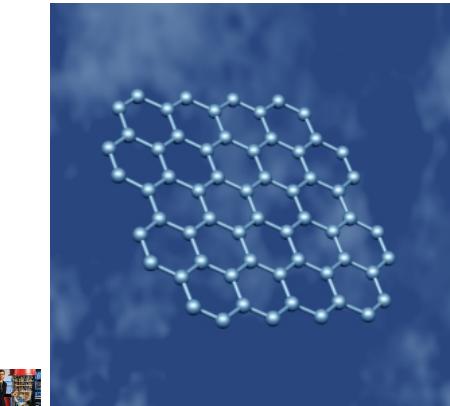


Figure 1.7: Left: Google CEO Sundar Pichai standing beside the quantum computer built in 2019 by Google. Right: Graphene, a single sheet of Carbon atoms, is a wonder material. Source: The internet.



Figure 1.8: (Left) The Meissner-Ochsenfeld effect for the expulsion of magnetic flux from a superconductor, observed spectacularly in the form of a block of a superconductor floating above a permanent magnet. (Right) A Sumo wrestler on a levitating superconductor.

experiments often lead the way in uncovering new phenomena and theories are then built to understand them. So it was with the birth of quantum mechanics. Thus, in beginning our journey into the world of quantum mechanics, it is well worth exploring the experimental puzzles that heralded the quantum revolution, and understanding their resolution.

Chapter 2

The Origins of Quantum Theory

2.1 Solving the Blackbody Radiation Spectrum Puzzle

2.1.1 Blackbody Radiation

Though it does not provide the most compelling evidence for quantum mechanics, it is of historical importance. The perfectly “black body” absorbs all radiation incident on it and reflects nothing. There is more: the blackbody is special in that it emits radiation of all frequencies.



Kirchoff's law: Conservation of heat current in a system which is in thermal equilibrium with its surroundings \Rightarrow the rate of heat absorption = the rate of emission.

Thermal equilibrium \Rightarrow Temperature of System = Temperature of surroundings.

Kirchoff

This law says nothing about the frequency (ν) of the radiation absorbed and emitted, i.e., it is independent of ν . Without this concept, a body would spontaneously heat up or cool down! A practical example of a blackbody is a cavity with a tiny aperture. Light inside the cavity is absorbed, reflected & emitted by its blackened walls and spends a very long time within the cavity before escaping. In this way, the cavity is filled with blackbody radiation, and the aperture acts like the blackbody absorber and emitter.



The total power emitted by a black body follows the Stefan-Boltzmann law

$$P = \sigma AT^4 , \quad (2.1)$$

Stefan

where $\sigma = 5.67 \times 10^{-8} \text{ Js}^{-1} \text{ m}^{-2} \text{ K}^{-4}$ is the Stefan-Boltzmann's constant, A is the surface area of the blackbody and T is its temperature. As we will soon see, Boltzmann showed how the T^4 could be obtained from thermodynamic considerations. Total energy density of radiation



Boltzmann

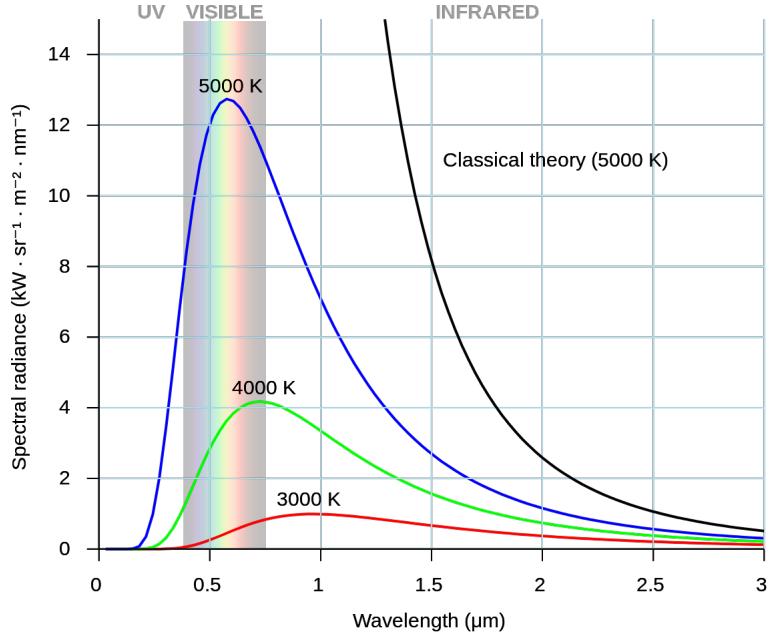
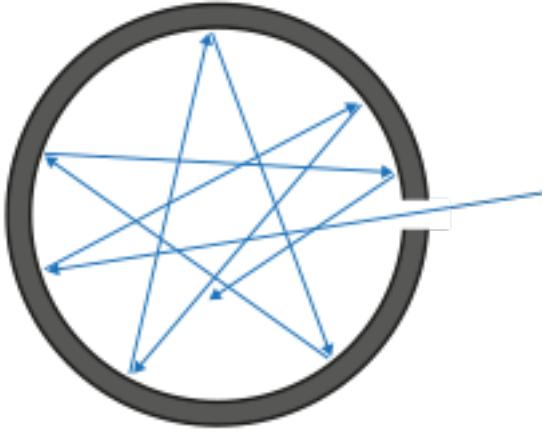


Figure 2.1: Left: A realisation of a blackbody cavity. Right: A plot of Spectral Radiance vs. wavelength for blackbody radiation. Source: The internet.

inside the blackbody

$$\rho = \frac{4P}{cA} = \frac{4\sigma}{c} T^4 = aT^4 \quad (2.2)$$

$$= \int_0^\infty \rho(\nu) d\nu \quad (2.3)$$

where $\rho(\nu)$ is the energy density in a given interval of the frequency of emitted radiation ranging from ν to $d\nu$. The constant $a = \frac{4\sigma}{c} = 7.56 \times 10^{-16} \text{ Jm}^{-3} \text{ K}^{-4}$. The spectral density $\rho(\nu)$ is the quantity which tells us how the radiated energy is distributed over the electromagnetic spectrum, and the total area under the curve gives us the Stefan-Boltzmann law.



A plot of $\rho(\lambda)$ versus wavelength is shown above in the right panel of Fig.2.1. The curves are for different values of temperature T , and show a non-monotonic behaviour (i.e., with a peak). Equivalent plots can also be obtained for $\rho(\nu)$ versus frequency ν (recall that $\nu \propto \frac{1}{\lambda}$). Wien's empirical observation was that the frequency of the peak was proportional to the temperature: $\nu_{peak} \propto T$.

Wien

Since $\nu \propto \frac{1}{\lambda}$, we obtain Wien's displacement law as

$$\lambda_{peak} = \frac{w}{T} , \quad w = 2.9 \times 10^{-3} \text{ mK} . \quad (2.4)$$

Consequences:

- (i) At $T \sim 300K$, λ_{peak} is in IR range \Rightarrow Thermal imaging glasses useful!
- (ii) At $T \sim 5000K$, λ_{peak} shifts into the optical range \Rightarrow , the temperature within a flame increases in going from the red part to the white part and finally the blue part!



Figure 2.2: Left: A view of wildlife through thermal imaging glasses, showing the thermal/heat map of IR radiation emitted by the body. Right: Pictures of a lit bunsen burner displaying various parts of the flame. Source: The internet.

2.1.2 Classical theory (heuristic derivation)

Consider a collection of E-M waves inside a blackbody cavity at temperature T , i.e., a superposition of harmonic waves corresponding to the various normal modes of oscillation of the cavity.

Energy density of Radiation with frequency ν is

$$\rho(\nu) = \bar{E} n(\nu) , \quad (2.5)$$

where $n(\nu)$ is the number density of wave modes within the cavity with frequency ν and \bar{E} corresponds to the average energy content of the radiation.

From the classical law of equipartition of energy,

$$\bar{E} = k_B T , \quad (2.6)$$

where $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

Now, from the fact that the wavenumber for modes within the cavity is given by

$$\vec{k} = \frac{2\pi}{L} \vec{n} , \quad \vec{n} = (n_x, n_y, n_z) , \quad n_x \in \mathcal{Z}, n_y \in \mathcal{Z}, n_z \in \mathcal{Z} , \quad (2.7)$$

where \vec{n} is the mode index (not to be confused with $n(\nu)!$) and L is the spatial extent of the system along any one of the dimensions of the cavity (assumed to be a very large 3D cube), we use the relation

$$\nu = \frac{c}{\lambda} = \frac{c|\vec{k}|}{2\pi} = \frac{c}{L} n , \quad n = \sqrt{n_x^2 + n_y^2 + n_z^2} \quad (2.8)$$

for e-m waves, together with the differential volume element for the case of $n \gg 1$ (cavity with a large number of wave modes, such that we can treat the integer n as a continuum variable) being $dV = 4\pi n^2 dn$ to obtain

$$\nu d\nu = \frac{8\pi}{c^3} \nu^2 d\nu . \quad (2.9)$$

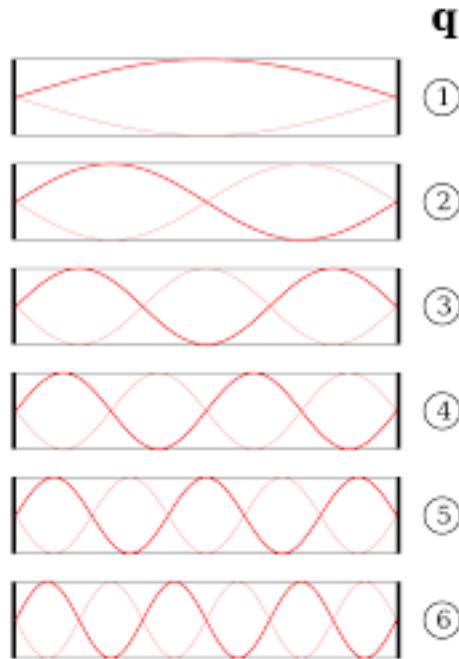


Figure 2.3: Normal modes/harmonics of a linear cavity. The topmost figure is the fundamental or first harmonic, $n = 1$, the next is the first higher harmonic ($n = 2$) and so on.
Source: The internet.

In turn, this leads to

$$\rho(\nu)d\nu = \bar{E} \cdot n(\nu)d\nu = \frac{8\pi k_B T}{c^3} \nu^2 d\nu . \quad (2.10)$$

The above formula is also called Rayleigh-Jeans formula, which as we shall see shortly, works only in the limit $\nu \rightarrow 0!$ Taking this expression for $\rho(\nu)$ at face value, we see that it is divergent: $\rho(\nu) \rightarrow \infty$ as $\nu \gg 1$, indicating a catastrophe in the UV part of the e-m spectrum! Clearly, something is wrong.

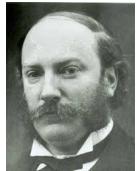


Jeans

2.1.3 Planck's Idea

The average energy is computed by using the probability distribution for the energy in the range E to $E + dE$

$$P(E) = \frac{e^{-\frac{E}{k_B T}}}{k_B T} , \quad (2.11)$$



Rayleigh

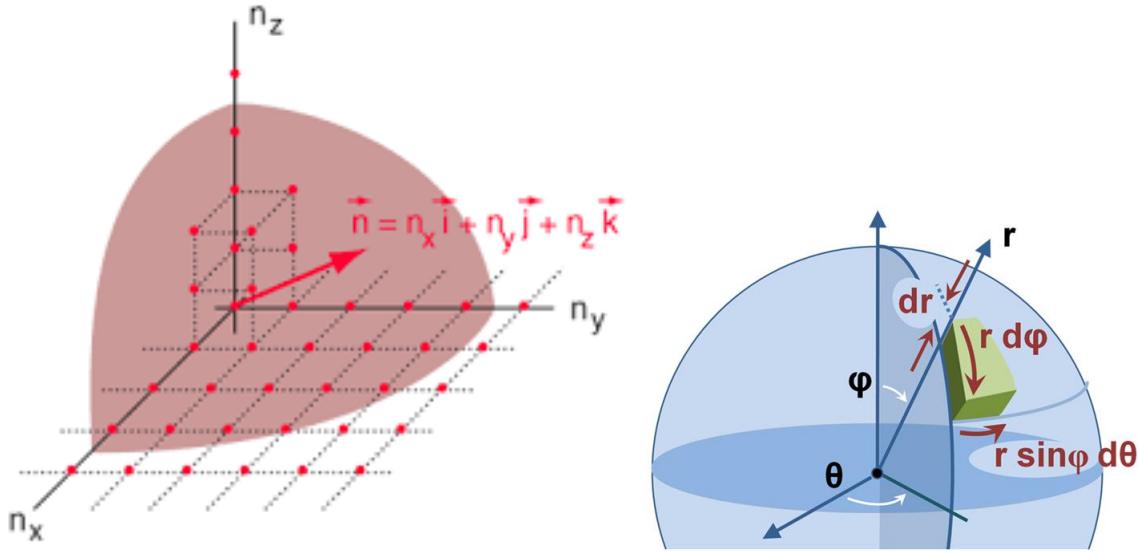


Figure 2.4: (Left) Normal modes of the cavity distributed in (n_x, n_y, n_z) space of integers. (Right) The Volume element in Spherical Polar Coordinates. Source: The internet.

which is the Boltzmann distribution. This gives us

$$\bar{E} = \frac{\int_0^\infty EP(E)dE}{\int_0^\infty P(E)dE} = k_B T \frac{\int_0^\infty d(\frac{E}{k_B T}) \frac{E}{k_B T} e^{-\frac{E}{k_B T}}}{\int_0^\infty d(\frac{E}{k_B T}) e^{-\frac{E}{k_B T}}} \quad (2.12)$$

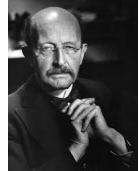
$$= k_B T \frac{\int_0^\infty dx x e^{-x}}{\int_0^\infty dx e^{-x}} \quad (2.13)$$

$$= k_B T . \quad (2.14)$$



Thus, we see that the Boltzmann distribution leads to the Rayleigh Jeans formula. Note that in the above, we used the following relation (recall Gamma function integrals)

$$\int_0^\infty dx x^{2n} e^{-x^2/a^2} = \sqrt{\pi} \frac{(2n)!}{n!} \left(\frac{a}{2}\right)^{2n+1} . \quad (2.15)$$



Planck started the quantum revolution in physics in the year 1900 by quantizing the energy scale in quanta of radiation frequency ν i.e. $E = 0, h\nu, 2h\nu, 3h\nu, \dots$, where h is the Planck constant. Then, recomputing the average energy for blackbody radiation, we obtain

$$\bar{E} = \frac{\sum_{E=0, h\nu, 2h\nu, \dots} EP(E)}{\sum_E P(E)} \quad (2.16)$$

Planck

$$= \frac{\sum_{n=0}^\infty \frac{n h \nu}{k_B T} e^{-n h \nu / k_B T}}{\sum_{n=0}^\infty \frac{e^{-n h \nu / k_B T}}{k_B T}} \\ = \frac{h \nu}{e^{n h \nu / k_B T} - 1} . \quad (2.17)$$

We can see that this answer for \bar{E} is quite different from that obtained from classical arguments. In obtaining the answer, we used the following relations

$$1 + x + x^2 + x^3 + \dots = \frac{1}{1-x} \quad (2.18)$$

$$1 + 2x + 3x^2 + 4x^3 + \dots = \frac{1}{(1-x)^2}. \quad (2.19)$$

This gives us

$$\rho(\nu)d\nu = \bar{E}n(\nu)d\nu \quad (2.20)$$

$$\begin{aligned} &= \frac{8\pi}{c^3} \nu^2 d\nu \frac{h\nu}{e^{nh\nu/k_B T} - 1} \\ &= \frac{8\pi h}{c^3} \frac{\nu^3}{e^{nh\nu/k_B T} - 1} d\nu \end{aligned} \quad (2.21)$$

$$\rightarrow \frac{8\pi k_B T}{c^3} \nu^2 d\nu \quad \text{for } h\nu \ll 1 \quad (\text{Rayleigh-Jeans limit}) \quad (2.22)$$

$$\rightarrow \frac{8\pi h\nu^3}{c^3} e^{-nh\nu/k_B T} \quad \text{for } h\nu \gg 1 \quad (\text{Wien limit}). \quad (2.23)$$

Thus, we find the total energy density ρ as

$$\rho = \int_0^\infty d\nu \rho(\nu) \quad (2.24)$$

$$\begin{aligned} &= \frac{8\pi}{c^3 h^3} (k_B T)^4 \int_{x=0}^\infty dx \frac{x^3}{e^x - 1} \quad (x = \frac{h\nu}{k_B T}) \\ &= \frac{8\pi^5 k_B^4}{15 c^3 h^3} T^4 \quad \text{as } \int_{x=0}^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}, \end{aligned} \quad (2.25)$$

$$= a T^4 \quad \text{where } a = \frac{8\pi^5 k_B^4}{15 c^3 h^3}. \quad (2.26)$$

This expression for ρ gives us the correct T^4 dependence of the Stefan-Boltzmann law, and gives the Stefan-Boltzmann constant as

$$\sigma = a \times \frac{c}{4} = \frac{8\pi^5 k_B^4}{15 c^3 h^3} \times \frac{c}{4} \quad (2.27)$$

$$= \frac{2\pi^4 k_B^4}{15 c^2 h^3}. \quad (2.28)$$

Using the values for $\sigma = 5.67 \times 10^{-8} \text{ Js}^{-1} \text{ m}^{-2} \text{ K}^{-4}$, $c = 3 \times 10^8 \text{ ms}^{-1}$ and $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$, we obtain $h = 6.6626 \times 10^{-34} \text{ Js}$.

Finally, from the expression for $\rho(\nu)$, we can find the ν_{max} for which $\rho(\nu)$ is a maxima

$$\begin{aligned} \frac{d\rho(\nu)}{d\nu} \Big|_{\nu_{max}} &= 0 \\ &= (3 - \frac{h\nu_{max}}{k_B T}) e^{h\nu_{max}/k_B T} - 3, \end{aligned} \quad (2.29)$$

which is numerically found to be

$$\nu_{max} \approx 2.8 \frac{k_B T}{h} \quad (\text{Wien's Law}). \quad (2.30)$$

Putting in the values of k_B , T and ν_{max} obtained from the experiments, we again obtain $h = 6.6626 \times 10^{-34} \text{ Js}$. In this way, Planck offered a comprehensive explanation of the nature of the blackbody spectrum, i.e., he resolved any fears of the UV catastrophe by explaining the origin of the non-monotonic behaviour of the curve for $\rho(\nu)$ plotted versus ν . His courageous step involved quantising the energy variable for e-m radiation. This was a first step taken towards the theory of quantum mechanics, and thus the proportionality constant h bears his name.



Planck

2.2 The Dual Nature of Light

2.2.1 Wave-like: Diffraction and Interference

Classical optics relies on the wave nature of light. For instance, take the phenomena of diffraction and interference.

Precisely the same can be done with water waves.

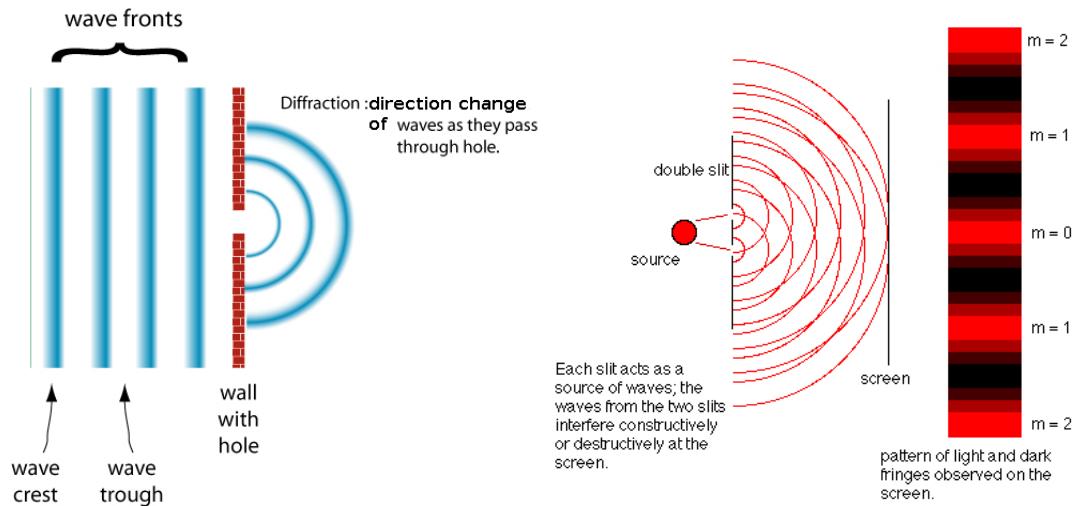


Figure 2.5: Left: Diffraction of waves from a single slit. Right: Interference of waves from a double-slit setup. Source: The internet.

2.2.2 Particle-like: the Photoelectric effect

Maxwell's equations correctly predict the wave nature of light as the propagation of oscillating Electric and magnetic fields. They are backed up by experiments; actually they are derived from there. But this is not a completely consistent picture of light.

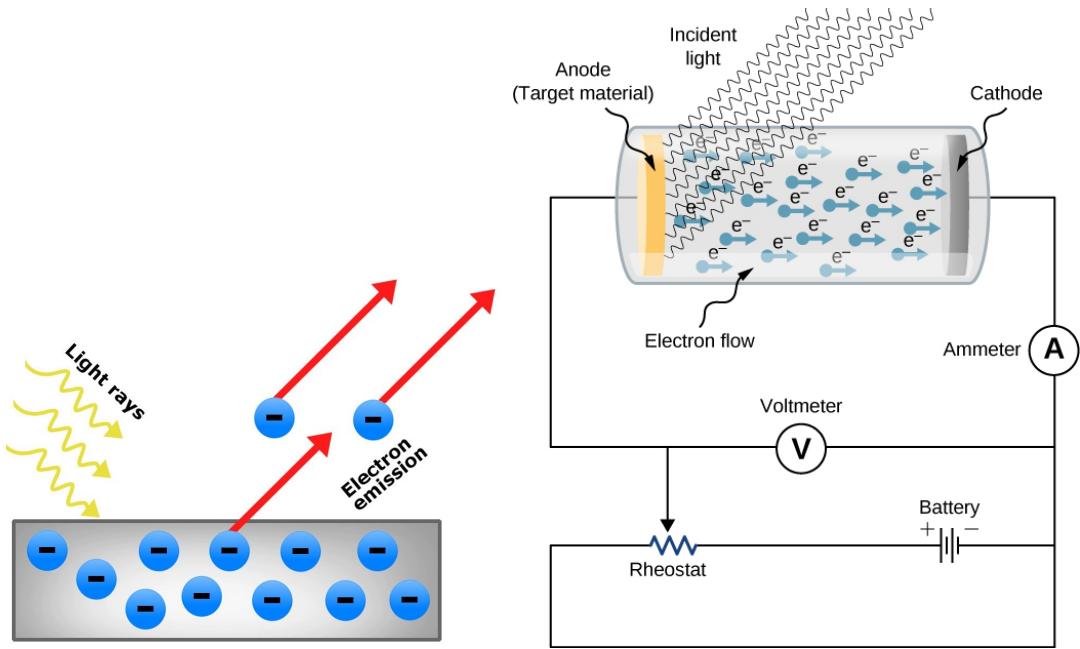


Figure 2.6: Left: The Photoelectric Effect. Right: A schematic diagram of the apparatus used for observing the Photoelectric effect. Source: The internet.

In the Photoelectric effect, shining light on a metal surface produces a current. We vary the frequency (ν) and intensity (I) of the incident light and in the process measure the current (i) and maximum energy $E_{max} = eV_0$ of the emitted electrons. This current is called the “photo-induced current” or “photocurrent”, and V_0 is the “stopping potential” required to cause the current flow to stop.

Typical observations include

$$(i) E_{max} = eV_0 \propto \nu$$

and with a universal slope for all metals given by the Planck constant h , and

$$(ii) \text{ photocurrent } i \propto I, \text{ and } I = \frac{W}{A}$$

where i is the photoelectric current, I is the intensity of light, W is the power of the incident radiation and A is the surface area of the metal on which radiation is incident.

(iii) non-universal intercept of i vs. ν line suggests a minimum (or threshold) energy $-eV_{0,min}$ that must be paid by the incident radiation $h\nu_{min} = -eV_{0,min}$ for a finite photocurrent to be observed.

Point (ii) is certainly logical, as we expect that the higher the intensity of the incident light, the greater the number of electrons will be liberated. But why is $E_{max} \propto \nu$?

From classical E-M theory, $E_{max} \propto I$ (or the energy of radiation). Einstein suggested in 1905 that light consists of a collection of particles called PHOTONS, carrying energy $h\nu$.

Experimental Results

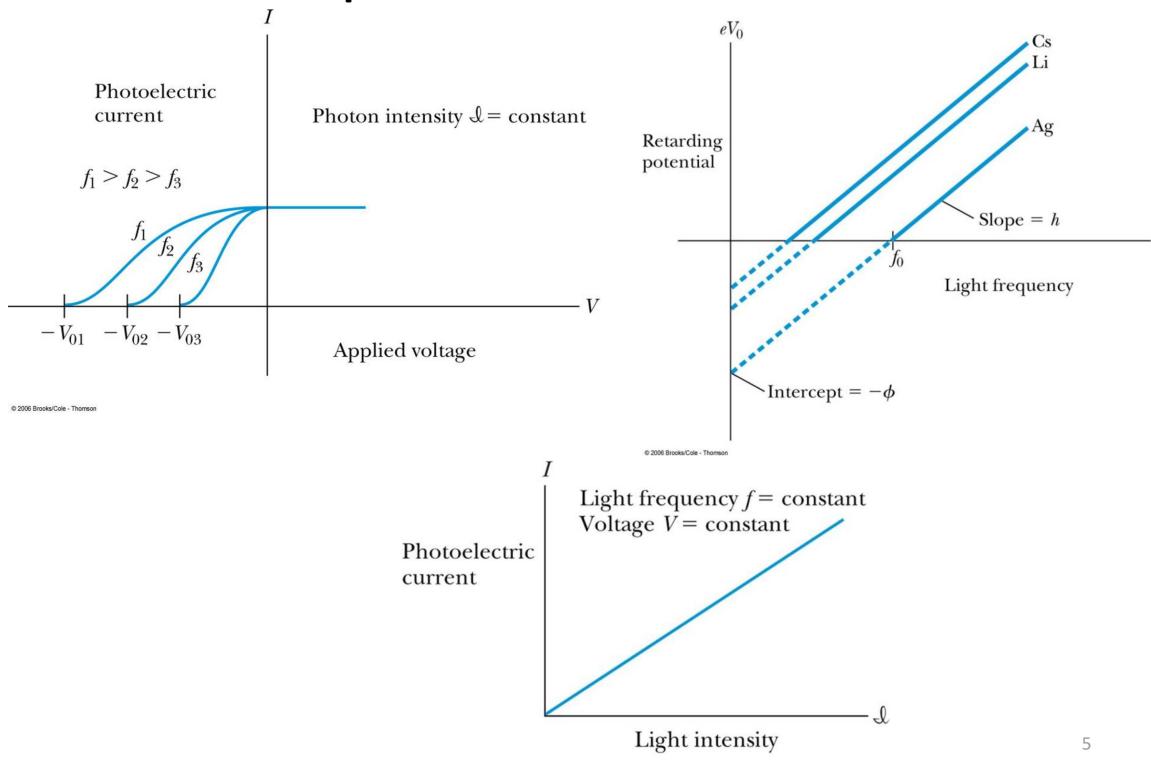


Figure 2.7: Typical experimental observations made for the Photoelectric Effect. Source: The internet.

Furthermore, he postulated that

$$E_B + E_{max} = h\nu ,$$

where the electrons are bound to the metal surface with a binding energy/work function E_B . E_B is therefore the minimum energy required to liberate the electron, and the rest can be transferred to the electrons as its kinetic energy (E_{max}). While the intercept (E_B) can vary between metals, the slope (h , Planck's constant) of the line is universal!

This gives another independent measurement measurement of h , suggesting its fundamental importance. It also establishes the particle-like nature of light. This explanation won Einstein the Nobel Prize in 1921.



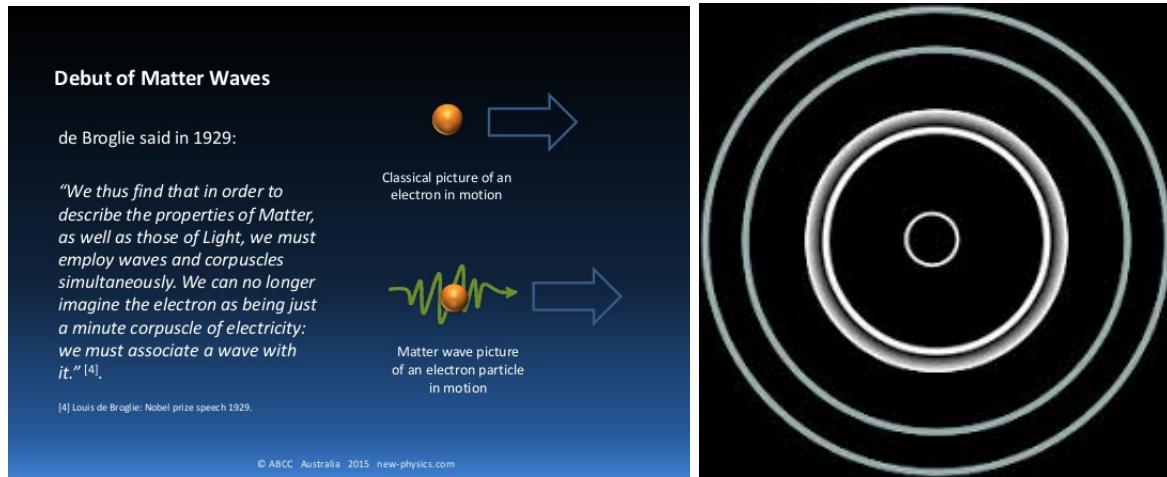
Einstein 2.2.3 de Broglie's Idea

Louis de Broglie postulated that all matter particles have associated with them a wave train whose wavelength is

$$\lambda_{matter} = \frac{h}{p} ,$$



where p is the particle momentum and h is the Planck constant. This suggests that h is truly a fundamental constant of nature. This can be observed in the Davisson-Germer experiment on diffraction of electrons.



Heisenberg

Figure 2.8: Left: de Broglie “Matter Waves”. Right: The characteristic rings observed in the electron diffraction experiment of Davisson and Germer. Source: The internet.

Heisenberg’s uncertainty principle can also be glimpsed here: for a particle possessing a definite momentum (i.e., with a vanishingly small variance), while its associated waveform is everywhere in space! This will render a large variance in its position. Contrast this with Classical Mechanics, where we can enumerate both its position and momentum with arbitrary accuracy!

Quantum tunneling through a barrier can also be understood with de Broglie’s idea. Recall that for $E < V$, the particle is forbidden classically to pass through the barrier. However, by replacing the particle by a wave in quantum mechanics, the waveform can exist under the barrier, as well as “leak through” the barrier to the other side! Tunnel diodes and scanning tunneling microscopy (STM) are all applications of quantum tunneling.



Born

2.3 The Dual Nature of Matter

We now turn to the discussion of Feynman on the double-slit interferometer with electrons (Feynman Lecture on Physics, Vol.III).

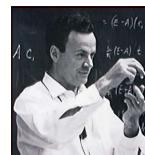
2.3.1 Double-slit experiment with pellets

We begin by investigating the case of 1mm sized pellets being sprayed from a gun at a double slit in a wall with a screen made of wood and a collector which is movable.

Assume that the pellets do not break in their passage through the slits. Also, that the pellets arrive in groups at the screen (this is similar to the assumption that the slits act as a source



Young



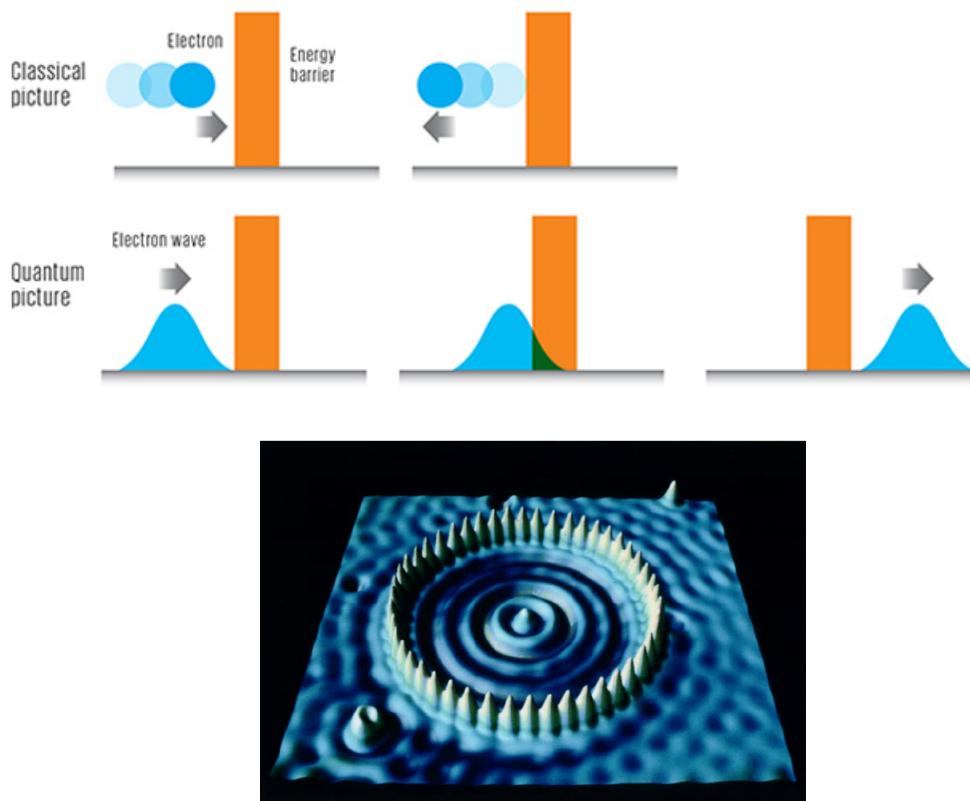


Figure 2.9: Above: The phenomenon of tunneling. Below: A “quantum corral” observed via STM measurements of Iron atoms placed on a Cu surface. Source: The internet.

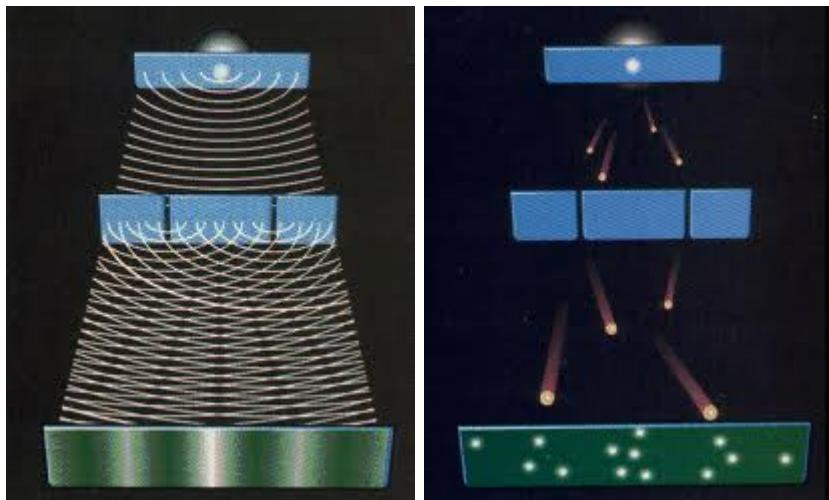


Figure 2.10: (Left) Double-slit Interference Experiment with Light waves. (Right) Double-slit Interference Experiment with Matter particles. Source: The internet.

of pellets); the size of these groups is independent of the rate of firing of the gun. Pellets are caught in the detector one at a time.

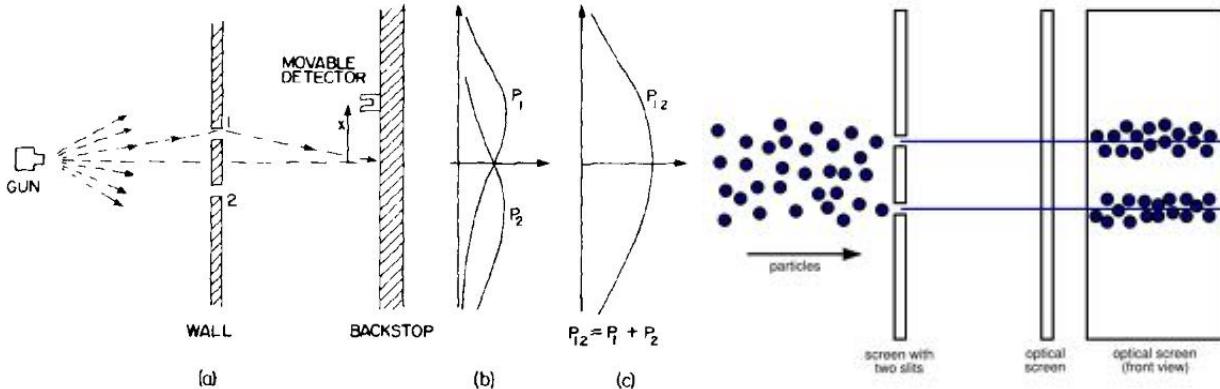


Figure 2.11: Double-slit experiment with pellets. Source: Feynman Lectures Vol.III and the Internet.

Q: What is the probability that a pellet that passes through the holes in the wall will arrive at the screen at a distance “x” from the center of the screen?

Probability means the chance that the pellet will reach the detector. It can be measured by counting the number that arrive at the detector within a particular interval of time, and then taking the ratio of this number to the total number that hit the screen within this interval. Or, for a fixed rate of firing, just the number that reached the detector in a given time interval. When either of hole 1 or 2 are closed, we get the probability distributions given by P_1 and P_2 , and with both both holes open we get

$$P_{12} = P_1 + P_2$$

which is the simple addition of probabilities, i.e., no interference as in the case of Young’s double slit experiment with a light source.

2.3.2 Double-slit experiment with electrons

Use an electron gun as the source (e.g., a tungsten wire heated by a electric current) surrounded by a metallic box with a pinhole. When the box is at a positive voltage with respect to the wire, electrons that are emitted from the wire will be accelerated towards the walls of the box; some will escape through the pinhole.

The electrons passing through the pinhole will be assumed to have the same energy. The double-slit wall can be a metallic sheet with two small holes, and the screen being another plate with the collector being an electron multiplier. Analogously, the entire screen can be an array of electron multipliers synchronised via a computer so as to be able to take simultaneous measurements.

Measurements can take the form of the impulse imparted on the detector: a ”click”, say. Note that all clicks are sharp, distinguishable but identical in, say, the amplitude of the impulse imparted. Note also that the clicks appear in no fixed sequence; they can be erratic/random.

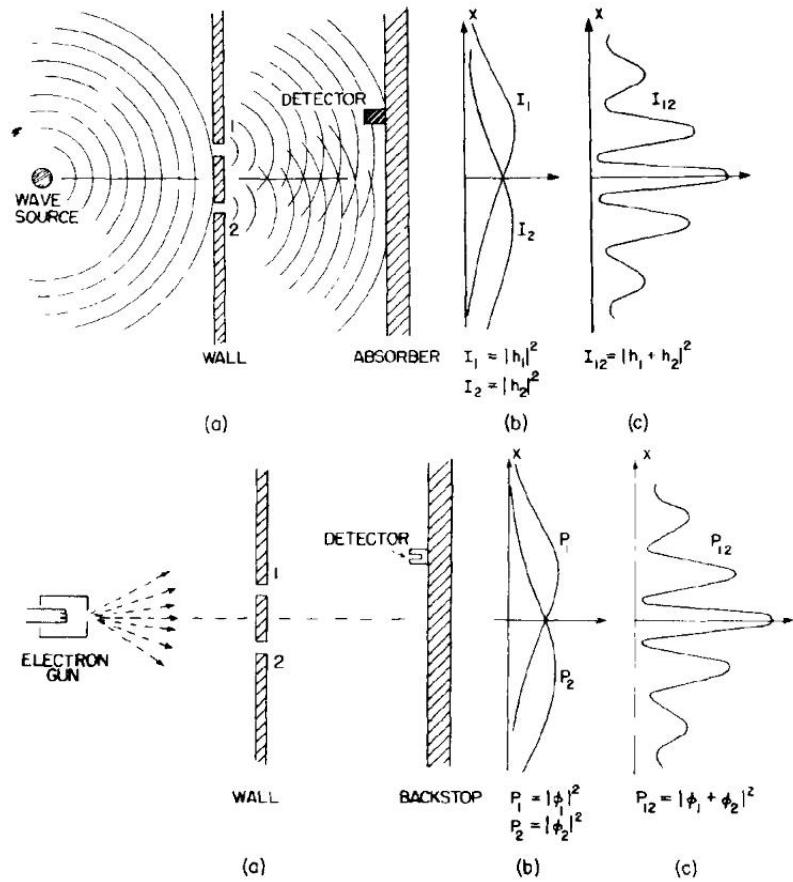


Figure 2.12: Above: Double-slit experiment with light waves. Below: Double-slit experiment with electron “matter waves”. Source: Feynman Lectures Vol.III.

Several counts made over identical time periods lead to similar results for the collected clicks: this makes a time-averaged rate of clicks helpful to keep track of.

Now, as the detector is moved up and down the screen, the rate at which the clicks appear can speed up or slow down, but the amplitude of each click remains unchanged. Also, changing the temperature of the wire gun slows or speeds up the rate of clicks, but doesn’t change the amplitude. Further, with two detectors in place, only a single one receives a click at any point in time (within our ability to resolve).

So far, everything suggests that the electrons are showing particle like behaviour, just as in the case of the double-slit experiment conducted with pellets.

Q: What is the probability that an electron arrives on the array at a distance “x” from the centre?

Keeping the operation of the gun fixed, measure the average rate of clicks at a distance “x” from the centre. Measurements of P_1 and P_2 with one of the slits closed appear quite reasonable!. But what about P_{12} (i.e., when both slits are open)?

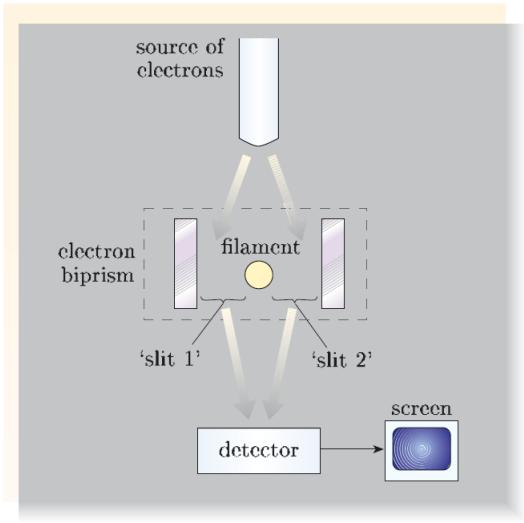


Figure 1.12 Schematic representation of an experimental arrangement used by Tonomura in 1989 to demonstrate the wave–particle duality of electrons. The two paths of the electrons around the filament are analogous to the paths through two slits in an otherwise absorbing screen.



Figure 2.13: Left: Double-slit experiment with electron “matter waves”. Right: Tonomura
Source: The Internet.

The outcome of the experiment:

$$P_{12} \neq P_1 + P_2!$$

The electrons shows interference when both slits are kept open! Not convinced? Take a look at Tonomura’s video showing a realisation of the experiment.

Proposition: Each electron goes through either hole 1 or hole 2.

Can this be right if P_{12} shows signature of interference?

Note that

- (i) electrons can’t split in two!
- (ii) the electrons are highly unlikely to take more complex paths (in through, reverse and out of the two holes)

This can be ruled out by noting that

- (i) the interference pattern shows zeros where either P_1 or P_2 would have shown a finite value. Thus, closing one hole suggests the mystery that the number through the other hole has somehow increased.
- (ii) at the center of the pattern, $P_{12} > 2(P_1 + P_2)$. This suggests that closing one hole somehow decreased the number through the other!

Both of the above cannot be true; i.e, they are mutually inconsistent. Thus, complex paths are ruled out.

Instead, let us define two complex numbers as A_1 and A_2 which we call Probability Amplitudes, such that the probabilities are

$$P_1 = |A_1|^2, P_2 = |A_2|^2 \text{ and } P_{12} = |A_1 + A_2|^2. \quad (2.31)$$

Conclusion: The electrons arrive like particles at the screen and the probability of arrival of the particles is distributed just like the distribution of intensity of a wave!

Since $P_{12} \neq P_1 + P_2$, the proposition given above is not verified: the experiment does not yield the information on whether the electron goes through either hole 1 or hole 2! This means that we cannot decide on which slit the electron goes through.

2.4 Spying on the Electrons

Let us try to watch on the electrons as they pass through the slits. We can do this by putting a light source in between the slits and the screen : on its way to the detector, an electron will scatter some light towards us. By placing the light source suitably, we will hopefully be able to distinguish the slit the electron passes through in terms of a flash of light in the vicinity of that slit.

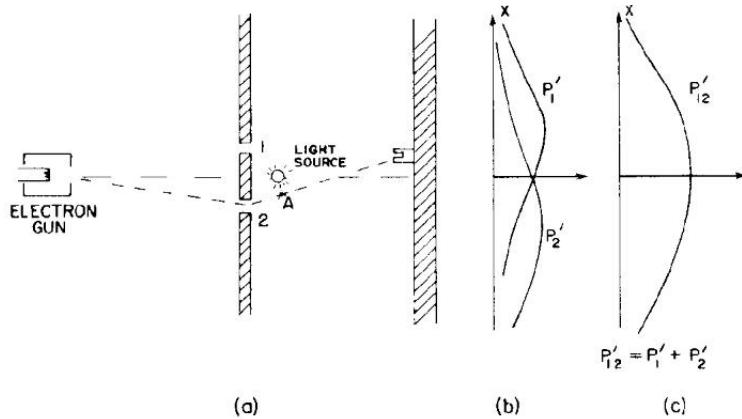


Figure 2.14: Double-slit experiment with electron “matter waves” and a light source by which to spy on which slit the electrons pass through. Source: Feynman Lectures Vol.III.

The result of this gedanken is that every time we find a “click” on the detector, we see a flash at either A (hole 1) or at B (hole 2), but never both at once! This is irrespective of the detector position. This leads to the belief that the electrons pass through either of the two slits, and the proposition holds true (in the presence of a light source) yielding a classical addition of probabilities (say, P'_{12}).

This means that watching the passage of the electrons seems to remove the quantum interference we noted earlier. However, if we switch off the light source and just look at the screen, we get back the P_{12} with the interference! Why is this happening?

Is the light source disturbing the electrons by imparting momentum to them, changing their trajectories so as to give us P'_{12} instead of P_{12} ? Lets check this out by repeating the gedanken, but by dimming the light source. As we do this, we should observe that the flashes caused by the scattering do not get weaker; rather, they become intermittent, i.e., there are occasions when the detector “clicks” but we get no flash.

This happens because some electrons are passing by unnoticed. This coincides with the reappearance of the P_{12} interference pattern! Further, this is happening because dimming the light source reduces the number of the photons that comprise the light source, leaving their energy unchanged ($\propto h\nu$, circa the photoelectric effect). Thus, some electrons escape without meeting any photons on the way.

We’re a little stuck here: since the flash amplitude is independent of the light source intensity, the only electrons we can observe through flashes are ones that we are disturbing. So, if we now plot separately (i) the flashes near point A, (ii) those near point B and (iii) those that pass by unobserved (but are accounted for by the detector clicks), we will get P_1 , P_2 and P_{12} respectively for them!

Conclusion: the electrons can they retain their ability to show quantum interference when they are not being observed.

We note the fact that since the photon momentum

$$p = \frac{h}{\lambda} ,$$

if we use a very large λ , $p \rightarrow 0$ and the momentum imparted will be almost negligible. So, lets use a very large λ light source (\rightarrow red end of the spectrum) for spying on the electrons. As we gradually increase λ , we will still get P_1 , P_2 and P'_{12} for the 3 kinds of observations. Then at some point when $\lambda \gtrsim d$ (the slit separation), we lose the ability to resolve between which slit the electron passed through, i.e., flashes for A and B are unresolvable and the flashes become fuzzy! Remarkably, it is for around this λ that the interference pattern emerges, i.e., $P'_{12} \rightarrow P_{12}$, indicating that the disturbance from scattering off the photons becomes negligible enough for the interference pattern to emerge.

Conclusion: We cannot find a way to tell which slit the electron went through, and yet not disturb the interference pattern.

This relates to a fundamental uncertainty of any quantum system and is not a limitation of the measuring apparatus: the Heisenberg uncertainty principle. So, what about our proposition: is it true or false? We can only say that it appears to be true when we are seeking to determine which hole/ slit the electron went through. But if we are not trying to do this (and is not doing so, are not disturbing the system in any way), we must conclude that the proposition cannot be true, i.e., we cannot determine which slit the electrons pass through! The inherent or intrinsic indeterminacy of the system has to be taken into account when

making any analysis and any conclusion/deductions.

For larger sized objects, the associated de Broglie wave form has an extremely short λ , i.e., oscillations and interference patterns become very fine and the maxima and minima are very hard to distinguish. Any detection typically involves length scales which encompass many wavelengths of the probability distribution curve. Thus, such detection will average over the rapid oscillations, sensing only the envelope. That's why macroscopic objects such as humans will always have a well-defined choice for which of the two slits they will go through, even though the electron doesn't!

“Once you eliminate the impossible, whatever remains, no matter how improbable, must be the truth.” Sherlock Holmes.

There is no mathematical theorem that renders quantum mechanics impossible.

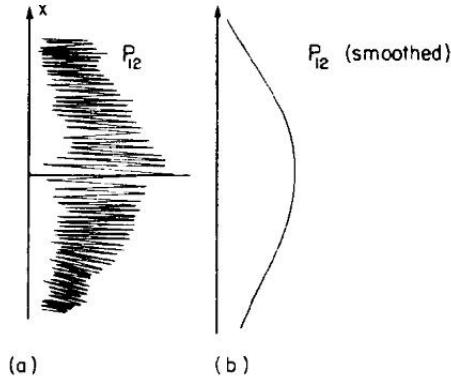


Figure 2.15: Smoothed out “envelope” of the rapid oscillations related to the matter waves.
Source: Feynman Lectures Vol.III.

2.5 Fundamental Postulates of Quantum mechanics

(1) Associated with every classical outcome of a quantum experiment/setup is a probability amplitude ψ . Remember that ψ is a complex valued quantity, $\psi \in \mathcal{C}$. Also, ψ is not directly observable, nevertheless ...

(2) The probability distribution given by $P = |\psi|^2$ is directly observable

(3) For the case of different classical outcomes, the correct way to take account of all of them is to write the probability amplitude for the entire system as a linear superposition of all possible outcomes:

$$\psi_{system} = \psi_1 + \psi_2 + \dots$$

Then, the probability distribution shows signature of quantum interference

$$P = |\psi_{system}|^2 = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + \dots + \text{Quantum Interference terms}$$

eg. for just $\psi_1 = |\psi_1|e^{i\delta_1}$ and $\psi_2 = |\psi_2|e^{i\delta_2}$

$$P = |\psi_1|^2 + |\psi_2|^2 + 2\psi_1^*\psi_2 \quad (2.32)$$

$$= P_1 + P_2 + 2\sqrt{P_1 P_2} \cos \delta \quad (2.33)$$

where $|\psi_1| = \sqrt{P_1}$, $|\psi_2| = \sqrt{P_2}$ and $\delta = \delta_2 - \delta_1$ is the difference between the phases of the waveforms ψ_1 and ψ_2 and leads to the quantum interference. For classical systems, averaging over rapidly oscillating δ removes the quantum interference terms.

Conclusion for the double-slit experiment for electrons:

Every electron passing through the slits has a matter-wave associated with it. If the wavelength is of the order of the slit-width, the matter waves will undergo *quantum interference*, and involve a probability distribution that has peaks and troughs. However, the observation of a single electron on the screen is classical, i.e., it appears as a bright dot in Tonomura's experiment. The quantum outcome of interference fringes is nevertheless manifested when we overlay the outcome from repeating this experiment with a million electrons! This is equivalent to recording the probabilistic pattern in the Schroedinger's Cat gedanken with a large ensemble of identical setups being observed by identical observers (as discussed earlier).

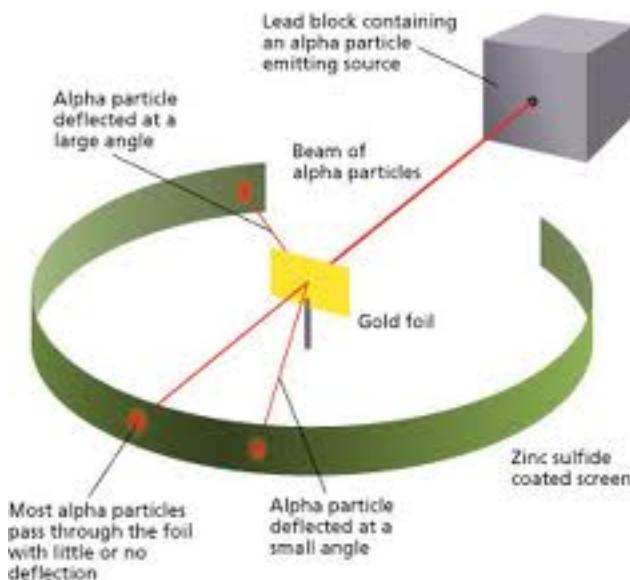
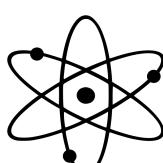


Figure 2.16: A schematic diagram of the experimental setup for the Rutherford gold foil scattering experiment, in which positively charged α particles (that emerge from the radioactive decay process of the source) are directed at a target thin gold foil. The observation of large-angle scattering provides strong evidence for the existence of a positively charged nuclear core within the atom. Source: The internet.

2.6 Bohr's Atom



Rutherford's experiment, in which positively charged α particles were scattered off a gold foil, had already helped establish the picture of a positively charged nucleus surrounded by negatively charged electrons (that are roaming in orbits).

However, this picture has two problems:

- (i) the electrons must undergo centripetal acceleration in their orbits. According to electro-magnetic theory, an accelerating charge must radiate e-m radiation and lose energy in doing so. Such an orbit will then become unstable and the electron should collapse into the positively charged nucleus! But no such radiation is observed; the electron orbits are stable. How can this be?
- (ii) an accelerated electron should radiate e-m radiation in a wide range of frequencies. Instead, radiation of certain discrete wavelengths is observed experimentally when H₂ gas is heated through electrical discharge:



Rydberg

$$\frac{1}{\lambda} = R \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad (2.34)$$

where $m = 1, 2, 3, \dots$, $n = 2, 3, 4, \dots$, $n > m$ and the Rydberg constant $R = 1.097 \times 10^7 \text{ m}^{-1}$. Note that this relation was first obtained empirically! The sequence of lines for $m = 1$ are called the Lyman series, $m = 2$ the Balmer series, $m = 3$ the Paschen series etc.

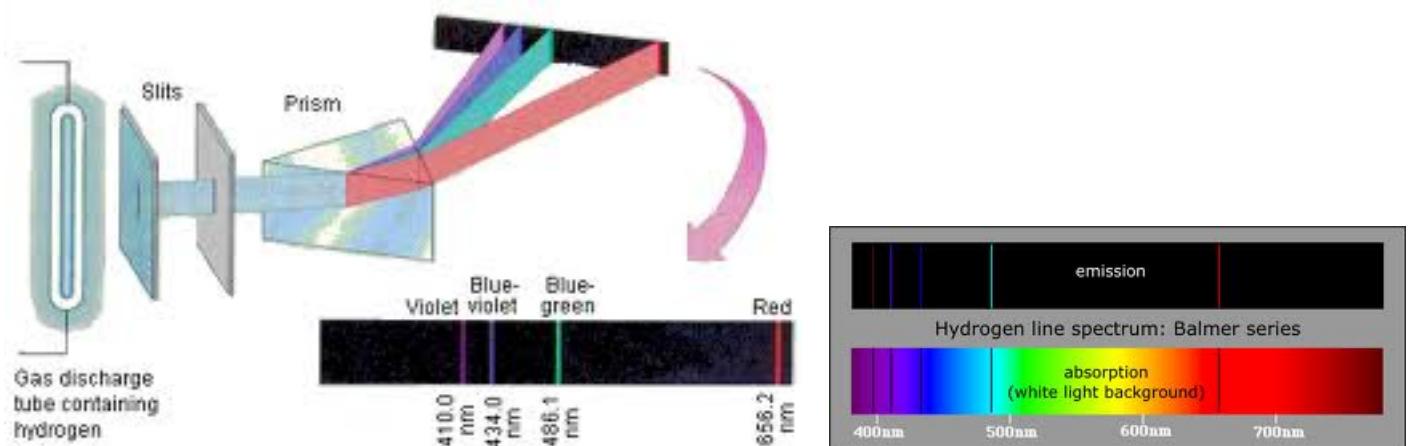


Figure 2.17: Left: A schematic diagram of the experimental setup for the observation of atomic spectra. Right: The atomic spectra of the Balmer series of the Hydrogen atom. Source: The internet.

What is the correct physical picture for the stable atom, and the radiation that is emitted? Enter Niels Bohr. He assumed that the **angular momentum of the electrons in their orbits is quantised**



$$L = pr = mvr = n \frac{\hbar}{2\pi} = n\hbar, \quad n = 1, 2, 3, \dots \quad (2.35)$$

This quantisation can be understood from de Broglie's hypothesis as follows: assume that

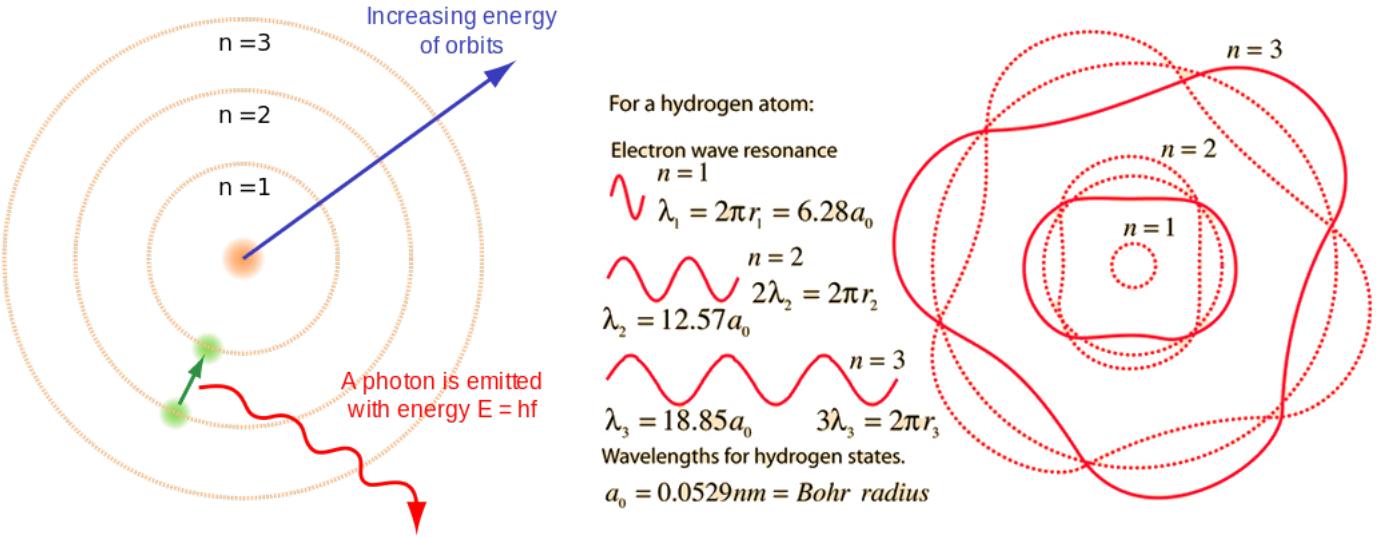


Figure 2.18: Left: A schematic diagram of the experimental setup for the observation of atomic spectra. Right: The atomic spectra of the Balmer series of the Hydrogen atom. Source: The internet.

the electron forms a standing wave in its orbit around the nucleus, with a circumference equal to an integer multiple of the wavelength λ

$$\begin{aligned} 2\pi r &= n\lambda = \frac{nh}{p} \\ L &= pr = \frac{nh}{2\pi}. \end{aligned} \quad (2.36)$$

The rest of the way is purely classical physics. For a classical orbit, we must equate Coulomb and centripetal forces

$$\begin{aligned} \frac{e^2}{4\pi\epsilon_0 r^2} &= \frac{mv^2}{r} \\ \Rightarrow r &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{mv^2} \\ \text{together with } v &= \frac{nh}{2\pi mr}. \end{aligned} \quad (2.37)$$

Solving these two relations together gives

$$\begin{aligned} r &= \frac{4\pi\epsilon_0\hbar^2}{me^2} n^2 = a_0 n^2, \quad \text{Bohr radius } a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11} \text{ m} \\ v &= \frac{e^2}{4\pi\epsilon_0\hbar} \frac{1}{n}. \end{aligned} \quad (2.38)$$

Putting these expressions for r and v in the total energy for the various orbits gives

$$\begin{aligned}
 E_n &= \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \\
 &= -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \\
 &= -\frac{13.6}{n^2} \text{ eV} \quad , \quad n = 1, 2, 3, \dots ,
 \end{aligned} \tag{2.39}$$



Balmer



Lyman



Pfund



Paschen

and $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$. The experimentally observed spectral lines are then given by (using Planck's formula)

$$h\nu = E_{n_1} - E_{n_2} \quad , \quad n_1 > n_2 , \tag{2.40}$$

and n_1 and n_2 have the meaning of the initial and final energy levels of the H-atom respectively, and ν is the frequency of the emitted photon. Written in terms of the wavelength λ , the above relation yields the Rydberg constant as $R = 13.6 \text{ eV}/hc = 1.097 \times 10^7 \text{ m}^{-1}$.

In fact, by using this model, we can understand the various spectral series mentioned earlier, and their corresponding wavelengths. Also, since $n = 1$ is the lowest possible energy state, the electron cannot lose any more energy by emitting radiation. This explains the stability of the H-atom. Nevertheless, this derivation uses too many notions of classical mechanics in a regime where they are not applicable: for instance, the electron does not have a well defined orbit radius or velocity. However, as we will see towards the end of these lectures, a fully quantum mechanical treatment of the H-atom gives the same spectrum. Clearly, Bohr's assumption hits the bulls eye!

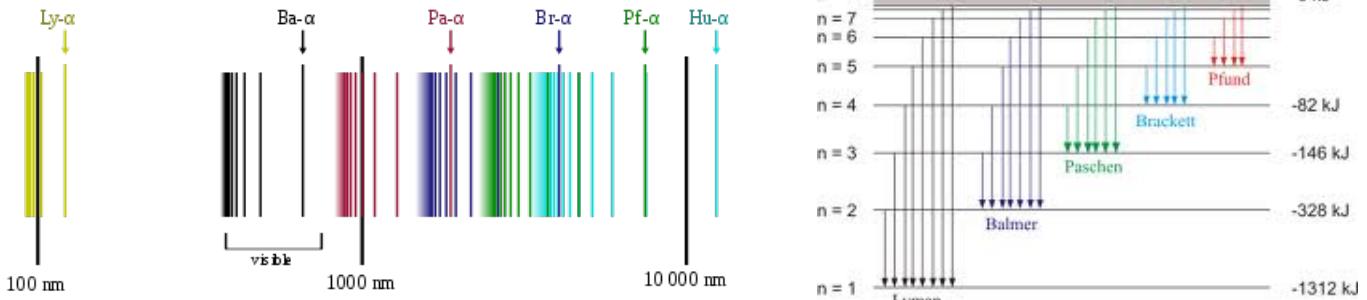


Figure 2.19: Left: Various Spectral Series in the e-m spectrum. Right: The electronic transitions in the Hydrogen atom associated with the respective spectral series. Source: The Internet.

2.7 Conclusions

We have, in this chapter, toured several of the impressive original demonstrations of the quantum world in the form of blackbody radiation, the photoelectric effect, the electron double-slit interference experiment and atomic spectra. It is worth noting that the explanations provided for each of these demonstrations needed the quantisation of an observable

(i.e., an experimentally measurable quantity) that would have taken any value in the classical world! In itself, this sets the stage for our entry into the world of the quantum.

Further, by carefully noting the duality between the particle and wave aspects of both electromagnetic radiation as well as matter, we confronted (say) the beautiful demonstration of interference of matter waves in a double-slit experiment. This led us to formulate certain postulates for the quantum world. We are now in a position to take our journey yet deeper by establishing the foundations of quantum mechanics on a firmer mathematical footing.

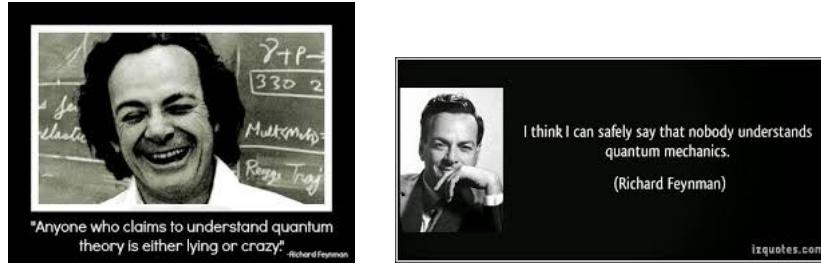


Figure 2.20: Source: The internet.

Chapter 3

The Foundations of Quantum Mechanics

3.1 Recap: Fundamental Postulates of Quantum mechanics

(1) Associated with every classical outcome of a quantum experiment/setup is a probability amplitude ψ . Remember that ψ is a complex valued quantity, $\psi \in \mathcal{C}$. Also, ψ is not directly observable, nevertheless ...

(2) The probability distribution given by $P = |\psi|^2$ is directly observable

(3) For the case of different classical outcomes, the correct way to take account of all of them is to write the probability amplitude for the entire system as a linear superposition of all possible outcomes:

$$\psi_{system} = \psi_1 + \psi_2 + \dots$$

Then, the probability distribution shows signature of quantum interference

$$P = |\psi_{system}|^2 = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + \dots + \text{Quantum Interference terms}$$

eg. for just $\psi_1 = |\psi_1|e^{i\delta_1}$ and $\psi_2 = |\psi_2|e^{i\delta_2}$

$$P = |\psi_1|^2 + |\psi_2|^2 + 2\psi_1^*\psi_2 \quad (3.1)$$

$$= P_1 + P_2 + 2\sqrt{P_1 P_2} \cos \delta \quad (3.2)$$

where $|\psi_1| = \sqrt{P_1}$, $|\psi_2| = \sqrt{P_2}$ and $\delta = \delta_2 - \delta_1$ is the difference between the phases of the waveforms ψ_1 and ψ_2 and leads to the quantum interference. For classical systems, averaging over rapidly oscillating δ removes the Q.I terms.

3.1.1 Heuristic derivation of the Schrödinger equation



Promulgated by Erwin Schrödinger in 1926, this equation gives a description for the behaviour of particles in the quantum world. Following the ideas of wave-particle duality of matter, the Schrödinger equation (SE) describes the mechanics and dynamics of matter waves.



Born

Unlike classical mechanics, a particle in quantum mechanics is no longer associated with a well defined trajectory $\vec{r}(t)$. Instead, we will deal with the wave amplitude for the particle Schrödinger as a function of (\vec{r}, t) .

What then is $\psi(\vec{r}, t)$? The straight forward answer, thanks to Max Born, is that

$$\int_V d\vec{r} |\psi(\vec{r}, t)|^2 \equiv \text{Probability of finding the particle within volume } V \text{ at time } t.$$

Also, $\int_{-\infty}^{\infty} d\vec{r} |\psi|^2 = 1$.

The second relation is called the “normalisation condition” (or “square integrability” condition) for ψ , and all physically realizable solutions ψ must obey this condition. Further, all other physical observables of the particle are also related to $\psi(\vec{r}, t)$.

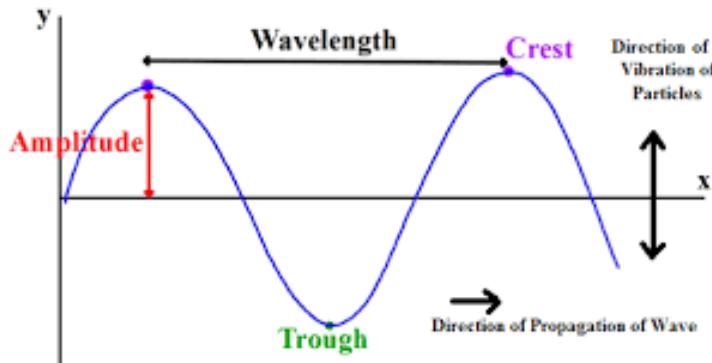


Figure 3.1: A simple waveform in 1D: $y = A \sin\left(\frac{2\pi x}{\lambda}\right)$. Source: The internet.

The derivation : Consider a wave in 1D

$$\psi(x, t) = A \cos\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right)$$

Denote $k = \frac{2\pi}{\lambda}$ (wave number) , $\omega = 2\pi\nu$ (angular frequency)

$$\psi(x, t) = A \cos(kx - \omega t)$$

This is a wave moving to the right with a phase velocity $v = \omega/k$ and group velocity $v_g = d\omega/dk$. In general, we could have written

$$\psi(\vec{r}, t) = A \cos(\vec{k} \cdot \vec{r} - \omega t) + B \sin(\vec{k} \cdot \vec{r} - \omega t),$$

or even

$$\psi(\vec{r}, t) = C \exp\left\{i(\vec{k} \cdot \vec{r} - \omega t)\right\}, \quad C \in \mathcal{C}$$

A quick recap on phase and group velocities. The phase velocity v is the velocity of propagation of points of constant phase $\phi = kx - \omega t$ for a single harmonic component of the full wavefunction ψ , i.e., stationarity of phase ϕ with respect to time t

$$\frac{d\phi}{dt} = k \frac{dx}{dt} - \omega = 0 \rightarrow \frac{dx}{dt} \equiv v = \frac{\omega}{k}. \quad (3.3)$$

On the other hand, in the neighbourhood of a point within a wavepacket, the phase $\phi = kx - \omega t$ is stationary with respect to the wavevector k , i.e., various k components of the wavepacket stand in constant phase relative to one another. Then, the group velocity (v_g) given by

$$\frac{d\phi}{dk} = x - \frac{d\omega}{dk}t = 0 \rightarrow \frac{x}{t} \equiv v_g = \frac{d\omega}{dk}, \quad (3.4)$$

and defines the motion of all such points that are in constant relative phase to one another.

Applying the properties of e-m waves to matter-waves, we already know that

$$(i) \quad E = h\nu = \hbar\omega \quad (\text{Planck})$$

$$(ii) \quad p = \frac{h}{\lambda} = \hbar k \quad (\text{de Broglie}),$$

where $\hbar = h/2\pi$. For a non-relativistic particle with mass m : $E = \frac{p^2}{2m}$.

Now, we can check that acting the following derivative on ψ

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = i\hbar(-i\omega)C \exp\left\{i(\vec{k} \cdot \vec{r} - \omega t)\right\} = E\psi(\vec{r}, t)$$

Note: in the language of linear algebra, we say that ψ is the eigenfunction of the linear operator $i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t}$ with eigenvalue E .

Now, for $\vec{k} \cdot \vec{r} = k_x x + k_y y + k_z z$, we can also see that $\psi(\vec{r}, t)$ is the eigenfunction of the linear operator $-i\hbar \frac{\partial}{\partial x}$ with eigenvalue $\hbar k_x$

$$-i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial x} = -i\hbar(ik_x)C \exp\left\{i(\vec{k} \cdot \vec{r} - \omega t)\right\} = \hbar k_x \psi(\vec{r}, t).$$

Similarly, $-i\hbar\frac{\partial}{\partial y}$ and $-i\hbar\frac{\partial}{\partial z}$ give eigenvalues $\hbar k_y$ and $\hbar k_z$ respectively.

$$\therefore -i\hbar\vec{\nabla}\psi(\vec{r}, t) = -i\hbar\left(\hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z}\right)\psi(\vec{r}, t) \quad (3.5)$$

$$= \hbar\left(\hat{x}k_x + \hat{y}k_y + \hat{z}k_z\right)\psi(\vec{r}, t) \quad (3.6)$$

$$= \hbar\vec{k}\psi(\vec{r}, t) \quad (3.7)$$

$$\Rightarrow -i\hbar\vec{\nabla}\psi = \vec{p}\psi \quad (3.8)$$

and

$$(-i\hbar\vec{\nabla}\psi) \cdot (-i\hbar\vec{\nabla}\psi) = \vec{p} \cdot \vec{p} \psi \quad (3.9)$$

$$\Rightarrow -\hbar^2\vec{\nabla}^2\psi = |\vec{p}|^2\psi = p^2\psi. \quad (3.10)$$

This gives us

$$\frac{-\hbar^2}{2m}\nabla^2\psi = \frac{p^2}{2m}\psi, \quad (3.11)$$

$$i\hbar\frac{\partial\psi(\vec{r}, t)}{\partial t} = E\psi. \quad (3.12)$$

Since $E = \frac{p^2}{2m}$, it is entirely plausible that

$$\frac{-\hbar^2}{2m}\nabla^2\psi = i\hbar\frac{\partial\psi(\vec{r}, t)}{\partial t}$$

Now assume that, in the presence of a spatially dependent potential energy $V(\vec{r})$, the extension to the above relation is

$$\hat{H}\psi \equiv -\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi = i\hbar\frac{\partial\psi(\vec{r}, t)}{\partial t},$$

where we have defined the Hamiltonian operator

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) = i\hbar\frac{\partial}{\partial t}. \quad (3.13)$$

Clearly, for $V(\vec{r}) \neq 0$, the solution $\psi \simeq \exp\{i(\vec{k}\vec{r} - \omega t)\}$ is not guaranteed to work (though it worked very well for $V = 0$).

Postulate: The above equation gives the correct $\psi(\vec{r}, t)$ for any potential $V(\vec{r})$.



Hamilton

This has been checked and verified rigorously in many cases for the past century! Thus, we can say with some comfort that the postulate holds, and that the Schrödinger equation correctly describes the dynamics of matter waves in various situations (i.e. described by different $V(\vec{r})$).

3.2 Physical Meaning of Ψ



$\Psi(\vec{r}, t)$ is a complex quantity in Quantum Mechanics, and thus it cannot represent a physically measurable quantity. Born argued that the probability density is, however, measurable:

$$|\psi|^2 = \psi^* \psi . \quad (3.14)$$

Now, just as ψ is a solution of the SE, so is $c\psi$ (where c is an arbitrary complex number). In this sense, the value of the complex number c cannot be determined from just the SE. Instead,

Born we need an additional requirement called the “Normalisation Condition” on the probability density to determine c

$$\int_{\text{all space}} d^3x \psi^* \psi = 1 . \quad (3.15)$$

As an example, consider the case of a particle in an infinite square well of extent a , with

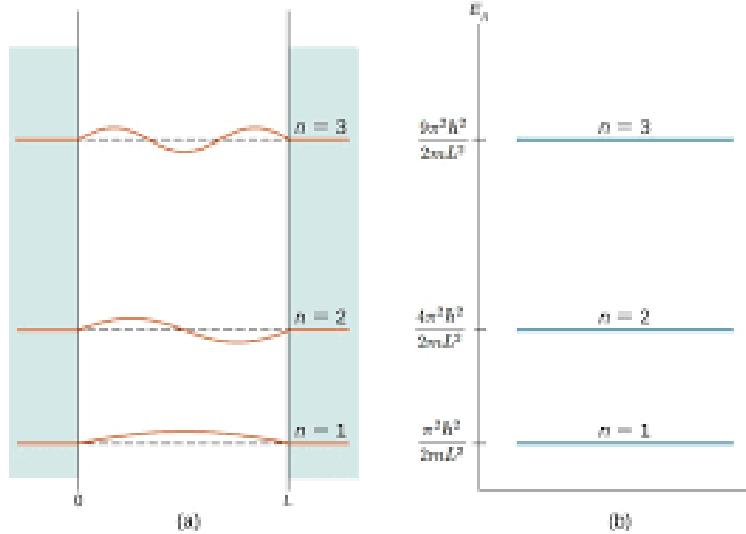


Figure 3.2: Wavefunctions (Left) and Energy Spectrum (Right) for the lowest three eigenstates of the particle in a box problem.

the ground state wavefunction given by

$$\begin{aligned} \psi &= A \sin\left(\frac{\pi x}{a}\right) \exp\left\{-\frac{i\hbar\pi^2}{2ma^2}t\right\} \quad 0 \leq x \leq a \\ &= 0 \text{ for } x < 0 \text{ and } x > a \end{aligned} \quad (3.16)$$

From the normalisation condition

$$\begin{aligned} \int_0^a dx |A|^2 \sin^2\left(\frac{\pi x}{a}\right) &= 1 \\ |A|^2 \frac{a}{2} &= 1 \implies A = \sqrt{\frac{2}{a}} \\ \implies \psi &= \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) e^{\frac{-i\hbar\pi^2}{2ma^2}t} \end{aligned}$$

We could have chosen $A = -\sqrt{\frac{2}{a}}$ or even $A = \exp\{i\phi\}\sqrt{\frac{2}{a}}$ where the phase ϕ is arbitrary. This choice doesn't matter, as all observables depend on the probability density ($\propto |A|^2$) and not on the probability amplitude.

Convention: We usually take A to be real and positive.

3.3 Observables, Operators and Expectation values

For a particle in state ψ , the expectation value of the position operator \hat{x} is defined as

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} dx \psi^* \hat{x} \psi = \int_{-\infty}^{\infty} dx x \times |\psi(x)|^2$$

Note: It is worth stressing that the quantity $\langle \hat{x} \rangle$ is the *average* (or *mean*) position obtained from measurements made from an entire ensemble of systems, all prepared in the state ψ . It is not the average obtained by taking repeated measurements on any one system.

Similarly, we have already seen linear operators for momentum and energy $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, $E = i\hbar \frac{\partial}{\partial t}$, such that we can write the expectation value for \hat{p}_x as

$$\langle \hat{p}_x \rangle = \int_{-\infty}^{\infty} dx \psi^*(x, t) (-i\hbar \frac{\partial}{\partial x}) \psi(x, t) .$$

These are all physically measurable quantities and are called **observables**. Very generally, in quantum mechanics,

OBSERVABLES are associated with LINEAR OPERATORS].

For any linear operator $\hat{\theta}$, its expectation value is

$$\langle \hat{\theta} \rangle = \int_v d\vec{r} \psi^*(\vec{r}, t) \hat{\theta} \psi(\vec{r}, t) \quad (3.17)$$

Note: One obtains definite results for the action of a linear operator on a state only if it is an eigenstate of that operator, i.e.,

$$\hat{\theta} \psi = \theta \psi$$

In this case, it is easy to see that

$$\begin{aligned} \langle \hat{\theta} \rangle &= \int_v d\vec{r} \psi^*(\vec{r}, t) \hat{\theta} \psi(\vec{r}, t) \\ &= \theta \int_v \psi^*(\vec{r}, t) \psi(\vec{r}, t) \\ &= \theta \quad (\text{as } \int_v \psi^*(\vec{r}, t) \psi(\vec{r}, t) = 1) . \end{aligned} \quad (3.18)$$

Conversely, if ψ is not an eigenstate of $\hat{\theta}$, acting with $\hat{\theta}$ on ψ will not give a value which will always be the same for repeated measurements on an ensemble with state ψ , i.e., we cannot predict the outcome of measuring θ on ψ with complete certainty. Instead, in such cases, the expectation value θ is always a well-defined quantity.

In fact, these **expectation values obey classical laws**. For instance,



$$\langle \hat{v} \rangle = \frac{d\langle \hat{x} \rangle}{dt},$$

$$\langle \hat{p}_x \rangle = m\langle \hat{v} \rangle = m \frac{d\langle \hat{x} \rangle}{dt},$$

Ehrenfest

$$\frac{d\langle \hat{p}_x \rangle}{dt} = \left\langle -\frac{d\hat{V}}{dx} \right\rangle.$$

These classical relations are examples of **Ehrenfest's theorem**, and are an expression of the correspondence principle for matter waves. Lets see how the third identity can be arrived at.

$$\begin{aligned} \frac{d\langle \hat{p}_x \rangle}{dt} &= \int dx \left(\frac{\partial \psi^*}{\partial t} \right) \hat{p}_x \psi + \int dx \psi^* \frac{\partial \hat{p}_x}{\partial t} \psi + \int dx \psi^* \hat{p}_x \frac{\partial \psi}{\partial t} \\ &= \frac{-1}{i\hbar} \int dx (\hat{H}\psi)^* \hat{p}_x \psi + \left\langle \frac{\partial \hat{p}_x}{\partial t} \right\rangle + \frac{1}{i\hbar} \int dx \psi^* \hat{p}_x (\hat{H}\psi) \quad (\text{using S.E: } \hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}) \\ &= \left\langle \frac{\partial \hat{p}_x}{\partial t} \right\rangle + \frac{1}{i\hbar} \int dx \psi^* (\hat{p}_x \hat{H} - \hat{H}^* \hat{p}_x) \psi \\ &= \frac{1}{i\hbar} \int dx \psi^* (\hat{p}_x \hat{H} - \hat{H} \hat{p}_x) \psi \quad (\text{as } \left\langle \frac{\partial \hat{p}_x}{\partial t} \right\rangle = 0, \hat{H}^* = \hat{H}, (\hat{H}\psi)^* = \psi^* \hat{H}^*) \\ &= \frac{1}{i\hbar} \int dx \psi^* (\hat{p}_x \hat{V} - \hat{V} \hat{p}_x) \psi \quad (\text{as the kinetic energy part vanishes}) \\ &= \frac{1}{i\hbar} \times -i\hbar \int dx \psi^* \left(\frac{\partial \hat{V}}{\partial x} \right) \psi \quad (\text{using the chain rule}) \\ &= \left\langle -\frac{d\hat{V}}{dx} \right\rangle. \end{aligned} \tag{3.19}$$

Note that the 4th line above involves the commutator of the two operators \hat{p}_x and \hat{H} , i.e.,

$$\begin{aligned} \hat{p}_x \hat{H} - \hat{H} \hat{p}_x &\equiv [\hat{p}_x, \hat{H}] \\ &= -\frac{\hbar^2}{2m} [\hat{p}_x, \hat{p}_x^2] + [\hat{p}_x, \hat{V}(\vec{r})] \\ &= [\hat{p}_x, \hat{V}(\vec{r})], \end{aligned} \tag{3.20}$$

where we have used the fact that $[\hat{p}_x, \hat{p}_x^2] = 0$, i.e., the kinetic energy term commutes with \hat{p}_x . The commutator for two linear operators $\hat{\theta}_1$ and $\hat{\theta}_2$ is defined as

$$[\hat{\theta}_1, \hat{\theta}_2] = \hat{\theta}_1 \hat{\theta}_2 - \hat{\theta}_2 \hat{\theta}_1. \tag{3.21}$$

The fact that $[\hat{p}_x, \hat{p}_x^2] = 0$ can be easily established by taking $\hat{p}_x = -i\hbar\partial/\partial x$ and evaluating $[\hat{p}_x, \hat{p}_x^2]f(x)$ where $f(x)$ is some smooth, differentiable function of x . Also, note that $\hat{H}^* = \hat{H}$ relates to the Hermitian nature of the linear operator \hat{H} , i.e., it must have a real eigenvalue. Further, $(\hat{H}\psi)^* = \psi^*\hat{H}^*$ is the Hermitian adjoint of $\hat{H}\psi$. We will see these relations in more detail in a later lecture.

The above Ehrenfest relation is nothing but an expression of Newton's second law for matter waves!

I leave it to you to prove some of the other examples of Ehrenfest's theorem as an exercise. Note that the form of the third type of Ehrenfest relation for an operator A will take

$$\frac{d\langle A(t) \rangle}{dt} = \frac{1}{i\hbar} \langle [H, A(t)] \rangle , \quad (3.22)$$

where $A(t) = U_t A U_t^\dagger$ and $U_t = e^{itH/\hbar}$. (Note that we have not assumed any explicit dependence of A on time t . Also, we have only been considering the expectation value (or "mean") of experimentally measurable quantities (observables) thus far. What about the fact that the such quantities will also have a variance (and therefore standard deviation), skew, kurtosis etc.? We will turn to this next.)

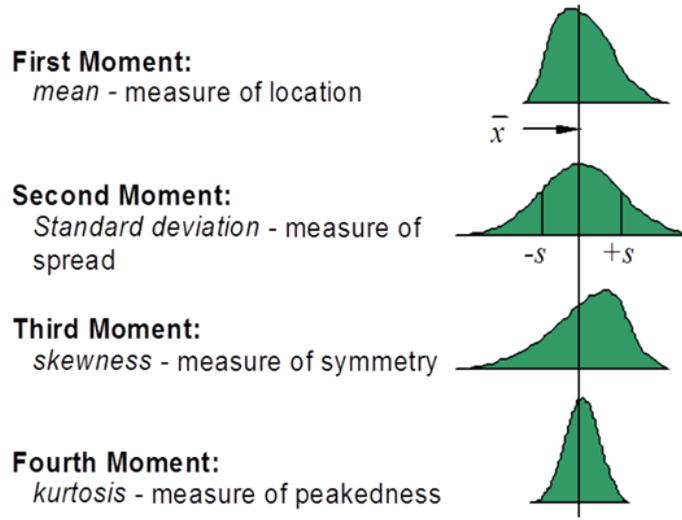


Figure 3.3: First four moments of a distribution. Source: The Internet.

Chapter 4

Formalism I : Operators, Eigenfunctions and Eigenvalues

4.1 Operators, Eigenfunctions and Eigenvalues

4.1.1 Definition of an operator

Recall that a Function is simply a rule for taking a number and changing it to another number, e.g., $f(x) = x^2$.

An operator is a rule for changing one function into another

$$D[f(x)] \equiv \frac{df(x)}{dx}$$

$$D[3x^2] = 6x$$

$$D[\cos x] = -\sin x$$

We are interested in a special class of operators called *linear* operators (L) such that:

$$(i) \quad L[f(x) + g(x)] = L[f(x)] + L[g(x)] \quad (4.1)$$

$$(ii) \quad L[cf(x)] = cL[f(x)] , \quad c \in \mathcal{R} \text{ or } c \in \mathcal{C} . \quad (4.2)$$

Note that the differential operator D satisfies the criteria for being a Linear Operator

$$D[f(x) + g(x)] = D[f(x)] + D[g(x)]$$

$$D[cf(x)] = cD[f(x)] ,$$

but the operator $A[f(x) + g(x)] = [f(x) + g(x)]^n$ does not

$$A[f(x) + g(x)] = [f(x) + g(x)]^n \neq f(x)^n + g(x)^n \quad \text{for } n > 1.$$

4.1.2 Eigenfunctions and Eigenvalues

For a linear operator L and a function $f(x)$ such that

$$L[f(x)] = cf(x), \quad c \in \mathcal{R} \text{ or } c \in \mathcal{C},$$

we call $f(x)$ an eigenfunction of L with eigenvalue c . The function $f(x)$ and the eigenvalue c will clearly depend on the form of the operator L . For instance, for the case of the differential operator D , we have for

$$D[f(x)] = cf(x) \Rightarrow f(x) = A \exp\{cx\}$$

is the general solution, where A is arbitrary constant. On the other hand, functions like $\ln x$, x^n and $\sin x$ are not eigenfunctions of the linear operator D .

In Quantum Mechanics, we postulate that linear operators associated with **all observables** (i.e., **experimentally measurable quantities**) have **real eigenvalues**. Such operators are called **Hermitian**

$$L[f(x)] = cf(x), \quad c \in \mathcal{R} \quad \text{and} \quad (4.3)$$

$$\langle L \rangle = \langle L^\dagger \rangle \in \mathcal{R}, \quad (4.4)$$

where the \dagger operation is defined as

$$\begin{aligned} \langle A \rangle &= \int_{-\infty}^{\infty} dx \psi^* A \psi, \quad \langle A^\dagger \rangle = \int_{-\infty}^{\infty} dx \psi^* A^\dagger \psi \\ \therefore \langle A \rangle &= \langle A^\dagger \rangle \\ \Rightarrow \langle A \rangle &= \int_{-\infty}^{\infty} dx \psi^* A \psi = \int_{-\infty}^{\infty} dx \underbrace{(A\psi)^*}_{=\psi^* A^\dagger} \psi = \langle A^\dagger \rangle. \end{aligned}$$

In the matrix formulation of quantum mechanics, the operator A is a $N \times N$ matrix, the state vector (wavefunction) ψ is a $1 \times N$ column vector and the state vector (wavefunction) ψ^* is a $N \times 1$ row vector, such that

$$\langle A \rangle = \int_V d^3r (\psi_1 \psi_2 \dots \psi_N)^* \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1N} \\ A_{21} & A_{22} & \dots & A_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ A_{N1} & A_{N2} & \dots & A_{NN} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix}. \quad (4.5)$$

Then, it becomes clear that the \dagger (i.e., Hermitian conjugation) operation involves taking both the complex conjugation *as well as* a transpose operation (i.e., such that A can be transferred from its action on a column vector to a row vector). Recall that the complex conjugation for the matrix must be done for every one of its elements.

For the special case of the row and column vector becoming a single state, say ψ_n^* and ψ_N respectively, and the operator A becoming a single element, say A_{NN} , there is now no longer any need to take the transpose action.

4.1.3 Commutators

As two linear operator \hat{A} and \hat{B} are not generally commutative under multiplication

$$\hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$$

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0 .$$

Why does this matter? For the case that $[\hat{A}, \hat{B}] = 0$,

$$(i) \quad \hat{A}\psi = a\psi , \tag{4.6}$$

$$(ii) \quad \hat{B}\psi = b\psi . \tag{4.7}$$

Now from (i)

$$\hat{B}(\hat{A}\psi) = \hat{B}a\psi = a\hat{B}\psi . \tag{4.8}$$

But since $\hat{A}\hat{B} = \hat{B}\hat{A}$, we can write the above as

$$\hat{B}(\hat{A}\psi) = \hat{A}(\hat{B}\psi) = a(\hat{B}\psi) , \tag{4.9}$$

i.e., $\hat{B}\psi$ is also an eigenfunction of \hat{A} with eigenvalue a . This indicates that $\hat{B}\psi$ must satisfy the eigenvalue equation: $\hat{B}\psi = b\psi$.

Note: For $[\hat{A}, \hat{B}] = 0$, we see that the state ψ is an eigenstate of both \hat{A} and \hat{B} , and we can simultaneously measure eigenvalues for both observables related to \hat{A} and \hat{B} .

On the other hand, for $[\hat{A}, \hat{B}] \neq 0$, it is clear that the operators \hat{A} and \hat{B} do not share the same eigenbasis, and we cannot simultaneously measure well-defined eigenvalues for both. For instance, consider the example of the conjugate observables $\hat{p} \equiv -i\hbar \frac{d}{dx}$ and $\hat{x} \equiv x$ (the spatial variable defined on \mathcal{R}) acting on wavefunctions defined on a wavefunction chosen to be in the x -representation, $\psi(x)$:

$$\begin{aligned} [\hat{p}, \hat{x}]\psi(x) &= (-i\hbar \frac{d}{dx})(x\psi(x)) - x(-i\hbar \frac{d}{dx})\psi(x) \\ &= -i\hbar x(\frac{d\psi(x)}{dx}) - i\hbar\psi + i\hbar x(\frac{d\psi(x)}{dx}) \\ &= -i\hbar\psi \\ \Rightarrow [\hat{p}, \hat{x}] &= -i\hbar \quad (\text{dropping the } \psi \text{ from both sides}) , \end{aligned} \tag{4.10}$$

i.e., confirming the fact \hat{p} and \hat{x} do not commute with one another. Note that you could have chosen to carry out this calculation with $\hat{p} \equiv p$ (the momentum variable defined on \mathcal{R}), $\hat{x} \equiv i\hbar \frac{d}{dp}$ and wavefunctions in the p -representation, $\psi(p)$. You will again obtain precisely the same result (check this for yourself!). This shows the representation independence of the relation $[\hat{p}, \hat{x}] = -i\hbar$.

This relation tells us that \hat{p} and \hat{x} do not share the same eigenbasis, and we cannot simultaneously measure well-defined eigenvalues for both \hat{p} and \hat{x} . This is basically a restatement of the Heisenberg uncertainty relation for \hat{p} and \hat{x} . Further, the appearance of the $i\hbar$ is actually signalling the wave-particle duality at the heart of quantum mechanics (we are playing with matter waves after all!). As you will learn in advanced courses up ahead, the $i\hbar$ factor is

also an indication of the fact that the quantum state (or Hilbert) space can be seen as the quantisation of the associated phase space for an equivalent classical mechanical system in terms of sub-blocks of side-length \hbar . If you don't know what I mean at this point, don't worry about it!

Further, the above commutator relation between conjugate operators such as \hat{p} and \hat{x} is itself a special case of a more generalised relation: $[\hat{O}_1, \hat{O}_2] \propto \hat{O}_3$, i.e., the commutation relation between two operators will typically lead to a third operator. We will encounter an example of this when we study the orbital angular momentum problem (in terms of the various components (L_x, L_y, L_z) of the orbital angular momentum operator).

Finally, a note on **symmetries**. The fact that an operator $\hat{\theta}$ commutes with the Hamiltonian operator \hat{H} , $[\hat{H}, \hat{\theta}] = 0$, implies that the corresponding physical observable satisfies a conservation law (i.e., an invariance in time) and reflects on a corresponding symmetry of the quantum system. Further, this symmetry (and its corresponding conservation law) will be preserved in time. This can be seen simply from the fact that since the unitary time evolution operator is given by $U = e^{-\frac{i\hat{H}t}{\hbar}}$ (i.e., U is a function of the Hamiltonian \hat{H}),

$$[\hat{H}, \hat{\theta}] = 0 \implies [U, \hat{\theta}] = 0 . \quad (4.11)$$

Let us consider a couple of simple examples to clarify these point.

- (a) For a free particle on the 1D line, $\hat{H} = \hat{p}^2/2m$ and $[\hat{H}, \hat{p}] = 0$, implying that the linear momentum \hat{p} is conserved in time and its eigenvalue is a “good” quantum number. This reflects on the fact that \hat{H} and \hat{p} have the same basis, and that there is a continuous translation symmetry in the problem, such that for the eigenfunction $\psi(x) = \mathcal{N}e^{-i\hat{p}x}$ (and where \mathcal{N} is the normalisation factor), we have

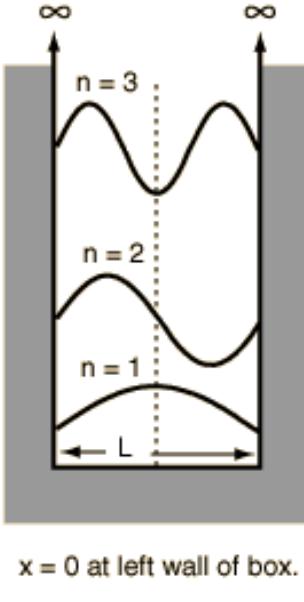
$$T_{\delta x}\psi(x) = e^{-i\hat{p}\delta x/\hbar}\psi(x) = \psi(x + \delta x) , \quad (4.12)$$

where $T_{\delta x} = e^{-i\hat{p}\delta x/\hbar}$ is the operator for a translation in real space along the 1D line by an amount δx . Thus, the linear momentum \hat{p} is the generator of infinitesimal translation δx .

- (b) For a quantum system in which the (say, 1D) potential has inversion symmetry $V(\hat{x}) = V(-\hat{x})$, the parity operation \hat{P} is such that its action on any eigenfunction ψ gives

$$\begin{aligned} \hat{P}\psi_0(x) &= \pm\psi_0(-x) \\ \text{This arises from the fact that } \hat{P}^2\psi_0(x) &= \psi_0(x) \\ \Rightarrow \psi_0(-x) &= \pm\psi_0(x) , \end{aligned} \quad (4.13)$$

i.e., eigenvalues of \hat{P} are ± 1 , such that all eigenstates have either even (+1) or odd (-1) parity eigenvalue. For such a parity symmetric system, $[\hat{H}, \hat{P}] = 0$. Consider the case of the wavefunctions of the particle in a box problem shown below. Can you think of any other well known potential in 1D that possesses parity symmetry?



$x = 0$ at left wall of box.

Figure 4.1: Wavefunctions for the lowest three eigenstates of the particle in a box problem.
Source: The internet.

4.2 Important properties of Eigenstates

(1) Eigenvalues of Hermitian Operators are real-valued.

Recall that this is important because Hermitian operators are associated with physical observables/ experimentally measurable quantities. Take a Hermitian Operator \hat{A} such that $\hat{A} = \hat{A}^\dagger = (\hat{A}^*)^T$, where $*$ and T refer, as discussed earlier, to complex conjugation and transpose operations respectively. Let

$$\hat{A}\psi_n = a_n\psi_n , \quad n = 1, 2, 3, \dots \quad (4.14)$$

Now, by computing the expectation value

$$\begin{aligned} \langle \hat{A} \rangle &= \int_{-\infty}^{\infty} dx \psi_n^* \hat{A} \psi_n = \int_{-\infty}^{\infty} dx \underbrace{(\hat{A} \psi_n)^*}_{=\psi_n^* \hat{A}^\dagger} \psi_n \\ &= \int_{-\infty}^{\infty} dx \psi_n^* a_n \psi_n = \int_{-\infty}^{\infty} dx (a_n \psi_n)^* \psi_n \\ &= a_n \int_{-\infty}^{\infty} dx \psi_n^* \psi_n = a_n^* \int_{-\infty}^{\infty} dx \psi_n^* \psi_n \\ \langle \hat{A} \rangle &= a_n = a_n^* \\ \text{or, } a_N &\in \mathcal{R} \quad (\text{QED}) \end{aligned} \quad (4.15)$$

(2) Different eigenstates of the same potential are orthogonal.

Note that the **Inner Product** is defined as

$$\int_{-\infty}^{\infty} dx \psi_n^* \psi_m = \delta_{n,m} = \begin{cases} 1, & n = m \\ 0, & \text{otherwise} \end{cases} \quad (4.16)$$

For a Hermitian operator \hat{A} with eigenstates ψ_n and corresponding eigenvalues a_n , such that $\hat{A}\psi_n = a_n\psi_n$ and $\hat{A}\psi_m = a_m\psi_m$. Now, since $\hat{A} = \hat{A}^\dagger$,

$$\begin{aligned} \int_{-\infty}^{\infty} dx \psi_m^* \hat{A}\psi_n &= \int_{-\infty}^{\infty} dx \underbrace{(\hat{A}\psi_m)^*}_{=\psi_n^* \hat{A}^\dagger} \psi_n \\ \int_{-\infty}^{\infty} dx \psi_m^* a_n \psi_n &= \int_{-\infty}^{\infty} dx (a_m \psi_m)^* \psi_n \\ a_n \int_{-\infty}^{\infty} dx \psi_m^* \psi_n &= a_m^* \int_{-\infty}^{\infty} dx \psi_m^* \psi_n = a_m \int_{-\infty}^{\infty} dx \psi_m^* \psi_n \quad (\text{as } \hat{A} \text{ is Hermitian}) \\ (a_n - a_m) \int_{-\infty}^{\infty} dx \psi_m^* \psi_n &= 0 . \end{aligned} \quad (4.17)$$

Now, for $a_n \neq a_m$ for $n \neq m$, $\int_{-\infty}^{\infty} dx \psi_m^* \psi_n = 0$.

On the other hand, for $n = m$, $\int_{-\infty}^{\infty} dx \psi_n^* \psi_n = 1 = \int_{-\infty}^{\infty} dx \psi_m^* \psi_m$. (QED)

What about the case of degenerate eigenstates? The above relation cannot distinguish between them, and we need to find the appropriate linear combinations of such degenerate eigenstates that are orthogonal to one another.

(3) Postulate of quantum mechanics: eigenstates of the TISE form a complete set of states, i.e, any other function $f(x)$ can be expressed as a linear combination of the eigenstates ψ_n

$$f(x) = \sum_{n=1} c_n \psi_n(x) . \quad (4.18)$$

The states $\psi_n(x)$ are then said to “span the vector space” or “form a suitable basis set”.

The superposition principle of quantum mechanics says that such linear combinations are valid solutions of the time-dependent Schrodinger’s equation as well

$$\Psi(x, t) = \sum_n C_n \psi_n(x) \exp\left\{\frac{-iE_n t}{\hbar}\right\} = \sum_n C_n \phi_n(x, t) ,$$

where $\phi_n(x, t)$ forms a complete basis of eigenstates.

Note that for such a linear combination of eigenstates with different E_n ,

$$H\Psi \neq E\Psi .$$

What does the superposition mean physically?

It means that QM allows for the possibility that a particle in a given potential can be

simultaneously in a mixture of different eigenstates (with different energy eigenvalues).

In order to make sense of any measurement of a physically observable quantity, the measurement process is often referred to as the collapse of the wavefunction $\Psi(x, t)$ into one of its constituent eigenstates $\phi_n(x, t)$. Further, the weight factors C_n refer to the probabilities that the measurement will lead to the eigenvalues of particular eigenstates ϕ_n . (At this point, recall our discussion of the Schrödinger cat gedanken, or the Feynman double slit experiment with electrons!)

Finally, if one knows the solution to the eigenvalue problem $H\psi_n = E_n\psi_n$, the superposition provides a means by which to determine the time dependence of any wavefunction Ψ . For this, we assume that at $t = 0$, $\Psi(x, t = 0) = \sum_n C_n \psi_n(x)$; then, we need to determine the coefficients C_n

$$\int_{-\infty}^{\infty} dx \psi_m^* \Psi(x) = \sum_n C_n \int_{-\infty}^{\infty} dx \psi_m^* \psi_n = \sum_n C_n \delta_{n,m} = C_m , \quad (4.19)$$

where we have used the orthogonality property of eigenstates we discussed earlier. Therefore, the coefficient $C_m = \int_{-\infty}^{\infty} dx \psi_m^* \Psi(x)$ gives the weight factors. This relation can be seen as implementing the “collapse” of the wavefunction in terms of a measurement of the coefficient C_m , and appears to be projective in the sense that it picks out one member of the entire Hilbert space from the rest. Such projections are typically non-unitary, i.e., they do not preserve the total probability. Nevertheless, this is one way in which to learn the C_m coefficients. It is not clear how to build in such processes involving measurement and wavefunction collapse within the Schrödinger equation formalism. We will discuss this in more detail towards the end of these lectures.

To continue, with the coefficients C_n having been computed, we can always obtain the full time-evolved state as

$$\Psi(x, t) = \sum_n C_n \psi_n(x) e^{-iE_n t / \hbar} . \quad (4.20)$$

It is safe to say that it is this “linear superposition” property of the wavefunction in the quantum world that scientists see as the power of a quantum computer. In some sense, such a computer will have all the answers (in a linear superposition) to a particular question you may ask of it (an oracle?) ... when you finally want the answer, a measurement causes the computer’s wavefunction to collapse onto your answer! Interesting, isn’t it? In this sense, the Schrödinger cat gedanken and the Feynman double slit experiment with electrons are simple quantum computation setups in which the cat and the electron can have only two possibilities that can exist in a linear superposition.

Similarly, the ammonia molecule lives in a linear superposition of the two positions of the Nitrogen atom (above and below the plane of three Hydrogen atoms), the Benzene molecule lives in a superposition (called the “resonance”) of the two configurations for the three alternating double bond structures. They can be thought of as molecular quantum computers ... but can we do some useful computation with them (or an array of such molecules)?

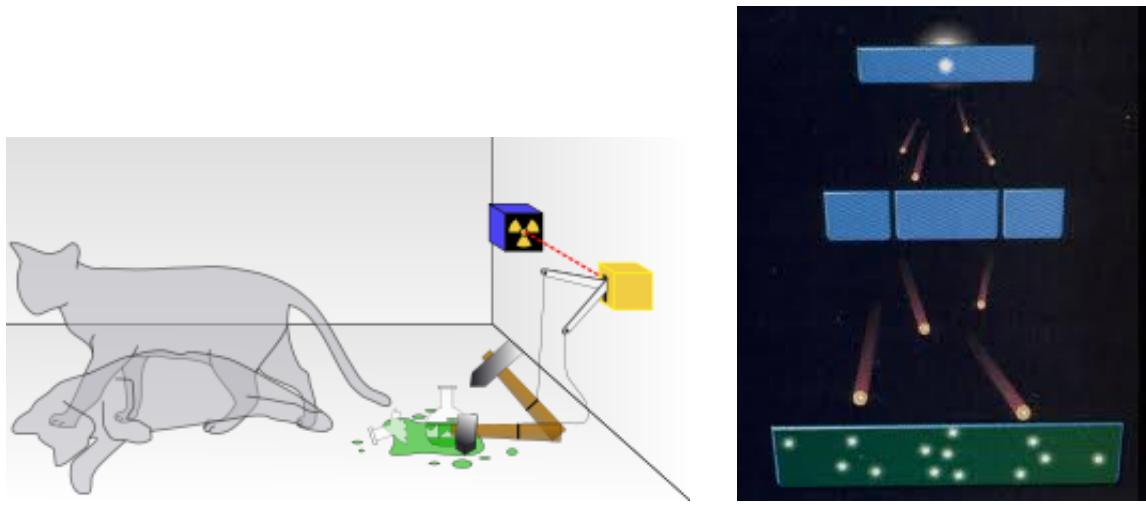


Figure 4.2: (Left) The Schrödinger Cat gedanken. (Right) Double-slit Interference Experiment with Matter particles. Source: The internet.

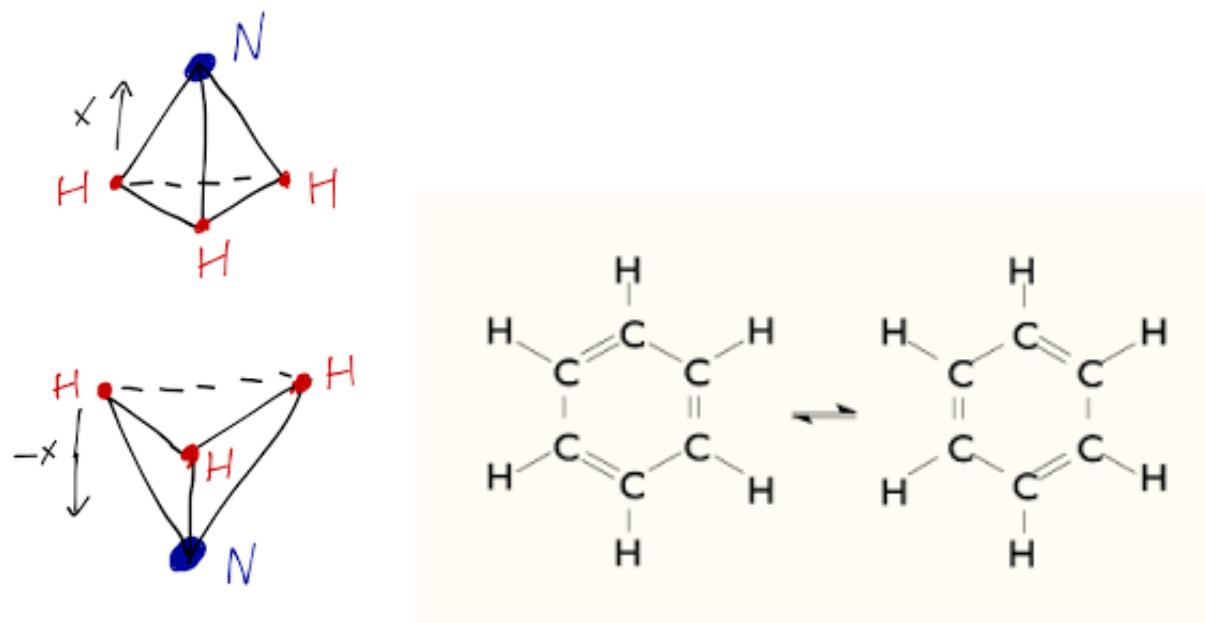


Figure 4.3: (Left) The two configurations of the Ammonia molecule. (Right) The two configurations of the Benzene molecule. Source: The internet.

Chapter 5

Formalism II : Vector Spaces in Quantum Mechanics

5.1 Vector Spaces

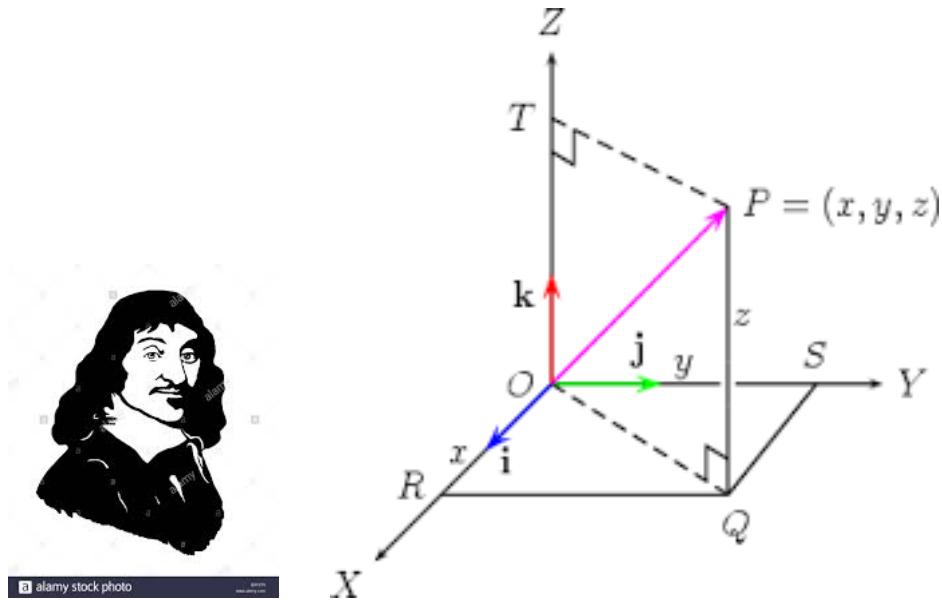


Figure 5.1: Left: Renée Descartes. Right: A vector in Cartesian coordinates. Source: The Internet.

We are already familiar with 2D and 3D spaces that can accommodate vectors. Generalising this to $n > 3$ dimensions means that for

(i) $\vec{u} = (u_1, u_2, u_3, \dots, u_n)$, $\vec{v} = (v_1, v_2, v_3, \dots, v_n)$, we need a “rule for vector addition”

$$\vec{u} + \vec{v} = (u_1 + v_1, u_2 + v_2, u_3 + v_3, \dots, u_n + v_n) = \vec{w}, \quad (5.1)$$

as well as

(ii) a “rule for the multiplication of a vector by a scalar”

$$\vec{r} = c\vec{u} , \quad (5.2)$$

where $c \in \mathcal{R}$ for a vector space of real-valued vectors and $c \in \mathcal{C}$ for a vector space of complex-valued vectors (as in quantum mechanics).

Finally, we also need a “rule for the dot product” between two vectors that leads to a scalar quantity

$$\vec{u} \cdot \vec{v} = u_1 v_1 + u_2 v_2 + \dots + u_n v_n . \quad (5.3)$$

Examples of vector spaces includes

- (a) the set of all real numbers, where each real number is a one-component vector and the entire set forms a 1D vector space, and
- (b) the set of (suitably defined) functions $f(x)$ is an infinite-dimensional vector space, since $f(x) + g(x) = h(x)$ and $g(x) = cf(x)$ are well-defined operations.

5.1.1 Dimension of a vector space:

The dimension of a vector space is the maximum number of linearly independent vectors the space can have (also known as “the basis”). This number can be infinite. For a N -dimensional vector space with a basis given by $(|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_N\rangle)$ such that any vector $|\psi\rangle$ can be written as

$$|\psi\rangle = \sum_{i=1}^N a_i |\phi_i\rangle , \quad (5.4)$$

i.e., a vector $|\psi\rangle$ can be written in terms of a linear superposition of the basis vectors $|\phi_i\rangle$ s, where the $|\phi_i\rangle$ s form a “complete basis which spans the entire set”. The coefficients (or weight factors) of the various components of the vector $|\psi\rangle$, a_i , are the projections of $|\psi\rangle$ onto the various “orthogonal” (or “normal”) directions given by $|\phi_i\rangle$. To understand this better, we need to define the “dot”, “scalar” or “inner product” $\langle\phi_i|\phi_j\rangle$ such that

$$a_i = \langle\psi|\phi_i\rangle , \quad (5.5)$$

and for a set of orthonormal basis vectors $\{|\phi_i\rangle\}$

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} , \quad (5.6)$$

where the Kronecker delta is defined as $\delta_{ij} = 1$ for $i = j$, and 0 otherwise.

5.1.2 More on the Inner Product

Defining a “dot” product for a finite dimensional vector space is easy, but what about for an infinite-dimensional vector space (e.g., the space of functions)? For such cases, we need to construct a more abstract concept called the “Inner Product”. Just as the dot product of two finite dimensional vectors gives a real number, by analogy, we consider the Inner

Product of two vectors, $|\psi\rangle$ and $|\phi\rangle$, of an abstract vector space to be a function which uses $|\psi\rangle$ and $|\phi\rangle$ as inputs and whose result is (in general) a complex number

$$\langle\psi|\phi\rangle = c, \quad c \in \mathcal{C}. \quad (5.7)$$

The Inner Product has the following properties:

- (i) $\langle\psi + \phi|\theta\rangle = \langle\psi|\theta\rangle + \langle\phi|\theta\rangle$
- (ii) $\langle\psi|c\phi\rangle = c\langle\psi|\phi\rangle$
- (iii) $\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*$
- (iv) $\langle\psi|\psi\rangle \geq 0$.

Using relations (ii) and (iii) from above, we can see that

$$\begin{aligned} \langle\phi|c\psi\rangle^* &= c^*\langle\phi|\psi\rangle^* \\ &= c^*\langle\psi|\phi\rangle \\ \text{But } \langle\phi|c\psi\rangle^* &= \langle c\psi|\phi\rangle \\ \Rightarrow \langle c\psi|\phi\rangle &= c^*\langle\psi|\phi\rangle. \end{aligned}$$

The inner product for the set of complex-valued functions defined in 3D is

$$\langle f(\vec{r})|g(\vec{r})\rangle = \int_{-\infty}^{\infty} dx dy dz f(\vec{r})^* g(\vec{r}). \quad (5.8)$$

In 1D, this becomes $\langle f(x)|g(x)\rangle = \int_{-\infty}^{\infty} dx f^*(x)g(x)$, such that for

$$\begin{aligned} f(x) &= \sin x, \quad g(x) = x \sin x \\ \langle f(x)|g(x)\rangle &= \int_{-\infty}^{\infty} dx f^*(x)g(x) \\ &= \int_{-\infty}^{\infty} dx x \sin^2 x \\ &\rightarrow 0, \end{aligned}$$

as the argument $x \sin^2 x$ is an odd function in x .

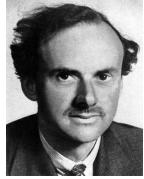
Finally, the requirement that the wavefunction $\psi(x)$ be normalised can now be recast as

$$\langle\psi|\psi\rangle = 1, \quad (5.9)$$

i.e., the “length” of the vector representing the state ψ is set of 1. Further, the Expectation value of an operator $\hat{\theta}$ can be defined as

$$\langle\hat{\theta}\rangle = \langle\psi|\hat{\theta}|\psi\rangle \equiv \langle\psi|\hat{\theta}\psi\rangle. \quad (5.10)$$

5.2 The Dirac Bra-Ket Notation



The vector space of function that we're interested in Quantum Mechanics is that of wavefunctions such that

$$\langle \psi | \psi \rangle = \int d^3x |\psi(r)|^2 = 1 , \quad (5.11)$$

i.e., the ψ s are both square-integrable and normalisable. Such a vector space is an example of a linear vector space called a **Hilbert space**. Thus, the physical state of a system is represented by elements of a Hilbert space called “state vectors”. We do have freedom in how to choose to represent these state vectors by means of an expansion using different functions. This is called the “choice of basis”, and is analogous to being able to representing a 3D coordinate system using the (x, y, z) , (r, θ, ϕ) or (ρ, ϕ, z) coordinates.



Hilbert

Dirac

It is, however, important to note that the meaning of the state of a system is independent of the basis of functions we choose. To highlight the usefulness of adopting the concept of an abstract vector space (from which all physical representations of the state vectors could be obtained), the physicist Dirac introduced the “bra-ket” notation of Quantum mechanics:

Ket: $|\psi\rangle$ belongs to (i.e, is an element of) an abstract Hilbert state vector space

Bra: $\langle \psi |$ belongs to an abstract Hilbert space dual to that whose elements are the Kets $|\psi\rangle$

Scalar/Inner Product: defined between members of the two dual Hilbert spaces $\langle \phi | \psi \rangle$

Expectation Value of an operator: $\langle \hat{\theta} \rangle = \langle \psi | \hat{\theta} | \psi \rangle \equiv \langle \psi | \hat{\theta} \psi \rangle$

Basis choice: $\psi(\vec{r}, t) = \langle \vec{r}, t | \psi \rangle$ (Position Representation) , $\psi(\vec{p}, t) = \langle \vec{p}, t | \psi \rangle$ (Momentum Representation) .

Thus, while the Kets are independent of any particular basis choice, they represent the system completely, and hence knowing the Hilbert space $\{|\psi\rangle\}$ means knowing all its amplitudes (read wavefunctions) in all possible representations.

5.3 Properties of $|\psi\rangle$, $\langle \psi |$ and $\langle \phi | \psi \rangle$

1. To every $|\psi\rangle$, there exists a unique $\langle \psi |$ and vice versa:

$$|\psi\rangle \leftrightarrow \langle \psi | \quad (5.12)$$

There is a one-to-one correspondence between bras and kets

$$a|\psi\rangle + b|\phi\rangle \leftrightarrow a^* \langle \psi | + b^* \langle \phi | \quad a, b \in \mathcal{C} \quad (5.13)$$

$$|a\psi\rangle = a|\psi\rangle \quad \& \quad \langle a\psi | = a^* \langle \psi | . \quad (5.14)$$

2. In Quantum Mechanics, as the scalar product is a complex number in general, the ordering matters, i.e., $\langle \psi | \phi \rangle$ is not necessarily the same as $\langle \phi | \psi \rangle$. Then,

$$\begin{aligned} \langle \phi | \psi \rangle^* &= (\int d\vec{r} \phi^*(\vec{r}, t) \psi(\vec{r}, t))^* = \int d\vec{r} \psi^*(\vec{r}, t) \phi(\vec{r}, t) = \langle \psi | \phi \rangle \\ \text{i.e., } \langle \phi | \psi \rangle^* &= \langle \psi | \phi \rangle . \end{aligned} \quad (5.15)$$

For the special case of $|\psi\rangle, |\phi\rangle \in \mathcal{R}$, $\langle \phi | \psi \rangle^* = \langle \phi | \psi \rangle = \langle \psi | \phi \rangle$.

Further,

$$\langle \psi | a_1 \psi_1 + a_2 \psi_2 \rangle = a_1 \langle \psi | \psi_1 \rangle + a_2 \langle \psi | \psi_2 \rangle \quad (5.16)$$

$$\langle a_1 \phi_1 + a_2 \phi_2 | \psi \rangle = a_1^* \langle \phi_1 | \psi \rangle + a_2^* \langle \phi_2 | \psi \rangle \quad (5.17)$$

$$\langle a_1 \phi_1 + a_2 \phi_2 | b_1 \psi_1 + b_2 \psi_2 \rangle = a_1^* b_1 \langle \phi_1 | \psi_1 \rangle + a_1^* b_2 \langle \phi_1 | \psi_2 \rangle + a_2^* b_1 \langle \phi_2 | \psi_1 \rangle + a_2^* b_2 \langle \phi_2 | \psi_2 \rangle . \quad (5.18)$$

3. For any state vector $|\psi\rangle$ of a Hilbert space \mathcal{H} , the norm (“length”) $\langle \psi | \psi \rangle$ is real and positive definite

$$\langle \psi | \psi \rangle \geq 0 , \quad \langle \psi | \psi \rangle \in \mathcal{R} . \quad (5.19)$$

Further, if the state $|\psi\rangle$ is normalised, $\langle \psi | \psi \rangle = 1$.

4. For two states $|\psi\rangle$ and $|\phi\rangle$ such that $\langle \psi | \phi \rangle = 0$, the two states are said to be “orthogonal”.

If in addition, $\langle \psi | \psi \rangle = 1 = \langle \phi | \phi \rangle$, the two states are said to be “orthonormal”.

5. Schwarz Inequality: $|\langle \psi | \phi \rangle|^2 \leq \langle \psi | \psi \rangle \langle \phi | \phi \rangle$ (equality holds for $|\psi\rangle = a|\phi\rangle$, $a \in \mathcal{C}$).

Analogy with relation between vectors in Euclidean space: $|\vec{A} \cdot \vec{B}|^2 \leq |\vec{A}|^2 |\vec{B}|^2$.

6. Triangle Inequality: $\sqrt{\langle \psi + \phi | \psi + \phi \rangle} \leq \sqrt{\langle \psi | \psi \rangle} + \sqrt{\langle \phi | \phi \rangle}$ (equality for $|\psi\rangle = a|\phi\rangle$, $a \in \mathcal{R}$ and $a > 0$).

Analogy with relation between vectors in Euclidean space: $|\vec{A} + \vec{B}| \leq |\vec{A}| + |\vec{B}|$.

Note that products like $|\psi\rangle |\phi\rangle$ and $\langle \psi | \langle \phi |$ are meaningless if $|\psi\rangle$ and $|\phi\rangle$ belong to the same Hilbert space \mathcal{H} . However, if $|\psi\rangle$ and $|\phi\rangle$ belong to different Hilbert spaces (e.g., real space wavefunctions and Spin angular momentum states), then products such as $|\psi\rangle |\phi\rangle$ and $\langle \psi | \langle \phi |$ are meaningful and are called “Direct Product”.

Physical meaning of $\langle \psi | \phi \rangle$: First, $\langle \psi | \phi \rangle$ represents the projection of the state vector $|\psi\rangle$ onto the state vector $|\phi\rangle$. Second, for the states $|\psi\rangle$ and $|\phi\rangle$ being normalised, and from Born’s probabilistic interpretation of Quantum Mechanics, the quantity $\langle \psi | \phi \rangle$ represents the probability amplitude that the system’s initial state $|\phi\rangle$ will, after measurement, be projected onto another state $|\psi\rangle$.

5.4 Operators

1. Operators are mathematical rules such that

$$\hat{A}|\psi\rangle = |\psi'\rangle , \quad \langle \phi | \hat{A} = \langle \phi' | . \quad (5.20)$$

2. Products of Operators: In general, the product

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0 \quad (5.21)$$

$$\Rightarrow \hat{A}\hat{B} \neq \hat{B}\hat{A}. \quad (5.22)$$

$$\text{Further, } \hat{A}\hat{B}\hat{C} = \hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \quad (5.23)$$

$$\hat{A}^m\hat{A}^n = \hat{A}^{m+n} \quad (5.24)$$

$$\hat{A}\hat{B}\hat{C}|\psi\rangle = \hat{A}\hat{B}(\hat{C}|\psi\rangle) = \hat{A}\{\hat{B}(\hat{C}|\psi\rangle)\}. \quad (5.25)$$

3. Linearity:

$$\hat{A}(a_1|\psi_1\rangle + a_2|\psi_2\rangle) = a_1\hat{A}|\psi_1\rangle + a_2\hat{A}|\psi_2\rangle \quad (5.26)$$

$$(a_1\langle\psi_1| + a_2\langle\psi_2|)\hat{A} = a_1\langle\psi_1|\hat{A} + a_2\langle\psi_2|\hat{A}. \quad (5.27)$$

4. Expectation Value:

$$\langle\hat{A}\rangle = \frac{\langle\psi|\hat{A}|\psi\rangle}{\langle\psi|\psi\rangle} \equiv \langle\psi|\hat{A}|\psi\rangle \quad (\text{if } |\psi\rangle \text{ is normalised}) \quad (5.28)$$

$$= \langle\psi|\hat{A}\psi\rangle. \quad (5.29)$$

5. Projection Operators: $|\phi\rangle\langle\psi|$ is a linear operator

$$|\phi\rangle\langle\psi|\psi'\rangle = \langle\psi|\psi'\rangle|\phi\rangle = c|\phi\rangle, \quad (5.30)$$

$$|\psi\rangle\langle\psi|\psi'\rangle = \langle\psi|\psi'\rangle|\psi\rangle = c|\psi\rangle, \quad (5.31)$$

where $c \equiv \langle\psi|\psi'\rangle \in \mathcal{C}$ is the probability amplitude arising from the projection.

6. Operations such as $|\psi\rangle\hat{A}$ and $\hat{A}\langle\psi|$ are not sensible.

7. The operator “adjoint” to $\hat{\theta}$ is $\hat{\theta}^\dagger$ such that

$$\langle\phi|\hat{\theta}\psi\rangle = \langle\hat{\theta}^\dagger\phi|\psi\rangle. \quad (5.32)$$

For example, let us work out the adjoint of the differential operator $\hat{D} \equiv \frac{d}{dx}$, i.e., \hat{D}^\dagger .

$$\langle\phi|\hat{D}\psi\rangle = \int_{-\infty}^{\infty} dx \phi^*(x) \frac{d\psi(x)}{dx} \quad (\text{in position basis}) \quad (5.33)$$

$$= [\phi^*(x)\psi(x)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx \frac{d\phi^*(x)}{dx} \psi(x) \quad (5.34)$$

$$= - \int_{-\infty}^{\infty} dx \frac{d\phi^*(x)}{dx} \psi(x) \quad (\text{as } \phi(x), \psi(x) \rightarrow 0 \text{ as } x \rightarrow \pm\infty) \quad (5.35)$$

$$\Rightarrow \langle\phi|\hat{D}\psi\rangle = \int_{-\infty}^{\infty} (-\hat{D}\phi^*(x))\psi(x) \quad (5.36)$$

$$= \langle -\hat{D}\phi|\psi\rangle \equiv \langle \hat{D}^\dagger\phi|\psi\rangle \quad (5.37)$$

$$\Rightarrow \hat{D}^\dagger = -\hat{D}. \quad (5.38)$$

Adjoint Operators have the following properties:

$$(i) \quad (c\hat{P})^\dagger = c^*\hat{P}^\dagger \quad (c \in \mathcal{C}) \quad (5.39)$$

$$(ii) \quad (\hat{P} + \hat{Q})^\dagger = \hat{P}^\dagger + \hat{Q}^\dagger \quad (5.40)$$

$$(iii) \quad (\hat{P}\hat{Q})^\dagger = \hat{Q}^\dagger\hat{P}^\dagger \quad (5.41)$$

$$(iv) \quad (\hat{P}^\dagger)^\dagger = \hat{P} . \quad (5.42)$$

Relation (iii) can also be seen as follows:

$$\langle \phi | \hat{P}(\hat{Q}\psi) \rangle = \langle \hat{P}^\dagger \phi | \hat{Q}\psi \rangle \quad (5.43)$$

$$= \langle \hat{Q}^\dagger \hat{P}^\dagger \phi | \psi \rangle . \quad (5.44)$$

8. Self-adjoint or “Hermitian” Operators: $\hat{\theta}^\dagger = \hat{\theta}$!

For example, the position operator \hat{x} is Hermitian: $\hat{x}^\dagger = \hat{x}$.

The momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$ is also Hermitian:

$$\hat{p}^\dagger = -\hat{p}^* = -(-i\hbar \frac{d}{dx})^* = \hat{p} . \quad (5.45)$$

Hermitian Operators are special, as their expectation values are real-valued:

$$\langle \hat{Q} \rangle = \langle \psi | \hat{Q} \psi \rangle \quad (5.46)$$

$$= \langle \psi | \hat{Q}^\dagger \psi \rangle \quad (\text{for } \hat{Q} = \hat{Q}^\dagger) \quad (5.47)$$

$$= \langle \hat{Q}\psi | \psi \rangle \quad (5.48)$$

$$= \langle \hat{Q} \rangle^* , \quad (5.49)$$

$$\Rightarrow \langle \hat{Q} \rangle \in \mathcal{R} . \quad (5.50)$$

Similarly, if $|\psi\rangle$ is an eigenfunction of a Hermitian operator \hat{Q} with eigenvalue q , i.e., $\hat{Q}|\psi\rangle = q|\psi\rangle$,

$$\langle \psi | \hat{Q} \psi \rangle = q \langle \psi | \psi \rangle = q \quad (5.51)$$

$$\text{But } \langle \psi | \hat{Q} \psi \rangle = \langle \hat{Q}^\dagger \psi | \psi \rangle \quad (5.52)$$

$$= \langle \hat{Q}\psi | \psi \rangle = q^* \langle \psi | \psi \rangle = q^* \quad (5.53)$$

$$\Rightarrow q \in \mathcal{R} . \quad (5.54)$$

Finally, writing

$$\langle \hat{Q} \rangle = \langle \psi | \hat{Q} | \psi \rangle \quad (\text{where the states } |\psi\rangle \text{ are not eigenstates of } \hat{Q}) \quad (5.55)$$

$$= \sum_{m,n} \langle \psi | \xi \rangle_{mm} \langle \xi | \hat{Q} | \xi \rangle_{nn} \langle \xi | \psi \rangle \quad (\text{where we've introduced the identity operator}) \quad (5.56)$$

$$I = \sum_n |\xi\rangle_{nn} \langle \xi| \quad \text{in terms of eigenstates of } \hat{Q}, \quad |\xi\rangle_n \quad (5.57)$$

$$= \sum_{m,n} \int \int dx dy \xi_m(x) \delta_{m,n} Q_n \xi_n^*(y) \quad (\text{as } \hat{Q}|\xi\rangle_n = Q_n|\xi\rangle_n) \quad (5.58)$$

where we have used $\langle \psi | \xi \rangle_m = \xi_m(x)$, $\langle \xi | \psi \rangle = \xi_n^*(y)$ and $\langle \xi | \hat{Q} | \xi \rangle_n = Q_n \langle \xi | \xi \rangle_n = Q_n \delta_{mn}$ in the last line.

5.5 Discrete & Continuous Basis

We have noted earlier that the quantum world is unlike the classical world: in the latter, all observables can take a continuum of values whereas in the former one can find examples of observables whose spectra can either be continuous or discrete. We have stressed considerably the quantisation phenomena of several observables that arises in many quantum systems in earlier chapters. Most generally, an identical form of the eigenvalue equation is obtained for operators \hat{A} and $\hat{\Gamma}$ acting on their eigenstates $|A\rangle$ and $|\psi\rangle$ so to obtain eigenvalues A and Γ that are discrete and continuous respectively

$$\hat{A}|A\rangle = A|A\rangle \leftrightarrow \hat{\Gamma}|\psi\rangle = \Gamma|\psi\rangle . \quad (5.59)$$

The inner product structure for the discrete ($|A\rangle$) and continuous ($|\psi\rangle$) states is, however, slightly different so as to signify their nature

$$(\text{discrete}) \quad \langle A|A' \rangle = \delta_{AA'} \leftrightarrow \langle \psi|\psi' \rangle = \delta(\psi - \psi') \quad (\text{continuous}) , \quad (5.60)$$

$$(\text{discrete}) \quad \sum_A |A\rangle \langle A| = 1 \leftrightarrow \int d\psi |\psi\rangle \langle \psi| = 1 \quad (\text{continuous}) , \quad (5.61)$$

$$(\text{discrete}) \quad |B\rangle = \sum_A |A\rangle \langle A|B\rangle \leftrightarrow |\phi\rangle = \int d\psi |\psi\rangle \langle \psi|\phi\rangle \quad (\text{continuous}) , \quad (5.62)$$

$$(\text{discrete}) \quad \langle B|B \rangle = \sum_A |\langle A|B \rangle|^2 = 1 \leftrightarrow \int d\psi |\langle \psi|\phi \rangle|^2 = 1 \quad (\text{continuous}) , \quad (5.63)$$

$$(\text{discrete}) \quad \langle C|B \rangle = \sum_A \langle C|A \rangle \langle A|B \rangle \leftrightarrow \langle \xi|\phi \rangle = \int d\psi \langle \xi|\psi \rangle \langle \psi|\phi \rangle \quad (\text{continuous}) \quad (5.64)$$

$$(\text{discrete}) \quad \langle A'|\hat{A}|A \rangle = A\delta_{AA'} \leftrightarrow \langle \psi'|\hat{\Gamma}|\psi \rangle = \Gamma\delta(\psi - \psi') \quad (\text{continuous}) \quad (5.65)$$

where we have used eq.(5.61) to obtain eq.(5.62) and eq.(5.64). Please note that the Dirac delta-functions $\delta(\psi - \psi')$ are mathematically well defined objects on the abstract Hilbert space $\{|\psi\rangle\}$. They are, however, better understood by projecting them onto some concrete basis related to some observable (such as position $\{|x\rangle\}$, momentum $\{|p\rangle\}$ etc.) in terms of which the Dirac delta-functions transform into their counterparts in the position (x), momentum (p) etc. variables.

5.6 Position and Momentum Basis

The eigenstates of the position operator \hat{x} for a one-dimensional quantum system satisfy

$$\hat{x}|x\rangle = x|x\rangle , \quad \langle x'|x \rangle = \delta(x' - x) , \quad (5.66)$$

where x is the eigenvalue obtained from the action of \hat{x} on $|x\rangle$, and has dimensions of length. An arbitrary physical state $|\alpha\rangle$ can always be written in terms of the set of eigenstates $\{|x\rangle\}$

$$|\alpha\rangle = \int_{-\infty}^{\infty} dx |x\rangle \langle x|\alpha\rangle = \int_{-\infty}^{\infty} dx \psi_{\alpha}(x) |x\rangle , \quad \psi_{\alpha}(x) = \langle x|\alpha\rangle , \quad (5.67)$$

$$\langle\alpha|\alpha\rangle = 1 \implies \int_{-\infty}^{\infty} dx \langle\alpha|x\rangle \langle x|\alpha\rangle = \int_{-\infty}^{\infty} dx |\langle\alpha|x\rangle|^2 = \int_{-\infty}^{\infty} dx |\psi_{\alpha}(x)|^2 = 1 , \quad (5.68)$$

$$\langle\beta|\alpha\rangle = \int_{-\infty}^{\infty} dx \langle\beta|x\rangle \langle x|\alpha\rangle = \int_{-\infty}^{\infty} dx \psi_{\beta}^{*}(x) \psi_{\alpha}(x) , \quad (5.69)$$

and where $\psi_{\alpha}(x) \equiv \langle x|\alpha\rangle$ is the real-space wavefunction for the physical state represented by $|\alpha\rangle$.

Extending this to three dimensions is straightforward. We now assume that the set of position eigenstates $|\vec{r}\rangle \equiv |x, y, z\rangle$ is a complete basis (i.e., where $\vec{r} = (x, y, z)$), such that we can write the physical state $|\psi\rangle$ in the real-space basis $\{|\vec{r}\rangle\}$ as

$$|\alpha\rangle = \int d^3x |\vec{r}\rangle \langle \vec{r}|\alpha\rangle . \quad (5.70)$$

Note that we are assuming that $|\vec{r}\rangle \equiv |x, y, z\rangle$ is a simultaneous eigenstate of the observables \hat{x}, \hat{y} and \hat{z}

$$\hat{x}|\vec{r}\rangle = x|\vec{r}\rangle , \quad \hat{y}|\vec{r}\rangle = y|\vec{r}\rangle , \quad \hat{z}|\vec{r}\rangle = z|\vec{r}\rangle . \quad (5.71)$$

Naturally, this means that the operators \hat{x}_i ($i = 1, 2, 3$) corresponds to the operators $(\hat{x}, \hat{y}, \hat{z})$ satisfy the following trivial commutation relations

$$[\hat{x}_i, \hat{x}_j] = 0 . \quad (5.72)$$

Starting from some arbitrary state $|\alpha\rangle$ that has been expanded in some basis $\{|A\rangle\}$ other than the position,

$$|\alpha\rangle = \sum_A |A\rangle \langle A|\alpha\rangle = \sum_A c_A |A\rangle , \quad \text{where } c_A = \langle A|\alpha\rangle \quad (5.73)$$

$$\langle x|\alpha\rangle = \sum_A \langle x|A\rangle \langle A|\alpha\rangle = \sum_A c_A \langle x|A\rangle ,$$

$$\implies \psi_{\alpha}(x) = \sum_A c_A \psi_A(x) , \quad \text{where } \psi_A(x) = \langle x|A\rangle . \quad (5.74)$$

Computing matrix elements of an operator \hat{A} is also found to be

$$\begin{aligned} \langle\beta|\hat{A}|\alpha\rangle &= \int dx' \int dx \langle\beta|x'\rangle \langle x'|\hat{A}|x\rangle \langle x|\alpha\rangle , \\ &= \int dx' \int dx \psi_{\beta}^{*}(x') \langle x'|\hat{A}|x\rangle \psi_{\alpha}(x) , \end{aligned} \quad (5.75)$$

such that computing the matrix element $\langle\beta|\hat{A}|\alpha\rangle$ requires the knowledge of the matrix element $\langle x'|\hat{A}|x\rangle$ (which is a function of x and x'). For the operator $\hat{A} \equiv \hat{f}(\hat{x})$ (where $\hat{f}(\hat{x})$

corresponds to an operator that is some function of \hat{x} , $f(\hat{x})$), we have

$$\begin{aligned}\langle x' | \hat{A} | x \rangle &= \langle x' | \hat{f}(\hat{x}) | x \rangle = f(x) \langle x' | x \rangle = f(x) \delta(x' - x) , \\ \implies \langle \beta | \hat{A} | \alpha \rangle &= \langle \beta | \hat{f}(\hat{x}) | \alpha \rangle ,\end{aligned}\quad (5.76)$$

$$\begin{aligned}&= \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dx \langle \beta | x' \rangle \langle x' | \hat{f}(\hat{x}) | x \rangle \langle x | \alpha \rangle , \\ &= \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dx \psi_{\beta}^{*}(x') \langle x' | \hat{f}(\hat{x}) | x \rangle \psi_{\alpha}(x) , \\ &= \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dx \psi_{\beta}^{*}(x') f(x) \delta(x' - x) \psi_{\alpha}(x) , \\ &= \int_{-\infty}^{\infty} dx \psi_{\beta}^{*}(x) f(x) \psi_{\alpha}(x) .\end{aligned}\quad (5.77)$$

The momentum, or p , basis is defined in the same way as observed above for the position (or x) basis

$$\hat{p} | p \rangle = p | p \rangle , \quad \langle p' | p \rangle = \delta(p' - p) , \quad (5.78)$$

where p is the eigenvalue obtained from the action of \hat{p} on $|p\rangle$, and has dimensions of momentum. An arbitrary physical state $|\alpha\rangle$ can always be written in terms of the set of eigenstates $\{|p\rangle\}$

$$|\alpha\rangle = \int_{-\infty}^{\infty} dp |p\rangle \langle p | \alpha \rangle = \int_{-\infty}^{\infty} dp \psi_{\alpha}(p) |p\rangle , \quad \psi_{\alpha}(p) = \langle p | \alpha \rangle , \quad (5.79)$$

$$\langle \alpha | \alpha \rangle = 1 \implies \int_{-\infty}^{\infty} dp \langle \alpha | p \rangle \langle p | \alpha \rangle = \int_{-\infty}^{\infty} dx |\langle \alpha | p \rangle|^2 = \int_{-\infty}^{\infty} dx |\psi_{\alpha}(p)|^2 = 1 , \quad (5.80)$$

$$\langle \beta | \alpha \rangle = \int_{-\infty}^{\infty} dp \langle \beta | p \rangle \langle p | \alpha \rangle = \int_{-\infty}^{\infty} dp \psi_{\beta}^{*}(p) \psi_{\alpha}(p) , \quad (5.81)$$

and where $\psi_{\alpha}(p) \equiv \langle p | \alpha \rangle$ is the momentum-space wavefunction for the physical state represented by $|\alpha\rangle$.

For the operator $\hat{A} \equiv \hat{f}(\hat{p})$ (where $\hat{f}(\hat{p})$ corresponds to an operator that is some function of \hat{p} , $f(\hat{p})$), we have

$$\begin{aligned}\langle p' | \hat{A} | p \rangle &= \langle p' | \hat{f}(\hat{p}) | p \rangle = f(p) \langle p' | p \rangle = f(p) \delta(p' - p) , \\ \implies \langle \beta | \hat{A} | \alpha \rangle &= \langle \beta | \hat{f}(\hat{p}) | \alpha \rangle ,\end{aligned}\quad (5.82)$$

$$\begin{aligned}&= \int_{-\infty}^{\infty} dp' \int_{-\infty}^{\infty} dp \langle \beta | p' \rangle \langle p' | \hat{f}(\hat{p}) | p \rangle \langle p | \alpha \rangle , \\ &= \int_{-\infty}^{\infty} dp' \int_{-\infty}^{\infty} dp \psi_{\beta}^{*}(p') \langle p' | \hat{f}(\hat{p}) | p \rangle \psi_{\alpha}(p) , \\ &= \int_{-\infty}^{\infty} dp' \int_{-\infty}^{\infty} dp \psi_{\beta}^{*}(p') f(p) \delta(p' - p) \psi_{\alpha}(p) , \\ &= \int_{-\infty}^{\infty} dp \psi_{\beta}^{*}(p) f(p) \psi_{\alpha}(p) .\end{aligned}\quad (5.83)$$

5.6.1 Momentum operator in Position Basis

Now, using the fact that the momentum operator \hat{p}_x in the position representation $\hat{p}_x \equiv -i\hbar \frac{\partial}{\partial x}$, we obtain

$$\begin{aligned}\hat{p}|\alpha\rangle &= \hat{p} \int dx |x\rangle \langle x|\alpha\rangle = \hat{p} \int dx \psi_\alpha(x) |x\rangle , \quad \psi_\alpha(x) = \langle x|\alpha\rangle , \\ &= \int dx (\hat{p}\psi_\alpha(x)) |x\rangle , \\ &= \int dx \left(-i\hbar \frac{\partial}{\partial x} \langle x|\alpha\rangle \right) |x\rangle ,\end{aligned}\tag{5.84}$$

$$\implies \langle x|\hat{p}|\alpha\rangle = -i\hbar \frac{\partial}{\partial x} \langle x|\alpha\rangle = -i\hbar \frac{\partial}{\partial x} \psi_\alpha(x) ,\tag{5.85}$$

using the fact that $\langle x'|x\rangle = \delta(x' - x)$. In general, the matrix element for \hat{p} in the x representation is given by

$$\langle x'|\hat{p}|x\rangle = -i\hbar \frac{\partial}{\partial x} \delta(x' - x) ,\tag{5.86}$$

and

$$\begin{aligned}\langle \beta|\hat{p}|\alpha\rangle &= \int dx \langle \beta|x\rangle \left(-i\hbar \frac{\partial}{\partial x} \langle x|\alpha\rangle \right) , \\ &= \int dx \psi_\beta^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi_\alpha(x) .\end{aligned}\tag{5.87}$$

We can now also obtain the wavefunction for the momentum eigenstate in the position representation, using

$$\langle x|\hat{p}|p\rangle = -i\hbar \frac{\partial}{\partial x} \langle x|p\rangle ,\tag{5.88}$$

$$\implies p \langle x|p\rangle = -i\hbar \frac{\partial}{\partial x} \langle x|p\rangle ,\tag{5.89}$$

$$\implies \langle x|p\rangle = \mathcal{N} e^{\frac{ipx}{\hbar}} ,\tag{5.90}$$

where the normalisation factor \mathcal{N} is obtained from

$$\langle x'|x\rangle = \delta(x' - x) = \int dp \langle x'|p\rangle \langle p|x\rangle ,\tag{5.91}$$

$$\begin{aligned}&= |\mathcal{N}|^2 \int dp e^{\frac{ip(x'-x)}{\hbar}} , \\ &= 2\pi\hbar |\mathcal{N}|^2 \delta(x' - x) , \\ \implies \mathcal{N} &= \frac{1}{\sqrt{2\pi\hbar}} .\end{aligned}\tag{5.92}$$

This gives us the so-called “transformation function” $\langle x|p\rangle$ as

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ipx}{\hbar}} ,\tag{5.93}$$

such that we can write the position-space ($\psi_\alpha(x)$) and momentum-space ($\psi_\alpha(p)$) wavefunctions for a general state $|\alpha\rangle$ as

$$\langle x|\alpha\rangle = \int dp \langle x|p\rangle \langle p|\alpha\rangle , \quad (5.94)$$

$$\text{or, } \psi_\alpha(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dp e^{\frac{ipx}{\hbar}} \psi_\alpha(p) , \quad (5.95)$$

$$\langle p|\alpha\rangle = \int dx \langle p|x\rangle \langle x|\alpha\rangle , \quad (5.96)$$

$$\text{or, } \psi_\alpha(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx e^{\frac{-ipx}{\hbar}} \psi_\alpha(x) . \quad (5.97)$$

Indeed, we can see that $\psi_\alpha(x)$ and $\psi_\alpha(p)$ are connected to one another through a Fourier transformation.

5.7 Change of Basis

Very generally, we can think of a change in basis (or representation) as a “generalised rotation of the old basis eigenfunctions into the new ones” through the application of a unitary operator U_Θ

$$|\phi_1\rangle = U_\Theta |\psi_1\rangle , \dots , |\phi_N\rangle = U_\Theta |\psi_N\rangle , \quad (5.98)$$

where Θ refers to the operator that acts as the “generator” of the transformation by an amount ϵ : $U_\Theta = e^{i\epsilon\Theta/\hbar}$. But why unitary operators? The answer lies in recognising the fact that transformations such as U_Θ which act on members of the Hilbert space $U_\Theta |\psi\rangle = |\psi'\rangle$ must preserve all inner products between them

$$\begin{aligned} \langle \phi|\psi\rangle \rightarrow \langle \phi'|\psi'\rangle &= (\langle \phi| U_\Theta^\dagger)(U_\Theta |\psi\rangle) = \langle \phi|\psi\rangle , \\ \implies U_\Theta^\dagger U_\Theta &= 1 , \\ \implies U_\Theta^\dagger &= U_\Theta^{-1} , \end{aligned} \quad (5.99)$$

indicating that U_Θ is a unitary operator. Indeed, transformation operators in quantum mechanics must be either unitary or anti-unitary (i.e., an operator U whose action on ψ leads to $U(c|\psi\rangle) = c^*U|\psi\rangle$, e.g., the time-reversal transformation operation).

Here are a few more interesting properties of unitary operators. First, for a Hermitian operator Θ , we can always form a unitary operator $U_\Theta(\lambda) = e^{i\lambda\Theta}$ where λ is real-valued:

$$U_\Theta^\dagger = e^{-i\lambda\Theta} , \quad U_\Theta^\dagger U_\Theta = 1 . \quad (5.100)$$

Further, the eigenvectors of Θ correspond to the eigenvectors of U_Θ , and the eigenvalues of Θ are related to those of U_Θ :

$$\begin{aligned} \hat{\Theta} |\psi\rangle &= \Theta |\psi\rangle , \\ U_\Theta |\psi\rangle &= e^{i\lambda\hat{\Theta}} |\psi\rangle = e^{i\lambda\Theta} |\psi\rangle , \end{aligned} \quad (5.101)$$

where the eigenvalues of U_Θ are phases given by $e^{i\lambda\Theta}$.

An important relation that will often prove useful is the following. For two Hermitian operators Θ and A , such that the unitary operator $U_\Theta = e^{i\lambda\Theta}$, we have the Baker-Campbell-Hausdorff relation (which we will not prove here)

$$\begin{aligned} U_\Theta A U_\Theta^\dagger &= e^{i\lambda\Theta} A e^{-i\lambda\Theta}, \\ &= A + i\lambda [\Theta, A] + \frac{(i\lambda)^2}{2!} [\Theta, [\Theta, A]] + \dots + \frac{(i\lambda)^n}{n!} [\Theta, [\Theta, [\Theta, \dots [\Theta, A]]] \dots] \end{aligned} \quad (5.102)$$

For the special case of $[\Theta, A] = 0$, all the commutators on the right hand side vanish identically, and the above simplifies to

$$U_\Theta A U_\Theta^\dagger = e^{i\lambda\Theta} A e^{-i\lambda\Theta} = A. \quad (5.103)$$

As we will now see, this relation indicates that, for an operator \hat{A} acting on its eigenbasis $\{|A\rangle\}$, there also exists an operator $\hat{B} \equiv U_\Theta \hat{A} U_\Theta^\dagger$ acting on its eigenbasis $\{|B\rangle\} \equiv \{U_\Theta |A\rangle\}$ with an identical set of eigenvalues

$$\begin{aligned} \hat{A} |A\rangle &= A |A\rangle, \\ \text{or, } U_\Theta \hat{A} U_\Theta^\dagger |A\rangle &= AU_\Theta |A\rangle, \\ \text{or, } \hat{B} |B\rangle &= A |B\rangle, \end{aligned} \quad (5.104)$$

where we have identified \hat{B} and $|B\rangle$ above. Thus, we say that \hat{A} and $\hat{B} \equiv U_\Theta \hat{A} U_\Theta^\dagger$ are unitarily equivalent observables with identical spectra (i.e., the set of eigenvalues $\{A\}$).

Now, using the fact that the matrix elements of the U_Θ transformation matrix between the two basis sets are given by $\langle A|B\rangle = \langle A|U_\Theta|A\rangle$, we can expand a given state $|\alpha\rangle$ as

$$|\alpha\rangle = \sum_A |A\rangle \langle A|\alpha\rangle, \quad (5.105)$$

$$\implies \langle B|\alpha\rangle = \sum_A \langle B|A\rangle \langle A|\alpha\rangle, \quad (5.106)$$

$$= \sum_A \langle A|U_\Theta^\dagger|A\rangle \langle A|\alpha\rangle = \sum_A \langle A|U_\Theta^{-1}|A\rangle \langle A|\alpha\rangle. \quad (5.107)$$

Similarly, we can relate the matrix elements of any operator \hat{X} in the new basis $|B\rangle$ to those in the old basis $|A\rangle$ as follows

$$\begin{aligned} \langle B_i|\hat{X}|B_j\rangle &= \sum_m \sum_n \langle B_i|A_m\rangle \langle A_m|\hat{X}|A_n\rangle \langle A_n|B_j\rangle, \\ &= \sum_m \sum_n \langle A_i|U_\Theta^\dagger|A_m\rangle \langle A_m|\hat{X}|A_n\rangle \langle A_n|U_\Theta|A_j\rangle. \end{aligned} \quad (5.108)$$

Defining the trace of an operator \hat{X} as the sum of its diagonal matrix elements computed in a basis, say $\{|A\rangle\}$

$$\text{Tr}_{|A\rangle} \hat{X} = \sum_A \langle A|\hat{X}|A\rangle, \quad (5.109)$$

we find that the trace is invariant under the transformations brought about by U_Θ

$$\text{Tr}_{|A\rangle} \hat{X} = \sum_A \langle A | \hat{X} | A \rangle = \sum_A \sum_B \sum_{B'} \langle A | B \rangle \langle B | \hat{X} | B' \rangle \langle B' | A \rangle , \quad (5.110)$$

$$= \sum_A \sum_B \sum_{B'} \langle B' | A \rangle \langle A | B \rangle \langle B | \hat{X} | B' \rangle ,$$

$$= \sum_B \sum_{B'} \langle B' | B \rangle \langle B | \hat{X} | B' \rangle \quad \text{as} \quad \sum_A |A\rangle \langle A| = 1 ,$$

$$= \sum_{B'} \langle B' | \hat{X} | B' \rangle \quad \text{as} \quad \sum_B |B\rangle \langle B| = 1 ,$$

$$= \sum_B \langle B | \hat{X} | B \rangle = \text{Tr}_{|B\rangle} \hat{X} . \quad (5.111)$$

Further, for $A(\lambda) = U_\Theta A U_\Theta^\dagger = e^{i\lambda\Theta} A e^{-i\lambda\Theta}$, it can be seen that

$$\frac{dA(\lambda)}{d\lambda} = i [\Theta, A(\lambda)] . \quad (5.112)$$

This can be easily derived by using the Baker-Campbell-Hausdorff relation for $A(\lambda)$ given above:

$$\begin{aligned} \frac{dA(\lambda)}{d\lambda} &= \frac{d}{d\lambda} (U_\Theta A U_\Theta^\dagger) = \frac{d}{d\lambda} (e^{i\lambda\Theta} A e^{-i\lambda\Theta}) , \\ &= \frac{d}{d\lambda} (A + i\lambda [\Theta, A] + \frac{(i\lambda)^2}{2!} [\Theta, [\Theta, A]] + \dots + \frac{(i\lambda)^n}{n!} [\Theta, [\Theta, [\Theta, \dots [\Theta, A]]] \dots] + \dots) , \\ &= i [\Theta, A] + \frac{2i^2\lambda}{2!} [\Theta, [\Theta, A]] + \frac{3i^3\lambda^2}{3!} [\Theta, [\Theta, [\Theta, A]]] + \dots , \\ &= i [\Theta, A] + i(i\lambda) [\Theta, [\Theta, A]] + i \frac{(i\lambda)^2}{2!} [\Theta, [\Theta, [\Theta, A]]] + \dots , \\ &= i \left[\Theta, (A + i\lambda [\Theta, A] + \frac{(i\lambda)^2}{2!} [\Theta, [\Theta, A]] + \frac{(i\lambda)^3}{3!} [\Theta, [\Theta, [\Theta, A]]] + \dots) \right] , \\ \Rightarrow \frac{dA(\lambda)}{d\lambda} &= i [\Theta, A(\lambda)] . \end{aligned} \quad (5.113)$$

A special case of the above relation corresponds to $\hat{\Theta}$ being the Hamiltonian H , $\hat{\Theta} \equiv H$, and $\lambda \equiv t$, such that $U_\Theta(t) \equiv U_t = e^{itH/\hbar}$ corresponds to the time (t) evolution operator, the time evolved operator $A(t)$ is given by

$$A(t) = U_t A U_t^\dagger = e^{itH/\hbar} A e^{-itH/\hbar} , \text{ and} \quad (5.114)$$

$$\hbar dA(t)/dt = i [H, A(t)] \quad (5.115)$$

is the Heisenberg equation of motion for the operator $A(t)$. We will explore the origin of this equation of motion for the operators such as A shortly.

5.8 Matrix representation of Operators & Matrix mechanics

From the above discussion, we can see that the matrix representation of the operator \hat{X} in the basis $\{|A\rangle\}$ is given by

$$\hat{X} = \sum_{|A'\rangle} \sum_{|A\rangle} |A'\rangle \langle A'| \hat{X} |A\rangle \langle A| , \quad (5.116)$$

where the matrix \tilde{X} whose elements are given by $\langle A' | \hat{X} | A \rangle$ can be written explicitly as

$$\tilde{X} = \begin{pmatrix} \langle A_1 | \hat{X} | A_1 \rangle & \langle A_1 | \hat{X} | A_2 \rangle & \dots \\ \langle A_2 | \hat{X} | A_1 \rangle & \langle A_2 | \hat{X} | A_2 \rangle & \dots \\ \vdots & \vdots & \ddots \\ \vdots & \vdots & \ddots \end{pmatrix} . \quad (5.117)$$

The matrix representation of \hat{X} becomes simple if we use the eigenstates ($|X\rangle$) of \hat{X} to compute the matrix elements

$$\hat{X} = \sum_{|X'\rangle} \sum_{|X\rangle} |X'\rangle \langle X' | \hat{X} |X\rangle \langle X| , \quad (5.118)$$

$$= \sum_{|X'\rangle} \sum_{|X\rangle} |X'\rangle (\langle X | \hat{X} | X \rangle \delta_{XX'}) \langle X | , \quad (5.119)$$

$$= \sum_{|X'\rangle} \sum_{|X\rangle} |X'\rangle X \delta_{XX'} \langle X | , \quad (5.120)$$

$$= \sum_{|X\rangle} X |X\rangle \langle X| = \sum_{|X\rangle} X P_{|X\rangle} , \quad (5.121)$$

where $P_{|X\rangle} \equiv |X\rangle \langle X|$ is the projector operator onto the state $|X\rangle$. Thus, we find that the operator in its diagonal basis can be written in terms of projectors onto its eigenstates.

Thus, we can use the above result to write the time-independent Schrödinger equation in the energy (or Hamiltonian) eigenbasis $\{|\psi\rangle\}$ as follows

$$H |\psi\rangle = \left(\sum_{|\psi'\rangle} E_{\psi'} |\psi'\rangle \langle \psi'| \right) |\psi\rangle , \quad (5.122)$$

$$= \sum_{|\psi'\rangle} E_{\psi'} |\psi'\rangle \langle \psi'| \psi \rangle , \quad (5.123)$$

$$= \sum_{|\psi'\rangle} E_{\psi'} |\psi'\rangle \delta_{\psi\psi'} \text{ as } \langle \psi' | \psi \rangle = \delta_{\psi\psi'} , \quad (5.124)$$

$$= E_\psi |\psi\rangle , \quad (5.125)$$

which gives the energy eigenvalues as the set $\{E_\psi\}$.

5.9 Quantum dynamics: the Schrödinger, Heisenberg and interaction pictures

We can now bring some more clarity to the time evolution (or dynamics) of the quantum mechanical universe. Recall that under time evolution, the state vectors transformed as $|\psi\rangle \rightarrow |\psi(t)\rangle = U_t^\dagger |\psi\rangle$ where $U_t = e^{-iHt/\hbar}$, but preserved the inner product (and norms) of the associated Hilbert space:

$$\langle\phi|\psi\rangle \rightarrow \langle\phi(t)|\psi(t)\rangle = (\langle\phi|U_t)(U_t^\dagger|\psi\rangle) = \langle\phi|\psi\rangle . \quad (5.126)$$

From what you have studied in earlier chapters, you will recall that we assumed that while state (vectors) such as $|\psi\rangle$ underwent time evolution as given above, operators acting on these states did not. Thus, for the time evolution of matrix elements such as $\langle\phi|\hat{A}|\psi\rangle$, we find that

$$\begin{aligned} \langle\phi|\hat{A}|\psi\rangle \rightarrow \langle\phi(t)|\hat{A}|\psi(t)\rangle &= (\langle\phi|U_t)\hat{A}(U_t^\dagger|\psi\rangle) , \\ &= \langle\phi|(U_t\hat{A}U_t^\dagger)|\psi\rangle , \\ &= \langle\phi|\hat{A}(t)|\psi\rangle , \end{aligned} \quad (5.127)$$

where $\hat{A}(t) = U_t\hat{A}U_t^\dagger$. If we ponder on this for a moment, this relation tells us something really interesting: computing the matrix element of the time-unevolved operator \hat{A} with time-evolved states $|\psi(t)\rangle$ and $|\phi(t)\rangle$ is equivalent to computing the matrix element of the time-evolved operator $\hat{A}(t)$ defined above but on the time-unevolved states $|\psi\rangle$ and $|\phi\rangle$. The first approach, where the states $|\psi\rangle$ evolve in time but the operators \hat{A} do not, is referred to as the Schrödinger picture of quantum mechanics. On the other hand, the second approach — where the states $|\psi\rangle$ are unchanged in time but the operators \hat{A} evolve in time, is referred to as the Heisenberg picture of quantum mechanics.

The earlier chapters dealt with the Schrödinger picture, where the only time evolution we considered was for problems where the Hamiltonian (or, the potential operator \hat{V}) had no explicit time dependence ($\hat{V} \equiv V(r)$). There, we studied the eigenstates $\{|\psi\rangle\}$ of the Hamiltonian H , and whose time evolution was simply given by $\{|\psi\rangle\} \rightarrow \{|\psi(t)\rangle\} = \{U_t^\dagger|\psi\rangle\}$ where $U_t = e^{-iHt/\hbar}$. On the other hand, in the Heisenberg picture, we would keep the states unchanged (i.e., precisely the same) with time, but allow the operators to evolve according to the Heisenberg equation of motion we derived earlier:

$$\begin{aligned} \frac{d\hat{A}(t)}{dt} &= \frac{d}{dt}\left(U_t\hat{A}U_t^\dagger\right) , \\ &= \frac{i}{\hbar}[H, A(t)] . \end{aligned} \quad (5.128)$$

Clearly, for the case of U_t (or equivalently, the Hamiltonian H) commuting with \hat{A} , $[U_t, \hat{A}] = 0$, the equation of motion tells us that the eigenvalues of \hat{A} are conserved in time.

It is also instructive to compare the Heisenberg equation of motion with the classical equation of motion for a quantity $A \equiv A(p, q)$ (where p and q are the generalised classical momenta

and coordinates respectively) that does not have any explicit time dependence, written in the Poisson bracket form

$$\frac{dA}{dt} = [A, H]_{\text{Classical}} , \quad (5.129)$$

where H is the Hamiltonian of the classical system. It can be argued that the the classical equation of motion can be obtained from it's quantum counterpart (the Heisenberg equation of motion) via the ansatz

$$\frac{[A, H]}{i\hbar} \rightarrow [A, H]_{\text{Classical}} . \quad (5.130)$$

This ansatz is believed to be one way in which to see the correspondence between the dynamics of the classical and quantum worlds. However, we must deal with the complication that the quantum world deals with experimentally observed quantities that arise from the action of operators on state vectors, while this is not true in the classical world. Thus, another way by which to see the correspondence is through the Ehrenfest theorem, which involves looking at the equation of motion for the expectation value of an operator $\langle \hat{A} \rangle$

$$\frac{d\langle \hat{A}(t) \rangle}{dt} = \frac{i}{\hbar} \langle [H, A(t)] \rangle \rightarrow [A, H]_{\text{Classical}} , \quad (5.131)$$

as leading to the equivalent classical experimentally observable quantity.

A word on “transition amplitudes” is due at this point. Imagine a system at time $t = 0$ prepared in an eigenstate of observable \hat{A} with eigenvalue a , $|a\rangle$. We can ask: what is the probability for the system to be found in an eigenstate of an observable B with eigenvalue b , $|b\rangle$, at a later time t ? This is known as the “transition amplitude” to go from $|a\rangle$ at time $t = 0$ to $|b\rangle$ at time t . In the Schrödinger picture, as $|a\rangle \rightarrow U_t |a\rangle$, this transition amplitude is given simply by the inner product $\langle b| (U_t |a\rangle)$. By contrast, in the Heisenberg picture $|a\rangle$ remains unchanged under time evolution. However, the transition amplitude in going from $|a\rangle$ to $|b\rangle$ with time cannot change dependent on the picture we have chosen for the time evolution. Thus, the invariance of the transition amplitude dictates that, in the Heisenberg picture, we interpret the transition amplitude as $(\langle b| U_t) |a\rangle$, i.e., the final state $|b\rangle$ in the Heisenberg picture undergoes a time evolution opposite to that of the initial state $|a\rangle$ in the Schrödinger picture. The same is true of the so-called “survival probability” $|\langle b| U_t |a\rangle|^2$, i.e., the probability corresponding to the transition amplitude.

5.9.1 The interaction picture

For the case when $\hat{V} \equiv V(r, t)$, we would have to treat the time-dependent Schrödinger equation

$$\hat{H}\Psi(\vec{r}, t) = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \Psi(\vec{r}, t) = i\hbar \frac{\partial\Psi(\vec{r}, t)}{\partial t} . \quad (5.132)$$

But how would we go about this? As we will now see, this involves working with neither the Schrödinger nor the Heisenberg pictures, but rather with a picture called the “Interaction” (or Dirac) picture which is intermediate between the Schrödinger and Heisenberg pictures. Consider a Hamiltonian H which can be split into two parts, one of which is time-independent

(H_0) while the other is time-dependent ($V(t)$): $H = H_0 + V(t)$. We assume that we know the eigenstates ($|n\rangle$) and energy eigenvalues (E_n) corresponding to H_0 : $H_0|n\rangle = E_n|n\rangle$.

The complication in dealing with $V(t)$ arises from the fact that we cannot presume that the time evolution of the eigenstates of the complete Hamiltonian H is simply a phase factor $e^{-iHt/\hbar}$, as H is now (through $V(t)$) itself changing in time t . Even if we start from the eigenstates of H_0 , $\{|n\rangle\}$, at time $t = 0$, the application of $V(t)$ for $t > 0$ can very generally lead to transitions between the states $\{|n\rangle\}$. How then would we determine how an arbitrary state vector $|\alpha\rangle$ evolves in time? Suppose at $t = 0$, we start from

$$|\alpha\rangle = \sum_n c_n(t=0)|n\rangle , \quad (5.133)$$

we wish to find $c_n(t)$ for $t > 0$ such that

$$|\alpha, t_0 = 0; t\rangle_S = \sum_n c_n(t)e^{-iE_nt/\hbar}|n\rangle , \quad (5.134)$$

where $|\alpha, t_0 = 0; t\rangle_S$ corresponds to a state vector in the Schrödinger picture at time t of a system whose state at time $t = 0$ is given by $|\alpha\rangle$ (see above). Note that in eq.(5.134), we have already explicitly accounted for the time evolution phase factor $e^{-iE_nt/\hbar}$ of the eigenstates $|n\rangle$ of the Hamiltonian H_0 (as this is present even if V is absent). In this way, we ensure that the time evolution of the coefficients $c_n \equiv c_n(t)$ arise purely from the presence of $V(t)$ and such that $c_n \equiv c_n(t=0)$ if $V(t)$ were set to zero. Clearly, the probability of finding $|n\rangle$ in $|\alpha, t_0 = 0; t\rangle$ is given by $|c_n(t)|^2$, and $\sum_n |c_n(t)|^2 = 1$ (i.e., unitarity is guaranteed). We will comment on the validity (or correctness) of the form of $|\alpha, t_0 = 0; t\rangle_S$ given in eq.(5.134) above at the end of this section.

We define the time dependent state in the interaction picture, $|\alpha, t_0; t\rangle_I$ (where the I subscript denotes the interaction picture), in terms of the state in the Schrödinger picture $|\alpha, t_0; t\rangle_S$

$$|\alpha, t_0; t\rangle_I = e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S . \quad (5.135)$$

Clearly, at $t = 0$, $|\alpha, t_0; t\rangle_I = |\alpha, t_0; t\rangle_S$. The operators related to observables are defined in the interaction picture as

$$\begin{aligned} \hat{A}_I &= \equiv e^{iH_0t/\hbar}\hat{A}_S e^{-iH_0t/\hbar}, \\ \implies V_I &= \equiv e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}, \end{aligned} \quad (5.136)$$

where the potential $V(t)$ is understood to be the time-dependent potential in the Schrödinger picture. Recalling that the Heisenberg picture is connected to the Schrödinger picture as follows

$$\begin{aligned} |\alpha\rangle_H &= e^{iHt/\hbar}|\alpha, t_0; t\rangle_S , \\ \hat{A}_H &= e^{iHt/\hbar}\hat{A}_S e^{-iHt/\hbar} , \end{aligned} \quad (5.137)$$

we see that the basic difference between the way in which the interaction picture is connected to the Schrödinger picture vis-a-vis the connection between the Heisenberg and Schrödinger pictures is given that the former connection relies on H_0 while the latter relies on H .

In order to obtain the differential equation that governs the time evolution of a state in the interaction picture, we take the time derivative of eq.(5.135)

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_I &= i\hbar \frac{\partial}{\partial t} (e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_S) , \\
&= -H_0 e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_S + e^{iH_0 t/\hbar} (i\hbar \frac{\partial}{\partial t}) |\alpha, t_0; t\rangle_S , \\
&= -H_0 e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_S + e^{iH_0 t/\hbar} (H_0 + V) |\alpha, t_0; t\rangle_S , \text{ using } i\hbar \frac{\partial}{\partial t} |\psi\rangle_S = H |\psi\rangle_S \\
&= e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} |\alpha, t_0; t\rangle_I , \\
\implies i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_I &= V_I |\alpha, t_0; t\rangle_I . \tag{5.138}
\end{aligned}$$

Clearly, this is a Schrödinger-like equation where the evolution of the state $|\alpha, t_0; t\rangle_I$ is dictated by V_I (instead of the total H), such that the state $|\alpha, t_0; t\rangle_I$ does not evolve if V_I vanishes. Similarly, if we take a time derivative of eq.(5.136) for an operator \hat{A} that does not contain time t explicitly, we find

$$\frac{d\hat{A}_I}{dt} = \frac{i}{\hbar} [H_0, \hat{A}_I] , \tag{5.139}$$

which is a Heisenberg-like equation for \hat{A}_I with H being replaced by H_0 . An explicit time dependence within \hat{A} will lead to an additional $\frac{\partial \hat{A}}{\partial t}$ term in the above expression.

Now, we continue to use the eigenstates of the H_0 , $|n\rangle$, as our state vectors:

$$|\alpha, t_0; t\rangle_I = \sum_n c_n(t) |n\rangle . \tag{5.140}$$

Thus, we can act with $e^{-iH_0 t/\hbar}$ on both sides, and use $H_0 |n\rangle = E_n |n\rangle$ to get

$$\begin{aligned}
e^{-iH_0 t/\hbar} |\alpha, t_0 = 0; t\rangle_I &= e^{-iH_0 t/\hbar} \sum_n c_n(t) |n\rangle , \\
\implies |\alpha, t_0 = 0; t\rangle_S &= \sum_n c_n(t) e^{-iH_0 t/\hbar} |n\rangle , \\
&= \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle , \tag{5.141}
\end{aligned}$$

giving us back eq.(5.134) once again. Thus, we see that eq.(5.140) is just another way of writing eq.(5.134); indeed, eq.(5.140) has a simpler form (as all the phase factors of $e^{-iE_n t/\hbar}$ are missing). We can now derive the differential equation for the coefficient $c_n(t)$ by acting on both side of the Schrödinger-like equation in the interaction picture (eq.5.138) with $\langle n|$

to obtain

$$i\hbar \frac{\partial}{\partial t} \langle n|\alpha, t_0; t \rangle_I = \sum_m \langle n| V_I |m\rangle \langle m|\alpha, t_0; t \rangle_I . \quad (5.142)$$

$$\begin{aligned} \text{But } \langle n| V_I |m\rangle &= \langle n| e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} |m\rangle , \\ &= e^{i(E_n - E_m)t/\hbar} \langle m| V(t) |n\rangle , \\ &= V_{nm}(t) e^{i(E_n - E_m)t/\hbar} . \end{aligned} \quad (5.143)$$

$$\text{And } c_n(t) = \langle n|\alpha, t_0; t \rangle_I . \quad (5.144)$$

$$\therefore i\hbar \frac{dc_n(t)}{dt} = \sum_m V_{nm}(t) e^{i\omega_{nm} t} c_m(t) , \quad (5.145)$$

where $\omega_{nm} = \frac{E_n - E_m}{\hbar}$. This is the basic differential equation for the time evolution of $c_n(t)$ that arises from the fact that $V(t)$ causes couplings with various other coefficients $c_m(t)$. Explicitly, this can be written out as

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12} e^{i\omega_{12} t} & V_{13} e^{i\omega_{13} t} & \dots \\ V_{21} e^{-i\omega_{12} t} & V_{22} & V_{23} e^{i\omega_{23} t} & \dots \\ V_{31} e^{-i\omega_{13} t} & V_{32} e^{-i\omega_{23} t} & V_{33} & \dots \\ \vdots & \vdots & \vdots & \ddots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ \vdots \end{pmatrix} . \quad (5.146)$$

The frequency ω_{mn} corresponds the energy cost of transitions between $|n\rangle$ and $|m\rangle$ brought about by the time-varying potential $V(t)$, i.e., $\langle m| V(t) |n\rangle \neq 0$. In this way, we have now arrived at an equation for the time evolution of the coefficients $c_n(t)$ in terms of the action of $V(t)$.

Finally, we end by asking: when is it safe to assume that eq.(5.134) for the time-evolved state in the Schrödinger picture is valid, i.e., when is the expansion of $|\alpha, t_0; t\rangle_S$ in terms of the eigenbasis of H_0 ($\{|n\rangle\}$) valid? Put another way, when can we be sure that the separation of the complete Hamiltonian into two separate parts, H_0 and $V(t)$, remains valid? The answer is that as long as the time-dependent potential $V(t)$ does not cause the ground state of H_0 , $|0\rangle$, to become orthogonal to itself. If this should happen, the eigenspectrum will undergo a huge shake-up and the application of the interaction picture in terms of H_0 and $V(t)$ is no longer valid. This is precisely what happens at a quantum phase transition in a many-body system comprised of a thermodynamically large number of interacting constituents. Thus, we are assuming that we are nowhere near any such interesting physics!

Chapter 6

Heisenberg's Uncertainty principle

6.1 The case of a wavepacket

In quantum mechanics, a particle is described by a wave packet (which itself is composed of many different waves!). The wave packet surrounds the expectation value of the position, and its “centre of gravity” moves with the group velocity along the classical trajectory. As we will see, such a wave packet has an intrinsic indeterminacy in its position and momentum.



Consider the wave packet through the Fourier integral at $t = 0$

Heisenberg

$$\psi(x, t = 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \ a(p) e^{\frac{ipx}{\hbar}} \quad \text{where} \quad a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx \psi(x) e^{-\frac{ipx}{\hbar}}$$

Using this relation, we can construct a wave packet localised within a region of width Δx and height $\frac{1}{\sqrt{\Delta x}}$, i.e., is a rectangular waveform $\psi(x)$ that is nonzero within a region of width Δx , and zero everywhere else.

The Fourier coefficient for this waveform is (for $p = \hbar k$)

$$a(p) = \sqrt{\frac{\Delta x}{2\pi\hbar}} \frac{\sin \frac{p\Delta x}{2\hbar}}{\frac{p\Delta x}{2\hbar}}$$

and $a(p)^2 \propto$ Probability that the particle has momentum p . Plotting $a(p)$ as a function of p shows maximum at $p = 0$, and the maximum contribution to the middle part comes from the narrow interval around the origin with a width

$$\Delta p \equiv \frac{\hbar}{\Delta x}$$

$\Rightarrow \Delta p \Delta x \equiv \hbar$ and this is irrespective of the shape of the wavepacket

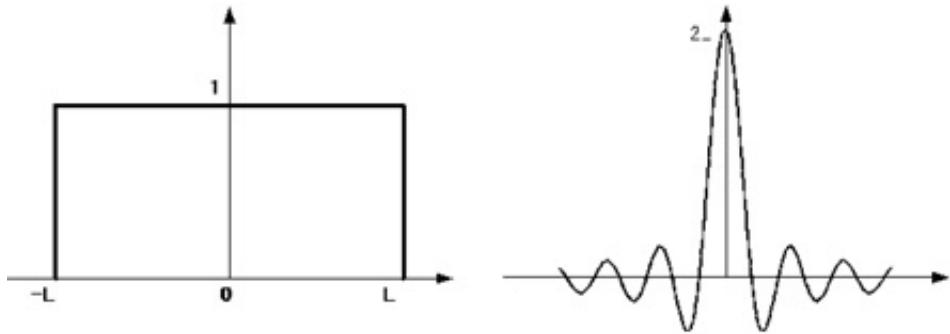


Figure 6.1: The square wavepacket and its Fourier transform (the sinc function, also known as the “Fraunhofer diffraction pattern”). Source: The internet.

It is not possible to build into the wavepacket more exact information on both the position and the momentum of the particle. This reflects the intrinsic indeterminacy of the wavepacket in terms of conjugate variables like (x, p) etc. This is the content of the Heisenberg uncertainty principle (HUP).

6.2 The γ -ray microscope gedanken

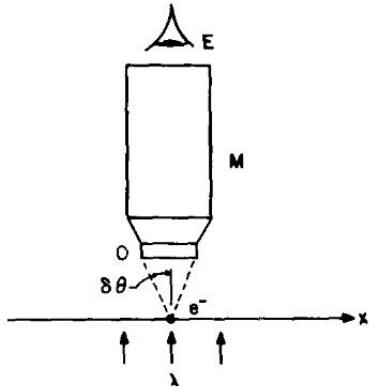


Figure 6.2: The γ -ray microscope gedanken. See text for discussion. Source: R. Shankar’s text “Principles of Quantum Mechanics”.

The Heisenberg Uncertainty Principle (HUP) sets a limit to the precision with which certain pairs of conjugate dynamical variables (e.g., linear position x and linear momentum p_x , angular momentum L and angular position θ etc.) can be defined *simultaneously*. There is no theoretical limit on the accuracy with which a single variable related to the wavepacket can be defined. The statement is that increasing the accuracy in the definition of a given variable makes manifest a decreasing accuracy in the definition of a variable conjugate to it, such that the uncertainty relation written in terms of both holds. It is important to note that **measurements make the intrinsic uncertainty manifest, but do not define them**.

A gedanken that highlights the intrinsic uncertainty in conjugate quantities is the γ -ray microscope. Here, light of wavelength λ shines on (i.e., scatters off) an electron (e^- in Fig.6.2 above) and then enters the objective lens (O) of a microscope (M) such that it finally reaches our eye (E). The aperture width of the lens is a , and the electron is placed at the focal distance f such that the gathering angle its position makes with respect to the lens is $2\delta\theta$ (i.e., the angle of the cone of light that enters O after scattering off the e^-). Ensure that the beam of electrons contains monoenergetic e^- s, such that we know the e^- -momentum precisely ($p = \sqrt{2mE}$) before its interaction with the light. According to the HUP, we can say nothing about the position related to the matter waves associated with such e^- s. Can we use a microscope to obtain some information on their position?

Since the classical resolving power of a microscope is inversely proportional to the wavelength (λ) of light used, why not try very short-wavelength λ , i.e., γ -rays? From physical optics, the accuracy of such a measurement is

$$\Delta x = \frac{\lambda}{\sin \delta\theta} \simeq \frac{\lambda f}{a}. \quad (6.1)$$

Now recall that quantum mechanically, the light being used is a flux of photons with momentum $p = h/\lambda$. Indeed, for us to be able to observe an e^- in M , a photon must be scattered such that the x -component of its momentum must lie in a range

$$0 \leq p_x \leq p \sin \delta\theta \simeq \frac{ha}{\lambda f} \Rightarrow \Delta p_x \simeq \frac{ha}{\lambda f}. \quad (6.2)$$

Thus, we can see that the product of Δx and Δp_x gives

$$\Delta x \cdot \Delta p_x \simeq h, \quad (6.3)$$

offering the HUP. This relation tells us that if we “soften the blow” imparted to the e^- by the photon by increasing λ or decreasing a (i.e., narrowing the objective lens width) such that $\Delta p_x \rightarrow 0$, we lose out on the resolution of the position of the e^- . Indeed, there is no way around the HUP: more elaborate schemes that attempt to take into account the recoil of the photon turn out to be equally futile. The appearance of the Planck constant h instead is telling us that the source of the HUP is intrinsic to the quantum world. Wave-particle duality is only another manifestation of this.

The only way out of this is to make measurement of macroscopic (i.e., classical) objects: for them, measurements typically have $h \rightarrow 0$ such that we can simultaneously have both $\Delta x \rightarrow 0$ as well as $\Delta p_x \rightarrow 0$. In this way, we can justify how the arbitrary precision of Newtonian mechanics emerges from the Heisenberg uncertainty principle quantum mechanics. Note, though, that taking the limit of $h \rightarrow 0$ is a heuristic tool ... we don't really understand at present how this emergence takes place!

6.3 A derivation of the HUP for wavepackets

Definition of Uncertainty in expectation value of an operator $\hat{\theta}$ is

$$\Delta\theta = \sqrt{\langle (\theta - \langle \theta \rangle)^2 \rangle} \text{ akin to the standard deviation in statistics}$$

Now,

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{\infty} dx \psi^* x \psi = \int_{-\infty}^{\infty} dx x |\psi(x)|^2 \\ \langle \hat{p}_x \rangle &= \int_{-\infty}^{\infty} dx \psi^*(x, t) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x, t) .\end{aligned}$$

Note that we are dropping the $\hat{}$ (hat) symbol above all operators for the sake of brevity; we assume henceforth that the reader will understand their presence from the context. In order to reach the HUP, let us start with

$$\begin{aligned}\int dx i\hbar \frac{d\psi^*}{dx} x \psi &= -i\hbar \int dx \psi^* \psi - i\hbar \int dx \frac{d\psi}{dx} x \psi^* \quad (\text{where } \psi^* x \psi|_{-\infty}^{\infty} \rightarrow 0 \text{ as } \psi, \psi^*|_{-\infty}^{\infty} \rightarrow 0) \\ &= -i\hbar \int dx \psi^* \psi + \left[i\hbar \int dx \frac{d\psi^*}{dx} x \psi \right]^* \quad (\text{as } x^* = x) .\end{aligned}\tag{6.4}$$

Since $c - c^* = 2i\text{Im}[c]$, $c \in \mathcal{C}$, we can rewrite the above as

$$i\hbar \int dx |\psi|^2 = 2i\text{Im} \left[\int i\hbar dx \frac{d\psi^*}{dx} x \psi \right] \tag{6.5}$$

$$\therefore \hbar^2 \left| \int dx |\psi|^2 \right|^2 = 4 \left| \text{Im} \int dx i\hbar \frac{d\psi^*}{dx} x \psi \right|^2 \leq 4 \left| i\hbar \int dx \frac{d\psi^*}{dx} x \psi \right|^2 , \tag{6.6}$$

where in the second line, we have used the relation $|\text{Im}[c]|^2 \leq |c|^2$, $c \in \mathcal{C}$. Now, using the Schwarz inequality $|c_1^* c_2|^2 \leq |c_1|^2 \times |c_2|^2$, we obtain

$$\begin{aligned}\left| \int dx i\hbar \frac{d\psi^*}{dx} x \psi \right|^2 &\leq \int dx x \psi^* x \psi \int dx \left(i\hbar \frac{\partial \psi^*}{\partial x} \right) \left(-i\hbar \frac{\partial \psi}{\partial x} \right) \\ \left| \int dx i\hbar \frac{d\psi^*}{dx} x \psi \right|^2 &\leq \int dx x^2 |\psi|^2 \int dx \left| -i\hbar \frac{\partial \psi}{\partial x} \right|^2 .\end{aligned}\tag{6.7}$$

Thus, the inequality relation eq.(6.6) becomes

$$\begin{aligned}\underbrace{\frac{\hbar^2}{4} \left| \int dx |\psi|^2 \right|^2}_{=1} &\leq \underbrace{\int dx x^2 |\psi|^2}_{\langle x^2 \rangle} \times \underbrace{\int dx \left(i\hbar \frac{\partial \psi^*}{\partial x} \right) \left(-i\hbar \frac{\partial \psi}{\partial x} \right)}_{\langle p^2 \rangle} \\ \Rightarrow \frac{\hbar^2}{4} &\leq \langle x^2 \rangle \langle p^2 \rangle .\end{aligned}\tag{6.8}$$

Recall that the relations for the standard deviations in x and p are

$$\Delta x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}, \quad \Delta p = \sqrt{\langle (p - \langle p \rangle)^2 \rangle} , \tag{6.9}$$

we replace x and p by their generalisations $x - \langle x \rangle$ and $p - \langle p \rangle$ respectively in eq.(6.8) to obtain

$$\frac{\hbar^2}{4} \leq \langle (x - \langle x \rangle)^2 \rangle \langle (p - \langle p \rangle)^2 \rangle \equiv \left(\Delta x \right)^2 \left(\Delta p \right)^2 \tag{6.10}$$

$$\Rightarrow \frac{\hbar}{2} \leq \Delta x \Delta p . \tag{6.11}$$

This is the celebrated form of the Heisenberg Uncertainty Principle (HUP) relation between x and p . It shows clearly the existence of a lower bound on the precisions that can be obtained on simultaneous measurement of x and its conjugate momentum p .

6.3.1 A generalised Uncertainty principle

Let us consider a state $|\psi\rangle$ and two Hermitian operators $A \equiv A^\dagger$ and $B \equiv B^\dagger$, such that

$$A|\psi\rangle = |X\rangle , \quad iB|\psi\rangle = |Y\rangle . \quad (6.12)$$

Now, we define the norms of $|X\rangle$, $|Y\rangle$ and $|X\rangle + |Y\rangle$ as

$$|X| = \sqrt{\langle X|X \rangle} , \quad |Y| = \sqrt{\langle Y|Y \rangle} , \quad |X + Y| = \sqrt{(\langle X| + \langle Y|)(|X\rangle + |Y\rangle)} . \quad (6.13)$$

Then, we start from the triangle inequality

$$|X| + |Y| \geq |X + Y| , \quad (6.14)$$

square it and simplify to get

$$\begin{aligned} (|X| + |Y|)^2 &\geq |X + Y|^2 , \\ \text{or, } |X|^2 + |Y|^2 + 2|X||Y| &\geq (\sqrt{(\langle X| + \langle Y|)(|X\rangle + |Y\rangle)})^2 , \\ &\geq (\langle X| + \langle Y|)(|X\rangle + |Y\rangle) , \\ &\geq |\langle X|X \rangle + \langle Y|Y \rangle + \langle X|Y \rangle + \langle Y|X \rangle| , \\ \implies 2|X||Y| &\geq |\langle X|Y \rangle + \langle Y|X \rangle| , \end{aligned} \quad (6.15)$$

which is the form of the Cauchy-Schwarz inequality we will use to obtain the uncertainty principle.

Substituting eq.(6.12) in eq.(6.15), we obtain (using $(iB|\psi\rangle)^\dagger = -i\langle\psi|B^\dagger = -i\langle\psi|B$)

$$\begin{aligned} 2\sqrt{\langle A^2 \rangle \langle B^2 \rangle} &\geq |\langle\psi|AB|\psi\rangle - \langle\psi|BA|\psi\rangle| , \quad (\text{removing an overall } i \text{ factor}) \\ \text{or, } 2\Delta A \Delta B &\geq |\langle\psi|[A, B]|\psi\rangle| , \quad \text{for } \langle A \rangle = 0 = \langle B \rangle , \quad \langle A^2 \rangle = (\Delta A)^2 , \quad \langle B^2 \rangle = (\Delta B)^2 \\ \implies \Delta A \Delta B &\geq \frac{1}{2}|\langle\psi|[A, B]|\psi\rangle| . \end{aligned} \quad (6.16)$$

This is the generalised uncertainty relation for the case of $\langle A \rangle = 0 = \langle B \rangle$. For the case of $\langle A \rangle \neq 0$, $\langle B \rangle \neq 0$, we can obtain the generalised uncertainty relation by redefine two new operators

$$\bar{A} = A - \langle A \rangle , \quad \bar{B} = B - \langle B \rangle . \quad (6.17)$$

Then, using the fact that the uncertainties in A and B are defined as $(\Delta A)^2 = \langle \bar{A}^2 \rangle$, $(\Delta B)^2 = \langle \bar{B}^2 \rangle$, and the fact that $[\bar{A}, \bar{B}] = [A, B]$, we obtain the generalised uncertainty relation as

$$\Delta A \Delta B \geq \frac{1}{2}|\langle\psi|[\bar{A}, \bar{B}]|\psi\rangle| . \quad (6.18)$$

Putting in $A \equiv x$ and $B \equiv p_x$, we obtain the results of the previous subsection: $\Delta x \Delta p_x \geq \frac{\hbar}{2}$, as the commutator $[x, p_x] = \hbar$.

Why did we choose the operator iB above, rather than B (even though B itself is Hermitian, i.e., $B^\dagger = B$)? Recall that the commutator of two Hermitian operators A and B , $[A, B]$ is actually anti-Hermitian in nature

$$([A, B])^\dagger = (AB - BA)^\dagger = B^\dagger A^\dagger - A^\dagger B^\dagger, \quad (6.19)$$

$$= BA - AB = -(AB - BA) = -[A, B]. \quad (6.20)$$

Such an anti-Hermitian operator has purely imaginary values: for an operator $C^\dagger = -C$

$$\langle \psi_n | C | \psi_n \rangle = c_n \langle \psi_n | \psi_n \rangle, \quad (6.21)$$

$$= (\langle \psi_n | -C^\dagger) | \psi_n \rangle = -c_n^* \langle \psi_n | \psi_n \rangle, \quad (6.22)$$

$$\implies c_n = -c_n^*, \quad (6.23)$$

which means that the eigenvalue c_N of the anti-Hermitian operator C is purely imaginary. Thus, we can see that the eigenvalue of the anti-Hermitian commutator $[A, B]$ is purely imaginary. Thus, in order to obtain a commutator that is Hermitian, we consider the anti-Hermitian operator iB , $(iB)^\dagger = -iB$ and its commutator with A

$$([A, iB])^\dagger = (A \times iB - iB \times A)^\dagger = (iB)^\dagger A^\dagger - A^\dagger (iB)^\dagger, \quad (6.24)$$

$$= (-iB) \times A - A \times (-iB) = i(AB - BA) = [A, iB]. \quad (6.25)$$

Thus, we now have a Hermitian commutator $[A, iB]$. Further, as we can see above, it yields real valued lower bound for the product of the uncertainties.

6.3.2 The Energy-time uncertainty relation

Note: As we have said earlier, there are several other examples of similar uncertainty relations in quantum mechanics, e.g., angular momentum and angular position etc. One such is that between energy E of a system and time t : $\Delta E \Delta t \geq \hbar/2$. This relation cannot be derived from the above approach as t is not a dynamical variable like x and p ; rather, t is a parameter in quantum mechanics. Thus, the content of this uncertainty relation is different from those that involve only dynamical variables. The uncertainty relation for E and t has the following (rough) meaning:

The energy E of a system that has only been in existence for a time (i.e., its “lifetime”) Δt has an uncertainty (or spread about its mean value) of atleast ΔE , such that the above quoted relation is satisfied. Clearly, for a stationary energy eigenstate, $\Delta E = 0$, and its lifetime $\Delta t \rightarrow \infty$. On the other hand, a non-stationary state (i.e., one with a finite lifetime) will undergo decay; such states have a finite and non-zero ΔE . More details on the origin of this relation will be revealed in further courses up ahead. For now, suffice it to say that there are several contexts in which such decay processes can show up, two being:

- (a) an open quantum system, i.e., a quantum system connected to its environment. Here, if the system is prepared in one (or a superposition) of the eigenstates of the isolated system, it will “decay” into the true eigenstates of the coupled system, and

(b) an interacting quantum system, i.e., a system with inter-constituent interactions. In such a many-body problem, if the system is prepared in one (or a superposition) of the eigenstates of the non-interacting system, it will “decay” into the true eigenstates of the full interacting system. This can give us an estimate (in the form of a lower bound) for time evolution between states, as was first pursued by Mandelstam and Tamm in 1945 (J. Phys. USSR **9**, 249-254 (1945))! They reasoned as follows.

Recall that the generalised uncertainty relation was given by

$$\Delta A \Delta B \geq \frac{1}{2} |\langle \psi | [A, B] | \psi \rangle| . \quad (6.26)$$

Further, the Ehrenfest relations for the operators A and B are given by

$$\frac{d\langle A(t) \rangle}{dt} = \frac{1}{i\hbar} \langle [H, A(t)] \rangle , \quad \frac{d\langle B(t) \rangle}{dt} = \frac{1}{i\hbar} \langle [H, B(t)] \rangle , \quad (6.27)$$

where $A(t) = U_t A U_t^\dagger$, $B(t) = U_t B U_t^\dagger$ and $U_t = e^{itH/\hbar}$. Taking $A \equiv H$ (the Hamiltonian), and using the Ehrenfest relation for B in the generalised uncertainty relation, we get the product of the uncertainties in the energy E and B

$$\begin{aligned} \Delta E \Delta B &\geq \frac{1}{2} |\langle \psi | [H, B] | \psi \rangle| = \frac{1}{2} |\langle \psi | i\hbar \frac{dB(t)}{dt} | \psi \rangle| , \\ \implies \Delta E \Delta B &\geq \frac{\hbar}{2} |\langle \psi | \frac{dB(t)}{dt} | \psi \rangle| . \end{aligned} \quad (6.28)$$

We now integrate this relation over a time period from t to $t + \Delta t$. For this, we note that (i) we are integrating over a total derivative in t on the right hand side, (ii) ΔE does not change over the time interval Δt and that (iii) ΔB is the average value of the variance in B computed over Δt . Thus, we obtain

$$\begin{aligned} \Delta E \times \Delta B \times \Delta t &\geq \frac{\hbar}{2} |\langle B_{t+\Delta t} \rangle - \langle B_t \rangle| , \\ \implies \Delta E \Delta t &\geq \frac{\hbar}{2} \left| \frac{\langle B_{t+\Delta t} \rangle - \langle B_t \rangle}{\Delta B} \right| , \end{aligned} \quad (6.29)$$

for ΔB computed over the time interval Δt . Now, for the time interval ΔT such that $\langle B_{t+\Delta T} \rangle - \langle B_t \rangle = \Delta B$, we have

$$\Delta E \Delta T \geq \frac{\hbar}{2} . \quad (6.30)$$

In this light, ΔT is referred to as the evolution time for the state $|\psi(t=0)\rangle$ to evolve to $|\psi(t=T)\rangle$ such that the condition $\langle B_{t+\Delta T} \rangle - \langle B_t \rangle = \Delta B$ is satisfied. Note that for the energy-time uncertainty relation to be satisfied, it is important that both $\Delta E \neq 0$ as well as $\Delta B \neq 0$ (as long as $\Delta E \neq \infty$). This means that the state $|\psi\rangle$ whose evolution we are considering can be neither an eigenstate of H nor of B .

Finally, we note that in both open as well as interacting quantum systems, the true eigenstates are very difficult to learn in general. Most of our theories for such complex quantum systems typically work with those that are almost isolated and weakly interacting.

Chapter 7

The Time Dependent and Independent Schrödinger Equations (TDSE & TISE)

The Schrödinger equation in its most general form is

$$\hat{H}\Psi(\vec{r}, t) \equiv \frac{-\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, t)\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi}{\partial t} ,$$

where the various cases we are interested in studying are characterized by different functional forms of $V(\vec{r}, t)$. This is the time dependent Schrödinger equation (TDSE).



Schrödinger

For a special case of potentials $V(\vec{r})$ (i.e., no explicit time dependence in the potential), we have

$$\hat{H}\Psi(\vec{r}, t) = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

Several cases of such potentials will be encountered in the days ahead. Concrete examples include the potential felt by an electron in an atom or in a crystal lattice.

We require that $\Psi(\vec{r}, t)$ be an eigenfunction of the energy operator $i\hbar \frac{\partial}{\partial t}$ with energy eigenvalue E

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = E\Psi(\vec{r}, t) ,$$

such that

$$\hat{H}\Psi(\vec{r}, t) = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi(\vec{r}, t) = E\Psi(\vec{r}, t) .$$

This is called the time independent Schrödinger equation (TISE). We can solve the equation above using separation of variables

$$\Psi(\vec{r}, t) = \psi(\vec{r})\chi(t) ,$$

such that

$$i\hbar\psi(\vec{r})\frac{\partial\chi(t)}{\partial t} = E\psi(\vec{r})\chi(t) \quad (7.1)$$

$$\implies \dot{\chi}(t) = \frac{-iE}{\hbar}\chi(t), \quad (7.2)$$

$$\chi(t) = e^{\frac{-iEt}{\hbar}}, \quad (7.3)$$

choosing $\chi(t=0) = 1$ as our normalisation choice.

Similarly,

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r})\chi(t) = E\psi(\vec{r})\chi(t)$$

$$\text{or, } \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \quad (7.4)$$

$$(7.5)$$

such that

$$\Psi(\vec{r}, t) = \psi(\vec{r})e^{\frac{-iEt}{\hbar}} \quad (7.6)$$

is the full wavefunction. We can also define a time evolution operator $U = e^{-\frac{i\hat{H}t}{\hbar}}$, such that

$$\begin{aligned} U\Psi(\vec{r}, t) &= e^{-\frac{i\hat{H}t}{\hbar}}\Psi(\vec{r}, t) \\ &= e^{-\frac{iEt}{\hbar}}\Psi(\vec{r}, t), \end{aligned} \quad (7.7)$$

where E is the eigenvalue of the Hamiltonian \hat{H} for the state $\Psi(\vec{r}, t)$. We will see later that the Hamiltonian corresponds to a **Hermitian** operator with real-valued eigenvalues $E \in \mathcal{R}$. In such cases, the unitary time evolution operator $U = e^{-\frac{i\hat{H}t}{\hbar}}$ (i.e., the exponentiation of a Hermitian operator) corresponds to a **Unitary** operator, whose eigenvalue is simply the phase factor $\chi(t) = e^{\frac{-iEt}{\hbar}}$.

Further, it is easily seen that

$$\text{Probability Density : } \Psi^*(\vec{r}, t)\Psi(\vec{r}, t) = \psi^*(\vec{r})e^{\frac{iEt}{\hbar}}\psi(\vec{r})e^{\frac{-iEt}{\hbar}} = \psi^*(\vec{r})\psi(\vec{r}) \text{ and} \quad (7.8)$$

$$\begin{aligned} \text{Expectation Value : } \langle \hat{\theta} \rangle &= \int_v d\vec{r} \psi^*(\vec{r})e^{\frac{iEt}{\hbar}}\hat{\theta}\psi(\vec{r})e^{\frac{-iEt}{\hbar}} \\ &= \int_v d\vec{r} \psi^*(\vec{r})\hat{\theta}\psi(\vec{r}). \end{aligned} \quad (7.9)$$

From these two relations for the Probability density and the Expectation value, we learn that the phase accrued from time evolution $\chi(t) = e^{\frac{-iEt}{\hbar}}$ does not change the total probability (or “norm”) associated with the state $\Psi(\vec{r})$ in time. We denote such a probability preserving time evolution as “**unitary**”.

As mentioned earlier, the time independent Schrödinger equation (TISE, eq.(7.5)) also helps us define the Hamiltonian operator

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}) \text{ whose eigenvalue is } E, \quad (7.10)$$

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}). \quad (7.11)$$

Further, time evolution of a system is neatly encoded by the (energy) eigenstates of the Hamiltonian operator. This makes them special.

Degenerate Eigenstates: Also, note that if

$$i\hbar \frac{\partial \Psi_1}{\partial t} = E\Psi_1, \quad \Psi_1 = \psi_1(\vec{r})\chi_1(t) \quad \& \quad i\hbar \frac{\partial \Psi_2}{\partial t} = E\Psi_2, \quad \Psi_2 = \psi_2(\vec{r})\chi_2(t), \quad (7.12)$$

$$\text{i.e., } \hat{H}\psi_1 = E\psi_1, \quad , \quad \hat{H}\psi_2 = E\psi_2, \quad (7.13)$$

then

$$\begin{aligned} \hat{H}(c_1\psi_1 + c_2\psi_2) &= Ec_1\psi_1 + Ec_2\psi_2 \quad (c_1, c_2 \in \mathcal{C}), \\ &= E(c_1\psi_1 + c_2\psi_2), \end{aligned} \quad (7.14)$$

i.e., $c_1\psi_1 + c_2\psi_2$ is also an eigenfunction of \hat{H} with the same energy eigenvalue E . In this case, the wavefunctions ψ_1 and ψ_2 are said to be **degenerate with respect to one other**.

7.1 Qualitative Solutions and the origin of Quantisation

We will now try to reach some qualitative conclusions on how “proper” wavefunctions ψ should look:

1. As $x \rightarrow \pm\infty$, $\psi(x) \rightarrow 0$; else, ψ is not normalisable (or square integrable). This is especially important in distinguishing the physically sensible wavefunctions in parts of the potential $V(x)$ that are classically forbidden.
2. The wavefunction ψ cannot be discontinuous. Physically, this makes no sense, as we would need extra information with which to make sense of missing probabilities $|\psi|^2$.
3. The spatial derivative $\frac{d\psi}{dx}$ is continuous for all x , unless the potential $V(x)$ is very peculiar (such that $\psi(x)$ has kinks). Can you think of such a peculiar $V(x)$?

For a wavefunction $\psi(x)$ that satisfies all these three conditions, the particle can exist classically in regions of x where the potential $V(x) < E$, while it is classically forbidden in regions where $E < V(x)$. In the classical world, a particle is bound to regions where $V(x) < E$. However, in the quantum world, perfectly legal $\psi(x)$ can be found for both $V(x) < E$ as well as $E < V(x)$. We will encounter this with bound states (e.g., in the simple harmonic oscillator problem) as well as with scattering (i.e., spatially extended) states (e.g., in the barrier tunneling problem).

The origin of the phenomenon of quantisation (or discretisation of the energy spectrum/allowed values of the eigenvalues E) lies in the fact that for states that are classically bound, the TISE has solutions ψ that satisfy all of the three criteria above *only at certain discrete values of E* . For instance, for a particle inside the infinitely deep well, it is easily seen that the simplest plausible $\psi(x)$ that satisfies curvature function $-\frac{\hbar^2}{2m}\vec{\nabla}^2$ as well as all three

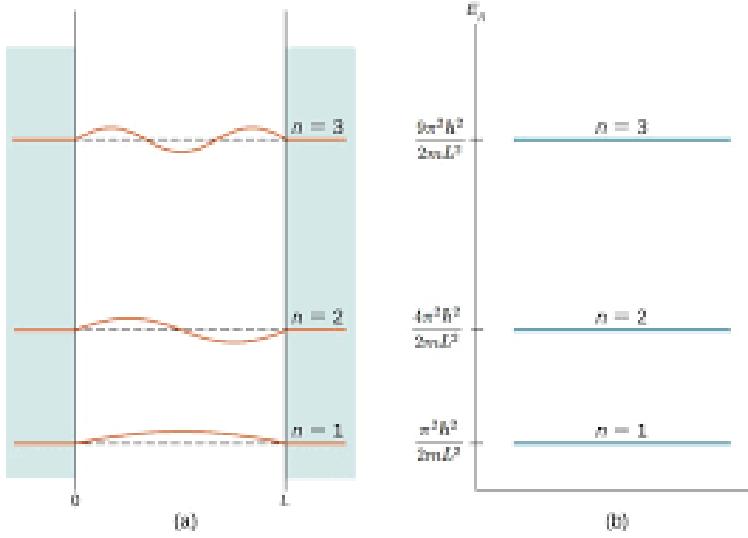
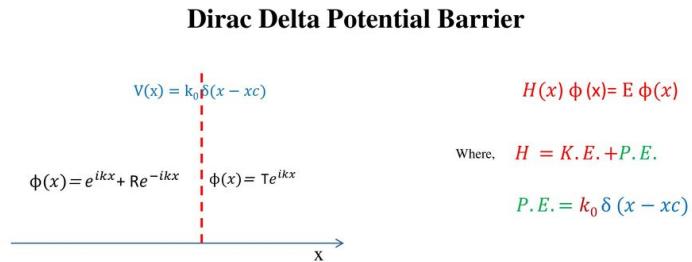
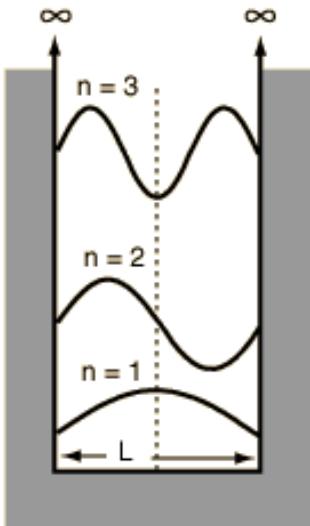


Figure 7.1: Wavefunctions (Left) and Energy Spectrum (Right) for the lowest three eigenstates of the particle in a box problem.

criteria given above is the one that characterises **the ground state** $\psi_{n=0}$: it has the minimum curvature (and thence the minimum kinetic energy) and vanishes at the walls of the potential (as $V \rightarrow \infty$ there). Tuning the energy E continuously does not reveal another solution $\psi_{n=1}$ vanishingly close by in energy to $\psi_{n=0}$. However, one finds other solutions at particular discrete values. Clearly, these will all have greater kinetic energy than the ground state, simply as they have greater curvature $-\frac{\hbar^2}{2m}\vec{\nabla}^2$.

Indeed, the next simplest and plausible ψ , $\psi_{n=1}$ is one that changes the curvature $\frac{d^2\psi(x)}{dx^2}$ qualitatively in comparison to that for $\psi_{n=0}$: $\psi_{n=1}$ crosses the x -axis once and is called **the first excited state**. A general result for excited bound states is that the n th excited state ($n \in \mathbb{Z}$) crosses the x -axis n times. Thus, the discrete bound states ψ_n have an energy E_n arising from an ever-increasing curvature due to n crossings of the x -axis. Also, if the potential $V(x)$ has a centre of symmetry, the eigenstates will be alternating even parity ($\psi(-x) = \psi(x)$) and odd parity ($\psi(-x) = -\psi(x)$) functions about that centre of symmetry.

For cases where $E > V(x)$ for all x , only unbound (or “scattering”) states exist. These states do not have a tendency to diverge at $x \rightarrow \pm\infty$ (though you have to be a little careful in showing that!) and their curvature $\frac{d^2\psi(x)}{dx^2}$ can vary continuously as E is varied. Thus, these unbound states form a continuous (rather than discrete) spectrum. For instance, the free particle with energy $E = p^2/2m$, $p \in \mathcal{R}$ and $V(x) = 0$ (or any constant with respect to which the kinetic energy can be defined) is a case of such a system with unbound states forming a continuous spectrum.



Where, $k^2 = \frac{2mE}{\hbar^2}$

Two Boundary Conditions

1. $\phi(xc + \epsilon) = \phi(xc - \epsilon)$

2. $\left[\frac{d\phi(x)}{dx} \right]_{xc-\epsilon}^{xc+\epsilon} - \frac{2mk_0}{\hbar^2} \phi(xc) = 0$

Analytical Solution possible!

Two Unknowns: R & T

x = 0 at left wall of box.

Quantum Physics: S. Gasiorowicz, John Wiley & Sons., USA, 1995.

Figure 7.2: (Left) Wavefunctions for the lowest three eigenstates of the particle in a box problem. (Right) Barrier Tunneling problem with a Dirac-Delta Function Potential. Source: The internet.

Chapter 8

Schrödinger Wave Mechanics: Bound states

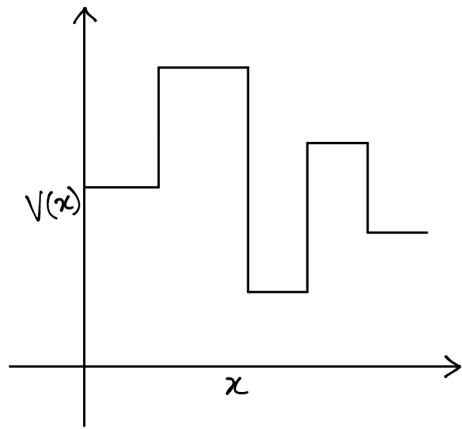


Figure 8.1: Schematic diagram for a piecewise constant potential in 1D.

For the case of piecewise constant potentials (i.e., potentials with step-like discontinuities as shown in figure 8.1), we consider a range of x over which the potential $V(x)$ is a constant then the TISE can be rewritten as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi = E\psi \quad (8.1)$$

$$\implies \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi = 0 \quad (8.2)$$

Trying a guess (or *ansatz*) solution $\psi(x) = Ce^{nx}$ in Eq. 8.2, we get

$$\begin{aligned} n^2Ce^{nx} + \frac{2m}{\hbar^2}(E - V_0)Ce^{nx} &= 0 \\ n^2 &= \frac{2m}{\hbar^2}(V_0 - E) \\ \therefore n &= \pm \sqrt{\frac{2m}{\hbar^2}(V_0 - E)} \end{aligned} \tag{8.3}$$

For $E < V_0$, $n \in \mathbb{R}$ (a classically forbidden solution!),

$$\psi(x) = C_1 e^{nx} + C_2 e^{-nx} \tag{8.4}$$

For $E > V_0$, $n = \pm i\bar{n}$ where $\bar{n} \in \mathbb{R}$ (a classically permitted solution!) and

$$\psi(x) = C_3 e^{i\bar{n}x} + C_4 e^{-i\bar{n}x} \tag{8.5}$$

$$= D_1 \cos(\bar{n}x) + D_2 \sin(\bar{n}x) \tag{8.6}$$

Here, $C_1, C_2, C_3, C_4, D_1, D_2$ are constants that are determined from boundary conditions appropriate to the problem at hand.

For the full wavefunction over several such piecewise constant potentials, we must “stitch together” the ψ s obtained from each section by demanding continuity in ψ and $d\psi/dx$, i.e., matching the wavefunction and its spatial derivative at various interfaces where the potential jumps. The continuity in ψ leads to the continuity in probability density, while that for $d\psi/dx$ leads to the continuity in probability current. This will give us the complete wavefunction for all x . It also tells us that ψ can be non-zero even in regions of x that are classically forbidden, e.g., inside a potential barrier. As we will see later, this is responsible for the quantum mechanical phenomenon of tunneling.

Chapter 9

Infinite square well/ Particle in a Box

Consider a potential as shown in figure 9.1.

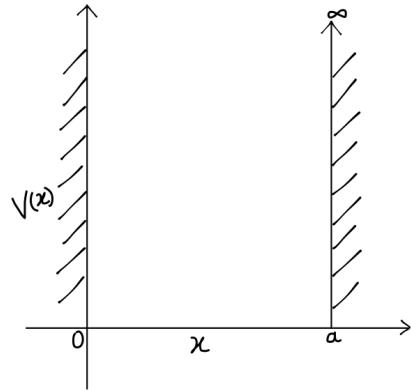


Figure 9.1: Schematic Diagram of the potential for the particle in a 1D Box.

$$V(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{otherwise} \end{cases} \quad (9.1)$$

The hard walls at $r = 0$ make the probability of finding the particle outside well to be zero i.e., $\psi(x) = 0$.

Inside the well, i.e., $0 < x < a$,

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad k = \frac{\sqrt{2mE}}{\hbar} \quad (E > 0) \quad (9.2)$$

Here, $E < 0$ does not give normalizable ψ . The general solutions are

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad (9.3)$$

Boundary Conditions

In general $\psi(x)$ & $\frac{d\psi(x)}{dx}$ must be continuous but where $V \rightarrow \infty$, only the first applies. Therefore,

$$\psi(0) = 0 = \psi(a) . \quad (9.4)$$

Using these two boundary conditions gives

$$\begin{aligned} \psi(0) = 0 \implies A \sin(0) + B \cos(0) &= 0 \\ B &= 0 \\ \therefore \psi(x) &= A \sin(kx) \end{aligned} \quad (9.5)$$

$$\begin{aligned} \psi(a) = 0 \implies A \sin(ka) &= 0 \\ \therefore k_n &= \frac{n\pi}{a}, \quad n \in \mathbb{Z} \end{aligned} \quad (9.6)$$

From Eq. 9.2,

$$\therefore E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, \quad n \in \mathbb{Z} = 1, 2, 3, \dots \dots \quad (9.7)$$

- E_n is discrete i.e., levels exist only for special values that are quantised in units of $\pi^2 \hbar^2 / 2ma^2$

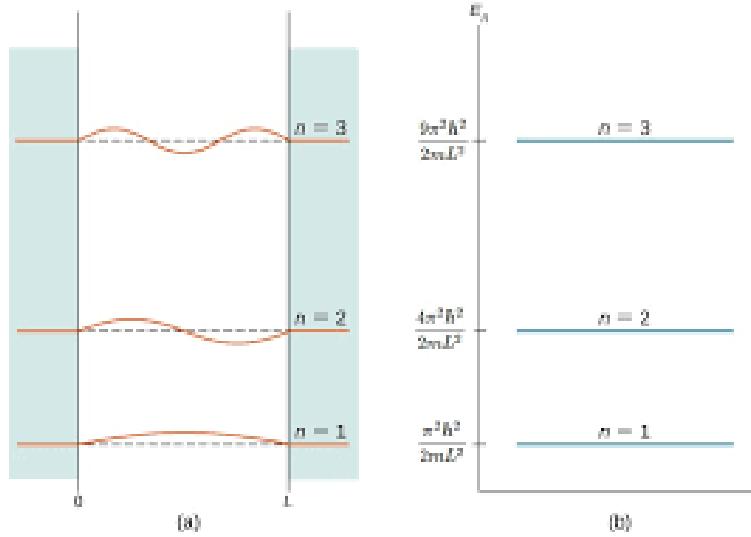


Figure 9.2: Wavefunctions (Left) and Energy Spectrum (Right) for the lowest three eigenstates of the particle in a box problem. Source: the internet.

Normalization

The normalizing condition given by Eq. 9.8 gives

$$\begin{aligned} & \int_{-\infty}^{\infty} |\psi_n|^2 dx = 1 \\ \implies & |A|^2 \int_0^a dx \sin^2(k_n x) = 1 \\ \therefore & A = \sqrt{\frac{2}{a}} \\ \psi_n(x) &= \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \end{aligned} \tag{9.9}$$

Discussion

An important point to note about this problem is the fact that the ground state energy is non-zero (while classically it should have been zero)! This, so called, **zero-point energy** arises from the fact that the particle is not sitting still in the quantum mechanical ground state. This can be seen from the fact that the ground state wavefunction, even if peaked at the centre of the well (as expected classically) is actually spread out all over the well. This “spreading out” of matter waves is typical of waves, who (unlike particles) hate being confined. Indeed, the ground state energy can be shown to arise completely from the Heisenberg uncertainty principle (and is left as an exercise to the interested reader).

Chapter 10

Simple Harmonic Oscillator

A spring block system is a classic oscillator problem in which force is linearly proportional to displacement. Note, however, that there is no such thing as a perfect oscillator and especially when applying forces beyond Hooke's law. However, for small forces applied such that the amplitude of motion is small, the motion can be taken to be harmonic. Put differently, about any local minima of any complicated potential, the parabolic approximation is decent as shown in figure 10.1

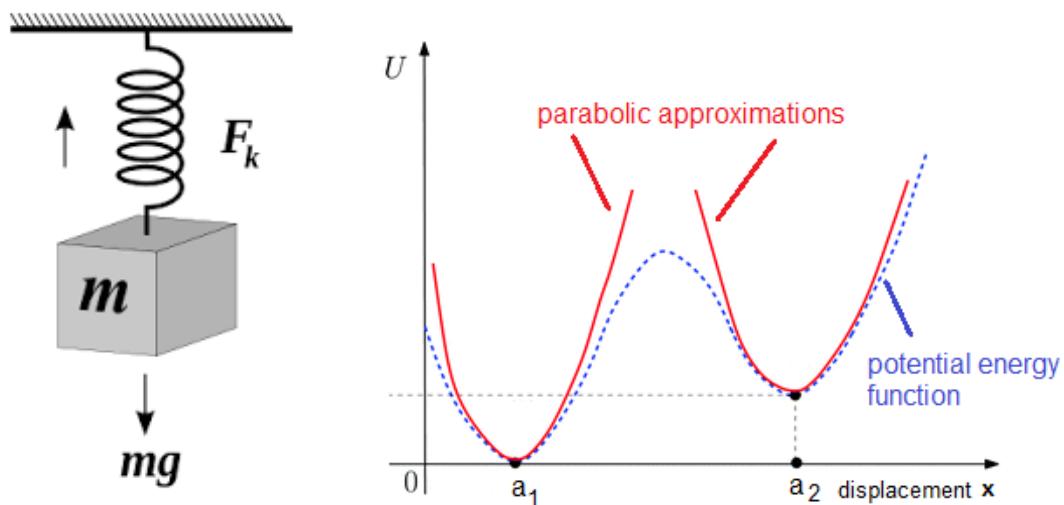


Figure 10.1: (Left) A classical mass spring oscillator system. (Right) Parabolic approximation at a minima

Let x_0 be the local minima of a potential $V(x)$ (i.e., $V'(x_0) = 0$, $V''(x_0) > 0$). Expanding $V(x)$ using taylor expansion about x_0 and looking at the close neighbourhood of x_0 (i.e.,

$|x - x_0| \ll 1$, we get

$$\begin{aligned} V(x) &= V(x_0) + \underbrace{V'(x_0)}_{=0}(x - x_0) + \frac{V''(x_0)}{2!}(x - x_0)^2 + \mathcal{O}((x - x_0)^3) \\ &\approx V(x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 \end{aligned} \quad (10.1)$$

By shifting our axes so that $V(x_0) = 0$, $x_0 = 0$ and taking $V''(x_0) = m\omega^2$ (the spring stiffness), we see that $V(x)$ in the close neighbourhood of x_0 behaves like a simple harmonic oscillator as seen in Eq. 10.2

$$V(x) = \frac{1}{2}m\omega^2x^2 \quad (10.2)$$

The time independent Schrödinger's equation can then be written as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x) \quad (10.3)$$

10.1 Algebraic Method

Eq. 10.3 could be written as

$$\frac{1}{2m}[p^2 + (m\omega x)^2]\psi = E\psi \quad (10.4)$$

Inspired by the following relation between two classical variables $(u, v) \in \mathcal{C}$

$$(u^2 + v^2) = (iu + v)(-iu + v) , \quad (10.5)$$

we rewrite

$$p^2 + (m\omega x)^2 = (ip + m\omega x)(-ip + m\omega x) + im\omega \underbrace{[x, p]}_{\neq 0} .$$

Raising & lowering operators

Defining new operators a_+ , a_-

$$a_{\pm} = \frac{1}{\sqrt{2m\omega\hbar}}(\mp ip + m\omega x) \quad (10.6)$$

$$\begin{aligned} [a_+, a_-] &= \frac{1}{2m\omega\hbar} [(-ip + m\omega x)(ip + m\omega x) - (ip + m\omega x)(-ip + m\omega x)] \\ &= \frac{1}{2m\omega\hbar} [p^2 - p^2 + m\omega^2x(1 - 1) + 2im\omega(xp - px)] \\ &= \frac{2im\omega}{2m\omega\hbar} [x, p] \\ &= -1 \end{aligned} \quad (10.7)$$

$$\& [a_-, a_+] = 1 \quad (10.8)$$

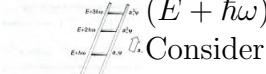
Here, a_{\pm} don't commute with each other as x, p don't commute. The Hamiltonian H can be written in terms of a_{\pm} as given by Eqs. 10.10, 10.11.

$$\begin{aligned} a_- a_+ &= \frac{1}{2m\hbar\omega} (ip + m\omega x)(-ip + m\omega x) \\ &= \frac{1}{2m\hbar\omega} (p^2 + m^2\omega^2x^2 - im\omega[x, p]) \\ &= \frac{1}{2\hbar m\omega} (p^2 + m^2\omega^2x^2) - \frac{i}{2\hbar}[x, p] \\ &= \frac{1}{\hbar\omega} H + \frac{1}{2} \end{aligned} \quad (10.9)$$

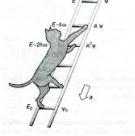
$$\therefore H = \hbar\omega \left(a_- a_+ - \frac{1}{2} \right) \quad (10.10)$$

$$= \hbar\omega \left(a_+ a_- + \frac{1}{2} \right) \quad \text{using } [a_-, a_+] = 1. \quad (10.11)$$

If ψ is an eigenstate of H with eigenvalue E , then $a_+\psi$ is also an eigenstate with eigenvalue $(E + \hbar\omega)$ and $a_-\psi$ is an eigenstate with eigenvalue $(E - \hbar\omega)$.



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$$\begin{aligned} H(a_+\psi) &= \hbar\omega \left(a_+ a_- + \frac{1}{2} \right) (a_+\psi) \\ &= \hbar\omega \left[a_+ a_- a_+ + \frac{1}{2} a_+ \right] \psi \\ &= \hbar\omega a_+ \left[a_- a_+ + \frac{1}{2} \right] \psi \\ &= \hbar\omega a_+ \left[a_- a_+ - \frac{1}{2} + 1 \right] \psi \\ &= \hbar\omega a_+ (H + \hbar\omega) \psi \\ &= (E + \hbar\omega) (a_+\psi) \end{aligned} \quad (10.12)$$

Similarly,

$$\begin{aligned} H(a_-\psi) &= \hbar\omega \left(a_- a_+ - \frac{1}{2} \right) (a_-\psi) \\ &= \hbar\omega \left[a_- a_+ a_- - \frac{1}{2} a_- \right] \psi \\ &= \hbar\omega a_- \left[a_+ a_- - \frac{1}{2} \right] \psi \\ &= \hbar\omega a_- \left[a_+ a_- + \frac{1}{2} - 1 \right] \psi \\ &= \hbar\omega a_- (H - \hbar\omega) \psi \\ &= (E - \hbar\omega) (a_-\psi) \end{aligned} \quad (10.13)$$

From Eqs. 10.12, 10.13, a_+ is called a **raising operator** while a_- is called a **lowering operator**.

Note that

$$a_+^\dagger = a_- \quad , \quad a_-^\dagger = a_+ \quad (10.14)$$

Thus, even though the operators a_\pm are not Hermitian (and therefore cannot be associated with experimental observables), we have seen that the Hamiltonian can be written in terms of the product a_+a_- (or a_-a_+).

Ground state

As the classical global minimum energy must be zero (bottom of the potential well) for the stability of such a confining (parabolic) potential, in order to get a normalizable (“legal”) $\psi(x)$, there must be a eigenstate $\psi_0(x)$ with lowest possible energy. As there are no other states below this state, it should vanish upon the action of lowering operator a_- . Thus, we impose the condition

$$\begin{aligned} a_-\psi_0(x) &= 0 \\ \Rightarrow \frac{1}{\sqrt{2\hbar m\omega}} \left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0(x) &= 0 \\ \frac{d\psi_0}{dx} &= -\frac{m\omega}{\hbar} x \psi_0 \\ \int \frac{d\psi_0}{\psi_0} &= -\frac{m\omega}{\hbar} \int x dx \\ \ln \psi_0 &= -\frac{m\omega}{2\hbar} x^2 + c \\ \psi_0 &= C_1 e^{-m\omega x^2/2\hbar} , \quad C_1 = \ln c . \end{aligned} \quad (10.16)$$

Here, C_1 can be calculated using the normalizing condition

$$\begin{aligned} \int_{-\infty}^{\infty} dx |\psi_0|^2 &= 1 \\ \Rightarrow |C_1|^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar} &= 1 \\ \Rightarrow |C_1|^2 \sqrt{\frac{\pi\hbar}{m\omega}} &= 1 \quad (\text{using } \int_{-\infty}^{\infty} dx e^{-x^2/a^2} = \sqrt{\frac{\pi}{a}}) , \\ \therefore C_1 &= \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \end{aligned} \quad (10.17)$$

$$\Rightarrow \psi_0 = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-m\omega x^2/2\hbar} \quad (10.18)$$

ψ_0 thus takes the shape of a Gaussian function in the spatial variable x , $\psi \propto e^{-ax^2}$. Let E_0

be the energy of ψ_0 ,

$$H\psi_0 = E_0\psi_0 \quad (10.19)$$

$$\begin{aligned} \hbar\omega \left(a_+ a_- + \frac{1}{2} \right) \psi_0 &= E_0 \psi_0 \\ \hbar\omega a_+ (a_- \psi_0) + \frac{1}{2} \hbar\omega \psi_0 &= E_0 \psi_0 \\ \implies \frac{1}{2} \hbar\omega \psi_0 &= E_0 \psi_0 \quad (\text{using } a_- \psi_0 = 0) \\ \therefore E_0 &= \frac{1}{2} \hbar\omega \end{aligned} \quad (10.20)$$

Here, E_0 is called as the **zero-point energy**. An important point to note about this problem is the fact that the ground state energy is non-zero (while classically it should have been zero)! In common with the particle in a box problem, this zero-point energy too arises from the fact that the particle is not sitting still in the quantum mechanical ground state. This can be seen from the fact that the ground state wavefunction, even if peaked at the centre of the well (as expected classically) is actually spread out all over the well. This “spreading out” of matter waves is typical of waves, who (unlike particles) hate being confined. Indeed, the ground state energy can be shown to arise completely from the Heisenberg uncertainty principle (and is left as an exercise to the interested reader). Next, we will see that applying a_+ on ψ_0 recursively will give us other eigenstates with higher energy.



James

A small humorous diversion on the stability of the system. Here is an anecdote that tells us why this concept is important. The philosopher and psychologist William James (1842-1910) was once giving a seminar on cosmology and the solar system, and was confronted by an elderly woman saying “Everything you’ve said is nonsense. It’s well known that the Earth is held up on the back of seven elephants, themself standing on the back of a giant turtle swimming through space!” Perplexed, James countered “But what, Madam, is the turtle standing on?” Without a thought, the old lady shot back, “Clever question, Professor James. The answer is simple: it’s turtles all the way down!” Perhaps the same could have been said of our search for the ground state of the harmonic oscillator in the absence of the condition imposed in eq.(10.15).



Turtles
all the
way
down!



Figure 10.2: Another view of the universe. Source: the internet.

The energy spectrum and excited states

Obtaining the energy spectrum is actually quite straightforward now. Given that we now have the ground state ψ_0 with energy eigenvalue $\frac{1}{2}\hbar\omega$, we can obtain an infinite tower of excited states by acting repeatedly on ψ_0 with the raising operator a_+ . From what we learnt earlier, the first excited eigenstate's energy eigenvalue will be $\hbar\omega$ greater than that of the ground state, i.e., $E_1 = \frac{3}{2}\hbar\omega$, $E_2 = \frac{5}{2}\hbar\omega$ and so on. We will now see this through an explicit calculation.

Thus, let us work out the energy eigenvalue of the first excited state $n = 1$ using $\psi_1 = A_1 a_+ \psi_0$ (where A_1 is a normalisation constant)

$$\begin{aligned}
 H\psi_1 &= (a_+ a_- + \frac{1}{2})\hbar\omega A_1 a_+ \psi_0 \\
 E_1 \psi_1 &= A_1 \hbar\omega (a_+ a_- a_+) \psi_0 + \frac{1}{2} \hbar\omega \psi_1 \\
 &= A_1 \hbar\omega a_+ (1 + a_+ a_-) \psi_0 + \frac{1}{2} \hbar\omega \psi_1 \quad (\text{using } [a_-, a_+] = 1) , \\
 &= A_1 \hbar\omega a_+ \psi_0 + \frac{1}{2} \hbar\omega \psi_1 \quad (\text{as } a_- \psi_0 = 0) , \\
 &= (1 + \frac{1}{2}) \hbar\omega A_1 a_+ \psi_0 \\
 &= \frac{3}{2} \hbar\omega \psi_1 \\
 \therefore E_1 &= \frac{3}{2} \hbar\omega . \tag{10.21}
 \end{aligned}$$

The entire spectrum can now be obtained by proceeding with the same strategy in an iterative fashion. To be precise, now that we know ψ_1 and its eigenvalue $E_1 = 3\hbar\omega/2$, we can now define $\psi_2 = A_2 a_+ \psi_1$ and proceed exactly as given above. This will show us that $E_2 = (2 + 1/2)\hbar\omega = 5\hbar\omega/2$:

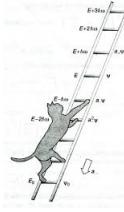


Turtles
all the
way
down!

$$\begin{aligned}
 H\psi_2 &= (a_+ a_- + \frac{1}{2})\hbar\omega A_2 a_+ \psi_1 \\
 E_2 \psi_2 &= A_2 \hbar\omega (a_+ a_- a_+) \psi_1 + \frac{1}{2} \hbar\omega \psi_2 \\
 &= A_2 \hbar\omega a_+ (1 + a_+ a_-) \psi_1 + \frac{1}{2} \hbar\omega \psi_2 \quad (\text{using } [a_-, a_+] = 1) , \\
 &= A_2 \hbar\omega a_+ (1 + 1) \psi_1 + \frac{1}{2} \hbar\omega \psi_2 \quad (\text{as } a_+ a_- \psi_1 = (E_1 - \frac{\hbar\omega}{2}) \psi_1 = \hbar\omega \psi_1) , \\
 &= (2 + \frac{1}{2}) \hbar\omega A_2 a_+ \psi_1 \\
 &= \frac{5}{2} \hbar\omega \psi_2 \\
 \therefore E_2 &= \frac{5}{2} \hbar\omega . \tag{10.22}
 \end{aligned}$$

Continuing in this way till the n th eigenstate ψ_n , using $\psi_n = A_n a_+ \psi_{n-1}$ and $E_{n-1} = (n - \frac{\hbar\omega}{2})$,

we find $E_n = (n + 1/2)\hbar\omega$:



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$$\begin{aligned}
 H\psi_n &= (a_+a_- + \frac{1}{2})\hbar\omega A_n a_+ \psi_{n-1} \\
 E_n \psi_n &= A_n \hbar\omega (a_+ a_- a_+) \psi_{n-1} + \frac{1}{2} \hbar\omega \psi_n \\
 &= A_2 \hbar\omega a_+ (1 + a_+ a_-) \psi_{n-1} + \frac{1}{2} \hbar\omega \psi_n \quad (\text{using } [a_-, a_+] = 1), \\
 &= A_2 \hbar\omega a_+ (n - 1 + 1) \psi_{n-1} + \frac{1}{2} \hbar\omega \psi_n \quad (\text{as } a_+ a_- \psi_{n-1} = (E_{n-1} - \frac{\hbar\omega}{2}) \psi_{n-1} = (n - 1) \hbar\omega \psi_{n-1}), \\
 &= (n + \frac{1}{2}) \hbar\omega A_n a_+ \psi_{n-1} \\
 &= (n + \frac{1}{2}) \hbar\omega \psi_n \\
 \therefore E_n &= (n + \frac{1}{2}) \hbar\omega. \tag{10.23}
 \end{aligned}$$

In this way, we find the entire spectrum for $n \in \mathbb{Z}$ and $n \geq 0$.

Now, the form of $\psi_n = A_n(a_+)^n \psi_0$ is exact in principle (while getting the exact form of $(a_+)^n \psi_0$ is quite tedious!), and all we need to do is to compute the normalisation constant A_n to be able to say that we have computed all the wavefunctions precisely. However, calculating A_n directly by performing the action of a_+ on ψ_0 n times is far too tedious. Instead, we compute A_n in a different way. Let us take

$$a_+ \psi_n = c_n \psi_{n+1}, \tag{10.24a}$$

$$a_- \psi_n = d_n \psi_{n-1}. \tag{10.24b}$$

Consider,

$$\begin{aligned}
 \int_{-\infty}^{\infty} (a_+ \psi_n)^* (a_+ \psi_n) dx &= \int_{-\infty}^{\infty} \psi_n^* a_- a_+ \psi_n dx \quad (\text{as } (a_+ \psi_n)^* = \psi_n^* a_-, a_+^\dagger = a_-), \\
 |c_n|^2 \int_{-\infty}^{\infty} \psi_{n+1}^* \psi_{n+1} dx &= \int_{-\infty}^{\infty} \psi_n^* \left(\frac{1}{\hbar\omega} H + \frac{1}{2} \right) \psi_n dx \quad (\text{using } H = (a_- a_+ - 1/2) \hbar\omega), \\
 |c_n|^2 &= \frac{1}{\hbar\omega} \int_{-\infty}^{\infty} \psi_n^* H \psi_n dx + \frac{1}{2} \int_{-\infty}^{\infty} \psi_n^* \psi_n dx \\
 &= \left(n + \frac{1}{2} \right) + \frac{1}{2} \quad (\text{using } \int_{-\infty}^{\infty} \psi_n^* \psi_n dx = 1), \\
 \Rightarrow |c_n|^2 &= n + 1 \\
 \therefore c_n &= \sqrt{n + 1} \tag{10.25}
 \end{aligned}$$

Similarly consider,

$$\begin{aligned}
\int_{-\infty}^{\infty} (a_- \psi_n)^* (a_- \psi_n) dx &= \int_{-\infty}^{\infty} \psi_n^* a_+ a_- \psi_n dx \quad (\text{as } (a_- \psi_n)^* = \psi_n^* a_+, a_+^\dagger = a_-) , \\
|d_n|^2 \int_{-\infty}^{\infty} \psi_{n-1}^* \psi_{n-1} dx &= \int_{-\infty}^{\infty} \psi_n^* \left(\frac{1}{\hbar\omega} H - \frac{1}{2} \right) \psi_n dx \quad (\text{using } H = (a_+ a_- + 1/2)\hbar\omega) , \\
|d_n|^2 &= \frac{1}{\hbar\omega} \int_{-\infty}^{\infty} \psi_n^* H \psi_n dx - \frac{1}{2} \int_{-\infty}^{\infty} \psi_n^* \psi_n dx \\
&= \left(n + \frac{1}{2} \right) - \frac{1}{2} \quad (\text{using } \int_{-\infty}^{\infty} \psi_n^* \psi_n dx = 1) , \\
\Rightarrow |d_n|^2 &= n \\
\therefore d_n &= \sqrt{n} \tag{10.26}
\end{aligned}$$

So, finally Eqs. 10.24a, 10.24b can be written as

$$\psi_{n+1} = (n+1)^{-1/2} a_+ \psi_n \tag{10.27a}$$

$$\psi_{n-1} = n^{-1/2} a_- \psi_n \tag{10.27b}$$

Using Eqs. 10.27, ψ_n can be written in terms of ψ_0 as

$$\psi_n = A_n (a_+)^n \psi_0 (x) = \frac{(a_+)^n}{\sqrt{n!}} \psi_0 \tag{10.28}$$

$$\Rightarrow A_n = \frac{1}{\sqrt{n!}} \tag{10.29}$$

We can also check orthogonality of ψ_n by using the following integral,

$$\begin{aligned}
\int_{-\infty}^{\infty} (a_{-}\psi_m)^* a_{-}\psi_n &= \int_{-\infty}^{\infty} \psi_m^* a_{+} a_{-}\psi_n = \int_{-\infty}^{\infty} \psi_m^* \left(\frac{1}{\hbar\omega} H - \frac{1}{2} \right) \psi_n \\
\int_{-\infty}^{\infty} (a_{-}\psi_m)^* a_{-}\psi_n &= n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \\
\int_{-\infty}^{\infty} (a_{+}a_{-}\psi_m)^* \psi_n &= n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \quad (\text{as } (a_{-}\psi_m)^* a_{-} = (a_{+}a_{-}\psi_m)^*) \\
\int_{-\infty}^{\infty} \left(\left(\frac{1}{\hbar\omega} H - \frac{1}{2} \right) \psi_m \right)^* \psi_n &= m \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \\
\therefore (m-n) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx &= 0 \\
\Rightarrow \int_{-\infty}^{\infty} \psi_m^* \psi_n dx &= \delta_{mn} \tag{10.30}
\end{aligned}$$

Figure 10.3 shows the first five energy levels of the harmonic oscillator [2], their wavefunctions (ψ) and their probability densities ($|\psi|^2$). Note that all the wavefunctions of the harmonic oscillator problem extend well into the classically forbidden region (i.e., outside the potential, where $V > E$); as expected, the ψ s decay exponentially to zero as $x \rightarrow \pm\infty$. This is a striking departure from our classical expectations. Further, the parity symmetry of the harmonic potential (in common with the particle in a box problem!) means that the ground state has even parity (i.e., is reflection symmetric), the first excited state has odd parity (i.e., is reflection anti-symmetric) and so on. Further, the excited states show the appearance of an increasing number of nodes (i.e., zeros of the wavefunction) as n increases. The fact that the nodes appear within the region where $E > V$ (i.e., inside the potential) reflects the fact that the kinetic energy (or curvature of the ψ) must increase substantially in the passage between neighbouring eigenstates resulting in the quantisation phenomenon marked by the quantum number n .

For $n \gg 1$, the “envelope” of the quantum probability distribution begins to resemble the large amplitude oscillations observed classically (as shown as the dashed line in Fig.10.4) [1]. Also, note that very little of the probability distribution of $|\psi_{100}|^2$ is in the classically forbidden region. Together, these observations are called the **Correspondence Principle**, and suggest how a quantum system will turn classical. We do not, however, have a well understood framework for understanding this passage between the two worlds as yet.

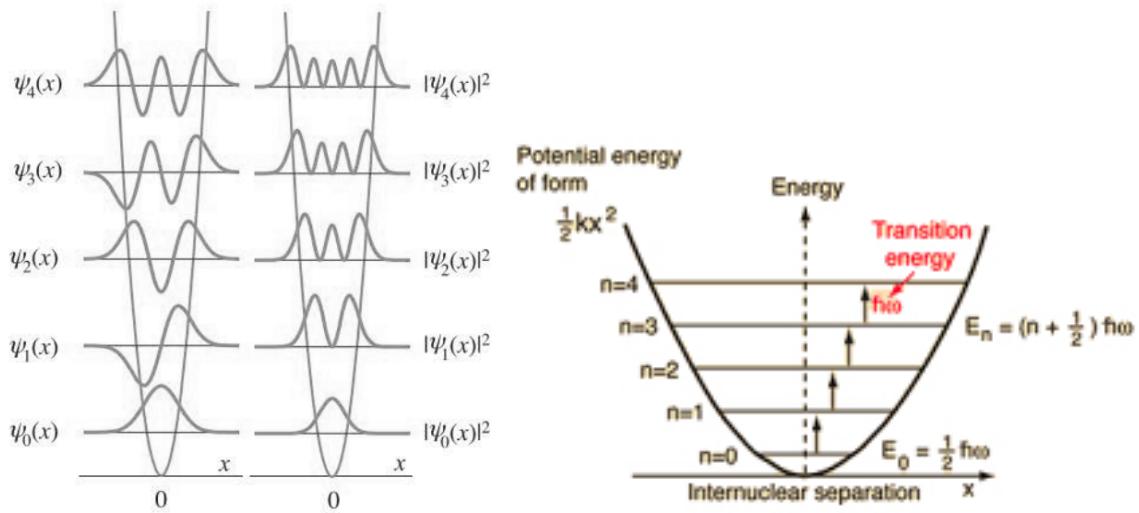


Figure 10.3: First few eigenstates (Left) and Energy Spectrum (Right) of the quantum mechanical harmonic oscillator.

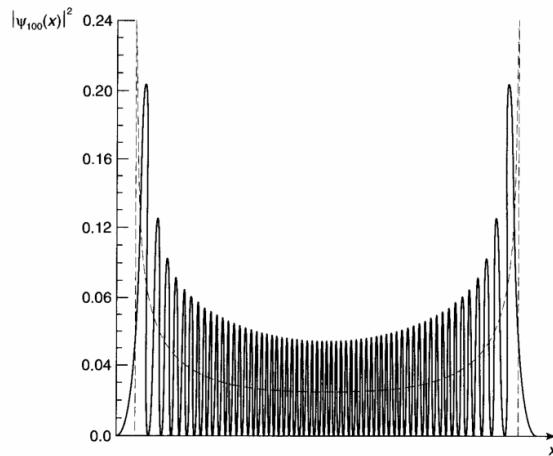


Figure 10.4: Probability distribution of high energy eigenstate ψ_{100} .

10.2 Analytic Method

We solve the TISE differential equation for the simple harmonic oscillator via a series solution. Recall that the starting point is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x) \quad (10.31)$$

Choosing $\xi = \sqrt{\frac{m\omega}{\hbar}}x$, $K = 2E/\hbar\omega$, Eq. 10.31 can be written as

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi \quad (10.32)$$

For $\xi^2 \gg K$, we can approximate the TISE as

$$\begin{aligned} \frac{d^2\psi}{d\xi^2} &\approx \xi^2\psi \\ \implies \psi(\xi) &\approx Ae^{-\xi^2/2} + Be^{\xi^2/2} \end{aligned} \quad (10.33)$$

$$\implies \psi(\xi) \approx Ae^{-\xi^2/2} \quad (10.34)$$

Here, $B = 0$ in Eq. 10.33, else $e^{\xi^2/2} \rightarrow \infty$ in the limit $x \rightarrow \pm\infty$ will cause ψ to diverge. Let us consider the following ansatz solution:

$$\psi(\xi) = h(\xi)e^{-\xi^2/2} \quad (10.35)$$

Note that we have already found the Gaussian part of the solution for ψ (as observed earlier from the algebraic solution).

Now, using Eq. 10.35, we obtain

$$\begin{aligned} \frac{d\psi}{d\xi} &= \left(\frac{dh(\xi)}{d\xi} - \xi h(\xi) \right) e^{-\xi^2/2} \\ \frac{d^2\psi}{d\xi^2} &= \left(\frac{d^2h(\xi)}{d\xi^2} - 2\xi \frac{dh(\xi)}{d\xi} + (\xi^2 - 1)h(\xi) \right) e^{-\xi^2/2} \end{aligned} \quad (10.36)$$

Using Eq. 10.36 in Eq. 10.32,

$$\begin{aligned} \left(\frac{d^2h(\xi)}{d\xi^2} - 2\xi \frac{dh(\xi)}{d\xi} + (\xi^2 - 1)h(\xi) \right) e^{-\xi^2/2} &= (\xi^2 - K)h(\xi)e^{-\xi^2/2} \\ \Rightarrow \frac{d^2h(\xi)}{d\xi^2} - 2\xi \frac{dh(\xi)}{d\xi} + (K - 1)h(\xi) &= 0 \end{aligned} \quad (10.37)$$

Solving Eq. 10.37 by the Frobenius method of a power series solution:

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j \xi^j \quad (10.38)$$

$$\frac{dh(\xi)}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + \cdots = \sum_{j=0}^{\infty} j a_j \xi^{j-1} \quad (10.39)$$

$$\frac{d^2h(\xi)}{d\xi^2} = 2a_2 + 6a_3\xi + \cdots = \sum_{j=0}^{\infty} (j+1)(j+2) a_{j+2} \xi^j \quad (10.40)$$

Putting Eqs. 10.38, 10.39, 10.40 in Eq. 10.37, we get

$$\sum_{j=0}^{\infty} [(j+1)(j+2) a_{j+2} - 2ja_j + (K-1)a_j] \xi^j = 0 \quad (10.41)$$

From the uniqueness of the power series expansion,

$$(j+1)(j+2) a_{j+2} - 2ja_j + (K-1)a_j = 0 \quad (10.42)$$

leading to the **recursion relation**

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)} a_j$$

Note that this recursion relation will relate the odd number indexed coefficients among themselves, and the even number indexed coefficients among themselves. This means that we can write $h(\xi) = h_{even}(\xi) + h_{odd}(\xi)$ where

$$h_{even}(\xi) = a_0 + a_2\xi^2 + a_4\xi^4 + \cdots, \quad (10.43a)$$

$$h_{odd}(\xi) = a_1\xi + a_3\xi^3 + a_5\xi^5 + \cdots, \quad (10.43b)$$

the recursion formula builds everything on 2 arbitrary constants, a_0 and a_1 , as would be expected from a 2nd order differential equation.

Now, for $j \gg 1, K$, we can approximate the recursion relation as

$$a_{j+2} \approx \frac{2}{j} a_j.$$

The relation $a_{j+2} = 2a_j/j$ has an approximate solution $a_j \approx c/(j/2)!$, where c is a constant. Then, for $\xi \gg 1$,

$$h(\xi) \approx c \sum_j \frac{1}{(j/2)!} \xi^j \approx c \sum_j \frac{1}{j!} \xi^{2j} \approx ce^{\xi^2}.$$

But since $\psi = h(\xi)e^{-\xi^2/2}$, we can see that with the $h(\xi)$ found above, $\psi \sim e^{\xi^2/2} \rightarrow \infty$ as $\xi \rightarrow \pm\infty$! The only way out of this divergent solution is if the power series expansion

terminates, i.e., if $a_{n+2} = 0$, which truncates either the even or the odd series, while the other series is zero right from the start:

$$\begin{aligned} a_{n+2} &= 0 \quad \text{and} \quad a_0 = 0 \quad \text{if } n \text{ is odd} \\ &\quad \text{or} \quad a_1 = 0 \quad \text{if } n \text{ is even} \end{aligned}$$

Put another way, for a truly ∞ series, the polynomial part of ψ always dominates and leads to a solution that diverges as $\xi \rightarrow \pm\infty$. On the other hand, for any finite polynomial series, the $e^{-\xi^2/2}$ part of ψ dominates and gives a convergent, normalizable solution.

Thus, from $a_{n+2} = 0$ (but $a_n \neq 0$), we get

$$\begin{aligned} \frac{2n+1-K}{(n+1)(n+2)} &= 0 \\ \implies K &= 2n+1 = \frac{2E}{\hbar\omega} \\ \therefore E &= \left(n + \frac{1}{2}\right)\hbar\omega \end{aligned} \tag{10.44}$$

It appears amazing that the quantization of the energy eigenvalue, E , should arise from a technical detail in finding the solutions to the TISE for the SHO, but the fact is that normalizable solutions (i.e., that satisfy the boundary conditions $\psi(x) \rightarrow 0$ for $x \rightarrow \pm\infty$) only appear for certain E values (all the other values of E give solutions but these diverge to $\pm\infty$ as $x \rightarrow \pm\infty$).

Thus for the allowed values of K ,

$$a_{j+2} = -\frac{2(n-j)}{(j+1)(j+2)} a_j . \tag{10.45}$$

For the ground state $n = 0$, we take $a_1 = 0$ to kill all terms in h_{odd} , while $j = 0$ gives $a_2 = 0$ (and hence all a_4, a_6 etc), such that

$$\begin{aligned} h_0(\xi) &= a_0 \\ \implies \psi_0(\xi) &= a_0 e^{-\xi^2/2} . \end{aligned} \tag{10.46}$$

For the first excited state $n = 1$, $a_0 = 0$ (such that all terms in h_{even} vanish) together with $j = 1$ (such that $a_3 = 0 = a_5 = \dots$) gives

$$\begin{aligned} h_1(\xi) &= a_1 \xi \\ \psi_1(\xi) &= a_1 \xi e^{-\xi^2/2} . \end{aligned} \tag{10.47}$$

For the second excited state $n = 2$, take $a_1 = 0$ (such that all terms in h_{odd} vanish) and $a_2 = -2a_0$, and $j = 2$ (such that $a_4 = 0 = a_6 = \dots$) gives

$$\begin{aligned} h_2(\xi) &= a_0 (1 - 2\xi^2) \\ \psi_2(\xi) &= a_0 (1 - 2\xi^2) e^{-\xi^2/2} . \end{aligned} \tag{10.48}$$

In general, $h_n(\xi)$ will be a polynomial in ξ of degree n , involving only even powers when n is even and only odd powers when n is odd. Apart from constants a_0, a_1 , these polynomials form are the so-called **Hermite Polynomials** $H_n(\xi)$:

$$\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \\ H_3(\xi) &= 8\xi^3 - 12\xi \\ H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12 \\ H_5(\xi) &= 32\xi^5 - 160\xi^3 + 120\xi \end{aligned}$$

where an arbitrary multiplicative factor is chosen such that the coefficient of the highest power of ξ is 2^n .

Thus, we obtain the eigenfunctions for the S.H.O. as

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \quad (10.49)$$

where the $(m\omega/\pi\hbar)^{1/4}$ factor comes from normalising ψ_0 and ψ_1 to learn the constants a_0 and a_1 respectively, and the $(n!)^{-1/2}$ factor we had already learnt from the algebraic solution.

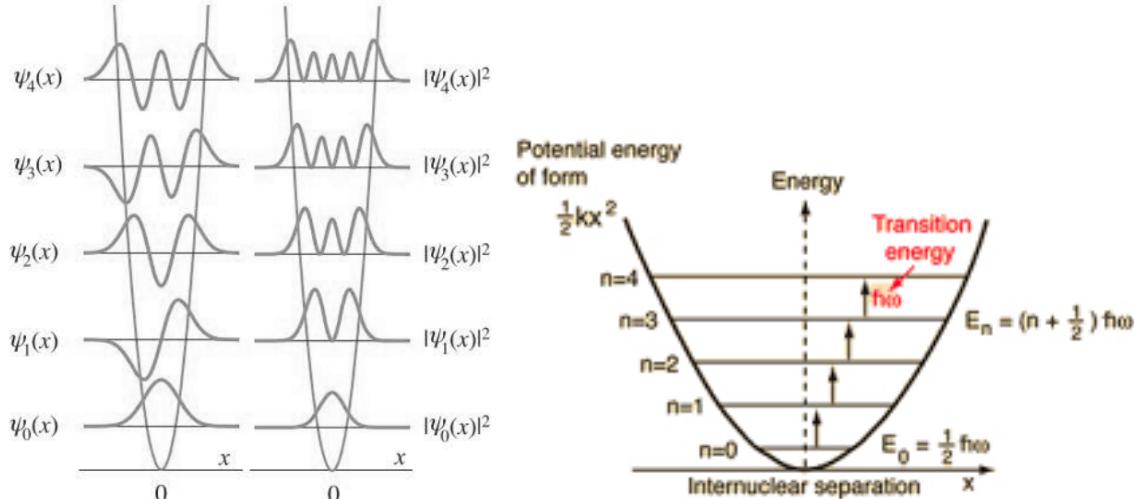


Figure 10.5: First few eigenstates (Left) and Energy Spectrum (Right) of the quantum mechanical harmonic oscillator.

It is important to note that the additional zeros (“nodes”) of the excited wavefunctions ψ_n ($n \geq 0$) (over and above the nodes at $x \rightarrow \pm\infty$ imposed by the boundary conditions) arises from the zeros of the Hermite polynomials $H_n(\xi)$. Further, the $H_n(\xi)$ are odd and even under the parity (reflection) transformation for $n \in$ odd and even respectively.

Chapter 11

Free particle

For a free particle, $V(x) = 0$ and the TISE is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (11.1)$$

$$\psi'' = -k^2\psi \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}, E \geq 0 \quad (11.2)$$

The general solution is:

$$\begin{aligned} \Psi(x, t) &= \psi(x) e^{-iEt/\hbar} \\ &= (Ae^{ikx} + Be^{-ikx}) e^{-iEt/\hbar} \\ &= Ae^{ik(x - \frac{\hbar k}{2m}t)} + Be^{-ik(x + \frac{\hbar k}{2m}t)} \end{aligned} \quad (11.3)$$

Eq. 11.3 shows a superposition of right going wave ($x - vt$) and a left going wave ($x + vt$) moving with speed $v = \hbar k/2m = \sqrt{E/2m}$, momentum $p = \hbar k$.

Note that the classical velocity of the particle $v_{cl} = \sqrt{2E/m}$. This paradox is resolved in the following way: The wavefunction given by Eq. 11.3 is not normalizable i.e., it doesn't die out at $\pm\infty$. This tells us that such separable solutions do not represent physically reasonable states for a free particle. Instead, a solution can be found by taking a linear combination of Eq. 11.3 (shown in Eq. 11.4) with different velocities so that they are normalizable. Indeed, this localizes the wave-function giving rise to the idea of “wave-packet”.

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk \quad (11.4)$$

This $\psi(x, t)$ can be normalized for appropriate $\phi(k)$. Note that it contains an entire range of k 's – hence the wavepacket. The simpler problem is to find the $\phi(k)$ for $\psi(x, t = 0)$ (the

initial wavefunction).

$$\Psi(x, 0) = \int_{-\infty}^{\infty} \frac{\phi(k)}{\sqrt{2\pi}} e^{ikx} dk \quad (11.5)$$

At this point, we can define the Fourier transform $F(k)$ of a function $f(x)$ (as well as the and inverse Fourier transform) as

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx \quad (11.6)$$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx} dk \quad (11.7)$$

Any normalizable $\psi(x, 0)$ will have a valid Fourier transform. So,

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} \Psi(x, 0) dx \quad (11.8)$$

Now the wave packet has a **phase velocity** $v_{ph} = \omega/k$ and a **group velocity** $v_g = d\omega/dk$. Taking $\omega = E/\hbar$,

$$\omega = \frac{\hbar k^2}{2m} \quad (11.9)$$

$$v_{ph} = \frac{\hbar k}{2m} \quad (11.10)$$

$$v_{gr} = \frac{\hbar k}{m} = 2v_{ph} \quad (11.11)$$

(Revise your concepts of phase and group velocity!)

Chapter 12

Scattering Processes and Quantum Tunneling

Having learnt the basics of the solution for the free particle problem in quantum mechanics, we will now study a couple of problems that involve us understand how matter waves can be scattered from some simple potentials. In doing so, we will be using the simple $e^{\pm ikx}$ type waveforms that we encountered in the previous chapter, and not the somewhat more complex matter wavepacket. This is more for ease of convenience, as the maths is somewhat harder for the wavepackets than it is for the simple $e^{\pm ikx}$ waveforms. For those who are worried about normalisability of the wavefunctions, you can view the wavepacket as being composed out of a huge number of such $e^{\pm ikx}$ waves. Thus, we can always learn the physics of scattering from the simpler situations, and then use the idea of wavepacket construction to create the mathematically correct solutions.

12.1 Step potential

Consider a step potential as shown in figure 12.1 given by

$$V(x) = \begin{cases} 0 & \text{if } x < 0 \quad (\text{region I}) \\ V_0 & \text{if } x \geq 0 \quad (\text{region II}) \end{cases} \quad (12.1)$$

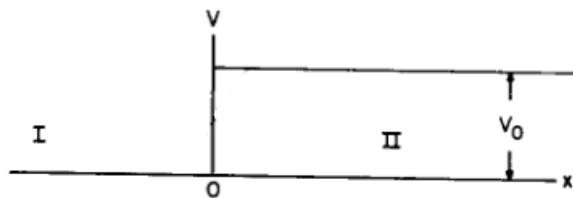


Figure 12.1: A schematic diagram of $V(x)$

Classically, an incoming particle from the left will bounce back from the step if $E < V_0$ and will be able to move to region II if $E > V_0$ with a changed momentum. Let's see what quantum mechanics tells us.

The TISE is:

$$\begin{aligned}\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi &= 0 \quad x < 0 \quad (\text{Region I}) \\ \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi &= 0 \quad x \geq 0 \quad (\text{Region II})\end{aligned}$$

Boundary conditions:

$$(i) \quad \psi(x \rightarrow 0^-) = \psi(x \rightarrow 0^+) \quad (12.2a)$$

$$(ii) \quad \left. \frac{d\psi}{dx} \right|_{x \rightarrow 0^-} = \left. \frac{d\psi}{dx} \right|_{x \rightarrow 0^+} \quad (12.2b)$$

For $E > V_0$, since $E > 0$ & $(E - V_0) > 0$, we can use the “free-particle” e^{ikx} type ψ everywhere.

$$\psi(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x} & x < 0, k_1 = \sqrt{\frac{2mE}{\hbar^2}} \\ Ce^{ik_2 x} + De^{-ik_2 x} & x \geq 0, k_2 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}} \end{cases} \quad (12.3)$$

For a particle coming towards the step from the left, $D = 0$ on physical grounds. Thus the two boundary conditions gives us:

$$(i) \quad A + B = C \quad (12.4)$$

$$(ii) \quad ik_1(A - B) = ik_2C \quad (12.5)$$

On general grounds, we can choose to measure all fluxes(or amplitudes) of particle relative to the incoming flux which is equivalent to taking $A = 1$. In this case

$$(i) \quad 1 + B = C \quad (12.6)$$

$$(ii) \quad k_1(1 - B) = k_2C \quad (12.7)$$

$$\implies B = \frac{k_1 - k_2}{k_1 + k_2} \quad \& \quad C = \frac{2k_1}{k_1 + k_2} \quad (12.8)$$

Then the coefficients B , C can be interpreted as the **reflection amplitude** r and the **transmission amplitude** t respectively. Do these relations for r and t appear familiar from something you may have seen in wave optics? The corresponding reflection and transmission

coefficients R, T are given by

$$\begin{aligned} R &= |r|^2 = B^2 \\ &= \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} = \frac{\left(\sqrt{E} - \sqrt{E - V_0}\right)^2}{\left(\sqrt{E} + \sqrt{E - V_0}\right)^2} \end{aligned} \quad (12.9)$$

$$\begin{aligned} T &= |t|^2 = C^2 \\ &= \frac{4k_1^2}{(k_1 + k_2)^2} = \frac{4E}{\left(\sqrt{E} + \sqrt{E - V_0}\right)^2} \end{aligned} \quad (12.10)$$

Also, note that

$$R + \frac{k_2}{k_1}T = 1 \quad (12.11)$$

In order to see such scattering, we have to take the length scale over which the step exists is much smaller compared to de Broglie λ of the quantum particle. In the opposite regime, we will see only classical results.

For $E < V_0$,

$$\psi(x) = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x} & x < 0, k_1 = \sqrt{\frac{2mE}{\hbar^2}} \\ Ce^{k_2x} + De^{-k_2x} & x \geq 0, k_2 = \sqrt{\frac{2m(V_0-E)}{\hbar^2}} \end{cases} \quad (12.12)$$

Unless $C = 0$, $\psi \rightarrow \infty$ as $x \rightarrow \infty$. So, $C = 0$ and $A = 1$ following the same logic as in the previous case. Applying boundary conditions given in Eq. 12.2 we get

$$1 + B = D \quad (12.13)$$

$$ik_1(1 - B) = -k_2D \quad (12.14)$$

$$\implies B = \frac{k_1 - ik_2}{k_1 + ik_2} \quad \& \quad D = \frac{2k_1}{k_1 + ik_2} \quad (12.15)$$

The reflection, transmission amplitudes will be

$$\begin{aligned} R &= |r|^2 = |B|^2 \\ &= \left| \frac{k_1 - ik_2}{k_1 + ik_2} \right|^2 = 1 \end{aligned} \quad (12.16)$$

$$\implies T = \frac{k_1}{k_2}(1 - R) = 0 \quad (12.17)$$

Even if the transmission amplitude T is zero, $\psi(x) \neq 0$ at $x \geq 0$. This means there is a non-zero probability to find the particle under the step (even though this may be experimentally quite challenging!). Note: only when $V_0 \rightarrow \infty$, $\psi(x) \rightarrow 0$ for $x \geq 0$. This phenomenon has no classical particle analog and is responsible for **tunneling** when we have a barrier of finite extent (the next case we will study!). However, an analogy can be drawn to the phenomenon of evanescent waves in total internal reflection of e-m waves at a boundary between dense and rare media. For this, revise Fresnel's theory for reflection and refraction of e-m waves.

12.2 Potential Barrier & Tunneling

Instead of the step potential shown in Figure 12.1, consider a barrier potential given by 12.18 and shown in Figure 12.2

$$V(x) = \begin{cases} 0 & \text{if } x < 0 \quad (\text{region I}) \\ V_0 & \text{if } 0 \leq x \leq a \quad (\text{region II}) \\ 0 & \text{if } x > a \quad (\text{region III}) \end{cases} \quad (12.18)$$

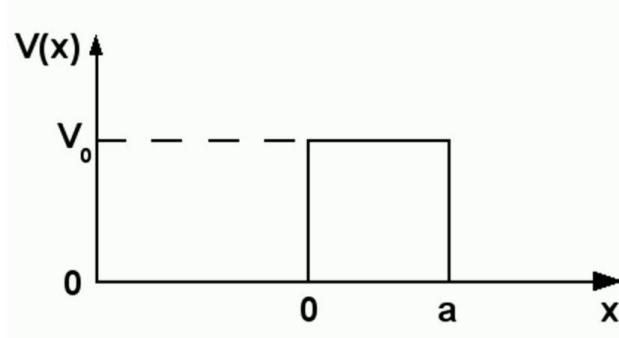


Figure 12.2: A potential barrier

Solving the TISE in each of the three regions individually means that we can take $\psi(x)$ as

$$\psi(x) = \begin{cases} e^{ik_1 x} + r e^{-ik_1 x} & x < 0, k_1 = \sqrt{\frac{2mE}{\hbar^2}} \\ A e^{ik_2 x} + B e^{-ik_2 x} & 0 \leq x \leq a, k_2 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}} \\ t e^{ik_1 x} & x > a, k_1 = \sqrt{\frac{2mE}{\hbar^2}} \end{cases} \quad (12.19)$$

Note that we have already used the boundary condition of an incoming particle from the left with a probability amplitude set to 1, while r and t give the probability amplitudes for reflection and transmission respectively. Further, E is the energy eigenvalue of the Hamiltonian for the full problem. It is also identical to the kinetic energy of the particle in regions I and III. To evaluate the four unknowns r , A , B , t , we use the continuity conditions on $\psi(x)$ and $d\psi/dx$ at both $x = 0$ & $x = a$, giving

$$\psi(x \rightarrow 0-) = \psi(x \rightarrow 0+) \Rightarrow 1 + r = A + B \quad (12.20a)$$

$$\psi'(x \rightarrow 0-) = \psi'(x \rightarrow 0+) \Rightarrow i k_1 (1 - r) = i k_2 (A - B) \quad (12.20b)$$

$$\psi(x \rightarrow a-) = \psi(x \rightarrow a+) \Rightarrow t e^{ik_1 a} = A e^{ik_2 a} + B e^{-ik_2 a} \quad (12.20c)$$

$$\psi'(x \rightarrow a-) = \psi'(x \rightarrow a+) \Rightarrow i k_1 t e^{ik_1 a} = i k_2 (A e^{ik_2 a} - B e^{-ik_2 a}) \quad (12.20d)$$

We set $\mu = k_2/k_1 = \sqrt{1 - V_0/E}$. Then solving the set of Eqs. 12.20 after some lengthy

algebra, we get

$$r = \frac{(1 - \mu^2) \sin(k_2 a)}{(1 + \mu^2) \sin k_2 a + 2i\mu \cos k_2 a} \quad (12.21a)$$

$$t = \frac{2i\mu e^{-ik_1 a}}{(1 + \mu^2) \sin k_2 a + 2i\mu \cos k_2 a} \quad (12.21b)$$

$$A = \frac{i(1 + \mu) e^{-ik_2 a}}{(1 + \mu^2) \sin k_2 a + 2i\mu \cos k_2 a} \quad (12.21c)$$

$$B = \frac{-i(1 - \mu) e^{ik_2 a}}{(1 + \mu^2) \sin k_2 a + 2i\mu \cos k_2 a} \quad (12.21d)$$

For $E > 0$ and $E \geq V_0$, k_1 , k_2 and $\mu \in \mathcal{R}$. Then, the transmission coefficient is given by

$$\begin{aligned} T = |t|^2 &= \frac{4\mu^2}{(1 + \mu^2)^2 \sin^2 k_2 a + 4\mu^2 \cos^2 k_2 a} \\ &= \frac{4\mu^2}{4\mu^2 + (1 - \mu^2)^2 \sin^2 k_2 a} = \frac{1}{1 + \frac{1}{4} \left(\frac{1-\mu^2}{\mu}\right)^2 \sin^2 k_2 a} \\ &= \frac{1}{1 + \frac{1}{4} \left(\frac{k_1^2 - k_2^2}{k_1 k_2}\right)^2 \sin^2 k_2 a} \end{aligned} \quad (12.22)$$

Note that the reflection coefficient $R = 1 - T$. Both R and T are plotted in Fig.12.3 as a function of E/V_0 . Whenever $k_2 a = n\pi$ the system is in resonance and there will be perfect

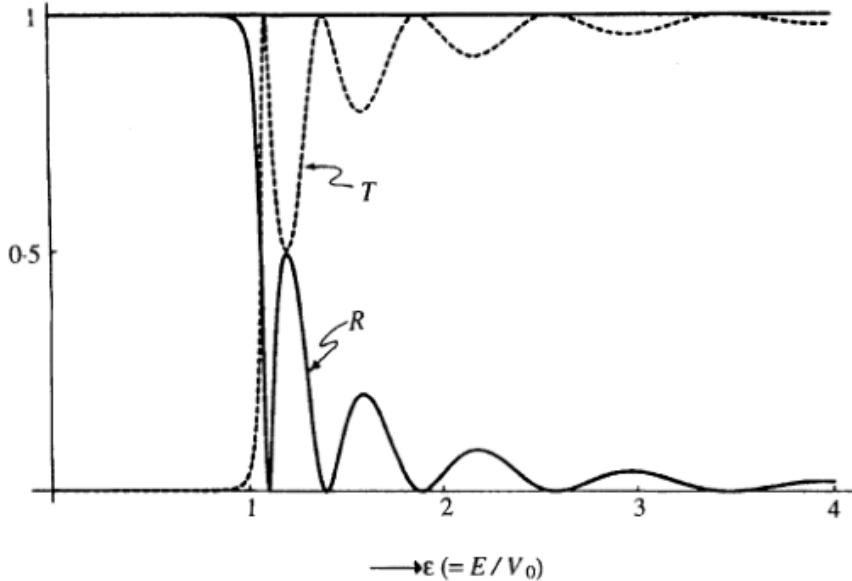


Figure 12.3: Transmission, Reflection coefficients as a function of $\epsilon = E/V_0$

transmission $T = 1$, $R = 0$ (see Fig.12.3). We also see that T oscillates and finally becomes

asymptotically equal to 1 for $E \gg V_0$; this is seen by taking $\mu \rightarrow 1$ in the expression for T in eq.(12.22). The criterion for the n th Resonance is given by the energy E_n

$$k_2 a = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} a = n\pi \quad (12.23)$$

$$E_n = V_0 + \frac{n^2\pi^2\hbar^2}{2ma^2} \quad (12.24)$$

Where do these resonances arise from? A simple way to picture them is to recall the Fabry-Perot resonances that arise within a cavity: light bouncing back and forth between the two “leaky” mirrors of the F-P cavity leads to a sequence of reflections and transmissions at the two mirrors, giving rise to standing waves within the cavity. A similar phenomenon is happening here for the wavefunction of the electron when over the barrier: there is a sequence of back and forth reflections and transmissions that happen at the two interfaces (at the two ends of the barrier) that fit together to form a perfect standing wave pattern at resonance. This is also indicated by the energy $n^2\pi^2\hbar^2/2ma^2$ (i.e., the eigenenergy of the standing waves formed in the particle in a box problem!) appearing in eq.(12.23). It is from this standing wave pattern that the perfect $T = 1$ arises from adding up the entire sequence of transmission probability amplitudes coherently. Similarly, $R = 0$ arises from adding up the entire sequence of reflection probability amplitudes coherently.

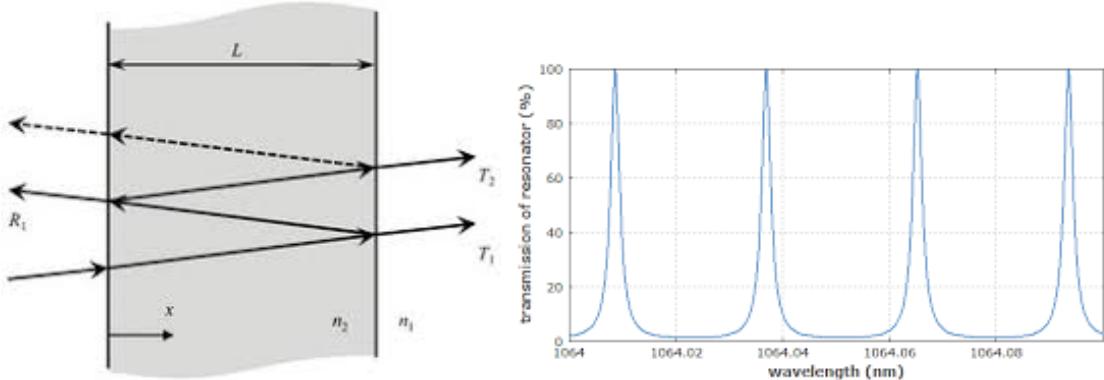


Figure 12.4: (Left) The Fabry-Perot Cavity, displaying the sequence of reflections and transmissions of e-m waves at the two leaky mirrors and (Right) the Transmission coefficient of the F-P cavity as a function the e-m wavelength. Source: The internet.

At the limit $E_0 \rightarrow V_0^+$, $k_2 \rightarrow 0 \implies \mu \rightarrow 0^+$,

$$\begin{aligned}
\frac{k_1^2 - k_2^2}{k_1 k_2} &\approx \frac{k_1^2}{k_1 k_2} \approx \frac{k_1}{k_2} \\
\implies T &\approx \left(1 + \frac{1}{4} \left(\frac{k_1}{k_2} \right)^2 k_2^2 a^2 \right)^{-1} \\
&\approx 1 - \frac{1}{4} k_1^2 a^2 \approx 1 - \frac{1}{4} \left(\frac{2mV_0}{\hbar^2} \right) a^2 \\
&\approx 1 - \frac{mV_0 a^2}{2\hbar^2}
\end{aligned} \tag{12.25}$$

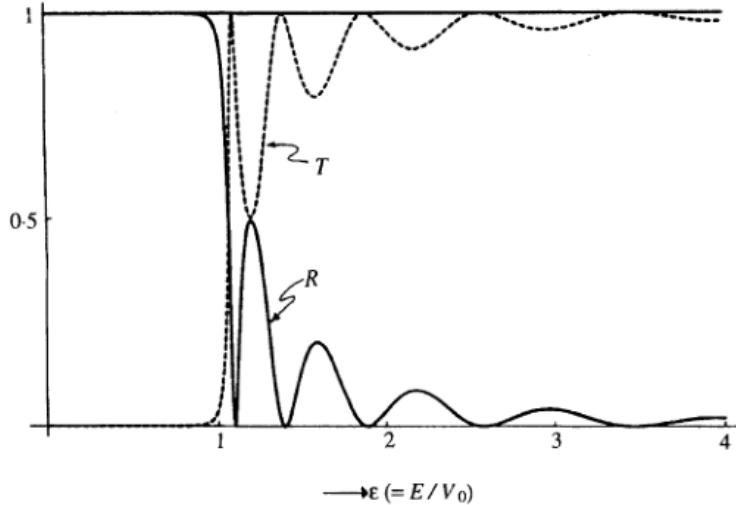


Figure 12.5: Transmission, Reflection coefficients as a function of Energy ϵ

For $E < V_0$, k_2 becomes imaginary

$$\begin{aligned}
k_2 &= iK = \frac{i}{\hbar} \sqrt{2m(V_0 - E)} \\
\implies T = |t|^2 &= \frac{(2k_1/K)^2}{\left(1 - \frac{k_1^2}{K^2} \right)^2 \sinh^2(Ka) + \left(\frac{2k_1}{K} \right)^2 \cosh^2(Ka)}
\end{aligned} \tag{12.26}$$

Thus, we can see that $T \rightarrow 0$ and $R = 1 - T \rightarrow 1$ as $E \rightarrow 0^+$, joining smoothly onto the expressions for T and R given by (12.25) as $E \rightarrow V_0^-$ (see Fig.12.3). An application of the phenomenon of quantum tunneling is realised in the scanning tunneling microscope (STM) shown below in Fig.12.6.

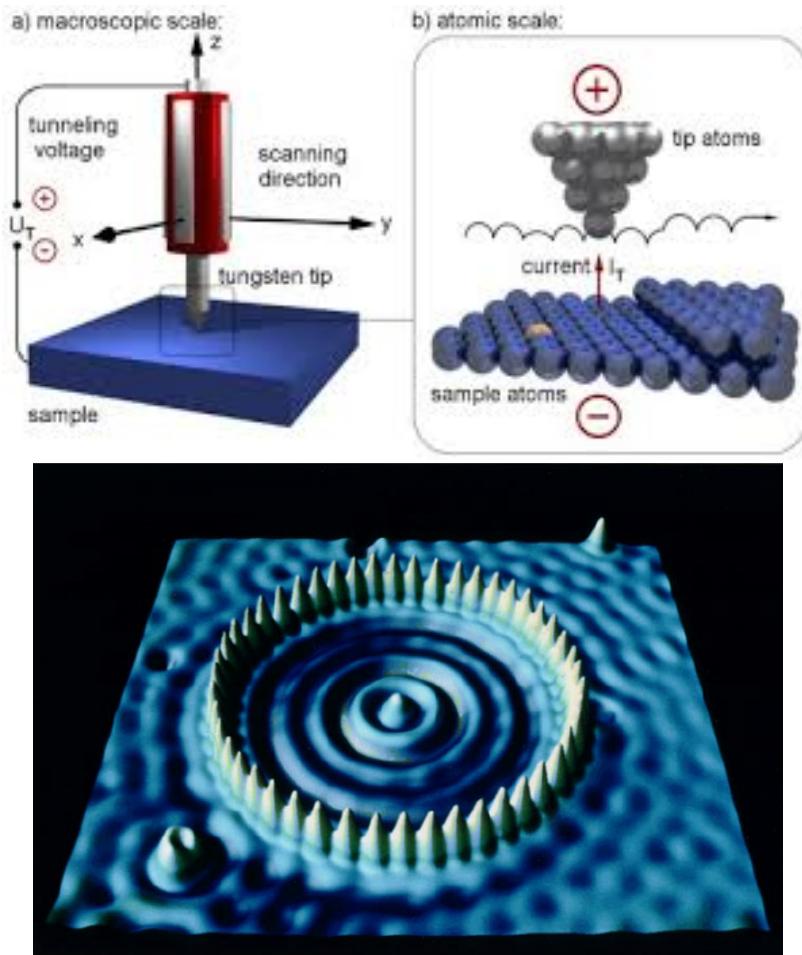


Figure 12.6: (Above) The physics of the scanning tunneling microscope (STM) is based on the phenomenon of quantum tunneling of electrons between the sample surface and the atoms of the STM tip and across a vacuum “barrier”. The tunnel current I_T depends on how easily sample surface electrons are available for such tunneling events, giving an indication of the nature of the atoms on the sample surface in terms of a picture. (Below) A “quantum corral” observed via STM measurements of Iron atoms placed on a Cu surface. Source: The internet.

Chapter 13

Time Independent Schrödinger Equation (TISE) in 3D

In 3D, the time dependant, independant Schrödinger equations is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} \quad (13.1)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (13.2)$$

In solving the TISE in 3D, we need to choose a system of coordinates: rectangular, cylindrical & spherical, which are best chosen by noting any symmetries of the potential $V(\mathbf{r})$, e.g., for a central force $F(\mathbf{r})$ which arises from a $V(|\mathbf{r}|)$ is most approximately (and easily) solved using spherical coordinates.

13.1 The Particle in a 3D Box

As a warm up, lets first consider the simpler problem of the infinite square well in 3D, which can be solved using rectangular coordinates.

$$V(\mathbf{r}) = \begin{cases} 0 & \text{when } 0 < x < a \\ & 0 < y < b \\ & 0 < z < c \\ \infty & \text{otherwise} \end{cases} \quad (13.3)$$

Thus inside the box,

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) &= E\psi(\mathbf{r}) \\ \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi &= -\frac{2mE}{\hbar^2}\psi \end{aligned} \quad (13.4)$$

Using the idea of separation of variables, we take the trial wavefunction

$$\psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z) \quad (13.5)$$

Putting Eq. 13.5 in Eq. 13.4,

$$\frac{1}{\psi_1(x)} \frac{\partial^2 \psi_1(x)}{\partial x^2} + \frac{1}{\psi_2(y)} \frac{\partial^2 \psi_2(y)}{\partial y^2} + \frac{1}{\psi_3(z)} \frac{\partial^2 \psi_3(z)}{\partial z^2} = -\frac{2mE}{\hbar^2}$$

Since the LHS has nicely factorized out into three separate equations & the RHS is a constant independant of (x, y, z) , we can take

$$\frac{1}{\psi_1} \frac{\partial^2 \psi_1}{\partial x^2} = -\frac{2mE_x}{\hbar^2} \quad \frac{1}{\psi_2} \frac{\partial^2 \psi_2}{\partial y^2} = -\frac{2mE_y}{\hbar^2} \quad \frac{1}{\psi_3} \frac{\partial^2 \psi_3}{\partial z^2} = -\frac{2mE_z}{\hbar^2}$$

Here, $E = E_x + E_y + E_z$. We thus have 3 independent 1D infinite square well problems with

$$\psi_1(x) = A_1 \sin \frac{n_x \pi x}{a}, \quad \psi_2(y) = A_2 \sin \frac{n_y \pi y}{a}, \quad \psi_3(z) = A_3 \sin \frac{n_z \pi z}{a} \quad (13.6)$$

$$E_x = \frac{\hbar^2 \pi^2}{2ma^2} n_x^2, \quad E_y = \frac{\hbar^2 \pi^2}{2mb^2} n_y^2, \quad E_z = \frac{\hbar^2 \pi^2}{2mc^2} n_z^2 \quad (13.7)$$

Then,

$$\psi(\mathbf{r}) = A \sin \left(\frac{n_x \pi x}{a} \right) \sin \left(\frac{n_y \pi y}{b} \right) \sin \left(\frac{n_z \pi z}{c} \right) \quad (13.8)$$

$$\begin{aligned} E &= E_x + E_y + E_z \\ &= \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \end{aligned} \quad (13.9)$$

where $A = A_1 A_2 A_3$. For the special case of a cube ($a = b = c$)

$$\psi(\mathbf{r}) = A \sin \left(\frac{n_x \pi x}{a} \right) \sin \left(\frac{n_y \pi y}{a} \right) \sin \left(\frac{n_z \pi z}{a} \right) \quad (13.10)$$

$$E = \frac{\hbar^2 \pi^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2) \quad (13.11)$$

The ground state is given by $(n_x = 1, n_y = 1, n_z = 1)$, as $\psi = 0$ for any one of these three indices being zero. The corresponding ground state energy is $E_{(1,1,1)} = 3\hbar^2 \pi^2 / 2ma^2$. Further, we can see that the three states $(n_x, n_y, n_z) = (1, 2, 1), (1, 1, 2), (2, 1, 1)$ all have the same energy $E_{(1,2,1)} = 6\hbar^2 \pi^2 / 2ma^2 = E_{(1,1,2)} = E_{(2,1,1)}$, and correspond to a triplet of the lowest lying excited states. This is the phenomenon of “degeneracy” (when 2 or more eigenstates with distinct ψ have the same E). Here, the wavefunctions are related by pairwise interchanges of the x, y & z axes (interchanges one face of the cube with another) which leaves the potential unchanged (the symmetry of the cube). However, such a degeneracy needs the tuning of atleast two parameters here (say, b and c with respect to a) so as to meet $a = b = c$. This means that this degeneracy is “accidental” (i.e., fragile), and is easily lifted by moving even slightly away from the condition $a = b = c$.

Chapter 14

The Angular Momentum problem: first passage

14.1 Introduction

For a classical particle, the angular momentum vector is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (14.1)$$

In quantum mechanics, the variables \mathbf{r} , \mathbf{p} are replaced by operators \mathbf{R} , $\mathbf{p} = -i\hbar\nabla$.

$$\begin{aligned} \mathbf{L} &= \mathbf{r} \times \mathbf{p} \\ &= L_x \hat{x} + L_y \hat{y} + L_z \hat{z} \end{aligned} \quad (14.2)$$

Here,

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x \end{aligned}$$

Are the components of \mathbf{L} Hermitian?

$$\begin{aligned} L_x^\dagger &= (yp_z)^\dagger - (zp_y)^\dagger = p_z^\dagger y^\dagger - p_y^\dagger z^\dagger \\ &= p_z y - p_y z \\ &= yp_z - zp_y = L_x \\ \mathbf{L}^\dagger &= \mathbf{L} \end{aligned} \quad (14.3)$$

Let us try computing $[L_x, L_y]$ now. First note that

$$[R_\alpha, p_\beta] = i\hbar\delta_{\alpha\beta} \quad (14.4)$$

$$[A + B, C] = [A, C] + [B, C] \quad (14.5)$$

$$[AB, C] = A[B, C] + [A, C]B \quad (14.6)$$

Thus,

$$\begin{aligned}
[L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\
&= [yp_z, zp_x] - [zp_y, zp_x] - [yp_z, xp_z] + [zp_y, xp_z] \\
&= y [p_z, zp_x] + [z, xp_z] p_y \quad (\text{as the second and third commutators vanish identically}) \\
&= y [p_z, z] p_x + x [z, p_z] p_y \\
&= i\hbar (xp_y - yp_x) = i\hbar L_z
\end{aligned} \tag{14.7}$$

Similarly, we can show that

$$[L_y, L_z] = i\hbar L_x , \tag{14.8}$$

$$[L_z, L_x] = i\hbar L_y . \tag{14.9}$$

Thus, simultaneous eigenstates of L_x , L_y , L_z (or even any pair from these 3) do not exist! This means that we can neither measure all three components precisely at once, nor any two components simultaneously. We can only make precise measurements for any one component of the angular momentum at a given instant.

We usually choose L_z for convenience, but this is still a matter of choice. Also, note that these three commutation relations show that L_x , L_y and L_z form, say, a right-handed triad (recall the right-hand corkscrew rule!) so as to remember the commutation relations as a mnemonic: a commutation relation that involves an anti-clockwise motion on the triad comes with a $+i\hbar$ factor in product with the third member of the triad, while a commutation relation that involves a clockwise motion on the triad comes with a $-i\hbar$ in product with the third member of the triad.

However, note that

$$\begin{aligned}
[L^2, L_z] &= [L_x^2 + L_y^2 + L_z^2, L_z] \\
&= [L_x^2, L_z] + [L_y^2, L_z] \\
&= L_x [L_x, L_z] + [L_x, L_z] L_x + L_y [L_y, L_z] + [L_y, L_z] L_y \\
&= -i\hbar L_x L_y - i\hbar L_y L_x + i\hbar L_y L_x + i\hbar L_x L_y = 0
\end{aligned} \tag{14.10}$$

L^2 is the square of the “length” of the angular momentum vector. Given that L^2 and L_z operators commute, we can define simultaneous eigenfunctions for them. In this way, we can simultaneously measure them both precisely, and these eigenvalues are “good quantum numbers”. Then what are the eigenvalues related to these operators? For this, we will fall back to the “ladder operators” formalism for angular momentum. (Recall that we encountered such objects in our discussion of the algebraic solution for the simple harmonic oscillator problem a few chapters ago.) By the way, it can be easily shown that $[L^2, L_x] = 0$ and $[L^2, L_y] = 0$, so that we could have equivalently chosen the simultaneous eigenstates for the pair (L^2, L_x) or (L^2, L_y) .

14.2 Total Angular Momentum

First, we should clarify that in any atomic system, the total angular momentum \mathbf{J} is given by the vector sum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (14.11)$$

\mathbf{L} = Orbital Angular Momentum

\mathbf{S} = Spin Angular Momentum

Here, \mathbf{L} literally relates to the classical orbital motion of a particle while \mathbf{S} is an internal degree of freedom and is quite different from the classical picture of rotational motion. Spin angular momentum arises from the internal structure of the state (i.e., Hilbert) space for the Lorentz transformation invariant relativistic Dirac equation. Thus, a more complete discussion of spin lies well beyond the purview of these lectures. We will, therefore, have to be content for now with a discussion of spin as simply a source of angular momentum that, unlike orbital angular momentum, cannot be visualised in terms of rotations in real space.

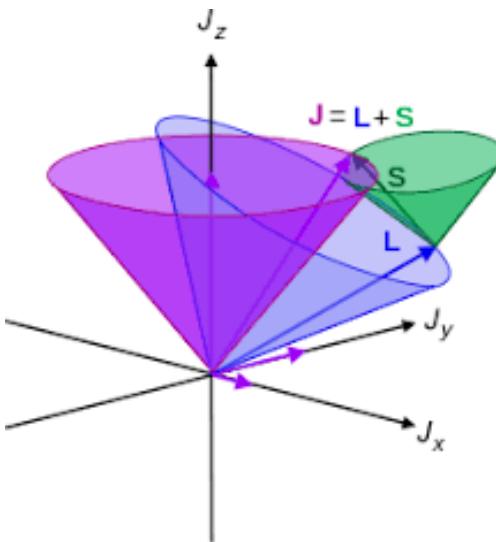


Figure 14.1: The angular momentum in quantum mechanics. Source: the internet.

Generally, in the absence of any physics that couples the \mathbf{L} and \mathbf{S} angular momenta, the commutation relations given earlier for the components of \mathbf{L} go through, as well as a similar algebra is found for \mathbf{S} . Thus, we may write

$$[J_x, J_y] = i\hbar J_z \quad (14.12)$$

$$[J_y, J_z] = i\hbar J_x \quad (14.13)$$

$$[J_z, J_x] = i\hbar J_y \quad (14.14)$$

$$[J^2, J_\alpha] = 0 \quad \text{for } \alpha = x, y, z \quad (14.15)$$

We are going to work here onwards with the eigenstates of J^2 and J_z . For them, we define the ladder operators as

$$J_+ = J_x + iJ_y \quad \text{Creation (raising) operator} \quad (14.16a)$$

$$J_- = J_x - iJ_y \quad \text{Annihilation (lowering) operator} \quad (14.16b)$$

$$[J_+, J_-] = -i [J_x, J_y] + i [J_y, J_x] = 2\hbar J_z. \quad (14.16c)$$

Note that $J_+^\dagger = J_-$, $J_-^\dagger = J_+$ which means that J_+ , J_- are not Hermitian, i.e., they do not correspond to observable quantities. But they can be used to go between different eigenfunctions (recall the ladder operators of the harmonic oscillator!).

For instance, starting with $J^2\psi = \alpha\psi$, $J_z\psi = \beta\psi$, assuming $J_+\psi = \phi$ (where ϕ is another normalised eigenstate of J^2 and J_z), let us try calculating $J^2\phi$, $J_z\phi$. Note that

$$[J^2, J_\pm] = 0 \quad \text{as} \quad [J^2, J_x] = 0 = [J^2, J_y]. \quad (14.17)$$

Thus,

$$J^2\phi = J^2(J_+\psi) = J_+(J^2\psi) = \alpha J_+\psi = \alpha\phi.$$

This shows that ϕ is an eigenstate of J^2 with the same eigenvalue α as that of ψ , i.e., the action of J_+ on ψ does not affect the eigenvalue of J^2 ! However, $[J_z, J_+] \neq 0$. In fact,

$$\begin{aligned} [J_z, J_+] &= [J_z, J_x + iJ_y] \\ &= [J_z, J_x] + i [J_z, J_y] \\ &= i\hbar J_y + i(-i\hbar) J_x \\ &= \hbar (J_x + iJ_y) = \hbar J_+ \end{aligned} \quad (14.18)$$

$$[J_z, J_-] = \hbar J_- \quad (14.19)$$

Calculating $J_z\phi$:

$$\begin{aligned} J_z\phi &= J_z J_+\psi = J_+ J_z\psi + \hbar J_+\psi \\ &= \beta J_+\psi + \hbar J_+\psi \\ &= (\beta + \hbar)\phi \end{aligned} \quad (14.20)$$

This means J_+ transforms ψ (with eigenvalues α , β for J^2 , J_z operators) into a new eigenfunction ϕ with eigenvalues α , $\beta + \hbar$. One more operation with J_+ will further increase the eigenvalue of J_z to $\beta + 2\hbar$ and so on.

Can we do this indefinitely (as done in simple harmonic oscillator)? No! This is because β^2 must have an upper bound that is defined in some way by α (the square of the length of the total angular momentum vector). This is simply seen from the fact that even classically, the z component of a vector is bounded by the magnitude of vector itself, i.e., $J_z^2 \leq J^2$.

More can be learnt about this upper bound on β by taking an eigenfunction ψ_{max} such that

$$J_+\psi_{max} = 0 \quad (14.21)$$

In the same way, we can argue that there must exist a ψ_{min} such that

$$J_- \psi_{min} = 0 \quad (14.22)$$

First, note that we can write J^2 in terms of J_\pm and J_z as follows

$$J^2 = J_x^2 + J_y^2 + J_z^2 \quad (14.23a)$$

$$= J_- J_+ + J_z^2 + \hbar J_z \quad (14.23b)$$

$$= J_+ J_- + J_z^2 - \hbar J_z , \quad (14.23c)$$

where we have used the fact that $J_x^2 + J_y^2 = J_+ J_- - \hbar J_z = J_- J_+ + \hbar J_z$.

Eqs. 14.23 are obtained by using the definition and commutation relations of J_\pm . Now, we can compute the values of α and β as follows

$$\begin{aligned} J^2 \psi_{max} &= (J_- J_+ + J_z^2 + \hbar J_z) \psi_{max} \\ \alpha \psi_{max} &= 0 + \beta_{max}^2 \psi_{max} + \hbar \beta_{max} \psi_{max} \\ \therefore \alpha &= \beta_{max}^2 + \hbar \beta_{max} \end{aligned} \quad (14.24)$$

Similarly, we find by operating $J^2 \psi_{min}$

$$\alpha = \beta_{min}^2 - \hbar \beta_{min} \quad (14.25)$$

From Eqs. 14.24, 14.25,

$$\begin{aligned} \beta_{min}^2 - \hbar \beta_{min} &= \beta_{max}^2 + \hbar \beta_{max} \\ \beta_{max}^2 - \beta_{min}^2 + \hbar (\beta_{max} + \beta_{min}) &= 0 \\ (\beta_{max} - \beta_{min} + \hbar) (\beta_{max} + \beta_{min}) &= 0 \\ \implies \beta_{max} &= -\beta_{min} \end{aligned} \quad (14.26)$$

as the other solution $\beta_{max} = \beta_{min} - \hbar$ does not make physical sense. Also, from the idea of ladder operators for J_z ,

$$\beta_{max} = \beta_{min} + n\hbar, \quad n \in \mathbb{Z} \quad (14.27)$$

$$\therefore \beta_{max} = \frac{n\hbar}{2} \quad (14.28)$$

The first line of the above equation is simply telling us that applying the raising operator an integer n number of times should take us from the state ψ_{min} to the state ψ_{max} . Now, defining $j = n/2$, $n \in \mathbb{Z}$, from Eq. 14.24, we obtain

$$\alpha = \hbar^2 j (j + 1), \quad (14.29)$$

$$\beta = m_j \hbar, \quad m_j = -j, -j + 1, \dots, j - 1, j \quad (14.30)$$

Therefore, we can write

$$J^2 \psi = \hbar^2 j (j + 1) \psi, \quad \text{where } j = \frac{n}{2}, n \in \mathbb{Z}, \quad (14.31)$$

$$J_z \psi = m_j \hbar \psi, \quad \text{where } m_j = -j, -j + 1, \dots, j - 1, j. \quad (14.32)$$

These relations are visualised in Fig.14.2 below. It is important to note that the integer parameter n has not been determined as yet. It turns out that nature appears to divide the odd valued integers and even valued integers for n into the world of Fermions (all matter particles) and Bosons (all force particles) respectively!

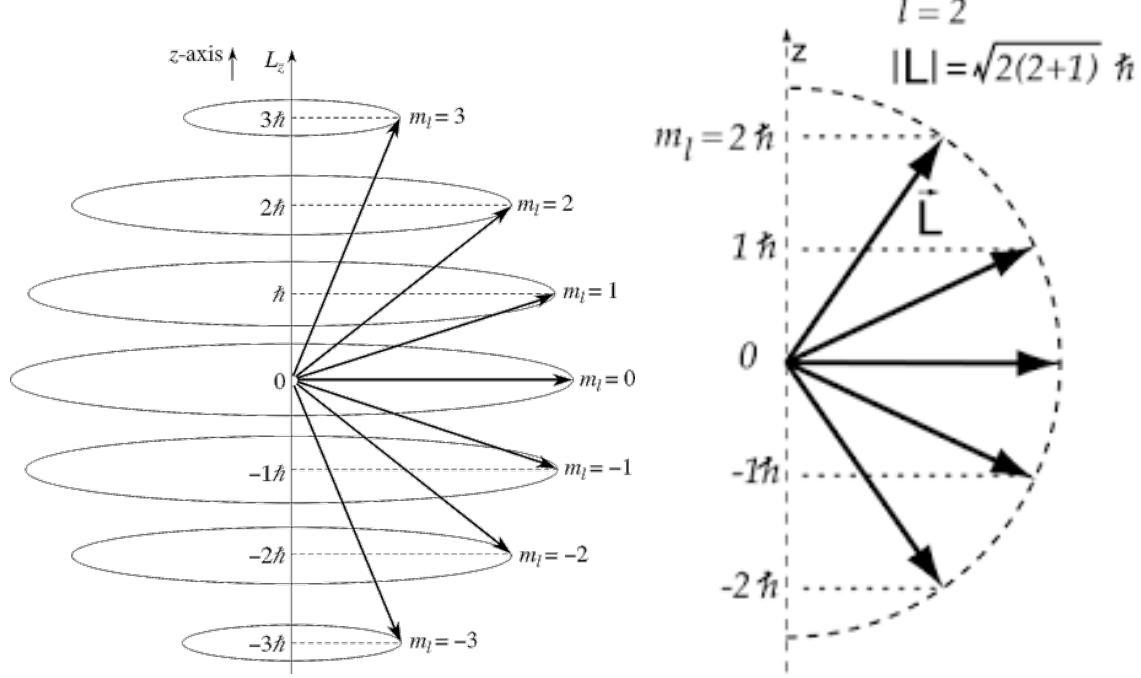


Figure 14.2: The angular momentum in quantum mechanics for the case of $n = 6$, $l = 3$ (left) and $n = 4$, $l = 2$ (right). Source: the internet.

Thus, we are now in a position to denote the common eigenstates of J^2 and J_z are denoted by the good quantum numbers j and m_j : $\psi \equiv |j, m_j\rangle$.

Finally, note that for $J_{\pm} |j, m_j\rangle = C_{j, m_j}^{\pm} |j, m_j \pm 1\rangle$, the constants C_{j, m_j}^{\pm} can be obtained by using the relations eq.(14.23b) and eq.(14.23c)

$$C_{j, m_j}^{\pm} = \hbar \sqrt{j(j+1) - m_j(m_j \pm 1)} . \quad (14.33)$$

To see how this is obtained, let us proceed as follows. Note that

$$\begin{aligned} J_+ |j, m_j\rangle &= C_{j, m_j}^+ |j, m_j + 1\rangle , \\ \Rightarrow (J_+ |j, m_j\rangle)^{\dagger} &= \langle j, m_j | (J_+)^{\dagger} = \langle j, m_j | J_- = C_{j, m_j}^{+*} \langle j, m_j + 1 | . \end{aligned} \quad (14.34)$$

Therefore, by using relation eq.(14.23b), we have

$$\begin{aligned} \langle j, m_j | J_- J_+ |j, m_j\rangle &= |C_{j, m_j}^+|^2 \langle j, m_j + 1 | j, m_j + 1 \rangle = |C_{j, m_j}^+|^2 , \\ \Rightarrow \langle j, m_j | J^2 - J_z^2 - \hbar J_z |j, m_j\rangle &= |C_{j, m_j}^+|^2 , \\ \Rightarrow |C_{j, m_j}^+|^2 &= [j(j+1) - m_j(m_j + 1)] \hbar^2 , \\ \Rightarrow C_{j, m_j}^+ &= \sqrt{j(j+1) - m_j(m_j + 1)} \hbar . \end{aligned} \quad (14.35)$$

Similarly, we can start from

$$\begin{aligned} J_- |j, m_j\rangle &= C_{j,m_j}^- |j, m_j - 1\rangle , \\ \implies (J_- |j, m_j\rangle)^\dagger &= \langle j, m_j | (J_-)^\dagger = \langle j, m_j | J_+ = C_{j,m_j}^{-*} \langle j, m_j - 1 | . \end{aligned} \quad (14.36)$$

Therefore, by using relation eq.(14.23c), we have

$$\begin{aligned} \langle j, m_j | J_+ J_- |j, m_j\rangle &= |C_{j,m_j}^-|^2 \langle j, m_j - 1 | j, m_j + 1 \rangle = |C_{j,m_j}^-|^2 , \\ \implies \langle j, m_j | J^2 - J_z^2 + \hbar J_z |j, m_j\rangle &= |C_{j,m_j}^-|^2 , \\ \implies |C_{j,m_j}^-|^2 &= [j(j+1) - m_j(m_j - 1)] \hbar^2 , \\ \implies C_{j,m_j}^- &= \sqrt{j(j+1) - m_j(m_j - 1)} \hbar . \end{aligned} \quad (14.37)$$

Chapter 15

Orbital Angular Momentum Eigenstates

As rotational symmetry in three dimensions is best visualised in spherical polar coordinates, we write the TISE in that coordinate system to obtain the eigenfunctions and eigenvalues of orbital angular momentum.

First, recall that the gradient in spherical coordinates is given by

$$\nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \quad (15.1)$$

! Revise the transformation of the gradient from Cartesian to spherical coordinates.

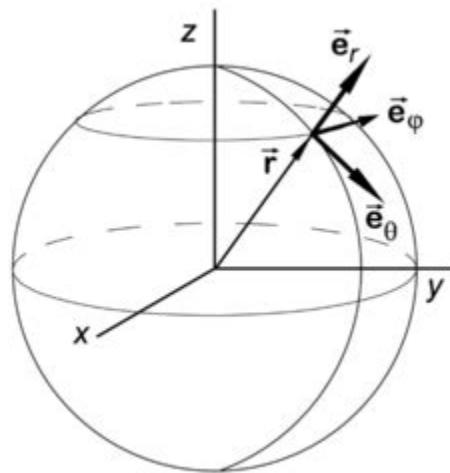


Figure 15.1: Spherical Coordinates

Then one can compute the components of the orbital angular momentum L_x , L_y , L_z

$$L_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) , \quad (15.2)$$

$$L_y = i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) , \quad (15.3)$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi} . \quad (15.4)$$

! Work these out for yourself carefully, following the definitions for the components of \vec{L} given in the previous chapter.

This gives us the norm of, and the raising and lowering operators for, the orbital angular momentum as

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] , \quad (15.5)$$

$$L_{\pm} = \hbar e^{\pm i\phi} \left(\pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) . \quad (15.6)$$

Thus, from our ladder operator analysis presented in the last chapter, we know that we can define eigenfunctions that are labelled by two good quantum l, m such that they satisfy the following eigenvalue equations

$$L^2 \psi_{lm}(\theta, \phi) = \hbar^2 l(l+1) \psi_{lm}(\theta, \phi) , \quad (15.7a)$$

$$L_z \psi_{lm}(\theta, \phi) = m\hbar \psi_{lm}(\theta, \phi) . \quad (15.7b)$$

This can be written as

$$\left[\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \right] \psi_{lm} = -l(l+1) \psi_{lm} , \quad (15.8)$$

$$\frac{\partial}{\partial \phi} \psi_{lm} = im \psi_{lm} . \quad (15.9)$$

The above prompts us to try the following trial solution using separation of variables: $\psi_{lm}(\theta, \phi) = \Theta(\theta) \Phi(\phi)$.

From eq.(15.9), it is easily seen that

$$\Phi(\phi) = e^{im\phi} \quad (15.10)$$

! Verify this by plugging it into eq.(15.9). Importantly, the solution for $\Phi(\phi)$ is simply a phase that can only be known modulo 2π . This means that since ϕ is an angular variable, the continuity of ψ_{lm} demands

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (\text{Periodic Boundary Condition}) \quad (15.11)$$

$$\text{i.e., } e^{im2\pi} = 1 \implies m \in \mathbb{Z} \quad (15.12)$$

! Note how the imposition of periodic boundary conditions leads immediately to the quantisation of the quantum number m . Further, it indicates that the orbital angular momentum orbits shown in Fig.14.2 must have a quantised period (m) for the matter waves. Recall that this was the assumption made by Bohr in formulating his solution to the Hydrogen atom problem.

From eq.(14.24), we know that $l = 0, 1, 2, \dots$. Then, putting eq.(15.10) in qq.(15.8) gives the “Legendre” differential equation

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} + l(l+1) \right] \Theta(\theta) = 0 . \quad (15.13)$$

The solutions to the above Legendre differential equation are the well-known **Legendre polynomials**. In this way, we find that the $\psi_{lm}(\theta, \phi)$ are the spherical harmonics $Y_{lm}(\theta, \phi)$:

$$\psi_{lm}(\theta, \phi) = Y_{lm}(\theta, \phi) = (-1)^{(m+|m|)/2} \left[\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \times e^{im\phi} \times P_{l|m|}(\cos \theta) , \quad (15.14)$$

where the $P_{lm}(\xi)$ ($m > 0$) are the Legendre functions (given below in eq.(15.15)) in terms of Legendre polynomials (given below in eq.(15.16)).

$$\text{Legendre Functions: } P_{lm}(\xi) = (1 - \xi^2)^{m/2} \frac{d^m}{d\xi^m} P_l(\xi) , \quad (\xi = \cos \theta) \quad (15.15)$$

$$\text{Legendre Polynomials: } P_l(\xi) = \frac{1}{2^l l!} \frac{d^l}{d\xi^l} (\xi^2 - 1)^l . \quad (15.16)$$

The $P_l(\xi)$ are l^{th} order polynomials in ξ ; the $P_{lm}(\xi)$ are thus $(l-m)^{th}$ order polynomials in ξ , and are multiplied by ξ^m . Further, the $P_{lm}(\xi)$ have $(l-m)$ nodes in $-1 < \xi < 1$. Some of the Legendre polynomials are given by

$$\begin{aligned} P_0 &= 1 , \\ P_1 &= \xi , \\ P_2 &= \frac{1}{2} (3\xi^2 - 1) , \\ P_3 &= \frac{1}{2} (5\xi^3 - 3\xi) , \text{ and so on.} \end{aligned}$$

Thus, we see that the $P_l(\xi)$ are either odd order or even order polynomials in ξ . Recall that we saw a similar phenomenon for the Hermite polynomial solutions for the wavefunctions of the harmonic oscillator problem as well. While the mathematical details given in the rest of this chapter are not essential for proceeding towards the Hydrogen atom problem, they are worth knowing for the overall completeness in our understanding of the angular momentum problem.

The Legendre polynomials satisfy the following recursion relation

$$(l+1) P_{l+1}(\xi) = (2l+1) \xi P_l(\xi) - l P_{l-1}(\xi) , \quad (15.17)$$

$$(1-\xi^2) \frac{dP_l}{d\xi} = l (P_{l-1} - \xi P_l) . \quad (15.18)$$

The associated Legendre functions satisfy

$$\text{Legendre differential equation : } \left[(1-\xi^2) \frac{d^2}{d\xi^2} - 2\xi \frac{d}{d\xi} + l(l+1) - \frac{m^2}{(1-\xi^2)} \right] P_{lm}(\xi) = 0 \quad (15.19)$$

$$\text{Parity transformation : } P_{lm}(-\xi) = (-1)^{l+m} P_{lm}(\xi) \quad (15.20)$$

$$\text{Orthogonality relation : } \int_{-1}^1 P_{lm}(\xi) P_{l'm'}(\xi) d\xi = \frac{2}{(2l+1)(l+m)!} \delta_{ll'} \delta_{mm'} \quad (15.21)$$

In particular, $P_{l0}(\xi) = P_l(\xi)$ and $P_{ll}(\xi) = (2l-1)!! (1-\xi^2)^{1/2}$, where $(2l-1)!! = (2l-1)(2l-3)\cdots 1$.

From these relations, we get the following properties of the spherical harmonics $Y_{lm}(\theta, \phi)$

$$\text{Orthogonality relation : } \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{mm'} , \quad (15.22)$$

$$\text{Completeness relation : } \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') = (\sin \theta)^{-1} \delta(\theta - \theta') \delta(\phi - \phi') . \quad (15.23)$$

Eqs.(15.22) and (15.23) prove the orthogonality and completeness of the spherical harmonics $Y_{lm}(\theta, \phi)$, thus making them suitable candidate for an eigenbasis. Eq.(15.24) below is called the **addition theorem**, which is a generalization of $\cos(\theta - \theta') = \cos \theta' \cos \theta + \sin \theta' \sin \theta$:

$$\sum_{m=-l}^l Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') = \frac{(2l+1)}{4\pi} P_l(\cos \theta) , \quad (15.24)$$

$$Y_{l,-m}(\theta, \phi) = (-1)^m Y_{lm}^*(\theta, \phi) . \quad (15.25)$$

For the unit vectors \hat{a}, \hat{b} , it can be shown that

$$P_l(\hat{a} \cdot \hat{b}) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi) ,$$

such that for $\hat{x} = \hat{y} \implies \sum_{m=-l}^l Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi) = \frac{2l+1}{4\pi} .$ \quad (15.26)

Eq.(15.26) is a generalization of $\cos^2 \theta + \sin^2 \theta = 1$ to 2D. Some of the spherical harmonics are given by

$$\begin{aligned} Y_{00} &= \frac{1}{\sqrt{4\pi}} , \\ Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta , \\ Y_{11} &= -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} , \\ Y_{20} &= \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) , \\ Y_{21} &= -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi} , \\ Y_{22} &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{i2\phi} , \text{ and so on.} \end{aligned}$$

Under the action of parity operator $\mathcal{P}\psi(\mathbf{r}) = \psi(-\mathbf{r})$,

$$\begin{aligned} \mathcal{P}Y_{lm}(\theta, \phi) &= Y_{lm}(\pi - \theta, \pi + \phi) \\ &= e^{im\pi} (-1)^{l+|m|} Y_{lm}(\theta, \phi) , \end{aligned} \quad (15.27)$$

$$\therefore \mathcal{P}Y_{lm}(\theta, \phi) = (-1)^l Y_{lm}(\theta, \phi) . \quad (15.28)$$

This means that Y_{lm} is even for even l and odd for odd l . Figure 15.2 shows the spherical harmonics $Y_{lm}(\theta, \phi)$ for $l = 0, 1, 2, 3$.

States with $l = 0$: s-orbitals

$l = 1$: p-orbitals

$l = 2$: d-orbitals

$l = 3$: f-orbitals

and so on ...

Below, in Fig.15.2, we see plots of the first few Spherical Harmonics. You may well recall having seen these somewhere as the orbitals for the Hydrogen atom.

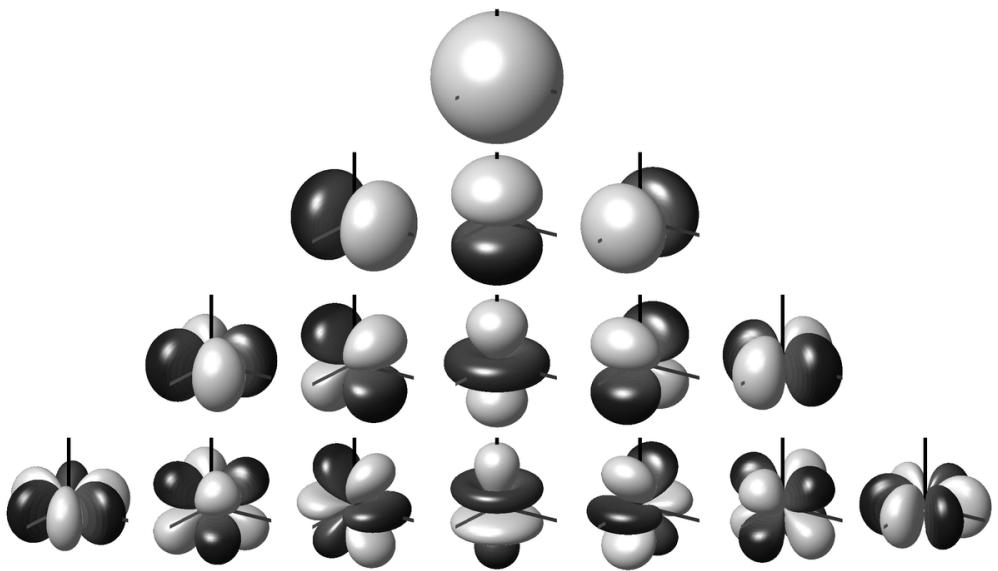


Figure 15.2: Spherical Harmonics

Chapter 16

Central Potential Problem

For a central force problem, $V(\mathbf{r}) = V(r)$ i.e., the potential only depends on the radial distance. Thus, the TISE will then be

$$H = \frac{1}{2m}\vec{p}^2 + V(r) \quad (16.1)$$

Now as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ such that $L_k = \epsilon_{ijk}x_ip_k$, the norm of the orbital angular momentum L^2 will be ($\mathbf{r} = x_1\hat{x} + x_2\hat{y} + x_3\hat{z}$)

$$\begin{aligned} L^2 &= \sum_{k=x,y,z} L_k^2 = (\epsilon_{ijk}x_ip_j)(\epsilon_{mnk}x_mp_n) \\ &= \epsilon_{ijk}\epsilon_{mnk}x_ip_jx_mp_n \\ &= (\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})x_ip_jx_mp_n \\ &= x_ip_jx_ip_j - x_ip_jx_jp_i \\ &= x_i(x_ip_j - i\hbar\delta_{ij})p_j - x_ip_j(p_ix_j + i\hbar\delta_{ij}) \\ &= x_i^2p_j^2 - i\hbar x_ip_i - x_ip_ip_jx_j - i\hbar x_ip_i \\ &= x_i^2p_j^2 - 2i\hbar x_ip_i - x_ip_i(x_jp_j - i\hbar) \\ &= x_i^2p_j^2 - x_ip_ix_jp_j - i\hbar x_ip_i \\ &= r^2p^2 - (\mathbf{r} \cdot \mathbf{p})^2 - i\hbar\mathbf{r} \cdot \mathbf{p} \end{aligned} \quad (16.2)$$

where ϵ_{ijk} is the totally anti-symmetric tensor of rank 3 (i, j, k can each take the values 1, 2, 3). ϵ_{ijk} has the following properties: (i) its value is zero for any two components being the same, all $\epsilon_{ijk} = 1$ for (i, j, k) arranged (say) in a clockwise manner and $\epsilon_{jik} = -\epsilon_{ijk} = \dots$ (i.e., the value is -1 for any two indices being swapped).

Further, the product $\epsilon_{ijk}\epsilon_{mnk} = (\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})$. Note that following the Einstein convention, we are summing over all repeated indices.

Finally, we have used the identity $(x_ip_j - p_jx_i) = i\hbar\delta_{ij}$. The last term on the RHS of Eq.

16.2 arises purely due to the non-commutativity of \mathbf{r} , \mathbf{p} . For $\mathbf{r} = r\hat{e}_r$ as $\hat{p} = i\hbar\nabla$

$$\begin{aligned}\nabla &= \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \\ \implies \mathbf{r} \cdot \mathbf{p} &= -i\hbar \mathbf{r} \cdot \nabla = -i\hbar r \frac{\partial}{\partial r}\end{aligned}\quad (16.3)$$

From Eq. 16.2,

$$\begin{aligned}\hat{p}^2 &= \frac{L^2}{r^2} - \frac{\hbar^2}{r^2} \left(\left(r \frac{\partial}{\partial r} \right)^2 + r \frac{\partial}{\partial r} \right) \\ &= \frac{L^2}{r^2} - \frac{\hbar^2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) \\ &= \frac{L^2}{r^2} - \hbar^2 \left(\frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \right)\end{aligned}\quad (16.4)$$

$$\hat{p}^2 = \frac{L^2}{r^2} + \hat{p}_r^2 \quad (16.5)$$

where \hat{p}_r is the radial momentum given by

$$\hat{p}_r = -i \frac{\hbar}{r} \frac{\partial}{\partial r} \cdot r = -i\hbar \left(\frac{1}{r} + \frac{\partial}{\partial r} \right) \quad (16.6)$$

$$\begin{aligned}[r, \hat{p}_r] &= \left[r, -i\hbar \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) \right] \\ &= i\hbar r \frac{\partial}{\partial r} - i\hbar + i\hbar \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) r \\ &= i\hbar\end{aligned}\quad (16.7)$$

$$(16.8)$$

Note that you have to be a little careful in carrying out the commutation relation here, so as not to miss out any terms. The best way to do this is to explicitly put in a wavefunction ψ on the right of the commutator, carry out the entire calculation, and remove it at the end.

Verify that the operator \hat{p}_r is Hermitian.

Putting Eq. 16.4 in Eq. 16.1,

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{2mr^2} L^2 + V(r) \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \quad (16.9)$$

For the case of a central potential, $V(r)$ has rotational symmetry. Then, $[H, L^2] = 0$, which means that $\psi(r, \theta, \phi)$ is a simultaneous eigenvalue of H , L^2 and L_z . So, we can take $\psi(r, \theta, \phi)$ as

$$\psi(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi) \quad \text{where } L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi), \quad (16.10)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2}{2mr^2} l(l+1) + V(r) \right] R(r) = ER(r) \quad (16.11)$$

Taking $R(r) = u(r)/r$,

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2mr^2} l(l+1) + V(r) \right] u(r) = Eu(r) \quad (16.12)$$

$$\implies V_{eff}(r) = V(r) + \frac{\hbar^2}{2mr^2} l(l+1) \quad (16.13)$$

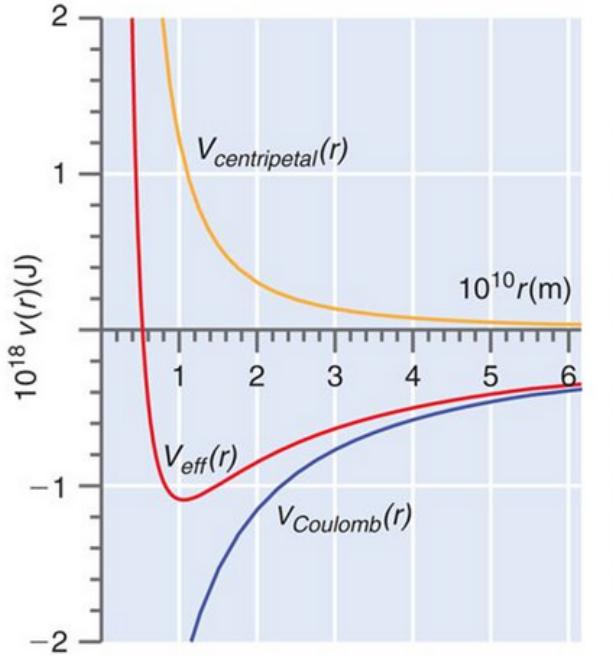


Figure 16.1: Effective potential for an atom with Coulomb and Centripetal potentials.

The plot in Fig.16.1 shows the effective potential V_{eff} for the Coulomb potential $V_{Coulomb}(r) \propto -1/r$ and the centripetal potential $V_{Centrifugal} = l(l+1)/2mr^2$.

The normalizability condition of ψ tells us that

$$\begin{aligned} \int d^3x |\psi|^2 &= \text{constant} \times \int_0^\infty dr r^2 \frac{|u(r)|^2}{r^2} < \infty \\ \implies \int_0^\infty dr |u(r)|^2 &< \infty \\ \implies \lim_{r \rightarrow \infty} |u(r)| &\leq \frac{a}{r^{1/2+\epsilon}} \quad \text{where } a = \text{constant}, \epsilon > 0 \end{aligned}$$

where the finite constant arise from the angular integrals $\int d\theta \int d\phi \sin^2\theta |Y_{lm}(\theta, \phi)|^2$. Thus, $u(r)$ must fall away faster than $1/\sqrt{r}$ as $r \rightarrow \infty$. Also, for the case of $\epsilon = 0$, you can easily see a logarithmic divergence of the integral with r in the limit of $r \rightarrow \infty$.

In the limit of $r \rightarrow 0$, we must have $u(r \rightarrow 0) \rightarrow 0$ faster than $r \rightarrow 0$ for the overall stability of the atomic system. Certainly, this is easily seen for $l \neq 0$ due to the overall repulsive nature of $V_{eff}(r \rightarrow 0)$. As

$$u(0) = 0 \text{ in the limit } r \rightarrow 0 , \quad (16.14)$$

we must have (for $l = 0$) a hard-wall boundary condition at $r = 0$

$$V_{eff}(r) = \begin{cases} V(r) & r > 0 , \\ \infty & r = 0 . \end{cases} \quad (16.15)$$

Do bound states exist in 3D for the case of the Coulomb potential problem?

Having set the stage for solving the Hydrogen atom problem, we now turn to this task in the next chapter.

Chapter 17

The Hydrogen Atom

For the Coulomb potential $V(r) = -e^2/4\pi\epsilon_0 r$ (note: a central potential!), let us first consider the two-body problem of the electron orbiting around the positively charged nucleus. For a classical system of two bodies of masses m_1, m_2 , at positions $\mathbf{r}_1, \mathbf{r}_2$, the problem can always be decomposed into center of mass and relative variables. The center of mass variables are given by

$$\begin{aligned}\mathbf{r}_{CM} &= \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} , \\ \mathbf{p}_{CM} &= \mathbf{p}_1 + \mathbf{p}_2 , \\ M &= m_1 + m_2 .\end{aligned}$$

The relative variables are given by

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 , \tag{17.1}$$

$$\begin{aligned}\mathbf{p} &= \mu(\mathbf{v}_1 - \mathbf{v}_2) , \quad \text{Reduced mass } \mu = \left[\frac{1}{m_1} + \frac{1}{m_2} \right]^{-1} = \frac{m_1 m_2}{m_1 + m_2} , \\ &= \frac{m_1 m_2}{m_1 + m_2} \left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2} \right) , \\ &= \frac{m_2 \mathbf{p}_1 - m_1 \mathbf{p}_2}{m_1 + m_2} .\end{aligned} \tag{17.2}$$

We now turn to the quantum mechanical case, where the position and momenta variables have been promoted to operators. Thus, denoting the particle index by μ, ν and the Cartesian components by i, j , we can write

$$[r_{\nu i}, p_{\mu j}] = i\hbar\delta_{ij}\delta_{\mu\nu} , \tag{17.3}$$

$$\implies [(\mathbf{r}_{CM})_i, (\mathbf{p}_{CM})_j] = i\hbar\delta_{ij} = [r_i, p_j] . \tag{17.4}$$

Thus, we can simplify the TISE for the 2-body system of the H-atom using

$$\begin{aligned} \mathbf{p}_{CM} &= -i\hbar\boldsymbol{\nabla}_{CM}, \\ \mathbf{p}_r &= -i\hbar\boldsymbol{\nabla}_r, \\ \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} &= \frac{p_{CM}^2}{M} + \frac{p^2}{2\mu}, \\ \implies H\Psi(\mathbf{r}_{CM}, \mathbf{r}) &= \left[\frac{p_{CM}^2}{M} + \frac{p^2}{2\mu} + V(r) \right] \Psi(\mathbf{r}_{CM}, \mathbf{r}) = E_{total}\Psi(\mathbf{r}_{CM}, \mathbf{r}). \end{aligned} \quad (17.5)$$

Now, given that there is no (external) potential experienced by the the 2-body system as a whole (i.e., there is no $V_{ext}(\mathbf{r}_{CM})$), the center of mass degree of freedom behaves effectively like a free particle, such that we can decompose the total wavefunction into $\Psi(\mathbf{r}_{CM}, \mathbf{r}) = \phi(\mathbf{r}_{CM})\psi_r$ such that

$$\begin{aligned} E_{CM} &= \frac{\hbar^2 k_{CM}^2}{2M}, \quad \phi(\mathbf{r}_{CM}) = e^{i\mathbf{k}_{CM} \cdot \mathbf{r}_{CM}}, \\ \left[\frac{p^2}{2\mu} + V(r) \right] \psi(\mathbf{r}) &= E_{rel}\psi(\mathbf{r}) \quad \text{where } E_{rel} = E_{total} - \frac{\hbar^2 k_{CM}^2}{2M}, \end{aligned} \quad (17.6)$$

where $m_e = 9.109 \times 10^{-31}$ kg, $m_p = 1.672 \times 10^{-27}$ kg and $\mu = m_e m_p / M = 0.9995 m_e$ for the H-atom problem. We have already studied the case of a TISE in the radial coordinate for a general central potential in the previous chapter. Thus, the equivalent 1D TISE for the H-atom is

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \right] u(r) = E_{rel}u(r). \quad (17.7)$$

Note that for $l = 0$,

$$V_{eff}(r) = \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \rightarrow -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} < 0.$$

Given that the Coulomb potential is overall confining, any bound state (if at all possible!) must exist for $E_{rel} < 0$ at $l = 0$. Thus, let us take $\varepsilon = -E_{rel}$ and simplify the TISE to

$$\frac{d^2u(r)}{dr^2} + \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2} \frac{u(r)}{r} - \frac{l(l+1)}{r^2} u(r) = \frac{2\mu}{\hbar^2} \varepsilon u(r) \quad \text{where } \varepsilon > 0. \quad (17.8)$$

At $r \rightarrow \infty$ limit, we can drop the V_{eff} term and take the approximate form $u(r) \sim u_{app}(r)$

$$\begin{aligned} \frac{d^2u_{app}}{dr^2} &= \frac{2\mu}{\hbar^2} \varepsilon u_{app} \\ \implies u_{app}(r) &\propto e^{-\sqrt{\frac{2\mu\varepsilon}{\hbar^2}}r}, \end{aligned} \quad (17.9)$$

where we have thrown away the possible solution of $u_{app}(r) \propto e^{\sqrt{\frac{2\mu\varepsilon}{\hbar^2}}r}$ on grounds of normalisability (as it diverges in the limit of $r \rightarrow \infty$). With this in mind, we consider the trial

solution

$$u(r) = v(r) e^{-\sqrt{\frac{2\mu\varepsilon}{\hbar^2}}r}, \quad (17.10)$$

$$v(r) = \sum_{p=1}^{\infty} A_p r^p. \quad (17.11)$$

Here, A_p are constants, and $A_0 = 0$ (from the constraint that $u(r \rightarrow 0) \rightarrow 0$, eq.16.14). Substituting Eq. 17.10 in Eq. 17.8 we get

$$\frac{d^2v(r)}{dr^2} - \frac{2\sqrt{2\mu\varepsilon}}{\hbar} \frac{dv(r)}{dr} + \frac{2\mu e^2}{4\pi\epsilon_0\hbar^2} \frac{v(r)}{r} - \frac{l(l+1)}{r^2} v(r) = 0 \quad (17.12)$$

Substituting Eq. 17.11 in Eq. 17.12 in seeking the Frobenius power-series solution and equating the coefficient of r^p to be zero, we obtain the recursion relation

$$[p(p+1) - l(l+1)] A_{p+1} = \left[\frac{2p\sqrt{2\mu\varepsilon}}{\hbar} - \frac{2\mu e^2}{\hbar^2 4\pi\epsilon_0} \right] A_p. \quad (17.13)$$

For $p = l$, $A_p = 0 \implies A_{p-1} = A_{p-2} = A_{p-3} = \dots$. Thus, the only non-zero coefficients have $p > l$. Also, as $r \rightarrow \infty$, $u(r) \rightarrow 0$ (for a normalisable solution to the TISE). This means that the power series $v(r)$ must terminate at a finite $p(> l)$, so that the exponential part can dominate as $r \rightarrow \infty$.

Thus, for some $p = n > l$, $A_{p+1} = 0$

$$\implies \frac{2n\sqrt{2\mu\varepsilon}}{\hbar} = \frac{2\mu e^2}{\hbar^2 4\pi\epsilon_0} \quad (17.14)$$

$$\therefore E_{rel}^n = -\varepsilon = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \quad (17.15)$$

$$= -\frac{13.6}{n^2} \text{eV}, \quad n \geq l+1 \quad (17.15)$$

$$R(r) = \frac{v(r)}{r} e^{-\frac{\sqrt{2\mu\varepsilon}}{\hbar}r} \quad (17.16)$$

$$= R_{nl}(r)$$

Thus, after such a long calculation, we do get back the Bohr formula (eq.(2.39))! The various $R_{nl}(r)$ can be found from getting various A_p from Eq. 17.13, and in terms of the characteristic lengthscale for the atom (the Bohr radius a_0):

$$R_{10}(r) = \left(\frac{1}{a_0} \right)^{3/2} 2e^{-r/a_0},$$

$$R_{20}(r) = \left(\frac{1}{2a_0} \right)^{3/2} 2 \left(1 - \frac{r}{2a_0} \right) e^{-r/2a_0},$$

$$R_{21}(r) = \left(\frac{1}{2a_0} \right)^{3/2} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0} \right) e^{-r/2a_0},$$



Bohr

and so on. Here, a_0 is the Bohr radius given by

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 5.3 \times 10^{-11} \text{ m} , \quad E_{rel}^n = -\frac{\hbar^2}{2\mu n^2 a_0^2} ,$$

and the full wavefunction of the H-atom is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad (17.17)$$

where the good quantum numbers are given by

$$\begin{aligned} n &= 1, 2, 3, \dots && \text{(Principal quantum number)} , \\ l &= 0, 1, \dots, n-1 && \text{(Orbital quantum number)} , \text{ and} \\ m &= -l, -l+1, \dots, l-1, l && \text{(Magnetic quantum number)} . \end{aligned}$$

While $R_{nl}(r)$ is dependent on both n & l , the energy E_{rel}^n is dependent on n alone. There must, therefore, be degeneracies for all the levels with different values of l and m that correspond to a given value of n . This degeneracy is, however, true only for the Coulomb central potential, and reflects a case of an “accidental” degeneracy. Quantifying this degeneracy, any n has $(n-1)$ possible values for l , and each l has $2l+1$ possible values of m . Thus, the total degeneracy for E_n will be

$$\begin{aligned} \text{Total degeneracy of } E_{rel}^n &= \sum_{l=0}^{n-1} (2l+1) , \\ &= 2 \frac{n(n-1)}{2} + n , \\ &= n^2 . \end{aligned} \quad (17.18)$$

Taking account of the spin internal degree of freedom (with its double degeneracy), the total degeneracy for E_{rel}^n will be $2n^2$. While the energy levels thus obtained match the Bohr model exactly, our earlier understanding of quantised electron orbits with a fixed trajectory is replaced by a probability distribution $P(r)$ obtained from $\psi_{nlm}(r, \theta, \phi)$

$$P(r) = \int_0^r dr r^2 \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi |\psi_{nlm}(r, \theta, \phi)|^2 , \quad \lim_{r \rightarrow \infty} P(r) = 1 . \quad (17.19)$$

We can also define radial probability density $P_{nl}(r)$ such that it gives the probability of finding the electron in a small interval dr at a distance r

$$P_{nlm}(r) = \int_0^\pi \int_0^{2\pi} r^2 \sin \theta d\phi d\theta |\psi_{nlm}(r, \theta, \phi)|^2 , \quad (17.20)$$

$$\begin{aligned} &= r^2 |R_{nl}(r)|^2 \int_0^\pi \int_0^{2\pi} |Y_{lm}(\theta, \phi)|^2 d\phi d\theta , \\ &= r^2 |R_{nl}(r)|^2 \times I_{lm} \end{aligned} \quad (17.21)$$

where $I_{lm} = \int_0^{\pi} \int_0^{2\pi} |Y_{lm}(\theta, \phi)|^2 d\phi d\theta$.

$$\therefore P_{nlm}(r) = r^2 |R_{nl}(r)|^2 \times I_{lm}, \quad (17.22)$$

$$\text{and } P(r) = \int_0^r P_{nlm}(r) dr. \quad (17.23)$$

Some plots of the $P_{nlm}(r)$ (as a function of r/a_0) are shown in Fig.17.1 below. The classical picture of orbits can (very roughly speaking) be understood as tracking the peaks of the radial probability density $P_{nlm}(r)$. Also, we display once again the solutions of the angular momentum problem in Fig.17.2 in order to visualise the “orbitals” of the Hydrogen atom.

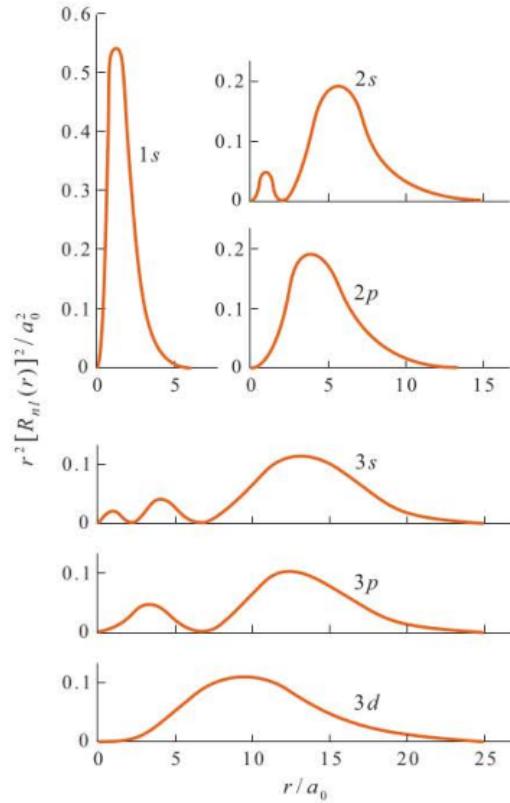


Figure 17.1: Radial Probability density function

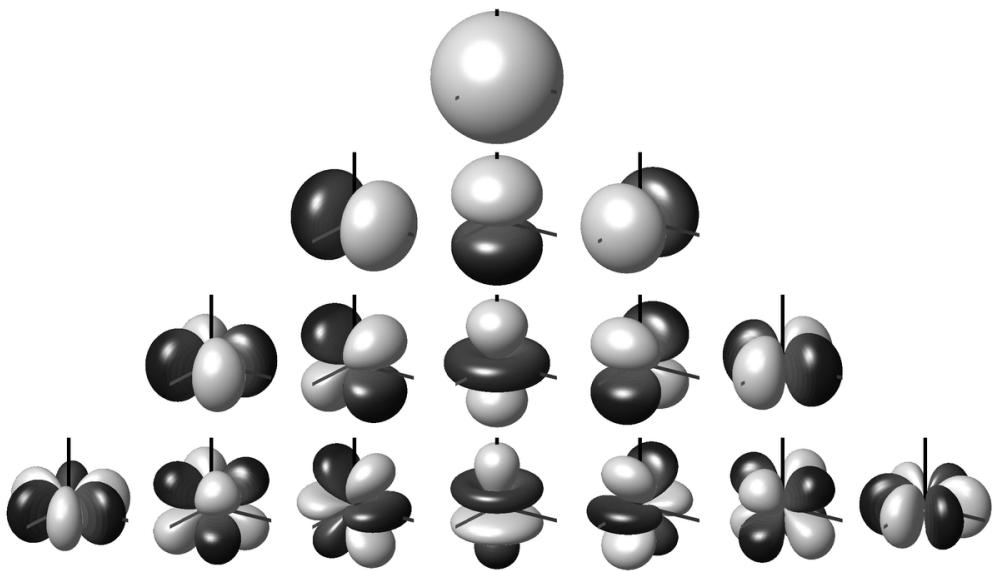


Figure 17.2: Spherical Harmonics

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