Advanced Quantum Physics

Handout 1

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Preface

Quantum mechanics underpins a variety of broad subject areas within physics and the physical sciences from high energy particle physics, solid state and atomic physics through to chemistry. As such, the subject resides at the core of every physics programme. By building upon the conceptual foundations introduced in the IB Quantum Physics course, the aim of Part II Advanced Quantum Physics is to develop further conceptual insights and technical fluency in the subject.

Although 24 lectures is a long course to prepare(!), it is still insufficient to cover all of the topics that different physicists will describe as "core". For example, some will argue that concepts of quantum computation should already be included as an established component of the core. Similarly, in the field of quantum optics, some will say that a detailed knowledge of atomic and molecular spectroscopy is key. In solid state physics, the concept of second quantization in many-body physics is considered central, while relativistic quantum mechanics can be seen as critical for high-energy physics. The material included in this course has been chosen to cover the key conceptual foundations, at a speed that should allow one to develop fluency in their application. This material will provide access to the more advanced subjects mentioned above, the majority of which will be covered in subsequent optional courses in Part II and Part III.

Syllabus

- **Review of Quantum Physics:** Postulates of quantum mechanics, operator methods, time-dependence. Solutions to the Schrödinger equation in one and three dimensions. Angular momentum and spin; matrix representations. Addition of anglar momentum, Clebsch-Gordan coefficients.

- **Approximate Methods:** Time-independent perturbation theory, first and second order expansion; degenerate perturbation theory. Variational method: ground state energy and eigenfunctions.

- **Motion of charged particle in electromagnetic fields:** Gauge invariance; Aharonov-Bohm effect. Particle magnetic moments; Stern-Gerlach experiment. Landau levels, two-dimensional electron gas.

- **Symmetries:** Translations and rotations, parity. Conservation laws. Wigner-Eckart theorem for scalar and vector operators. Selection rules. Landé projection formula.

- **Identical particles:** Particle indistinguishability and quantum statistics; exchange interactions. The helium atom.

- **Atomic and molecular structure:** The 'real' Hydrogen atom; fine structure: relativistic corrections; spin-orbit coupling; hyperfine structure. Multi-electron atoms: LS coupling; Hund's rules; Stark effect; Zeeman effect. Born-Oppenheimer approximation; H_2+ ion; molecular orbitals; H_2 molecule; ionic and covalent bonding.

- **Time-dependent perturbation theory:** Transitions in two-level system, Rabi oscillations, magnetic resonance. Spin transitions. Time-dependent perturbation theory, Fermi's Golden rule. Scattering and the Born approximation.

- **Elements of quantum field theory:** Quantization of the electromagnetic field, photons; number states. Radiative transitions, electric dipole approximation, selection rules, spontaneous emission and absorption, stimulated emission, Einstein's A and B coefficients; Cavity rate equations and lasers, coherent states.

Handout

To accompany the course, a substantial handout has been prepared.[1] In some cases, the handout contains material (usually listed as INFO blocks) that goes beyond the scope of the lectures. Needless to say, the examination will be limited to material that is covered in lectures and not the handout.

Problem Sets

The problem sets are a vital and integral part of the course providing the means to reinforce key ideas as well as practice techniques. Problems indicated by a † symbol are regarded as challenging. Throughout these notes are included a number of simpler exercises which may be completed "along the way", and aim to reinforce some of the ideas developed in the text.

Books

As a core of every undergraduate and graduate physics programme, there is a wealth of excellent textbooks on the subject. Choosing books that suit is a subjective exercise. Apart from the handout, I am not aware of a text that addresses all of the material covered in this course: Most are more dense and far-reaching, and others are simply more advanced or imbalanced towards specialist topics. At the same time, I would not recommend relying solely on the handout. Apart from the range of additional examples they offer, the textbooks will often provide a more erudite and engaging discussion of the material. Although there are too many texts on the subject to discuss every one, I have included below some of the books that I believe to be particularly useful.

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[1]This detailed handout is thanks entirely to the work of Prof. N. Cooper and Prof. B. Simons, two previous lecturers of this course.

Bibliography

[1] B. H. Bransden and C. J. Joachain, **Quantum Mechanics**, (2nd edn, Pearson, 2000). This is a classic text which covers core elements of advanced quantum mechanics. It is particularly strong in the area of atomic physics, but weaker on many-particle physics.

[2] S. Gasiorowicz, **Quantum Physics**, (2nd edn, Wiley 1996, 3rd edn, Wiley, 2003). This is an excellent textbook that covers material at approximately the right level for the course. However, the published text (as opposed to the supplementary material available online) omits some topics which are addressed in this course.

[3] H. Haken and H. C. Wolf, **The Physics of Atoms and Quanta**, (6th edn, Springer, 2000). This is a more advanced text which addresses many aspects of atomic physics and quantum optics in a readable manner.

[4] K. Konishi and G. Paffuti, **Quantum Mechanics: A New Introduction**, (OUP, 2009). This is a new text which includes some entertaining new topics within an old field. It also has a useful set of mathematica-based examples if you can get hold of the disk!

[5] L. D. Landau and L. M. Lifshitz, **Quantum Mechanics: Non-Relativistic Theory, Volume 3**, (Butterworth-Heinemann, 3rd edn, 1981). This is a rich and classic text which covers many of the core topics in this course, in most cases at a level that goes well beyond our target.

[6] F. Schwabl, **Quantum Mechanics**, (Springer, 4th edn, 2007). This book provides a clear exposition of the core topics addressed at the same level as the current text.

[7] R. Shankar, **Principles of Quantum Mechanics**, (Springer; 2nd edn, 1994). This is a very interesting and idiosyncratic text which I particularly like. It is not comprehensive enough to cover every topic in this course. But where there is overlap, it provides an excellent and interesting commentary.

[8] G. L. Squires, **Problems in Quantum Mechanics**, (CUP 1995). A clear presentation of core ideas, illustrated by a very useful collection of worked examples.

Contents

Chapter 1

Wave mechanics and the Schrödinger equation

Although this lecture course will assume a familiarity with the basic concepts of wave mechanics, to introduce more advanced topics in quantum theory, it makes sense to begin with a concise review of the foundations of the subject. In particular, in the first chapter of the course, we will begin with a brief discussion of the historical challenges that led to the development of quantum theory almost a century ago.

The formulation of a consistent theory of statistical mechanics, electrodynamics and special relativity during the latter half of the 19th century and the early part of the 20th century had been a triumph of "unification". However, the undoubted success of these theories gave an impression that physics was a mature, complete, and predictive science. Nowhere was confidence expressed more clearly than in the famous quote made at the time by Lord Kelvin: *There is nothing new to be discovered in physics now. All that remains is more and more precise measurement.* However, there were a number of seemingly unrelated and unsettling problems that challenged the prevailing theories.

1.1 Historical foundations of quantum physics

1.1.1 Black-body radiation

In 1860, Gustav Kirchhoff introduced the concept of a "black body", an object that absorbs all electromagnetic radiation that falls upon it – none passes through and none is reflected. Since no light is reflected or transmitted, the object appears black when it is cold. However, above absolute zero, a black body emits thermal radiation with a spectrum that depends on temperature. To determine the spectrum of radiated energy, it is helpful to think of a black body as a thermal cavity at a temperature, T. The energy radiated by the cavity can be estimated by considering the resonant modes. In three-dimensions, the number of modes, per unit frequency per unit volume is given by

$$N(\nu)d\nu = \frac{8\pi\nu^2}{c^3}d\nu \,,$$

where, as usual, c is the speed of light.[1]

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[1] If we take the cavity to have dimension L^3, the modes of the cavity involve wave numbers $\mathbf{k} = \pi\mathbf{n}/L$ where $\mathbf{n} = (n_x, n_y, n_z)$ denote the vector of integers $n_x = 0, 1, 2, \cdots \infty$, etc. The corresponding frequency of each mode is given by $\nu = c|\mathbf{k}|/2\pi$, where c is the velocity of light. The number of modes (per unit volume) having frequencies between ν and $\nu + d\nu$ is therefore given by $N(\nu)d\nu = \frac{1}{L^3} \times 2 \times \frac{1}{8} \times \frac{(4\pi k^2)dk}{(\pi/L)^3}$, where the factor of 2 accounts for the two

William Thomson, 1st Baron Kelvin 1824-1907
Kelvin was educated at Glasgow and Cambridge. He became professor of natural philosophy at Glasgow in 1846. From 1846 to 1851 Kelvin edited the "Cambridge and Dublin Mathematical Journal," to which he contributed several important papers. Some of his chief discoveries are announced in the "Secular Coating of the Earth," and the Bakerian lecture, the "Electrodynamic Qualities of Metals." He invented the quadrant, portable, and absolute electrometers, and other scientific instruments. In January 1892, he was raised to the peerage as Lord Kelvin.

Gustav Robert Kirchhoff 1824-1887
A German physicist who contributed to the fundamental understanding of electrical circuits, spectroscopy, and the emission of black-body radiation by heated objects. He coined the term "black body" radiation in 1862, and two sets of independent concepts in both circuit theory and thermal emission are named "Kirchhoff's laws" after him.

John William Strutt, 3rd Baron Rayleigh OM (1842-1919)
An English physicist who, with William Ramsay, discovered the element argon, an achievement for which he earned the Nobel Prize in 1904. He also discovered the phenomenon of Rayleigh scattering, explaining why the sky is blue, and predicted the existence of surface waves known as Rayleigh waves.

Figure 1.1: The COBE (Cosmic Background Explorer) satellite made careful measurements of the shape of the spectrum of the emission from the cosmic microwave background. As one can see, the behaviour at low-frequencies (long-wavelengths) conforms well with the predicted Rayleigh-Jeans law translating to a temperature of 2.728K. However, at high frequencies, there is a departure from the predicted ν^2 dependence.
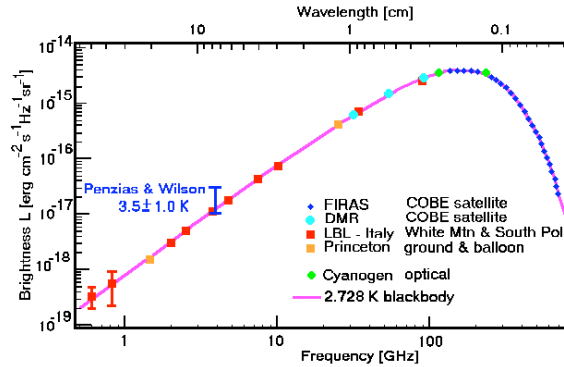
The amount of radiation emitted in a given frequency range should be proportional to the number of modes in that range. Within the framework of classical statistical mechanics, each of these modes has an equal chance of being excited, and the average energy in each mode is $k_B T$ (equipartition), where k_B is the Boltzmann constant. The corresponding energy density is therefore given by the **Rayleigh-Jeans law**,

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} k_B T \,.$$

This result predicts that $\rho(\nu, T)$ increases without bound at high frequencies, ν — the ultraviolet (UV) catastrophe. However, such behaviour stood in contradiction with experiment which revealed that the high-frequency dependence is quite benign (see, e.g., Fig. 1.1).

To resolve difficulties presented by the UV catastrophe, Planck hypothesized that, for each mode ν, energy is quantized in units of $h\nu$, where h denotes the Planck constant. In this case, the energy of each mode is given by[2]

$$\langle \varepsilon(\nu) \rangle = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/k_B T}}{\sum_{n=0}^{\infty} e^{-nh\nu/k_B T}} = \frac{h\nu}{e^{h\nu/k_B T} - 1} \,,$$

leading to the anticipated suppression of high frequency modes. From this result one obtains the celebrated Planck radiation formula,

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle \varepsilon(\nu) \rangle = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} \,.$$

This result conforms with experiment (Fig. 1.1), and converges on the Rayleigh-Jeans law at low frequencies, $h\nu/k_B T \to 0$.

Planck's result suggests that electromagnetic energy is quantized: light of wavelength $\lambda = c/\nu$ is made up of quanta each of which has energy $h\nu$. The equipartition law fails for oscillation modes with high frequencies, $h\nu \gg k_B T$.

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polarizations, the factor $(4\pi k^2)dk$ is the volume of the shell from k to $k + dk$ in reciprocal space, the factor of $1/8$ accounts for the fact that only positive wavenumbers are involved in the closed cavity, and the factor of $(\pi/L)^3$ denotes the volume of phase space occupied by each mode. Rearranging the equation, and noting that $dk = 2\pi d\nu/c$, we obtain the relation in the text.

[2]If we define the partition function, $\mathcal{Z} = \sum_{n=0}^{\infty} e^{-\beta n h\nu}$, where $\beta = 1/k_B T$, then $\langle E \rangle = -\partial_\beta \ln \mathcal{Z}$. Making use of the formula for the sum of a geometric progression, $\sum_{n=0}^{\infty} r^n = 1/(1-r)$, we obtain the relation.

Max Karl Ernst Ludwig Planck 1858-1947 German physicist whose work provided the bridge between classical and modern physics. Around 1900 Planck developed a theory explain the nature of blackbody radiation. He proposed that energy is emitted and absorbed in discrete packets or "quanta," and that these had a definite size − Planck's constant. Planck's finding didn't get much attention until the idea was furthered by Albert Einstein in 1905 and Niels Bohr in 1913. Planck won the Nobel Prize in 1918, and, together with Einstein's theory of relativity, his quantum theory changed the field of physics.

Albert Einstein 1879-1955 was a German-born theoretical physicist. He is best known for his theory of relativity and specifically mass-energy equivalence, expressed by the equation $E = mc^2$. Einstein received the 1921 Nobel Prize in Physics "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect."
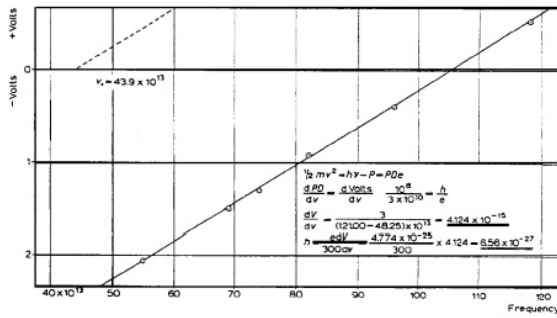
Figure 1.2: Measurements of the photoelectric effect taken by Robert Millikan showing the variation of the stopping voltage, eV, with variation of the frequency of incident light. Figure reproduced from Robert A. Millikan's Nobel Lecture, *The Electron and the Light-Quanta from the Experimental Point of View*, The Nobel Foundation, 1923.

A quantum theory for the specific heat of matter, which takes into account the quantization of lattice vibrational modes, was subsequently given by Debye and Einstein.

1.1.2 Photoelectric effect

We turn now to the second ground-breaking experiment in the development of quantum theory. When a metallic surface is exposed to electromagnetic radiation, above a certain threshold frequency, the light is absorbed and electrons are emitted (see figure, right). In 1902, Philipp Eduard Anton von Lenard observed that the energy of individual emitted electrons increases with the frequency of the light. This was at odds with Maxwell's wave theory of light, which predicted that the electron energy would be proportional to the intensity of the radiation.

In 1905, Einstein resolved this paradox by describing light as composed of discrete quanta (photons), rather than continuous waves. Based upon Planck's theory of black-body radiation, Einstein theorized that the energy in each quantum of light was proportional to the frequency. A photon above a threshold energy, the "work function" W of the metal, has the required energy to eject a single electron, creating the observed effect. In particular, Einstein's theory was able to predict that the maximum kinetic energy of electrons emitted by the radiation should vary as

$$\text{K.E.}_{\max} = h\nu - W .$$

Later, in 1916, Millikan was able to measure the maximum kinetic energy of the emitted electrons using an evacuated glass chamber. The kinetic energy of the photoelectrons was found by measuring the potential energy of the electric field, eV, needed to stop them. As well as confirming the linear dependence of the kinetic energy on frequency (see Fig. 1.2), by making use of his estimate for the electron charge, e, established from his oil drop experiment in 1913, he was able to determine Planck's constant to a precision of around 0.5%. This discovery led to the quantum revolution in physics and earned Einstein the Nobel Prize in 1921.

1.1.3 Compton scattering

In 1923, Compton investigated the scattering of high energy X-rays and γ-ray from electrons in a carbon target. By measuring the spectrum of radiation at different angles relative to the incident beam, he found two scattering peaks. The first peak occurred at a wavelength which matched that of the incident beam, while the second varied with angle. Within the framework of a purely
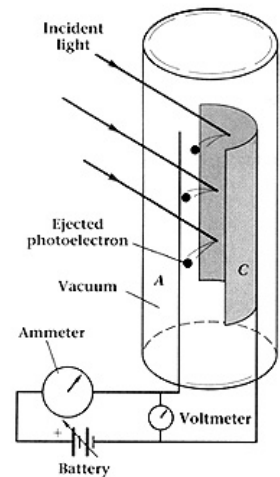
Robert Andrews Millikan 1868-1853
He received his doctorate from Columbia University and taught physics at the University of Chicago (1896-1921) and the California Institute of Technology (from 1921). To measure electric charge, he devised the Millikan oil-drop experiment. He verified Albert Einstein's photoelectric equation and obtained a precise value for the Planck constant. He was awarded the 1923 Nobel Prize in physics.

Arthur Holly Compton 1892-1962:
An American physicist, he shared the 1927 Nobel Prize in Physics with C. T. R. Wilson for his discovery of the Compton effect. In addition to his work on X rays he made valuable studies of cosmic rays and contributed to the development of the atomic bomb.

classical theory of the scattering of electromagnetic radiation from a charged particle – Thomson scattering – the wavelength of a low-intensity beam should remain unchanged.

Compton's observation demonstrated that light cannot be explained purely as a classical wave phenomenon. Light must behave as if it consists of particles in order to explain the low-intensity Compton scattering. If one assumes that the radiation is comprised of photons that have a well defined momentum as well as energy, $p = \frac{h\nu}{c} = \frac{h}{\lambda}$, the shift in wavelength can be understood: The interaction between electrons and high energy photons (ca. keV) results in the electron being given part of the energy (making it recoil), and a photon with the remaining energy being emitted in a different direction from the original, so that the overall momentum of the system is conserved. By taking into account both conservation of energy and momentum of the system, the Compton scattering formula describing the shift in the wavelength as function of scattering angle θ can be derived,[3]

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

The constant of proportionality $h/m_e c = 0.002426$ nm, the Compton wavelength, characterizes the scale of scattering. Moreover, as $h \to 0$, one finds that $\Delta\lambda \to 0$ leading to the classical prediction.

1.1.4 Atomic spectra

The discovery by Rutherford that the atom was comprised of a small positively charged nucleus surrounded by a diffuse cloud of electrons led naturally to the consideration of a planetary model of the atom. However, a classical theory of electrodynamics would predict that an accelerating charge would radiate energy leading to the eventual collapse of the electron into the nucleus. Moreover, as the electron spirals inwards, the emission would gradually increase in frequency leading to a broad continuous spectra. Yet, detailed studies of electrical discharges in low-pressure gases revealed that atoms emit light at discrete frequencies.

The clue to resolving these puzzling observations lay in the discrete nature of atomic spectra. For the hydrogen atom, light emitted when the atom is thermally excited has a particular pattern: Balmer had discovered in 1885 that the emitted wavelengths follow the empirical law, $\lambda = \lambda_0(1/4 - 1/n^2)$ where $n = 3, 4, 5, \cdots$ and $\lambda_0 = 3645.6\overset{\circ}{A}$ (see Fig. 1.4). Neils Bohr realized that these discrete values of the wavelength reflected the emission of individual photons having energy equal to the energy difference between two allowed orbits of the electron circling the nucleus (the proton), $E_n - E_m = h\nu$, leading to the conclusion that the allowed energy levels must be quantized and varying as $E_n = -\frac{hcR_H}{n^2}$, where $R_H = 109678\,\mathrm{cm}^{-1}$ denotes the Rydberg constant.

How could the quantum $h\nu$ restricting allowed radiation energies also restrict the allowed electron orbits? In 1913 Bohr proposed that the angular momentum of an electron in one of these orbits is quantized in units of Planck's

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[3]If we assume that the total energy and momentum are conserved in the scattering of a photon (γ) from an initially stationary target electron (e), we have $E_\gamma + E_e = E_{\gamma'} + E_{e'}$ and $\mathbf{p}_\gamma = \mathbf{p}_{\gamma'} + \mathbf{p}_{e'}$. Here $E_\gamma = h\nu$ and $E_e = m_e c^2$ denote the energy of the photon and electron before the collision, while $E_{\gamma'} = h\nu'$ and $E_{e'} = \sqrt{(p_{e'}c)^2 + (mc^2)^2}$ denote the energies after. From the equation for energy conservation, one obtains $(p_{e'}c)^2 = (h(\nu - \nu') + m_e c^2)^2 - (m_e c^2)^2$. From the equation for momentum conservation, one obtains $p_{e'}^2 = p_\gamma^2 + p_{\gamma'}^2 - 2|p_\gamma||p_{\gamma'}|\cos\theta$. Then, noting that $E_\gamma = p_\gamma c$, a rearrangement of these equations obtains the Compton scattering formula.
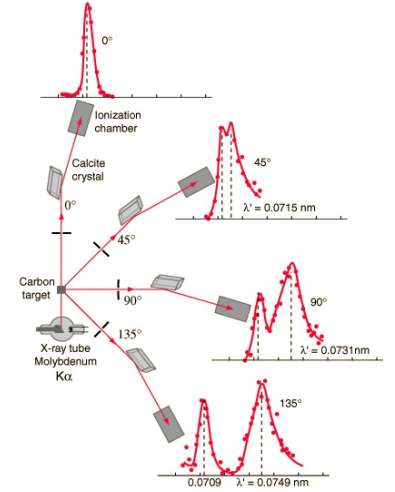
Figure 1.3: Variation of the wavelength of X rays scattered from a Carbon target. A. H. Compton, Phys. Rev. **21**, 483; **22**, 409 (1923)
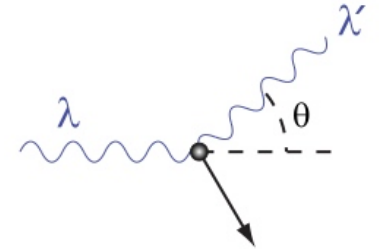
Ernest Rutherford, 1st Baron Rutherford of Nelson, 1871-1937 was a New Zealand born British chemist and Physicist who became known as the father of nuclear physics. He discovered that atoms have a small charged nucleus, and thereby pioneered the Rutherford model (or planetary model of the atom, through his discovery of Rutherford scattering. He was awarded the Nobel Prize in Chemistry in 1908. He is widely credited with splitting the atom in 1917 and leading the first experiment to "split the nucleus" in a controlled manner by two students under his direction, John Cockcroft and Ernest Walton in 1932.
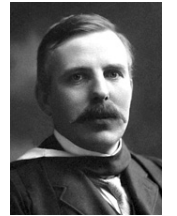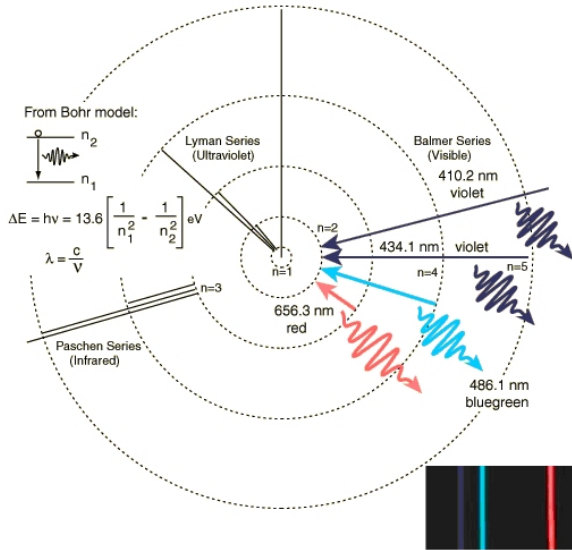
Figure 1.4: Schematic describing various transitions (and an image with the corresponding visible spectral lines) of atomic hydrogen.

constant,

$$L = m_e v r = n\hbar, \qquad \hbar = \frac{h}{2\pi}\,. \tag{1.1}$$

As a result, one finds that $R_{\rm H} = (\frac{e^2}{4\pi\epsilon_0})^2 \frac{2\pi^2 m}{ch^3}$.

▷ EXERCISE. Starting with the Bohr's planetary model for atomic hydrogen, find how the quantization condition (1.1) restricts the radius of the allowed (circular) orbits. Determine the allowed energy levels and obtain the expression for the Rydberg constant above.

But why should only certain angular momenta be allowed for the circling electron? A heuristic explanation was provided by de Broglie: just as the constituents of light waves (photons) are seen through Compton scattering to act like particles (of definite energy and momentum), so particles such as electrons may exhibit wave-like properties. For photons, we have seen that the relationship between wavelength and momentum is $p = h/\lambda$. de Broglie hypothesized that the inverse was true: for particles with a momentum p, the wavelength is

$$\lambda = \frac{h}{p}, \qquad \text{i.e. } p = \hbar k\,,$$

where k denotes the wavevector of the particle. Applied to the electron in the atom, this result suggested that the allowed circular orbits are standing waves, from which Bohr's angular momentum quantization follows. The de Broglie hypothesis found quantitative support in an experiment by Davisson and Germer, and independently by G. P. Thomson in 1927. Their studies of electron diffraction from a crystalline array of Nickel atoms (Fig. 1.5) confirmed that the diffraction angles depend on the incident energy (and therefore momentum).

This completes the summary of the pivotal conceptual insights that paved the way towards the development of quantum mechanics.

1.2 Wave mechanics

de Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in

Niels Henrik David Bohr 1885-1962
A Danish physicist who made fundamental contributions to the understanding atomic structure and quantum mechanics, for which he received the Nobel Prize in Physics in 1922. Bohr mentored and collaborated with many of the top physicists of the century at his institute in Copenhagen. He was also part of the team of physicists working on the Manhattan Project. Bohr married Margrethe Norlund in 1912, and one of their sons, Aage Niels Bohr, grew up to be an important physicist who, like his father, received the Nobel prize, in 1975.

Louis Victor Pierre Raymond, 7th duc de Broglie 1892-1987
A French physicist, de Broglie had a mind of a theoretician rather than one of an experimenter or engineer.
de Broglie's 1924 doctoral thesis Recherches sur la théorie des quanta introduced his theory of electron waves. This included the particle-wave property duality theory of matter, based on the work of Einstein and Planck. He won the Nobel Prize in Physics in 1929 for his discovery of the wave nature of electrons, known as the de Broglie hypothesis or mécanique ondulatoire.
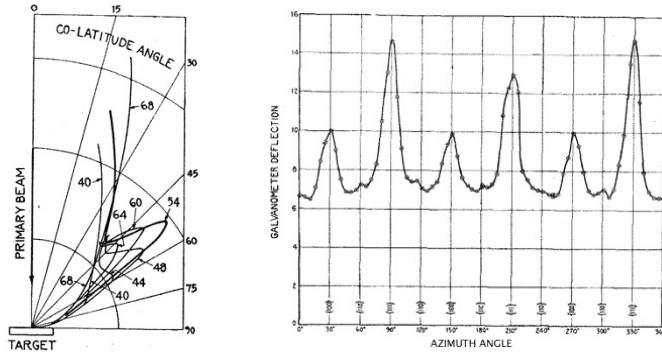
Figure 1.5: In 1927, Davisson and Germer bombarded a single crystal of nickel with a beam of electrons, and observed several beams of scattered electrons that were almost as well defined as the incident beam. The phenomenological similarities with X-ray diffraction were striking, and showed that a wavelength could indeed be associated with the electrons. The first figure shows the intensity of electron scattering against co-latitude angle for various bombarding voltages. The second figure shows the intensity of electron scattering vs. azimuth angle —- 54V, co-latitude 50. Figures taken taken from C. Davisson and L. H. Germer, *Reflection of electrons by a crystal of nickel*, Nature **119**, 558 (1927).

the Autumn of 1925, Pieter Debye, a theorist in Zurich, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end, Debye remarked that he considered the whole theory rather childish: Why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string; real waves in space diffracted and diffused; in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem, and constructing his equation.

There is no rigorous derivation of Schrödinger's equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and constructing an analogous structure for de Broglie's waves and electrons (and, of course, other particles).

1.2.1 Maxwell's wave equation

For a monochromatic wave in vacuum, with no currents or charges present, Maxwell's wave equation,

$$\nabla^2 \mathbf{E} - \frac{1}{c^2}\ddot{\mathbf{E}} = 0 \,, \qquad (1.2)$$

admits the plane wave solution, $\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$, with the linear dispersion relation $\omega = c|\mathbf{k}|$ and c the velocity of light. Here, (and throughout the text) we adopt the convention, $\ddot{\mathbf{E}} \equiv \partial_t^2 \mathbf{E}$. We know from the photoelectric effect and Compton scattering that the photon energy and momentum are related to the frequency and wavelength of light through the relations $E = h\nu = \hbar\omega$, $p = \frac{h}{\lambda} = \hbar k$. The wave equation tells us that $\omega = c|\mathbf{k}|$ and hence $E = c|\mathbf{p}|$. If we think of $e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ as describing a particle (photon) it would be more natural to write the plane wave in terms of the energy and momentum of the particle as $\mathbf{E_0}e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$. Then, one may see that the wave equation applied to the plane wave describing particle propagation yields the familiar energy-momentum relationship, $E^2 = (c\mathbf{p})^2$ for a massless relativistic particle.

This discussion suggests how one might extend the wave equation from the photon (with zero rest mass) to a particle with rest mass m_0. We require
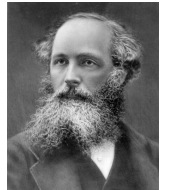
a wave equation that, when it operates on a plane wave, yields the relativistic energy-momentum invariant, $E^2 = (c\mathbf{p})^2 + m_0^2 c^4$. Writing the plane wave function $\phi(\mathbf{r}, t) = A e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar}$, where A is a constant, we can recover the energy-momentum invariant by adding a constant mass term to the wave operator,

$$\left(\nabla^2 - \frac{\partial_t^2}{c^2} - \frac{m_0^2 c^2}{\hbar^2} \right) e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar} = -\frac{\left((c\mathbf{p})^2 - E^2 + m_0^2 c^4 \right)}{(\hbar c)^2} e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar} = 0 \,.$$

This wave equation is called the **Klein-Gordon equation** and correctly describes the propagation of relativistic particles of mass m_0. However, its form is inappropriate for non-relativistic particles, like the electron in hydrogen.

Continuing along the same lines, let us assume that a non-relativistic electron in free space is also described by a plane wave of the form $\Psi(x, t) = A e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar}$. We need to construct an operator which, when applied to this wave function, just gives us the ordinary non-relativistic energy-momentum relation, $E = \frac{\mathbf{p}^2}{2m}$. The factor of $\mathbf{p}^2$ can be recovered from two derivatives with respect to $\mathbf{r}$, but the only way we can get E is by having a single differentiation with respect to time, i.e.

$$i\hbar \partial_t \Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) \,.$$

This is Schrödinger's equation for a free non-relativistic particle. One remarkable feature of this equation is the factor of i which shows that the wavefunction is complex.

How, then, does the presence of a spatially varying scalar potential affect the propagation of a de Broglie wave? This question was considered by Sommerfeld in an attempt to generalize the rather restrictive conditions in Bohr's model of the atom. Since the electron orbit was established by an inverse-square force law, just like the planets around the Sun, Sommerfeld couldn't understand why Bohr's atom had only circular orbits as opposed to Kepler-like elliptical orbits. (Recall that all of the observed spectral lines of hydrogen were accounted for by energy differences between circular orbits.)

de Broglie's analysis of the allowed circular orbits can be formulated by assuming that, at some instant, the spatial variation of the wavefunction on going around the orbit includes a phase term of the form $e^{ipq/\hbar}$, where here the parameter q measures the spatial distance around the orbit. Now, for an acceptable wavefunction, the total phase change on going around the orbit must be $2\pi n$, where n is integer. For the usual Bohr circular orbit, where $p = |\mathbf{p}|$ is constant, this leads to quantization of the angular momentum $L = pr = n\hbar$.

Sommerfeld considered a general Keplerian elliptical orbit. Assuming that the de Broglie relation $p = h/\lambda$ still holds, the wavelength must vary as the particle moves around the orbit, being shortest where the particle travels fastest, at its closest approach to the nucleus. Nevertheless, the phase change on moving a short distance Δq should still be $p\Delta q/\hbar$. Requiring the wavefunction to link up smoothly on going once around the orbit gives the **Bohr-Sommerfeld quantization condition**

$$\oint p \, dq = nh \,, \tag{1.3}$$

where $\oint$ denotes the line integral around a closed orbit. Thus only certain *elliptical* orbits are allowed. The mathematics is non-trivial, but it turns out

> **Arnold Johannes Wilhelm Sommerfeld 1868-1951**
> A German theoretical physicist who pioneered developments in atomic and quantum physics, and also educated and groomed a large number of students for the new era of theoretical physics. He introduced the fine-structure constant into quantum mechanics.

that every allowed elliptical orbit has the same energy as one of the allowed circular orbits. That is why Bohr's theory gave the correct energy levels. This analysis suggests that, in a varying potential, the wavelength changes in concert with the momentum.

1.2.2 Schrödinger's equation

Following Sommerfeld's considerations, let us then consider a particle moving in one spatial dimension subject to a "roller coaster-like" potential. How do we expect the wavefunction to behave? As discussed above, we would expect the wavelength to be shortest where the potential is lowest, in the minima, because that's where the particle is going the fastest. Our task then is to construct a wave equation which leads naturally to the relation following from (classical) energy conservation, $E = \frac{p^2}{2m} + V(x)$. In contrast to the free particle case discussed above, the relevant wavefunction here will no longer be a simple plane wave, since the wavelength (determined through the momentum via the de Broglie relation) varies with the potential. However, at a given position x, the momentum is determined by the "local wavelength". The appropriate wave equation is the one-dimensional Schrödinger equation,

$$i\hbar\partial_t\Psi(x,t) = -\frac{\hbar^2\partial_x^2}{2m}\Psi(x,t) + V(x)\Psi(x,t)\,, \qquad (1.4)$$

with the generalization to three-dimensions leading to the Laplacian operator ∇^2 in place of ∂_x^2 (cf. Maxwell's equation).

So far, the validity of this equation rests on plausibility arguments and hand-waving. Why should anyone believe that it really describes an electron wave? Schrödinger's test of his equation was the hydrogen atom. He looked for Bohr's "stationary states": states in which the electron was localized somewhere near the proton, and having a definite energy. The time dependence would be the same as for a plane wave of definite energy, $e^{-iEt/\hbar}$; the spatial dependence would be a time-independent function decreasing rapidly at large distances from the proton. From the solution of the stationary wave equation for the Coulomb potential, he was able to deduce the allowed values of energy and momentum. These values were exactly the same as those obtained by Bohr (except that the lowest allowed state in the "new" theory had zero angular momentum): impressive evidence that the new theory was correct.

With this background, we are now in a position to summarize the basic postulates of quantum mechanics.

Erwin Rudolf Josef Alexander Schrödinger 1887-1961
was an Austrian theoretical physicist who achieved fame for his contributions to quantum mechanics, especially the Schrödinger equation, for which he received the Nobel Prize in 1933. In 1935, after extensive correspondence with personal friend Albert Einstein, he proposed the Schrödinger's cat thought experiment.

1.3 Postulates of quantum theory

Since there remains no "first principles" derivation of the quantum mechanical equations of motion, the theory is underpinned by a set of "postulates" whose validity rest on experimental verification. Needless to say, quantum mechanics remains perhaps the most successful theory in physics.

▷ **Postulate 1.** The state of a quantum mechanical system is completely specified by a function $\Psi(\mathbf{r}, t)$ that depends upon the coordinates of the particle(s) and on time. This function, called the wavefunction or state function, has the important property that $|\Psi(\mathbf{r}, t)|^2\, d\mathbf{r}$ represents the probability that the particle lies in the volume element $d\mathbf{r} \equiv d^d r$ located at position $\mathbf{r}$ at time t.

The wavefunction must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the net probability of finding it at some point in space must be unity leading to the normalization condition, $\int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 \, d\mathbf{r} = 1$. It is customary to also normalize many-particle wavefunctions to unity. The wavefunction must also be single-valued, continuous, and finite.

▷ **Postulate 2.** To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

If we require that the expectation value of an operator $\hat{A}$ is real, then it follows that $\hat{A}$ must be a Hermitian operator. If the result of a measurement of an operator $\hat{A}$ is the number a, then a must be one of the eigenvalues, $\hat{A}\Psi = a\Psi$, where Ψ is the corresponding eigenfunction. This postulate captures a central point of quantum mechanics – the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states).

▷ **Postulate 3.** If a system is in a state described by a normalized wavefunction Ψ, then the average value of the observable corresponding to $\hat{A}$ is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\mathbf{r}\,.$$

If the system is in an eigenstate of $\hat{A}$ with eigenvalue a, then any measurement of the quantity A will yield a. Although measurements must always yield an eigenvalue, the state does not have to be an eigenstate of $\hat{A}$ initially. An arbitrary state can be expanded in the complete set of eigenvectors of $\hat{A}$ ($\hat{A}\Psi_i = a_i \Psi_i$) as $\Psi = \sum_i^n c_i \Psi_i$, where n may go to infinity. In this case, the probability of obtaining the result a_i from the measurement of $\hat{A}$ is given by $P(a_i) = |\langle \Psi_i | \Psi \rangle|^2 = |c_i|^2$. The expectation value of $\hat{A}$ for the state Ψ is the sum over all possible values of the measurement and given by

$$\langle A \rangle = \sum_i a_i |\langle \Psi_i | \Psi \rangle|^2 = \sum_i a_i |c_i|^2\,.$$

Finally, a measurement of Ψ which leads to the eigenvalue a_i, causes the wavefunction to "collapses" into the corresponding eigenstate Ψ_i. (In the case that a_i is degenerate, then Ψ becomes the projection of Ψ onto the degenerate subspace). Thus, measurement affects the state of the system.

▷ **Postulate 4.** The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi(\mathbf{r}, t)\,,$$

where $\hat{H}$ is the Hamiltonian of the system. If Ψ is an eigenstate of $\hat{H}$, it follows that $\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}, 0)e^{-iEt/\hbar}$.

Chapter 2

Quantum mechanics in one dimension

Following the rules of quantum mechanics, we have seen that the state of a quantum particle, subject to a scalar potential $V(\mathbf{r}, t)$, is described by the time-dependent Schrödinger equation,

$$
i\hbar\partial_t\Psi(\mathbf{r}, t) = -\frac{\hbar^2\nabla^2}{2m}\Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t). \qquad (2.1)
$$

As with all second order linear differential equations, if the potential $V(\mathbf{r}, t) = V(\mathbf{r})$ is time-independent, the time-dependence of the wavefunction can be separated from the spatial dependence. Setting $\Psi(\mathbf{r}, t) = T(t)\psi(\mathbf{r})$, and separating the variables, the Schrödinger equation takes the form,

$$
\frac{\left(-\frac{\hbar^2\nabla^2}{2m}\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})\right)}{\psi(\mathbf{r})} = \frac{i\hbar\partial_t T(t)}{T(t)} = \text{const.} = E.
$$

Since we have a function of only $\mathbf{r}$ set equal to a function of only t, they both must equal a constant. In the equation above, we call the constant E (with some knowledge of the outcome). We now have an equation in t set equal to a constant, $i\hbar\partial_t T(t) = ET(t)$, which has a simple general solution, $T(t) = Ce^{-iEt/\hbar}$, where C is some constant. The corresponding equation in $\mathbf{r}$ is then given by the stationary, or **time-independent Schrödinger equation**,

$$
-\frac{\hbar^2\nabla^2}{2m}\psi(x) + V(x)\psi(x) = E\psi(x).
$$

The full time-dependent solution is given by $\Psi(\mathbf{r}, t) = e^{-iEt/\hbar}\psi(\mathbf{r})$ with definite energy, E. Their probability density $|\Psi(\mathbf{r}, t)|^2 = |\psi(\mathbf{r})|^2$ is constant in time – hence they are called stationary states! The operator

$$
\hat{H} = -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r})
$$

defines the **Hamiltonian** and the stationary wave equation can be written as the eigenfunction equation, $\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$, i.e. $\psi(\mathbf{r})$ is an eigenstate of $\hat{H}$ with eigenvalue E.

To explore its properties, we will first review some simple and, hopefully, familiar applications of the equation to one-dimensional systems. In addressing the one-dimensional geometry, we will divide our consideration between potentials, $V(x)$, which leave the particle free (i.e. unbound), and those that bind the particle to some region of space.

2.1 Wave mechanics of unbound particles

2.1.1 Particle flux and conservation of probability

In analogy to the Poynting vector for the electromagnetic field, we may want to know the probability current. For example, for a free particle system, the probability density is uniform over all space, but there is a net flow along the direction of momentum. We can derive an equation showing conservation of probability by differentiating the probability density, $P(x,t) = |\Psi(x,t)|^2$, and using the Schrödinger equation, $\partial_t P(x,t) + \partial_x j(x,t) = 0$. This translates to the usual conservation equation if $j(x,t)$ is identified as the probability current,

$$j(x,t) = -\frac{i\hbar}{2m} \left[\Psi^* \partial_x \Psi - \Psi \partial_x \Psi^* \right] . \qquad (2.2)$$

If we integrate over some interval in x, $\int_a^b \partial_t P(x,t) dx = -\int_a^b \partial_x j(x,t) dx$ it follows that $\partial_t \int_a^b P(x,t) dx = j(x=a,t) - j(x=b,t)$, i.e. the rate of change of probability is equal to the net flux entering the interval.

To extending this analysis to three space dimensions, we use the general form of the continuity equation, $\partial_t P(\mathbf{r},t) + \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0$, from which follows the particle flux,

$$\mathbf{j}(\mathbf{r},t) = -\frac{i\hbar}{2m} \left[\Psi^*(\mathbf{r},t) \nabla \Psi(\mathbf{r},t) - \Psi(\mathbf{r},t) \nabla \Psi^*(\mathbf{r},t) \right] . \qquad (2.3)$$

2.1.2 Free particle

In the absence of an external potential, the time-dependent Schrödinger equation (2.1) describes the propagation of travelling waves. In one dimension, the corresponding complex wavefunction has the form

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

where A is the amplitude, and $E(k) = \hbar\omega(k) = \frac{\hbar^2 k^2}{2m}$ represents the free particle energy dispersion for a non-relativistic particle of mass, m, and wavevector $k = 2\pi/\lambda$ with λ the wavelength. Each wavefunction describes a plane wave in which the particle has definite energy $E(k)$ and, in accordance with the de Broglie relation, momentum $p = \hbar k = h/\lambda$. The energy spectrum of a freely-moving particle is therefore continuous, extending from zero to infinity and, apart from the spatially constant state $k = 0$, has a two-fold degeneracy corresponding to right and left moving particles.

For an infinite system, it makes no sense to fix the amplitude A by the normalization of the total probability. Instead, it is useful to fix the flux associated with the wavefunction. Making use of Eq. (2.2) for the particle current, the plane wave is associated with a constant (time-independent) flux,

$$j(x,t) = -\frac{i\hbar}{2m} \left(\Psi^* \partial_x \Psi - \text{c.c.} \right) = |A|^2 \frac{\hbar k}{m} = |A|^2 \frac{p}{m} .$$

For a given value of the flux j, the amplitude is given, up to an arbitrary constant phase, by $A = \sqrt{mj/\hbar k}$.

To prepare a **wave packet** which is localized to a region of space, we must superpose components of different wave number. In an open system, this may be achieved using a Fourier expansion. For any function,[1] $\psi(x)$, we have the

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[1]More precisely, we can make such an expansion providing we meet some rather weak conditions of smoothness and differentiability of $\psi(x)$ – conditions met naturally by problems which derive from physical systems!
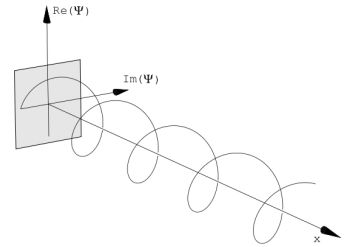
Fourier decomposition,[2]

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k)\, e^{ikx} dk \, ,$$

where the coefficients are defined by the inverse transform,

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x)\, e^{-ikx} dx \, .$$

The normalization of $\psi(k)$ follows automatically from the normalization of $\psi(x)$, $\int_{-\infty}^{\infty} \psi^*(k)\psi(k)dk = \int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1$, and both can represent probability amplitudes. Applied to a wavefunction, $\psi(x)$ can be understood as a wave packet made up of contributions involving definite momentum states, e^{ikx}, with amplitude set by the Fourier coefficient $\psi(k)$. The probability for a particle to be found in a region of width dx around some value of x is given by $|\psi(x)|^2 dx$. Similarly, the probability for a particle to have wave number k in a region of width dk around some value of k is given by $|\psi(k)|^2 dk$. (Remember that $p = \hbar k$ so the momentum distribution is very closely related. Here, for economy of notation, we work with k.)

The Fourier transform of a normalized Gaussian wave packet, $\psi(k) = (\frac{2\alpha}{\pi})^{1/4} e^{-\alpha(k-k_0)^2}$, is also a Gaussian (exercise),

$$\psi(x) = \left(\frac{1}{2\pi\alpha}\right)^{1/4} e^{ik_0 x} e^{-\frac{x^2}{4\alpha}} \, .$$

From these representations, we can see that it is possible to represent a *single* particle, localized in real space as a superposition of plane wave states localized in Fourier space. But note that, while we have achieved our goal of finding localized wave packets, this has been at the expense of having some non-zero width in x and in k.

For the Gaussian wave packet, we can straightforwardly obtain the width (as measured by the root mean square – RMS) of the probability distribution, $\Delta x = (\langle (x - \langle x \rangle)^2 \rangle)^{1/2} \equiv (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} = \sqrt{\alpha}$, and $\Delta k = \frac{1}{\sqrt{4\alpha}}$. We can again see that, as we vary the width in k-space, the width in x-space varies to keep the following product constant, $\Delta x \Delta k = \frac{1}{2}$. If we translate from the wavevector into momentum $p = \hbar k$, then $\Delta p = \hbar \Delta k$ and

$$\Delta p\, \Delta x = \frac{\hbar}{2} \, .$$

If we consider the width of the distribution as a measure of the "uncertainty", we will prove in section (3.1.3) that the Gaussian wave packet provides the minimum uncertainty. This result shows that we cannot know the position of a particle and its momentum at the same time. If we try to localize a particle to a very small region of space, its momentum becomes uncertain. If we try to make a particle with a definite momentum, its probability distribution spreads out over space.

With this introduction, we now turn to consider the interaction of a particle with a non-uniform potential background. For non-confining potentials, such systems fall into the class of **scattering problems**: For a beam of particles incident on a non-uniform potential, what fraction of the particles are transmitted and what fraction are reflected? In the one-dimensional system,

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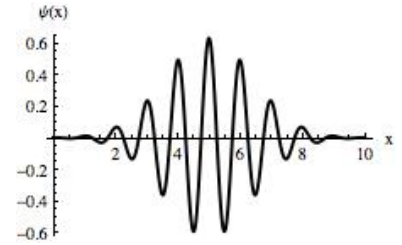
[2]Here we will adopt an economy of notation using the same symbol ψ to denote the wavefunction and its Fourier coefficients. Their identity will be disclosed by their argument and context.

the classical counterpart of this problem is trivial: For particle energies which exceed the maximum potential, all particles are eventually transmitted, while for energies which are lower, all particles are reflected. In quantum mechanics, the situation is richer: For a generic potential of finite extent and height, some particles are always reflected and some are always transmitted. Later in the course we will consider the general problem of scattering from a localized potential in arbitrary dimension. But for now, we will focus on the one-dimensional system, where many of the key concepts can be formulated.

2.1.3 Potential step

As we have seen, for a time-independent potential, the wavefunction can be factorized as $\Psi(x, t) = e^{-iEt/\hbar}\psi(x)$, where $\psi(x)$ is obtained from the stationary form of the Schrödinger equation,

$$\left[-\frac{\hbar^2 \partial_x^2}{2m} + V(x) \right] \psi(x) = E\psi(x),$$

and E denotes the energy of the particle. As $|\Psi(x, t)|^2$ represents a probability density, it must be everywhere finite. As a result, we can deduce that the wavefunction, $\psi(x)$, is also finite. Moreover, since E and $V(x)$ are presumed finite, so must be $\partial_x^2 \psi(x)$. The latter condition implies that

▷ both $\psi(x)$ and $\partial_x \psi(x)$ must be continuous functions of x, even if V has a discontinuity.

Consider then the influence of a potential step (see figure) on the propagation of a beam of particles. Specifically, let us assume that a beam of particles with kinetic energy, E, moving from left to right are incident upon a potential step of height V_0 at position $x = 0$. If the beam has unit amplitude, the reflected and transmitted (complex) amplitudes are set by r and t. The corresponding wavefunction is given by

$$\begin{aligned} \psi_<(x) &= e^{ik_< x} + r e^{-ik_< x} \quad &x < 0 \\ \psi_>(x) &= t e^{ik_> x} \quad &x > 0 \end{aligned}$$

where $k_< = \sqrt{\frac{2mE}{\hbar^2}}$ and $k_> = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$. Applying the continuity conditions on ψ and $\partial_x \psi$ at the step $(x = 0)$, one obtains the relations $1 + r = t$ and $ik_<(1 - r) = ik_> t$ leading to the reflection and transmission amplitudes,

$$r = \frac{k_< - k_>}{k_< + k_>}, \qquad t = \frac{2k_<}{k_< + k_>}.$$

The reflectivity, R, and transmittivity, T, are defined by the ratios,

$$R = \frac{\text{reflected flux}}{\text{incident flux}}, \qquad T = \frac{\text{transmitted flux}}{\text{incident flux}}.$$

With the incident, reflected, and transmitted fluxes given by $|A|^2 \frac{\hbar k_<}{m}$, $|Ar|^2 \frac{\hbar k_<}{m}$, and $|At|^2 \frac{\hbar k_>}{m}$ respectively, one obtains

$$R = \left| \frac{k_< - k_>}{k_< + k_>} \right|^2 = |r|^2, \qquad T = \left| \frac{2k_<}{k_< + k_>} \right|^2 \frac{k_>}{k_<} = |t|^2 \frac{k_>}{k_<} = \frac{4k_< k_>}{(k_< + k_>)^2}.$$

From these results one can confirm that the total flux is, as expected, conserved in the scattering process, i.e. $R + T = 1$.

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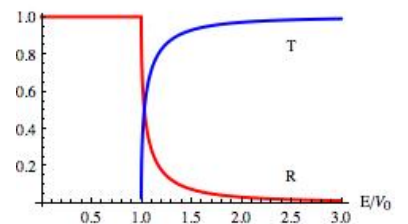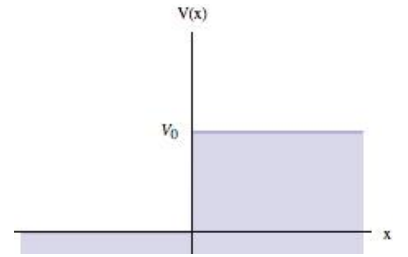
▷ EXERCISE. While $E - V_0$ remains positive, show that the beam is able to propagate across the potential step (see figure). Show that the fraction of the beam that is reflected depends on the relative height of the step while the phase depends on the sign of V_0. In particular, show that for $V_0 > 0$, the reflected beam remains in phase with the incident beam, while for $V_0 < 0$ it is reversed. Finally, when $E - V_0 < 0$, show that the beam is unable to propagate to the right ($R = 1$). Instead show that there is an evanescent decay of the wavefunction into the barrier region with a decay length set by $2\pi\sqrt{\hbar^2/2m(V_0 - E)}$. If $V_0 \to \infty$, show that the system forms a standing wave pattern.

2.1.4 Potential barrier

Having dealt with the potential step, we now turn to consider the problem of a beam of particles incident upon a square potential barrier of height V_0 (presumed positive for now) and width a. As mentioned above, this geometry is particularly important as it includes the simplest example of a scattering phenomenon in which a beam of particles is "deflected" by a local potential. Moreover, this one-dimensional geometry also provides a platform to explore a phenomenon peculiar to quantum mechanics – **quantum tunneling**. For these reasons, we will treat this problem fully and with some care.

Since the barrier is localized to a region of size a, the incident and transmitted wavefunctions have the same functional form, $e^{ik_1 x}$, where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$, and differ only in their complex amplitude, i.e. after the encounter with the barrier, the transmitted wavefunction undergoes only a change of amplitude (some particles are reflected from the barrier, even when the energy of the incident beam, E, is in excess of V_0) and a phase shift. To determine the relative change in amplitude and phase, we can parameterise the wavefunction as

$$\begin{array}{ll} \psi_1(x) = e^{ik_1 x} + re^{-ik_1 x} & x \le 0 \\ \psi_2(x) = Ae^{ik_2 x} + Be^{-ik_2 x} & 0 \le x \le a \\ \psi_3(x) = te^{ik_1 x} & a \le x \end{array}$$

where $k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$. Here, as with the step, r denotes the reflected amplitude and t the transmitted.

Applying the continuity conditions on the wavefunction, ψ, and its derivative, $\partial_x \psi$, at the barrier interfaces at $x = 0$ and $x = a$, one obtains

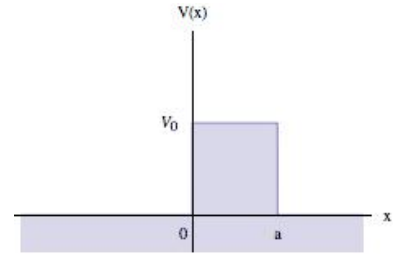$$\begin{cases} 1 + r = A + B \\ Ae^{ik_2 a} + Be^{-ik_2 a} = te^{ik_1 a} \end{cases}, \quad \begin{cases} k_1(1 - r) = k_2(A - B) \\ k_2(Ae^{ik_2 a} - Be^{-ik_2 a}) = k_1 te^{ik_1 a} \end{cases}.$$

Together, these four equations specify the four unknowns, r, t, A and B. Solving, one obtains (exercise)

$$t = \frac{2k_1 k_2 e^{-ik_1 a}}{2k_1 k_2 \cos(k_2 a) - i(k_1^2 + k_2^2)\sin(k_2 a)},$$

translating to a transmissivity of

$$T = |t|^2 = \frac{1}{1 + \frac{1}{4}\left(\frac{k_1}{k_2} - \frac{k_2}{k_1}\right)^2 \sin^2(k_2 a)},$$

Transmission probability of a finite potential barrier for $\sqrt{2mV_0}a/\hbar = 7$. Dashed: classical result. Solid line: quantum mechanics.

and the reflectivity, $R = 1 - T$. As a consistency check, we can see that, when $V_0 = 0$, $k_2 = k_1$ and $t = 1$, as expected. Moreover, T is restricted to the interval from 0 to 1 as required. So, for barrier heights in the range $E > V_0 > 0$,

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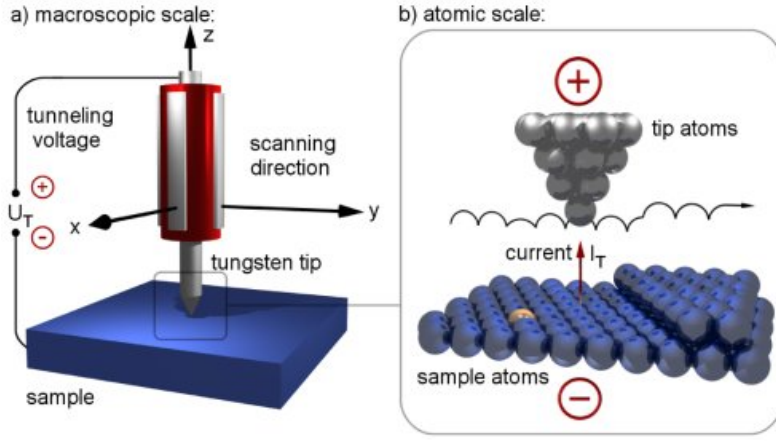
Figure 2.1: Principle of scanning tunneling microscopy: Applying a negative sample voltage yields electron tunneling from occupied states at the surface into unoccupied states of the tip. Keeping the tunneling current constant while scanning the tip over the surface, the tip height follows a contour of constant local density of states.

the transmittivity T shows an oscillatory behaviour with k_2 reaching unity when $k_2 a = n\pi$ with n integer. At these values, there is a conspiracy of interference effects which eliminate altogether the reflected component of the wave leading to perfect transmission. Such a situation arises when the width of the barrier is perfectly matched to an integer or half-integer number of wavelengths inside the barrier.

When the energy of the incident particles falls below the energy of the barrier, $0 < E < V_0$, a classical beam would be completely reflected. However, in the quantum system, particles are able to **tunnel** through the barrier region and escape leading to a non-zero transmission coefficient. In this regime, $k_2 = i\kappa_2$ becomes pure imaginary leading to an evanescent decay of the wavefunction under the barrier and a suppression, but not extinction, of transmission probability,

$$T = |t|^2 = \frac{1}{1 + \frac{1}{4}\left(\frac{k_1}{\kappa_2} + \frac{\kappa_2}{k_1}\right)^2 \sinh^2 \kappa_2 a} .$$

For $\kappa_2 a \gg 1$ (the weak tunneling limit), the transmittivity takes the form

$$T \simeq \frac{16 k_1^2 \kappa_2^2}{(k_1^2 + \kappa_2^2)^2} e^{-2\kappa_2 a} .$$

Finally, on a cautionary note, while the phenomenon of quantum mechanical tunneling is well-established, it is difficult to access in a convincing experimental manner. Although a classical particle with energy $E < V_0$ is unable to penetrate the barrier region, in a physical setting, one is usually concerned with a thermal distribution of particles. In such cases, thermal activation may lead to transmission *over* a barrier. Such processes often overwhelm any contribution from true quantum mechanical tunneling.

Real part of the wavefunction for $E/V_0 = 0.6$ (top), $E/V_0 = 1.6$ (middle), and $E/V_0 = 1 + \pi^2/2$ (bottom), where $mV_0 a^2/\hbar^2 = 1$. In the first case, the system shows tunneling behaviour, while in the third case, $k_2 a = \pi$ and the system shows resonant transmission.

▷ INFO. **Scanning tunneling microscopy (STM)** is a powerful technique for viewing surfaces at the atomic level. Its development in the early eighties earned its inventors, Gerd Binnig and Heinrich Rohrer (at IBM Zürich), the Nobel Prize in Physics in 1986. STM probes the density of states of a material using the tunneling current. In its normal operation, a lateral resolution of 0.1 nm and a depth resolution of 0.01 nm is typical for STM. The STM can be used not only in ultra-high vacuum, but also in air and various other liquid or gas ambients, and at temperatures ranging from near zero kelvin to a few hundred degrees Celsius.

The STM is based on the concept of quantum tunnelling (see Fig. 2.1). When a conducting tip is brought in proximity to a metallic or semiconducting surface, a bias between the two can allow electrons to tunnel through the vacuum between them. For low voltages, this tunneling current is a function of the local density of states at the Fermi level, E_F, of the sample.[3] Variations in current as the probe passes over the surface are translated into an image. STM can be a challenging technique, as it requires extremely clean surfaces and sharp tips.
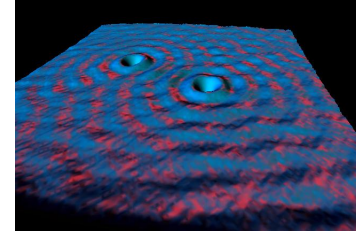
STM image showing two point defects adorning the copper (111) surface. The point defects (possibly impurity atoms) scatter the surface state electrons resulting in circular standing wave patterns.

2.1.5 The rectangular potential well

Finally, if we consider scattering from a potential well (i.e. with $V_0 < 0$), while $E > 0$, we can apply the results of the previous section to find a continuum of unbound states with the corresponding **resonance** behaviour. However, in addition to these unbound states, for $E < 0$ we have the opportunity to find bound states of the potential. It is to this general problem that we now turn.

▷ EXERCISE. Explore the phase dependence of the transmission coefficient in this regime. Consider what happens to the phase as resonances (bound states) of the potential are crossed.

2.2 Wave mechanics of bound particles

In the case of unbound particles, we have seen that the spectrum of states is continuous. However, for bound particles, the wavefunctions satisfying the Schrödinger equation have only particular quantized energies. In the one-dimensional system, we will find that all binding potentials are capable of hosting a bound state, a feature particular to the low dimensional system.

2.2.1 The rectangular potential well (continued)

As a starting point, let us consider a rectangular potential well similar to that discussed above. To make use of symmetry considerations, it is helpful to reposition the potential setting
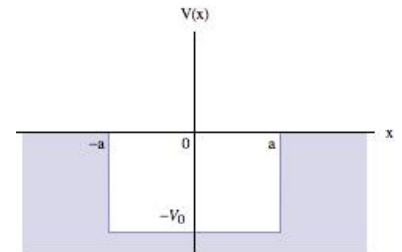
$$V(x) = \begin{cases} 0 & x \leq -a \\ -V_0 & -a \leq x \leq a \\ 0 & a \leq x \end{cases} ,$$

where the potential depth V_0 is assumed positive. In this case, we will look for bound state solutions with energies lying in the range $-V_0 < E < 0$. Since the Hamiltonian is invariant under **parity transformation**, $[\hat{H}, \hat{P}] = 0$ (where $\hat{P}\psi(x) = \psi(-x)$), the eigenstates of the Hamiltonian $\hat{H}$ must also be eigenstates of parity, i.e. we expect the eigenfunctions to separate into those symmetric and those antisymmetric under parity.[4]

For $E < 0$ (bound states), the wavefunction outside the well region must have the form

$$\psi(x < -a) = Ce^{\kappa x}, \qquad \psi(x > a) = De^{-\kappa x},$$

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[3]Although the meaning of the Fermi level will be addressed in more detail in chapter **??**, we mention here that it represents the energy level to which the electron states in a metal are fully-occupied.

[4]Later, in section 3.2, we will discuss the role of symmetries in quantum mechanics.

with $\kappa = \sqrt{-\frac{2mE}{\hbar^2}}$ while in the central well region, the general solution is of the form

$$\psi(-a < x < a) = A\cos(kx) + B\sin(kx),$$

where $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$. Once again we have four equations in four unknowns. The calculation shows that either A or B must be zero for a solution. This means that the states separate into solutions with even or odd parity.

For the even states, the solution of the equations leads to the quantization condition, $\kappa = \tan(ka)k$, while for the odd states, we find $\kappa = -\cot(ka)k$. These are transcendental equations, and must be solved numerically. The figure (right) compares $\kappa a = \left(\frac{2mV_0 a^2}{\hbar^2} - (ka)^2\right)^{1/2}$ with $ka\tan(ka)$ for the even states and to $-ka\cot(ka)$ for the odd states. Where the curves intersect, we have an allowed energy. From the structure of these equations, it is evident that an even state solution can always be found for arbitrarily small values of the binding potential V_0 while, for odd states, bound states appear only at a critical value of the coupling strength. The wider and deeper the well, the more solutions are generated.

Comparison of $\kappa a = \left(\frac{2mV_0 a^2}{\hbar^2} - (ka)^2\right)^{1/2}$ with $ka\tan(ka)$ and $-ka\cot(ka)$ for $\frac{2mV_0 a^2}{\hbar^2} = 14$. For this potential, there are a total of three solutions labelled A, B and C. Note that, from the geometry of the curves, there is always a bound state no matter how small is the potential V_0.

▷ EXERCISE. Determine the pressure exerted on the walls of a rectangular potential well by a particle inside.

2.2.2 The δ-function potential well

Let us now consider perhaps the simplest binding potential, the δ-function, $V(x) = -aV_0\delta(x)$. Here the parameter 'a' denotes some microscopic length scale introduced to make the product $a\delta(x)$ dimensionless.[5] For a state to be bound, its energy must be negative. Moreover, the form of the potential demands that the wavefunction is symmetric under parity, $x \to -x$. (A wavefunction which was antisymmetric must have $\psi(0) = 0$ and so could not be influenced by the δ-function potential.) We therefore look for a solution of the form

$$\psi(x) = A \begin{cases} e^{\kappa x} & x < 0 \\ e^{-\kappa x} & x > 0 \end{cases},$$

where $\kappa = \sqrt{-2mE/\hbar^2}$. With this choice, the wavefunction remains everywhere continuous including at the potential, $x = 0$. Integrating the stationary form of the Schrödinger equation across an infinitesimal interval that spans the region of the δ-function potential, we find that

$$\partial_x\psi|_{+\epsilon} - \partial_x\psi|_{-\epsilon} = -\frac{2maV_0}{\hbar^2}\psi(0).$$

From this result, we obtain that $\kappa = maV_0/\hbar^2$, leading to the bound state energy

$$E = -\frac{ma^2V_0^2}{2\hbar^2}.$$

Indeed, the solution is unique. An attractive δ-function potential hosts only one bound state.

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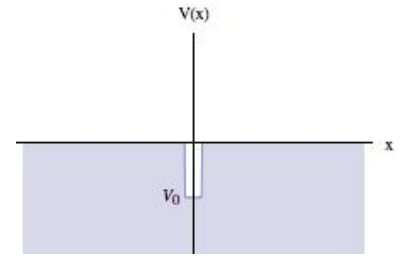
[5]Note that the dimensions of $\delta(x)$ are $[\text{Length}^{-1}]$.

▷ EXERCISE. Explore the bound state properties of the "molecular" binding potential $V(x) = -aV_0[\delta(x+d)+\delta(x-d)]$. Show that it consists of two bound states, one bonding (nodeless) and one anti-bonding (single node). How does the energy of the latter compare with two isolated δ-function potential wells?

2.2.3 INFO: **The δ-function model of a crystal**

Finally, as our last example of a one-dimensional quantum system, let us consider a particle moving in a periodic potential. The **Kronig-Penney model** provides a caricature of a (one-dimensional) crystalline lattice potential. The potential created by the ions is approximated as an infinite array of potential wells defined by a set of repulsive δ-function potentials,

$$V(x) = aV_0 \sum_{n=-\infty}^{\infty} \delta(x - na).$$

Since the potential is repulsive, it is evident that all states have energy $E > 0$. This potential has a new symmetry; a translation by the lattice spacing a leaves the potential unchanged, $V(x+a) = V(x)$. The probability density must therefore exhibit the same translational symmetry,

$$|\psi(x + a)|^2 = |\psi(x)|^2,$$

which means that, under translation, the wavefunction differs by at most a phase, $\psi(x + a) = e^{i\phi}\psi(x)$. In the region from $(n - 1)a < x < na$, the general solution of the Schrödinger equation is plane wave like and can be written in the form,

$$\psi_n(x) = A_n \sin[k(x - na)] + B_n \cos[k(x - na)],$$

where $k = \sqrt{2mE/\hbar^2}$ and, following the constraint on translational invariance, $A_{n+1} = e^{i\phi}A_n$ and $B_{n+1} = e^{i\phi}B_n$. By applying the boundary conditions, one can derive a constraint on k similar to the quantized energies for bound states considered above.

Consider the boundary conditions at position $x = na$. Continuity of the wavefunction, $\psi_n|_{x=na} = \psi_{n+1}|_{x=na}$, translates to the condition, $B_n = A_{n+1}\sin(-ka) + B_{n+1}\cos(-ka)$ or

$$B_{n+1} = \frac{B_n + A_{n+1}\sin(ka)}{\cos(ka)}.$$

Similarly, the discontinuity in the first derivative, $\partial_x\psi_{n+1}|_{x=na} - \partial_x\psi_n|_{na} = \frac{2maV_0}{\hbar^2}\psi_n(na)$, leads to the condition, $k[A_{n+1}\cos(ka) + B_{n+1}\sin(ka) - A_n] = \frac{2maV_0}{\hbar^2}B_n$. Substituting the expression for B_{n+1} and rearranging, one obtains

$$A_{n+1} = \frac{2maV_0}{\hbar^2 k}B_n \cos(ka) - B_n \sin(ka) + A_n \cos(ka).$$

Similarly, replacing the expression for A_{n+1} in that for B_{n+1}, one obtains the parallel equation,

$$B_{n+1} = \frac{2maV_0}{\hbar^2 k}B_n \sin(ka) + B_n \cos(ka) + A_n \sin(ka).$$

With these two equations, and the relations $A_{n+1} = e^{i\phi}A_n$ and $B_{n+1} = e^{i\phi}B_n$, we obtain the quantization condition,[6]

$$\boxed{\cos\phi = \cos(ka) + \frac{maV_0}{\hbar^2 k}\sin(ka).}$$

As $\hbar k = \sqrt{2mE}$, this result relates the allowed values of energy to the real parameter,

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[6]Eliminating A_n and B_n from the equations, a sequence of cancellations obtains

$$e^{2i\phi} - e^{i\phi}\left(\frac{2maV_0}{\hbar^2 k}\sin(ka) + 2\cos(ka)\right) + 1 = 0.$$

Then multiplying by $e^{-i\phi}$, we obtain the expression for $\cos\phi$.

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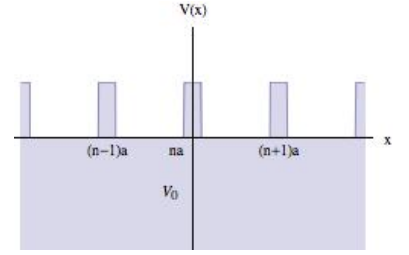
Figure 2.2: Solid line shows the variation of $\cos\phi$ with ka over a range from -1 to 1 for $V_0 = 2$ and $ma^2\hbar^2 = 1$. The blue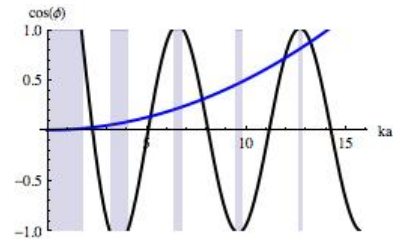 line shows $0.01 \times E = (\hbar k)^2/2m$. The shaded region represents values of k and energy for which there is no solution.

ϕ. Since $\cos\phi$ can only take values between -1 and 1, there are a sequence of allowed **bands** of energy with energy gaps separating these bands (see Fig. 2.2).

Such behaviour is characteristic of the spectrum of periodic lattices: In the periodic system, the wavefunctions – known as **Bloch states** – are indexed by a "quasi"-momentum index k, and a band index n where each Bloch band is separated by an energy gap within which there are no allowed states. In a **metal**, electrons (fermions) populate the energy states starting with the lowest energy up to some energy scale known as the **Fermi energy**. For a partially-filled band, low-lying excitations associated with the continuum of states allow electrons to be accelerated by a weak electric field. In a **band insulator**, all states are filled up to an energy gap. In this case, a small electric field is unable to excite electrons across the energy gap – hence the system remains insulating.

$\triangleright$ EXERCISE. In the Kronig-Penney model above, we took the potential to be repulsive. Consider what happens if the potential is attractive when we also have to consider the fate of the states that were bound for the single δ-function potential. In this case, you will find that the methodology and conclusions mirror the results of the repulsive potential: all states remain extended and the continuum of states exhibits a sequence of band gaps controlled by similar sets of equations.

2.3 Wentzel, Kramers and Brillouin (WKB) method

The WKB (or Wentzel, Kramers and Brillouin) approximation describes a "quasi-classical" method for solving the one-dimensional time-independent Schrödinger equation. Note that the consideration of one-dimensional systems is less restrictive that it may sound as many symmetrical higher-dimensional problems are rendered effectively one-dimensional (e.g. the radial equation for the hydrogen atom). The WKB method is named after physicists Wentzel, Kramers and Brillouin, who all developed the approach independently in 1926.[7] Earlier, in 1923, the mathematician Harold Jeffreys had developed a general method of approximating the general class of linear, second-order differential equations, which of course includes the Schrödinger equation.[8] But since the Schrödinger equation was developed two years later, and Wentzel, Kramers, and Brillouin were apparently unaware of this earlier work, the contribution of Jeffreys is often neglected.

The WKB method is important both as a practical means of approximating solutions to the Schrödinger equation, and also as a conceptual framework for understanding the classical limit of quantum mechanics. The WKB approximation is valid whenever the wavelength, λ, is small in comparison to other relevant length scales in the problem. This condition is not restricted to quantum mechanics, but rather can be applied to any wave-like system (such as fluids, electromagnetic waves, etc.), where it leads to approximation schemes which are mathematically very similar to the WKB method in quantum mechanics. For example, in optics the approach is called the **eikonal method**, and in general the method is referred to as **short wavelength asymptotics**. Whatever the name, the method is an old one, which predates

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[7]L. Brillouin, (1926). "La mécanique ondulatoire de Schrödinger: une méthode générale de resolution par approximations successives", Comptes Rendus de l'Academie des Sciences **183**: 24–26; H. A. Kramers, (1926). "Wellenmechanik und halbzählige Quantisierung", Z. Phys. **39**: 828–840; G. Wentzel (1926). "Eine Verallgemeinerung der Quantenbedingungen für die Zwecke der Wellenmechanik". Z. Phys. **38**: 518–529.

[8]H. Jeffreys, (1924). "On certain approximate solutions of linear differential equations of the second order", Proc. Lon. Math. Soc. **23**: 428–436.

quantum mechanics – indeed, it was apparently first used by Liouville and Green in the first half of the nineteenth century. In quantum mechanics, λ is interpreted as the de Broglie wavelength, and L is normally the length scale of the potential. Thus, the WKB method is valid if the wavefunction oscillates many times before the potential energy changes significantly.

2.3.1 Semi-classical approximation to leading order

Consider then the propagation of a quantum particle in a slowly-varying one-dimensional potential, $V(x)$. Here, by "slowly-varying" we mean that, in any small region the wavefunction is well-approximated by a plane wave, and that the wavelength only changes over distances that are long compared with the local value of the wavelength. We're also assuming for the moment that the particle has positive kinetic energy in the region. Under these conditions, we can anticipate that the solution to the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\partial_x^2\psi(x) + V(x)\psi(x) = E\psi(x)\,,$$

will take the form $A(x)e^{\pm ip(x)x/\hbar}$ where $p(x)$ is the "local" value of the momentum set by the classical value, $p^2/2m + V(x) = E$, and the amplitude, $A(x)$, is slowly-varying compared with the phase factor. Clearly this is a *semi-classical* limit: $\hbar$ has to be sufficiently small that there are many oscillations in the typical distance over which the potential varies.[9]

To develop this idea more rigorously, and to emphasize the rapid *phase* variation in the semi-classical limit, we can parameterize the wavefunction as

$$\psi(x) = e^{i\sigma(x)/\hbar}\,.$$

Here the complex function $\sigma(x)$ encompasses both the amplitude and phase. Then, with $-\hbar^2\partial_x^2\psi(x) = -i\hbar e^{i\sigma(x)/\hbar}\partial_x^2\sigma(x) + e^{i\sigma(x)/\hbar}(\partial_x\sigma)^2$, the Schrödinger equation may be rewritten in terms of the phase function as

$$-i\hbar\partial_x^2\sigma(x) + (\partial_x\sigma)^2 = p^2(x)\,. \tag{2.4}$$

Now, since we're assuming the system is semi-classical, it makes sense to expand $\sigma(x)$ as a power series in $\hbar$, setting

$$\sigma = \sigma_0 + (\hbar/i)\sigma_1 + (\hbar/i)^2\sigma_2 + \cdots\,.$$

At the leading (zeroth) order of the expansion, we can drop the first term in (2.4), leading to $(\partial_x\sigma_0)^2 = p^2(x)$. Defining $p(x) = +\sqrt{2m(E - V(x))}$, this equation permits the two solutions $\partial_x\sigma_0 = \pm p(x)$, from which we conclude

$$\sigma_0(x) = \pm\int^x p(x')dx'\,.$$

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[9]To avoid any point of confusion, it is of course true that $\hbar$ is a fundamental constant – not easily adjusted! So what do we mean when we say that the semi-classical limit translates to $\hbar \to 0$? The validity of the semi-classical approximation relies upon $\lambda/L \ll 1$. Following the de Broglie relation, we may write this inequality as $h/pL \ll 1$, where p denotes the particle momentum. Now, in this correspondence, both p and L can be considered as "classical" scales. So, formally, we can think of accessing the semi-classical limit by adjusting $\hbar$ so that it is small enough to fulfil this inequality. Alternatively, at fixed $\hbar$, we can access the semi-classical regime by reaching to higher and higher energy scales (larger and larger p) so that the inequality becomes valid.

From the form of the Schrödinger equation (2.4), it is evident that this approximate solution is only valid if we can ignore the first term. More precisely, we must have

$$\left| \frac{\hbar \partial_x^2 \sigma(x)}{(\partial_x \sigma(x))^2} \right| \equiv |\partial_x (\hbar / \partial_x \sigma)| \ll 1 \,.$$

But, in the leading approximation, $\partial_x \sigma \simeq p(x)$ and $p(x) = 2\pi \hbar / \lambda(x)$, so the condition translates to the relation

$$\frac{1}{2\pi} |\partial_x \lambda(x)| \ll 1 \,.$$

This means that the change in wavelength over a distance of one wavelength must be small. This condition can not always be met: In particular, if the particle is confined by an attractive potential, at the edge of the classically allowed region, where $E = V(x)$, $p(x)$ must be zero and the corresponding wavelength infinite. The approximation is only valid well away from these **classical turning points**, a matter to which we will return shortly.

2.3.2 Next to leading order correction

Let us now turn to the next term in the expansion in $\hbar$. Retaining terms from Eq. (2.4) which are of order $\hbar$, we have

$$-i\hbar \partial_x^2 \sigma_0 + 2\partial_x \sigma_0 (\hbar / i) \partial_x \sigma_1 = 0 \,.$$

Rearranging this equation, and integrating, we find

$$\partial_x \sigma_1 = -\frac{\partial_x^2 \sigma_0}{2\partial_x \sigma_0} = -\frac{\partial_x p}{2p} \,, \qquad \sigma_1(x) = -\frac{1}{2} \ln p(x) + \text{const.} \,.$$

So, to this order of approximation, the wavefunction takes the form,

$$\psi(x) = \frac{C_1}{\sqrt{p(x)}} e^{(i/\hbar) \int^x p \, dx'} + \frac{C_2}{\sqrt{p(x)}} e^{-(i/\hbar) \int^x p \, dx'} \,, \tag{2.5}$$

where C_1 and C_2 denote constants of integration.

To interpret the factors of $\sqrt{p(x)}$, consider the first term: a wave moving to the right. Since $p(x)$ is real (remember we are currently considering the classically allowed region where $E > V(x)$), the exponential has modulus unity, and the local probability density is proportional to $1/p(x)$, i.e. to $1/v(x)$, where $v(x)$ denotes the velocity of the particle. This dependence has a simple physical interpretation: The probability of finding the particle in any given small interval is proportional to the time it spends there. Hence it is inversely proportional to its speed.

We turn now to consider the wavefunction in the classically forbidden region where

$$\frac{p^2(x)}{2m} = E - V(x) < 0 \,.$$

Here $p(x)$ is of course pure imaginary, but the same formal phase solution of the Schrödinger equation applies provided, again, that the particle is remote from the classical turning points where $E = V(x)$. In this region, the wavefunction takes the general form,

$$\psi(x) = \frac{C_1'}{\sqrt{|p(x)|}} e^{-(1/\hbar) \int |p| \, dx'} + \frac{C_2'}{\sqrt{|p(x)|}} e^{(1/\hbar) \int |p| \, dx'} \,. \tag{2.6}$$

This completes our study of the wavefunction in the regions in which the semi-classical approach can be formally justified. However, to make use of this approximation, we have to understand how to deal with the regions close to the classical turning points. Remember that in our treatment of the Schrödinger equation the energy quantization derived from the implementation of boundary conditions.

2.3.3 Connection formulae, boundary conditions and quantization rules

Let us assume that we are dealing with a one-dimensional confining potential where the classically allowed region is unique and spans the interval $b \leq x \leq a$. Clearly, in the classically forbidden region to the right, $x > a$, only the first term in Eq. (2.6) remains convergent and can contribute, while for $x < b$ it is only the second term that contributes. Moreover, in the classically allowed region, $b \leq x \leq a$, the wavefunction has the oscillating form (2.5).

But how do we connect the three regions together? To answer this question, it is necessary to make the assumption that the potential varies sufficiently smoothly that it is a good approximation to take it to be linear in the vicinity of the classical turning points. That is to say, we assume that a linear potential is a sufficiently good approximation out to the point where the short wavelength (or decay length for tunneling regions) description is adequate. Therefore, near the classical turning at $x = a$, we take the potential to be

$$E - V(x) \simeq F_0(x - a),$$

where F_0 denotes the (constant) force. For a strictly linear potential, the wavefunction can be determined analytically, and takes the form of an Airy function.[10] In particular, it is known that the Airy function to the right of the classical turning point has the asymptotic form

$$\lim_{x \gg a} \psi(x) = \frac{C}{2\sqrt{|p(x)|}} e^{-(1/\hbar) \int_a^x |p| \, dx'},$$

translating to a decay into the classically forbidden region while, to the left, it has the asymptotic oscillatory solution,

$$\lim_{b \ll x < a} \psi(x) = \frac{C}{\sqrt{|p(x)|}} \cos\left[\frac{1}{\hbar} \int_x^a p \, dx' - \frac{\pi}{4}\right] \equiv \frac{C}{\sqrt{|p(x)|}} \cos\left[\frac{\pi}{4} - \frac{1}{\hbar} \int_x^a p \, dx'\right].$$

At the second classical turning point at $x = b$, the same argument gives

$$\lim_{b < x \ll a} \psi(x) = \frac{C'}{\sqrt{|p(x)|}} \cos\left[\frac{1}{\hbar} \int_b^x p \, dx' - \frac{\pi}{4}\right].$$

For these two expressions to be consistent, we must have $C' = \pm C$ and

$$\left(\frac{1}{\hbar} \int_b^x p(x') \, dx' - \frac{\pi}{4}\right) - \left(\frac{\pi}{4} - \frac{1}{\hbar} \int_x^a p(x') \, dx'\right) = n\pi,$$

where, for n even, $C' = C$ and for n odd, $C' = -C$. Therefore, we have the condition $\frac{1}{\hbar} \int_b^a p(x) \, dx = (n + 1/2)\pi$, or when cast in terms of a complete periodic cycle of the classical motion,

$$\boxed{\oint p(x) \, dx = 2\pi\hbar(n + 1/2).}$$

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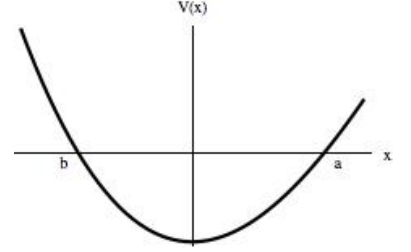
[10]For a detailed discussion in the present context, we refer to the text by Landau and Lifshitz.

This is just the **Bohr-Sommerfeld quantization condition**, and n can be interpreted as the number of nodes of the wavefunction.

▷ INFO. Note that the integrated action, $\oint p\,dx$, represents the area of the classical path in phase space. This shows that each state is associated with an element of phase space $2\pi\hbar$. From this, we can deduce the approximate energy splitting between levels in the semi-classical limit: The change in the integral with energy ΔE corresponding to one level must be $2\pi\hbar$ – one more state and one more node, i.e. $\Delta E\,\partial_E \oint p\,dx = 2\pi\hbar$. Now $\partial_p E = v$, so $\oint \partial_E p\,dx = \oint dx/v = T$, the period of the orbit. Therefore, $\Delta E = 2\pi\hbar/T = \hbar\omega$: In the semi-classical limit, if a particle emits one photon and drops to the next level, the frequency of the photon emitted is just the orbital frequency of the particle.

▷ EXAMPLE: For the **quantum harmonic oscillator**, $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = E$, the classical momentum is given by

$$p(x) = \sqrt{2m\left(E - \frac{m\omega^2 x^2}{2}\right)}.$$

The classical turning points are set by $E = m\omega^2 x_0^2/2$, i.e. $x_0 = \pm 2E/m\omega^2$. Over a periodic cycle, the classical action is given by

$$\oint p(x)dx = 2\int_{-x_0}^{x_0} dx\sqrt{2m\left(E - \frac{m\omega^2 x^2}{2}\right)} = 2\pi\frac{E}{\omega}.$$

The WKB wavefunction (dashed) and the exact wavefunction (solid) for the $n = 0$ and $n = 10$ states of the quantum harmonic oscillator.

According to the WKB method, the latter must be equated to $2\pi\hbar(n + 1/2)$, with the last term reflecting the two turning points. As a result, we find that the energy levels are as expected specified by $E_n = (n + 1/2)\hbar\omega$.

In the WKB approximation, the corresponding wavefunctions are given by

$$\psi(x) = \frac{C}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int_{-x_0}^{x} p(x')dx' - \frac{\pi}{4}\right)$$

$$= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{2\pi}{4}(n + 1/2) + \frac{1}{\hbar}\int_{0}^{x} p(x')dx' - \frac{\pi}{4}\right)$$

$$= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{n\pi}{2} + \frac{E}{\hbar\omega}\left[\arcsin\left(\frac{x}{x_0}\right) + \frac{x}{x_0}\sqrt{1 - \frac{x^2}{x_0^2}}\right]\right),$$

for $0 < x < x_0$ and

$$\psi(x) = \frac{C}{2\sqrt{p(x)}}\exp\left(-\frac{E}{\hbar\omega}\left[\frac{x}{x_0}\sqrt{\frac{x^2}{x_0^2} - 1} - \operatorname{arccosh}\left(\frac{x}{x_0}\right)\right]\right).$$

for $x > a$. Note that the failure of the WKB approximation is reflected in the appearance of discontinuities in the wavefunction at the classical turning points (see figures). Nevertheless, the wavefunction at high energies provides a strikingly good approximation to the exact wavefunction.

▷ EXAMPLE: Consider the problem of **quantum tunneling**. Suppose that a beam of particles is incident upon a localized potential barrier, $V(x)$. Further, let us assume that, over a single continuous region of space, from b to a, the potential rises above the incident energy of the incoming particles so that, classically, all particles would be reflected. In the quantum system, the some particles incident from the left may tunnel through the barrier and continue propagating to the right. We are interested in finding the transmission probability.

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From the WKB solution, to the left of the barrier (region 1), we expect a wavefunction of the form

$$\psi_1(x) = \frac{1}{\sqrt{p}} \exp\left[\frac{i}{\hbar} \int_b^x p\, dx'\right] + r(E)\frac{1}{\sqrt{p}} \exp\left[-\frac{i}{\hbar} \int_b^x p\, dx'\right],$$

with $p(E) = \sqrt{2m(E - V(x))}$, while, to the right of the barrier (region 3), the wavefunction is given by

$$\psi_3(x) = t(E)\frac{1}{\sqrt{p}} \exp\left[\frac{i}{\hbar} \int_a^x p\, dx'\right].$$

In the barrier region, the wavefunction is given by

$$\psi_2(x) = \frac{C_1}{\sqrt{|p(x)|}} \exp\left[-\frac{1}{\hbar} \int_a^x |p|\, dx'\right] + \frac{C_2}{\sqrt{|p(x)|}} \exp\left[\frac{1}{\hbar} \int_a^x |p|\, dx'\right].$$

Applying the matching conditions on the wavefunction at the classical turning points, one obtains the transmissivity,

$$\boxed{T(E) \simeq \exp\left[-\frac{2}{\hbar} \int_a^b |p|\, dx\right].}$$

▷ INFO. For a particle strictly confined to one dimension, the connection formulae can be understood within a simple picture: The wavefunction "spills over" into the classically forbidden region, and its twisting there collects an $\pi/4$ of phase change. So, in the lowest state, the total phase change in the classically allowed region need only be $\pi/2$. For the **radial equation**, assuming that the potential is well behaved at the origin, the wavefunction goes to zero there. A bound state will still spill over beyond the classical turning point at r_0, say, but clearly there must be a total phase change of $3\pi/4$ in the allowed region for the lowest state, since there can be no spill over to negative r. In this case, the general quantization formula will be

$$\frac{1}{\hbar} \int_0^{r_0} p(r)\, dr = (n + 3/4)\pi, \qquad n = 0, 1, 2, \cdots,$$

with the series terminating if and when the turning point reaches infinity. In fact, some potentials, including the Coulomb potential and the centrifugal barrier for $\ell \neq 0$, are in fact singular at $r = 0$. These cases require special treatment.

Chapter 3

Operator methods in quantum mechanics

While the wave mechanical formulation has proved successful in describing the quantum mechanics of bound and unbound particles, some properties can not be represented through a wave-like description. For example, the electron spin degree of freedom does not translate to the action of a gradient operator. It is therefore useful to reformulate quantum mechanics in a framework that involves only operators.

Before discussing properties of operators, it is helpful to introduce a further simplification of notation. One advantage of the operator algebra is that it does not rely upon a particular basis. For example, when one writes $\hat{H} = \frac{\hat{p}^2}{2m}$, where the hat denotes an operator, we can equally represent the momentum operator in the spatial coordinate basis, when it is described by the differential operator, $\hat{p} = -i\hbar\partial_x$, or in the momentum basis, when it is just a number $\hat{p} = p$. Similarly, it would be useful to work with a basis for the wavefunction which is coordinate independent. Such a representation was developed by Dirac early in the formulation of quantum mechanics.

In the parlons of mathematics, square integrable functions (such as wavefunctions) are said form a vector space, much like the familiar three-dimensional vector spaces. In the **Dirac notation**, a state vector or wavefunction, ψ, is represented as a "ket", $|\psi\rangle$. Just as we can express any three-dimensional vector in terms of the basis vectors, $\mathbf{r} = x\hat{\mathbf{e}}_1 + y\hat{\mathbf{e}}_2 + z\hat{\mathbf{e}}_3$, so we can expand any wavefunction as a superposition of basis state vectors,

$$|\psi\rangle = \lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle + \cdots .$$

Alongside the ket, we can define the "bra", $\langle\psi|$. Together, the bra and ket define the **scalar product**

$$\langle\phi|\psi\rangle \equiv \int_{-\infty}^{\infty} dx\, \phi^*(x)\psi(x)\,,$$

from which follows the identity, $\langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle$. In this formulation, the real space representation of the wavefunction is recovered from the inner product $\psi(x) = \langle x|\psi\rangle$ while the momentum space wavefunction is obtained from $\psi(p) = \langle p|\psi\rangle$. As with a three-dimensional vector space where $\mathbf{a} \cdot \mathbf{b} \leq |a|\,|b|$, the magnitude of the scalar product is limited by the magnitude of the vectors,

$$\langle\psi|\phi\rangle \leq \sqrt{\langle\psi|\psi\rangle\langle\phi|\phi\rangle}\,,$$

a relation known as the **Schwartz inequality**.

3.1 Operators

An operator $\hat{A}$ is a mathematical object that maps one state vector, $|\psi\rangle$, into another, $|\phi\rangle$, i.e. $\hat{A}|\psi\rangle = |\phi\rangle$. If

$$\boxed{\hat{A}|\psi\rangle = a|\psi\rangle\,,}$$

then $|\psi\rangle$ is said to be an **eigenstate** (or **eigenfunction**) of $\hat{A}$ with eigenvalue a. For example, the plane wave state $\psi_p(x) = \langle x|\psi_p\rangle = A\,e^{ipx/\hbar}$ is an eigenstate of the **momentum operator**, $\hat{p} = -i\hbar\partial_x$, with eigenvalue p. For a free particle, the plane wave is also an eigenstate of the Hamiltonian, $\hat{H} = \frac{\hat{p}^2}{2m}$ with eigenvalue $\frac{p^2}{2m}$.

In quantum mechanics, for any observable A, there is an operator $\hat{A}$ which acts on the wavefunction so that, if a system is in a state described by $|\psi\rangle$, the expectation value of A is

$$\boxed{\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \int_{-\infty}^{\infty} dx\,\psi^*(x)\hat{A}\psi(x)\,.} \tag{3.1}$$

Every operator corresponding to an observable is both linear and Hermitian: That is, for any two wavefunctions $|\psi\rangle$ and $|\phi\rangle$, and any two complex numbers α and β, **linearity** implies that

$$\hat{A}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha(\hat{A}|\psi\rangle) + \beta(\hat{A}|\phi\rangle)\,.$$

Moreover, for any linear operator $\hat{A}$, the **Hermitian conjugate** operator (also known as the adjoint) is defined by the relation

$$\boxed{\langle\phi|\hat{A}\psi\rangle = \int dx\,\phi^*(\hat{A}\psi) = \int dx\,\psi(\hat{A}^\dagger\phi)^* = \langle\hat{A}^\dagger\phi|\psi\rangle\,.} \tag{3.2}$$

From the definition, $\langle\hat{A}^\dagger\phi|\psi\rangle = \langle\phi|\hat{A}\psi\rangle$, we can prove some useful relations: Taking the complex conjugate, $\langle\hat{A}^\dagger\phi|\psi\rangle^* = \langle\psi|\hat{A}^\dagger\phi\rangle = \langle\hat{A}\psi|\phi\rangle$, and then finding the Hermitian conjugate of $\hat{A}^\dagger$, we have

$$\langle\psi|\hat{A}^\dagger\phi\rangle = \langle(\hat{A}^\dagger)^\dagger\psi|\phi\rangle = \langle\hat{A}\psi|\phi\rangle, \qquad \text{i.e. } (\hat{A}^\dagger)^\dagger = \hat{A}\,.$$

Therefore, if we take the Hermitian conjugate twice, we get back to the same operator. It's easy to show that $(\lambda\hat{A})^\dagger = \lambda^*\hat{A}^\dagger$ and $(\hat{A}+\hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$ just from the properties of the dot product. We can also show that $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$ from the identity, $\langle\phi|\hat{A}\hat{B}\psi\rangle = \langle\hat{A}^\dagger\phi|\hat{B}\psi\rangle = \langle\hat{B}^\dagger\hat{A}^\dagger\phi|\psi\rangle$. Note that operators are **associative** but not (in general) **commutative**,

$$\hat{A}\hat{B}|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle) = (\hat{A}\hat{B})|\psi\rangle \neq \hat{B}\hat{A}|\psi\rangle\,.$$

It is helpful to define the **commutator** of two operators by

$$\boxed{\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}\,.}$$

A physical variable must have real expectation values (and eigenvalues). This implies that the operators representing physical variables have some special properties. By computing the complex conjugate of the expectation value of a physical variable, we can easily show that physical operators are their own Hermitian conjugate,

$$\langle\psi|\hat{H}|\psi\rangle^* = \left[\int_{-\infty}^{\infty}\psi^*(x)\hat{H}\psi(x)dx\right]^* = \int_{-\infty}^{\infty}\psi(x)(\hat{H}\psi(x))^*dx = \langle\hat{H}\psi|\psi\rangle\,.$$

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i.e. $\langle \hat{H}\psi|\psi\rangle = \langle\psi|\hat{H}\psi\rangle = \langle\hat{H}^\dagger\psi|\psi\rangle$, and $\hat{H}^\dagger = \hat{H}$. Operators that are their own Hermitian conjugate are called **Hermitian** (or self-adjoint).

▷ EXERCISE. Prove that the momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$ is Hermitian. Further show that the parity operator, defined by $\hat{P}\psi(x) = \psi(-x)$ is also Hermitian.

3.1.1 Matrix representations of operators

Eigenfunctions of Hermitian operators $\hat{H}|i\rangle = E_i|i\rangle$ form an orthonormal (i.e. $\langle i|j\rangle = \delta_{ij}$) complete basis. For any complete basis $\{|i\rangle\}$, we can expand a state $|\psi\rangle$ as

$$|\psi\rangle = \sum_i \psi_i |i\rangle \qquad (3.3)$$

This is a "representation" of $|\psi\rangle$ in this particular basis: e.g. if $\{|i\rangle\}$ are energy eigenstates, then we say that ψ_i is the "energy-representation" of $|\psi\rangle$.

▷ EXERCISE. Show that the overlap of two vectors is $\langle\phi|\psi\rangle = \sum_i \phi_i^* \psi_i$.

To obtain an explicit form for ψ_i, we note that we can for any orthonormal complete set of states $\{|i\rangle\}$, we can always write

$$|\psi\rangle = \sum_i |i\rangle\langle i|\psi\rangle . \qquad (3.4)$$

Thus, we see that the complex numbers $\langle i|\psi\rangle$ are the components of the state vector in the basis states $\{|i\rangle\}$, that is $\psi_i \equiv \langle i|\psi\rangle$.

A 'ket' state vector followed by a 'bra' state vector is an example of an operator. The **projection operator** onto a state $|j\rangle$ is given by $|j\rangle\langle j|$. First the bra vector dots into the state, giving the coefficient of $|j\rangle$ in the state, then it is multiplied by the unit vector $|j\rangle$, turning it back into a vector, with the right length to be a projection. An operator maps one vector into another vector, so this is an operator. If we sum over a complete orthonormal set of states, like the eigenstates of a Hermitian operator, we obtain the (useful) **resolution of the identity**

$$\boxed{\hat{I} = \sum_i |i\rangle\langle i| .}$$

Using the resolution of the identity, it is possible to express any operator as

$$\hat{A} = \hat{I}\hat{A}\hat{I} = \sum_i \sum_j |j\rangle\langle j|A|i\rangle\langle i| . \qquad (3.5)$$

The complex numbers $A_{ji} \equiv \langle j|A|i\rangle$ are the "matrix representation" of $\hat{A}$ in this basis,

$$\hat{A} = \sum_{ij} A_{ji}|j\rangle\langle i| . \qquad (3.6)$$

Consider the action of $\hat{A}$ on a state $|\psi\rangle$

$$
\begin{aligned}
|\phi\rangle &\equiv \hat{A}|\psi\rangle & (3.7)\\
&= \sum_i \sum_j |j\rangle\langle j|A|i\rangle\langle i|\psi\rangle = \sum_{i,j} |j\rangle A_{ji}\psi_i & (3.8)
\end{aligned}
$$

The representation of $|\phi\rangle$ in this basis is

$$
\begin{aligned}
\phi_i \;\equiv\; \langle i|\phi\rangle &= \langle i|\left(\sum_{k,j}|j\rangle A_{jk}\psi_k\right) = \sum_{k,j}\delta_{i,j}A_{jk}\psi_k & (3.9)\\
&= \sum_k A_{ik}\psi_k & (3.10)
\end{aligned}
$$

Thus the action of the operator $\hat{A}$ is via matrix multiplication of A_{ik} on the components of the vector ψ_k. Any complete orthonormal set of vectors can be used as the basis. Each gives rise to a different (vector) representation of the states and (matrix) representation of the operators.

In the above discussion, we have assumed that the basis $\{|i\rangle\}$ is discrete (i.e. we can sum over the projectors $|i\rangle\langle i|$). How do we interpret these sums when the basis is described by a continuous variable? For example, we could consider the eigenstates $\{|x\rangle\}$ of the position operator $\hat{x}$, or the eigenstates $\{|p\rangle\}$ of the momentum operator $\hat{p}$.

For a continuous set of states, the resolution of the identity becomes

$$
\boxed{\hat{I} = \int dx\, |x\rangle\langle x|\,.}
$$

and the orthonormality condition becomes

$$
\langle x'|x\rangle = \delta(x-x') \qquad (3.11)
$$

where $\delta(x)$ is the **Dirac delta function**. Thus, for a state $|\psi\rangle$ we can write

$$
|\psi\rangle = \int dx\, |x\rangle\langle x|\psi\rangle = \int dx\, \psi(x)|x\rangle \qquad (3.12)
$$

If $\{|x\rangle\}$ are the position eigenstates, then the complex function $\psi(x)$ the position representation of $|\psi\rangle$. This function $\psi(x)$ is nothing but the wavefunction of the Schrödinger equation. Eqn. (3.12) shows how the Schrödinger wavefunction should be interpreted within the more abstract Dirac notation.

▷ EXERCISE. Show that the overlap of two vectors is $\langle\phi|\psi\rangle = \int \phi^*(x)\psi(x)\,dx$.

▷ EXAMPLE: The basis states can be formed from any complete set of orthogonal states. In particular, they can be formed from the basis states of the position or the momentum operator, i.e. $\int_{-\infty}^{\infty} dx|x\rangle\langle x| = \int_{-\infty}^{\infty} dp|p\rangle\langle p| = \hat{I}$. If we apply these definitions, we can then recover the familiar Fourier representation,

$$
\psi(x) \equiv \langle x|\psi\rangle = \int_{-\infty}^{\infty} dp\, \underbrace{\langle x|p\rangle}_{e^{ipx/\hbar}/\sqrt{2\pi\hbar}}\,\langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dp\, e^{ipx/\hbar}\,\psi(p)\,,
$$

where $\langle x|p\rangle$ is the position representation of the momentum eigenstate $|p\rangle$.

3.1.2 Time-evolution operator

The ability to develop an eigenfunction expansion provides the means to explore the time evolution of a general wave packet, $|\psi\rangle$ under the action of a Hamiltonian. Formally, we can evolve a wavefunction forward in time

by applying the time-evolution operator. For a Hamiltonian which is time-independent, we have $|\psi(t)\rangle = \hat{U}|\psi(0)\rangle$, where

$$\boxed{\hat{U} = e^{-i\hat{H}t/\hbar},}$$

denotes the time-evolution operator.[1] By inserting the resolution of identity, $\mathbb{I} = \sum_i |i\rangle\langle i|$, where the states $|i\rangle$ are eigenstates of the Hamiltonian with eigenvalue E_i, we find that

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} \sum_i |i\rangle\langle i|\psi(0)\rangle = \sum_i |i\rangle\langle i|\psi(0)\rangle e^{-iE_i t/\hbar}.$$

▷ EXAMPLE: Consider the harmonic oscillator Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$. Later in this chapter, we will see that the eigenstates, $|n\rangle$, have equally-spaced eigenvalues, $E_n = \hbar\omega(n + 1/2)$, for $n = 0, 1, 2, \cdots$. Let us then consider the time-evolution of a general wavepacket, $|\psi(0)\rangle$, under the action of the Hamiltonian. From the equation above, we find that $|\psi(t)\rangle = \sum_n |n\rangle\langle n|\psi(0)\rangle e^{-iE_n t/\hbar}$. Since the eigenvalues are equally spaced, let us consider what happens when $t = t_r \equiv 2\pi r/\omega$, with r integer. In this case, since $e^{2\pi i n r} = 1$, we have

$$|\psi(t_r)\rangle = \sum_n |n\rangle\langle n|\psi(0)\rangle e^{-i\omega t_r/2} = (-1)^r |\psi(0)\rangle.$$

From this result, we can see that, up to an overall phase, the wave packet is perfectly reconstructed at these times. This recurrence or "echo" is not generic, but is a manifestation of the equal separation of eigenvalues in the harmonic oscillator.

▷ EXERCISE. Using the symmetry of the harmonic oscillator wavefunctions under parity show that, at times $t_r = (2r + 1)\pi/\omega$, $\langle x|\psi(t_r)\rangle = e^{-i\omega t_r/2}\langle -x|\psi(0)\rangle$. Explain the origin of this recurrence.

The time-evolution operator is an example of a **unitary operator**. The latter are defined as transformations which preserve the scalar product, $\langle\phi|\psi\rangle = \langle\hat{U}\phi|\hat{U}\psi\rangle = \langle\phi|\hat{U}^\dagger\hat{U}\psi\rangle \overset{!}{=} \langle\phi|\psi\rangle$, i.e.

$$\boxed{\hat{U}^\dagger\hat{U} = \mathbb{I}.}$$

3.1.3 Uncertainty principle for non-commuting operators

For non-commuting Hermitian operators, $[\hat{A}, \hat{B}] \neq 0$, it is straightforward to establish a bound on the uncertainty in their expectation values. Given a state $|\psi\rangle$, the mean square uncertainty is defined as

$$(\Delta A)^2 = \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^2\psi\rangle = \langle\psi|\hat{U}^2\psi\rangle$$
$$(\Delta B)^2 = \langle\psi|(\hat{B} - \langle\hat{B}\rangle)^2\psi\rangle = \langle\psi|\hat{V}^2\psi\rangle,$$

where we have defined the operators $\hat{U} = \hat{A} - \langle\psi|\hat{A}\psi\rangle$ and $\hat{V} = \hat{B} - \langle\psi|\hat{B}\psi\rangle$. Since $\langle\hat{A}\rangle$ and $\langle\hat{B}\rangle$ are just constants, $[\hat{U}, \hat{V}] = [\hat{A}, \hat{B}]$. Now let us take the scalar product of $\hat{U}|\psi\rangle + i\lambda\hat{V}|\psi\rangle$ with itself to develop some information about the uncertainties. As a modulus, the scalar product must be greater than or equal to zero, i.e. expanding, we have $\langle\psi|\hat{U}^2\psi\rangle + \lambda^2\langle\psi|\hat{V}^2\psi\rangle + i\lambda\langle\hat{U}\psi|\hat{V}\psi\rangle -$

---

[1]This equation follows from integrating the time-dependent Schrödinger equation, $\hat{H}|\psi\rangle = i\hbar\partial_t|\psi\rangle$.

$i\lambda\langle\hat{V}\psi|\hat{U}\psi\rangle \geq 0$. Reorganising this equation in terms of the uncertainties, we thus find

$$(\Delta A)^2 + \lambda^2(\Delta B)^2 + i\lambda\langle\psi|[\hat{U},\hat{V}]|\psi\rangle \geq 0\,.$$

If we minimise this expression with respect to λ, we can determine when the inequality becomes strongest. In doing so, we find

$$2\lambda(\Delta B)^2 + i\langle\psi|[\hat{U},\hat{V}]|\psi\rangle = 0, \qquad \lambda = -\frac{i}{2}\frac{\langle\psi|[\hat{U},\hat{V}]|\psi\rangle}{(\Delta B)^2}\,.$$

Substituting this value of λ back into the inequality, we then find,

$$(\Delta A)^2(\Delta B)^2 \geq -\frac{1}{4}\langle\psi|[\hat{U},\hat{V}]|\psi\rangle^2\,.$$

We therefore find that, for non-commuting operators, the uncertainties obey the following inequality,

$$\boxed{\Delta A\,\Delta B \geq \left|\frac{1}{2}\langle[\hat{A},\hat{B}]\rangle\right|\,.}$$

If the commutator is a constant, as in the case of the conjugate operators $[\hat{p},\hat{x}] = -i\hbar$, the expectation values can be dropped, and we obtain the relation, $(\Delta A)(\Delta B) \geq \frac{i}{2}[\hat{A},\hat{B}]$. For momentum and position, this result recovers **Heisenberg's uncertainty principle**,

$$\boxed{\Delta p\,\Delta x \geq \left|\frac{1}{2}\langle[\hat{p},\hat{x}]\rangle\right| = \frac{\hbar}{2}\,.}$$

3.1.4 Time-evolution of expectation values

Finally, to close this section on operators, let us consider how their expectation values evolve. To do so, let us consider a general operator $\hat{A}$ which may itself involve time. The time derivative of a general expectation value has three terms.

$$\frac{d}{dt}\langle\psi|\hat{A}|\psi\rangle = \partial_t(\langle\psi|)\hat{A}|\psi\rangle + \langle\psi|\partial_t\hat{A}|\psi\rangle + \langle\psi|\hat{A}(\partial_t|\psi\rangle)\,.$$

If we then make use of the time-dependent Schrödinger equation, $i\hbar\partial_t|\psi\rangle = \hat{H}|\psi\rangle$, and the Hermiticity of the Hamiltonian, we obtain

$$\frac{d}{dt}\langle\psi|\hat{A}|\psi\rangle = \underbrace{\frac{i}{\hbar}\left(\langle\psi|\hat{H}\hat{A}|\psi\rangle - \langle\psi|\hat{A}\hat{H}|\psi\rangle\right)}_{\frac{i}{\hbar}\langle\psi|[\hat{H},\hat{A}]|\psi\rangle} + \langle\psi|\partial_t\hat{A}|\psi\rangle\,.$$

This is an important and general result for the time derivative of expectation values which becomes simple if the operator itself does not explicitly depend on time,

$$\boxed{\frac{d}{dt}\langle\psi|\hat{A}|\psi\rangle = \frac{i}{\hbar}\langle\psi|[\hat{H},\hat{A}]|\psi\rangle\,.}$$

From this result, which is known as **Ehrenfest's theorem**, we see that expectation values of operators that commute with the Hamiltonian are constants of the motion.

Paul Ehrenfest 1880-1933 An Austrian physicist and mathematician, who obtained Dutch citizenship in 1922. He made major contributions to the field of statistical mechanics and its relations with quantum mechanics, including the theory of phase transition and the Ehrenfest theorem.

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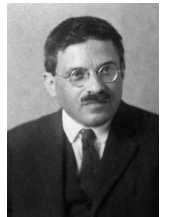
▷ EXERCISE. Applied to the non-relativistic Schrödinger operator for a single particle moving in a potential, $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$, show that $\frac{d\langle \hat{x}\rangle}{dt} = \frac{\langle \hat{p}\rangle}{m}$, $\frac{d\langle \hat{p}\rangle}{dt} = -\langle \partial_x V\rangle$.

Show that these equations are consistent with the relations,

$$\frac{d}{dt}\langle \hat{x}\rangle = \left\langle \frac{\partial H}{\partial p} \right\rangle, \qquad \frac{d}{dt}\langle \hat{p}\rangle = -\left\langle \frac{\partial H}{\partial x} \right\rangle,$$

the counterpart of Hamilton's classical equations of motion.

3.2 Symmetry in quantum mechanics

Symmetry considerations are very important in quantum theory. The structure of eigenstates and the spectrum of energy levels of a quantum system reflect the symmetry of its Hamiltonian. As we will see later, the transition probabilities between different states under a perturbation, such as that imposed by an external electromagnetic field, depend in a crucial way on the transformation properties of the perturbation and lead to "selection rules". Symmetries can be classified into two types, discrete and continuous, according to the transformations that generate them. For example, a mirror symmetry is an example of a discrete symmetry while a rotation in three-dimensional space is continuous.

Formally, the symmetries of a quantum system can be represented by a group of unitary transformations (or operators), $\hat{U}$, that act in the Hilbert space.[2] Under the action of such a unitary transformation, operators corresponding to observables $\hat{A}$ of the quantum model will then transform as,

$$\hat{A} \to \hat{U}^\dagger \hat{A} \hat{U}\,.$$

For unitary transformations, we have seen that $\hat{U}^\dagger \hat{U} = \mathbb{I}$, i.e. $\hat{U}^\dagger = \hat{U}^{-1}$. Under what circumstances does such a group of transformations represent a **symmetry group**? Consider a Schrödinger particle in three dimensions:[3] The basic observables are the position and momentum vectors, $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$. We can always define a transformation of the coordinate system, or the observables, such that a vector $\hat{\mathbf{A}} = \hat{\mathbf{r}}$ or $\hat{\mathbf{p}}$ is mapped to $\mathbf{R}[\hat{\mathbf{A}}]$.[4] If $\mathbf{R}$ is an element of the group of transformations, then this transformation will be represented by a unitary operator $\hat{U}(\mathbf{R})$, such that

$$\hat{U}^\dagger \hat{\mathbf{A}} \hat{U} = \mathbf{R}[\hat{\mathbf{A}}]\,.$$

Such unitary transformations are said to be **symmetries of a general operator** $\hat{O}(\hat{\mathbf{p}}, \hat{\mathbf{r}})$ if

$$\boxed{\hat{U}^\dagger \hat{O} \hat{U} = \hat{O}, \qquad \text{i.e.} \quad [\hat{O}, \hat{U}] = 0\,.}$$

---

[2]In quantum mechanics, the possible states of a system can be represented by unit vectors (called "state vectors") residing in "state space" known as the **Hilbert space**. The precise nature of the Hilbert space is dependent on the system; for example, the state space for position and momentum states is the space of square-integrable functions.

[3]In the following, we will focus our considerations on the realm of "low-energy" physics where the relevant space-time transformations belong to the **Galilei group**. For discussions of **Lorentz invariance** and relativistic quantum mechanics see TP2.

[4]e.g., for a clockwise spatial rotation by an angle θ around $\mathbf{e}_z$, we have,

$$\mathbf{R}[\mathbf{r}] = R_{ij}\hat{x}_j, \qquad \mathbf{R} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}\,.$$

Similarly, for a spatial translation by a vector $\mathbf{a}$, $\mathbf{R}[\mathbf{r}] = \mathbf{r} + \mathbf{a}$. (Exercise: construct representations for transformations corresponding to spatial reflections, and inversion.)

If $\hat{O}(\hat{\mathbf{p}}, \hat{\mathbf{r}}) \equiv \hat{H}$, the quantum Hamiltonian, such unitary transformations are said to be symmetries of the quantum system.

3.2.1 Observables as generators of transformations

The vector operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{r}}$ for a Schrödinger particle are themselves generators of space-time transformations. From the standard commutation relations one can show that, for a constant vector $\mathbf{a}$, the unitary operator

$$\hat{U}(\mathbf{a}) = \exp\left[-\frac{i}{\hbar}\mathbf{a}\cdot\hat{\mathbf{p}}\right],$$

acting in the Hilbert space of a Schrödinger particle performs a **spatial translation**, $\hat{U}^\dagger(\mathbf{a})f(\mathbf{r})\hat{U}(\mathbf{a}) = f(\mathbf{r} + \mathbf{a})$, where $f(\mathbf{r})$ denotes a general algebraic function of $\mathbf{r}$.

> ▷ INFO. The **proof** runs as follows: With $\hat{\mathbf{p}} = -i\hbar\nabla$,
>
> $$\hat{U}^\dagger(\mathbf{a}) = e^{\mathbf{a}\cdot\nabla} = \sum_{n=0}^{\infty}\frac{1}{n!}a_{i_1}\cdots a_{i_n}\nabla_{i_1}\cdots\nabla_{i_n},$$
>
> where summation on the repeated indices, i_m is assumed. Then, making use of the **Baker-Hausdorff identity** (exercise)
>
> $$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!}[\hat{A}, [\hat{A}, \hat{B}]] + \cdots, \tag{3.13}$$
>
> it follows that
>
> $$\hat{U}^\dagger(\mathbf{a})f(\mathbf{r})\hat{U}(\mathbf{a}) = f(\mathbf{r}) + a_{i_1}(\nabla_{i_1}f(\mathbf{r})) + \frac{1}{2!}a_{i_1}a_{i_2}(\nabla_{i_1}\nabla_{i_2}f(\mathbf{r})) + \cdots = f(\mathbf{r} + \mathbf{a}),$$
>
> where the last identity follows from the Taylor expansion.

> ▷ EXERCISE. Prove the Baker-Hausdorff identity (3.13).

Therefore, a quantum system has spatial translation as an invariance group if and only if the following condition holds,

$$\hat{U}(\mathbf{a})\hat{H} = \hat{H}\hat{U}(\mathbf{a}), \qquad \text{i.e.} \quad \hat{\mathbf{p}}\hat{H} = \hat{H}\hat{\mathbf{p}}.$$

This demands that the Hamiltonian is independent of position, $\hat{H} = \hat{H}(\hat{\mathbf{p}})$, as one might have expected! Similarly, the group of unitary transformations, $\hat{U}(\mathbf{b}) = \exp[-\frac{i}{\hbar}\mathbf{b}\cdot\hat{\mathbf{r}}]$, performs **translations in momentum space**. Moreover, **spatial rotations** are generated by the transformation $\hat{U} = \exp[-\frac{i}{\hbar}\theta\mathbf{e}_n\cdot\hat{\mathbf{L}}]$, where $\hat{\mathbf{L}} = \hat{\mathbf{r}}\times\hat{\mathbf{p}}$ denotes the angular momentum operator.

> ▷ EXERCISE. For an infinitesimal rotation by an angle θ by a fixed axis, $\hat{\mathbf{e}}_n$, construct $\mathbf{R}[\mathbf{r}]$ and show that $\hat{U} = \mathbb{I} - \frac{i}{\hbar}\theta\hat{\mathbf{e}}_n\cdot\mathbf{L} + O(\theta^2)$. Making use of the identity $\lim_{N\to\infty}(1 - \frac{a}{N})^N = e^{-a}$, show that "large" rotations are indeed generated by the unitary transformations $\hat{U} = \exp\left[-\frac{i}{\hbar}\theta\hat{\mathbf{e}}_n\cdot\mathbf{L}\right]$.

As we have seen, **time translations** are generated by the time evolution operator, $\hat{U}(t) = \exp[-\frac{i}{\hbar}\hat{H}t]$. Therefore, every observable which commutes with the Hamiltonian is a constant of the motion (invariant under time translations),

$$\hat{H}\hat{A} = \hat{A}\hat{H} \implies e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar} = \hat{A}, \qquad \forall t.$$

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We now turn to consider some examples of discrete symmetries. Amongst these, perhaps the most important in low-energy physics are parity and time-reversal. The **parity** operation, denoted $\hat{P}$, involves a reversal of sign on all coordinates.

$$\boxed{\hat{P}\psi(\mathbf{r}) = \psi(-\mathbf{r})\,.}$$

This is clearly a discrete transformation. Application of parity twice returns the initial state implying that $\hat{P}^2 = 1$. Therefore, the eigenvalues of the parity operation (if such exist) are ± 1. A wavefunction will have a defined parity if and only if it is an even or odd function. For example, for $\psi(x) = \cos(x)$, $\hat{P}\psi = \cos(-x) = \cos(x) = \psi$; thus ψ is even and $P = 1$. Similarly $\psi = \sin(x)$ is odd with $P = -1$. Later, in the next chapter, we will encounter the spherical harmonic functions which have the following important symmetry under parity, $\hat{P}Y_{\ell m} = (-1)^{\ell}Y_{lm}$. Parity will be conserved if the Hamiltonian is invariant under the parity operation, i.e. if the Hamiltonian is invariant under a reversal of sign of all the coordinates.[5]

▷ INFO.   In classical mechanics, the **time-reversal** operation involves simply "running the movie backwards". The time-reversed state of the phase space coordinates $(x(t), p(t))$ is defined by $(x_T(t), p_T(t))$ where $x_T(t) = x(t)$ and $p_T(t) = -p(t)$. Hence, if the system evolved from $(x(0), p(0))$ to $(x(t), p(t))$ in time t and at t we reverse the velocity, $p(t) \to -p(t)$ with $x(t) \to x(t)$, at time $2t$ the system would have returned to $x(2t) = x(0)$ while $p(2t) = -p(0)$. If this happens, we say that the system is time-reversal invariant. Of course, this is just the statement that Newton's laws are the same if $t \to -t$. A notable case where this is not true is that of a charged particle in a magnetic field.

As with classical mechanics, time-reversal in quantum mechanics involves the operation $t \to -t$. However, referring to the time-dependent Schrödinger equation, $i\hbar \partial_t \psi(x,t) = \hat{H}\psi(x,t)$, we can see that the operation $t \to -t$ is equivalent to complex conjugation of the wavefunction, $\psi \to \psi^*$ if $\hat{H}^* = \hat{H}$. Let us then consider the time-evolution of $\psi(x,t)$,

$$\psi(x,0) \to e^{-\frac{i}{\hbar}\hat{H}(x)t}\psi(x,0) \stackrel{\text{c.c.}}{\to} e^{+\frac{i}{\hbar}\hat{H}^*(x)t}\psi^*(x,0) \stackrel{\text{evolve}}{\to} e^{-\frac{i}{\hbar}\hat{H}(x)t}e^{+\frac{i}{\hbar}\hat{H}^*(x)t}\psi^*(x,0)\,.$$

If we require that $\psi(x, 2t) = \psi^*(x,0)$, we must have $\hat{H}^*(x) = \hat{H}(x)$. Therefore, $\hat{H}$ is invariant under time-reversal if and only if $\hat{H}$ is real.

▷ INFO.   Although the group of space-transformations covers the symmetries that pertain to "low-energy" quantum physics, such as atomic physics, quantum optics, and quantum chemistry, in nuclear physics and elementary particle physics new observables come into play (e.g. the isospin quantum numbers and the other quark charges in the standard model). They generate symmetry groups which lack a classical counterpart, and they do not have any obvious relation with space-time transformations. These symmetries are often called **internal symmetries** in order to underline this fact.

3.2.2   Consequences of symmetries: multiplets

Having established how to identify whether an operator belongs to a group of symmetry transformations, we now consider the consequences. Consider

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[5]In high energy physics, parity is a symmetry of the strong and electromagnetic forces, but does not hold for the weak force. Therefore, parity is conserved in strong and electromagnetic interactions, but is violated in weak interactions.

a single unitary transformation $\hat{U}$ in the Hilbert space, and an observable $\hat{A}$ which commutes with $\hat{U}$, $[\hat{U}, \hat{A}] = 0$. If $\hat{A}$ has an eigenvector $|a\rangle$, it follows that $\hat{U}|a\rangle$ will be an eigenvector with the same eigenvalue, i.e.

$$\hat{U}\hat{A}|a\rangle = \hat{A}\hat{U}|a\rangle = a\hat{U}|a\rangle \, .$$

This means that either:

1. $|a\rangle$ is an eigenvector of both $\hat{A}$ and $\hat{U}$, or

2. the eigenvalue a is degenerate: the linear space spanned by the vectors $\hat{U}^n|a\rangle$ (n integer) are eigenvectors with the same eigenvalue.

This mathematical argument leads to the conclusion that, given a group G of unitary operators $\hat{U}(x)$, $x \in$ G, for any observable which is invariant under these transformations, i.e.

$$[\hat{U}(x), \hat{A}] = 0 \quad \forall x \in \text{G} \, ,$$

its discrete eigenvalues and eigenvectors will show a characteristic multiplet structure: there will be a degeneracy due to the symmetry such that the eigenvectors belonging to each eigenvalue form an invariant subspace under the group of transformations.

▷ EXAMPLE: For example, if the Hamiltonian commutes with the angular momentum operators, $\hat{L}_i$, $i = x, y, z$, i.e. it is invariant under three-dimensional rotations, an energy level with a given orbital quantum number ℓ is at least $(2\ell + 1)$-fold degenerate. Such a degeneracy can be seen as the result of non-trivial actions of the operator $\hat{L}_x$ and $\hat{L}_y$ on an energy (and $\hat{L}_z$) eigenstate $|E, \ell, m\rangle$ (where m is the magnetic quantum number associated with $\hat{L}_z$).

3.3 The Heisenberg picture

Until now, the time dependence of an evolving quantum system has been placed within the wavefunction while the operators have remained constant – this is the **Schrödinger picture** or **representation**. However, it is sometimes useful to transfer the time-dependence to the operators. To see how, let us consider the expectation value of some operator $\hat{B}$,

$$\langle \psi(t)|\hat{B}|\psi(t)\rangle = \langle e^{-i\hat{H}t/\hbar}\psi(0)|\hat{B}|e^{-i\hat{H}t/\hbar}\psi(0)\rangle = \langle \psi(0)|e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle \, .$$

According to rules of associativity, we can multiply operators together before using them. If we define the operator $\hat{B}(t) = e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}$, the time-dependence of the expectation values has been transferred from the wavefunction. This is called the **Heisenberg picture** or **representation** and in it, the operators evolve with time (even if, as in this case, they have no explicit time dependence) while the wavefunctions remain constant. In this representation, the time derivative of the operator is given by

$$\frac{d}{dt}\hat{B}(t) = \frac{i\hat{H}}{\hbar}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar} - e^{i\hat{H}t/\hbar}\hat{B}\frac{i\hat{H}}{\hbar}e^{-i\hat{H}t/\hbar}$$

$$= \frac{i}{\hbar}e^{i\hat{H}t/\hbar}[\hat{H}, \hat{B}]e^{-i\hat{H}t/\hbar} = \frac{i}{\hbar}[\hat{H}, \hat{B}(t)] \, .$$

▷ EXERCISE. For the general Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$, show that the position and momentum operators in the Heisenberg picture obey Hamilton's classical equations of motion.

Werner Heisenberg 1901-76
A German physicist and one of the founders of the quantum theory, he is best known for his uncertainty principle which states that it is impossible to determine with arbitrarily high accuracy both the position and momentum of a particle. In 1926, Heisenberg developed a form of the quantum theory known as matrix mechanics, which was quickly shown to be fully equivalent to Erwin Schrödinger's wave mechanics. His 1932 Nobel Prize in Physics cited not only his work on quantum theory but also work in nuclear physics in which he predicted the subsequently verified existence of two allotropic forms of molecular hydrogen, differing in their values of nuclear spin.

3.4 Quantum harmonic oscillator

As we will see time and again in this course, the harmonic oscillator assumes a privileged position in quantum mechanics and quantum field theory finding numerous and sometimes unexpected applications. It is useful to us now in that it provides a platform for us to implement some of the technology that has been developed in this chapter. In the one-dimensional case, the quantum harmonic oscillator Hamiltonian takes the form,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \,,$$

where $\hat{p} = -i\hbar\partial_x$. To find the eigenstates of the Hamiltonian, we could look for solutions of the linear second order differential equation corresponding to the time-independent Schrödinger equation, $\hat{H}\psi = E\psi$, where $\hat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2}m\omega^2 x^2$. The integrability of the Schrödinger operator in this case allows the stationary states to be expressed in terms of a set of orthogonal functions known as Hermite polynomials. However, the complexity of the exact eigenstates obscure a number of special and useful features of the harmonic oscillator system. To identify these features, we will instead follow a method based on an operator formalism.

The form of the Hamiltonian as the sum of the squares of momenta and position suggests that it can be recast as the "square of an operator". To this end, let us introduce the operator

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + i\frac{\hat{p}}{m\omega}\right), \qquad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - i\frac{\hat{p}}{m\omega}\right) \,,$$

where, for notational convenience, we have not drawn hats on the operators a and its Hermitian conjugate $a^\dagger$. Making use of the identity,

$$a^\dagger a = \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{\hat{p}^2}{2\hbar m\omega} + \frac{i}{2\hbar}[\hat{x}, \hat{p}] = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2}$$

and the parallel relation, $aa^\dagger = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$, we see that the operators fulfil the commutation relations

$$\boxed{[a, a^\dagger] \equiv aa^\dagger - a^\dagger a = 1 \,.}$$

Then, setting $\hat{n} = a^\dagger a$, the Hamiltonian can be cast in the form

$$\boxed{\hat{H} = \hbar\omega(\hat{n} + 1/2) \,.}$$

Since the operator $\hat{n} = a^\dagger a$ must lead to a positive definite result, we see that the eigenstates of the harmonic oscillator must have energies of $\hbar\omega/2$ or higher. Moreover, the ground state $|0\rangle$ can be identified by finding the state for which $a|0\rangle = 0$. Expressed in the coordinate basis, this translates to the equation,[6]

$$\left(x + \frac{\hbar}{m\omega}\partial_x\right)\psi_0(x) = 0, \qquad \psi_0(x) = \langle x|0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar} \,.$$

First few states of the quantum harmonic oscillator. Not that the parity of the state changes from even to odd through consecutive states.

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[6]Formally, in coordinate basis, we have $\langle x'|a|x\rangle = \delta(x'-x)(a + \frac{\hbar}{m\omega}\partial_x)$ and $\langle x|0\rangle = \psi_0(x)$. Then making use of the resolution of identity $\int dx|x\rangle\langle x| = \mathbb{I}$, we have

$$\langle x|a|0\rangle = 0 = \int dx \,\langle x|a|x'\rangle\langle x'|0\rangle = \left(x + \frac{\hbar}{m\omega}\partial_x\right)\psi_0(x) \,.$$

Since $\hat{n}|0\rangle = a^\dagger a|0\rangle = 0$, this state is an eigenstate with energy $\hbar\omega/2$. The higher lying states can be found by acting upon this state with the operator $a^\dagger$. The proof runs as follows: If $\hat{n}|n\rangle = n|n\rangle$, we have

$$\hat{n}(a^\dagger|n\rangle) = a^\dagger \underbrace{aa^\dagger}_{a^\dagger a+1} |n\rangle = (a^\dagger \underbrace{a^\dagger a}_{\hat{n}} + a^\dagger)|n\rangle = (n+1)a^\dagger|n\rangle$$

or, equivalently, $[\hat{n}, a^\dagger] = a^\dagger$. In other words, if $|n\rangle$ is an eigenstate of $\hat{n}$ with eigenvalue n, then $a^\dagger|n\rangle$ is an eigenstate with eigenvalue $n+1$.

From this result, we can deduce that the eigenstates for a "tower" $|0\rangle$, $|1\rangle = C_1 a^\dagger|0\rangle$, $|2\rangle = C_2 (a^\dagger)^2|0\rangle$, etc., where C_n denotes the normalization. If $\langle n|n\rangle = 1$ we have

$$\langle n|aa^\dagger|n\rangle = \langle n|(\hat{n}+1)|n\rangle = (n+1)\,.$$

Therefore, with $|n+1\rangle = \frac{1}{\sqrt{n+1}} a^\dagger|n\rangle$ the state $|n+1\rangle$ is also normalized, $\langle n+1|n+1\rangle = 1$. By induction, we can deduce the general normalization,

$$\boxed{|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle\,,}$$

with $\langle n|n'\rangle = \delta_{nn'}$, $\hat{H}|n\rangle = \hbar\omega(n+1/2)|n\rangle$ and

$$\boxed{a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \qquad a|n\rangle = \sqrt{n}|n-1\rangle\,.}$$

The operators a and $a^\dagger$ represent **ladder operators** and have the effect of lowering or raising the energy of the state.

In fact, the operator representation achieves something quite remarkable and, as we will see, unexpectedly profound. The quantum harmonic oscillator describes the motion of a *single* particle in a one-dimensional potential well. Its eigenvalues turn out to be equally spaced – a ladder of eigenvalues, separated by a constant energy $\hbar\omega$. If we are energetic, we can of course translate our results into a coordinate representation $\psi_n(x) = \langle x|n\rangle$.[7] However, the operator representation affords a second interpretation, one that lends itself to further generalization in quantum field theory. We can instead interpret the quantum harmonic oscillator as a simple system involving many fictitious particles, each of energy $\hbar\omega$. In this representation, known as the **Fock space**, the vacuum state $|0\rangle$ is one involving no particles, $|1\rangle$ involves a single particle, $|2\rangle$ has two and so on. These fictitious particles are created and annihilated by the action of the raising and lowering operators, $a^\dagger$ and a with canonical commutation relations, $[a, a^\dagger] = 1$. Later in the course, we will find that these commutation relations are the hallmark of **bosonic** quantum particles and this representation, known as the **second quantization** underpins the quantum field theory of the electromagnetic field.

This completes our abridged survey of operator methods in quantum mechanics.

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[7]Expressed in real space, the harmonic oscillator wavefunctions are in fact described by the Hermite polynomials,

$$\psi_n(x) = \langle x|n\rangle = \sqrt{\frac{1}{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \exp\left[-\frac{m\omega x^2}{2\hbar}\right],$$

where $H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}$.

Chapter 4

Quantum mechanics in more than one dimension

Previously, we have explored the manifestations of quantum mechanics in one spatial dimension and discussed the properties of bound and unbound states. The concepts developed there apply equally to higher dimension. However, for a general two or three-dimensional potential, without any symmetry, the solutions of the Schrödinger equation are often inaccessible. In such situations, we may develop approximation methods to address the properties of the states (e.g. WKB method, and see chapter 7). However, in systems where there is a high degree of symmetry, the quantum mechanics of the system can often be reduced to a tractable low-dimensional theory.

4.1 Rigid diatomic molecule

As a pilot example let us consider the quantum mechanics of a rigid diatomic molecule with nuclear masses m_1 and m_2, and (equilibrium) bond length, R_e (see figure). Since the molecule is rigid, its coordinates can be specified by its centre of mass, $\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$, and internal orientation, $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ (with $|\mathbf{r}| = R_e$). Defining the total mass $M = m_1 + m_2$, and moment of inertia, $I = \mu R_e^2$, where $\mu = m_1 m_2/(m_1 + m_2)$ denotes the reduced mass, the corresponding Hamiltonian can be then separated into the kinetic energy associated with the centre of mass motion and the rotational kinetic energy,

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{L}}^2}{2I} , \qquad (4.1)$$

where $\hat{\mathbf{P}} = -i\hbar\nabla_{\mathbf{R}}$ and $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ denotes the angular momentum associated with the internal degrees of freedom. Since the internal and centre of mass degrees of freedom separate, the wavefunction can be factorized as $\psi(\mathbf{r}, \mathbf{R}) = e^{i\mathbf{K}\cdot\mathbf{R}}Y(\mathbf{r})$, where the first factor accounts for the free particle motion of the body, and the second factor relates to the internal angular degrees of freedom.

As a result of the coordinate separation, we have reduced the problem of the rigid diatomic molecule to the study of the quantum mechanics of a particle moving on a sphere – the **rigid rotor**,

$$\hat{H}_{\mathrm{rot}} = \frac{\hat{\mathbf{L}}^2}{2I} .$$

The eigenstates of this component of the Hamiltonian are simply the states of the angular momentum operator. Indeed, in *any* quantum mechanical system involving a radial potential, the angular momentum will be conserved, i.e.
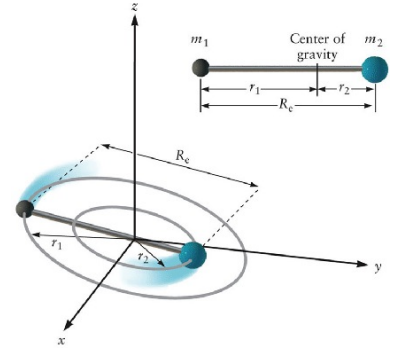
$[\hat{H}, \hat{\mathbf{L}}] = 0$ meaning that the angular component of the wavefunction can be indexed by the states of the angular momentum operator. We therefore now digress to discuss the quantum mechanics of angular momentum.

4.2 Angular momentum

4.2.1 Commutation relations

Following the usual canonical quantization procedure, the angular momentum operator is defined by $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ where, as usual, $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ obey the commutation relations, $[\hat{p}_i, \hat{r}_j] = -i\hbar\delta_{ij}$.[1] Using this relation, one may then show that the angular momentum operators obey the **spin commutation relations**, (exercise)

$$\boxed{[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k \,.} \tag{4.2}$$

where, as usual, ϵ_{ijk} denotes the totally antisymmetric tensor — the Levi-Civita symbol.[2]

▷ EXERCISE. Show that the angular momentum operator commutes with the Hamiltonian of a particle moving in a central potential, $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{r})$. Show that the Hamiltonian of a free particle of mass m confined to a sphere of radius R is given by $\hat{H} = \frac{\hat{\mathbf{L}}^2}{2mR^2}$.

4.2.2 Eigenvalues of angular momentum

In the following, we will construct a basis set of angular momentum states. Since the angular momentum is a *vector* quantity, it may be characterized by its magnitude and direction. For the former, let us define the operator $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. With the latter, since the separate components of the angular momentum are all mutually non-commuting, we cannot construct a common set of eigenstates for any two of them. They do, however, commute with $\hat{\mathbf{L}}^2$ (exercise). Therefore, in the following, we will look for an eigenbasis of $\hat{\mathbf{L}}^2$ and *one* direction, say $\hat{L}_z$,

$$\hat{\mathbf{L}}^2|a, b\rangle = a|a, b\rangle, \qquad \hat{L}_z|a, b\rangle = b|a, b\rangle \,.$$

To find $|a, b\rangle$, we could simply proceed by looking for a suitable coordinate basis to represent $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ in terms of differential operators. However, although we will undertake such a programme in due course, before getting to this formalism, we can make substantial progress without resorting to an explicit coordinate representation.

▷ INFO. **Raising and lowering operators for angular momentum:** The set of eigenvalues a and b can be obtained by making use of a trick based on a "ladder operator" formalism which parallels that used in the study of the quantum harmonic oscillator in section 3.4. Specifically, let us define the raising and lowering operators,

$$\boxed{\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \,.}$$

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[1]In this chapter, we will index the angular momentum operators with a 'hat'. Later, we will become lazy and the hat may well disappear.

[2]Recall that $\epsilon_{ijk} = 1$ if (i, j, k) is an even permutation of (1,2,3), -1 if it is an odd permutation, and 0 if any index is repeated.

With this definition, one may then show that (exercise)

$$[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm \,.$$

Since each component of the angular momentum commutes with $\hat{\mathbf{L}}^2$, we can deduce that the action of $\hat{L}_\pm$ on $|a, b\rangle$ cannot affect the value of a relating to the magnitude of the angular momentum. However, they do affect the projection:

$$\hat{L}_z\hat{L}_\pm|a,b\rangle = \hat{L}_\pm\hat{L}_z|a,b\rangle + [\hat{L}_z, \hat{L}_\pm]|a,b\rangle = (b \pm \hbar)\hat{L}_\pm|a,b\rangle \,.$$

Therefore, if $|a, b\rangle$ is an eigenstate of $\hat{L}_z$ with eigenvalue b, $\hat{L}_\pm|a,b\rangle$ is either zero, or an eigenstate of $\hat{L}_z$ with eigenvalue $b \pm \hbar$, i.e. $\hat{L}_\pm|a,b\rangle = C_\pm(a,b)|a, b \pm \hbar\rangle$ where $C_\pm(a,b)$ is a normalisation constant.

To fix the normalisation, we may note that the norm,

$$\left|\left|\hat{L}_\pm|a,b\rangle\right|\right|^2 = \langle a, b|\hat{L}_\pm^\dagger\hat{L}_\pm|a,b\rangle = \langle a, b|\hat{L}_\mp\hat{L}_\pm|a,b\rangle \,,$$

where we have used the identity $\hat{L}_\pm^\dagger = \hat{L}_\mp$. Then, making use of the relation $\hat{L}_\mp\hat{L}_\pm = \hat{L}_x^2 + \hat{L}_y^2 \pm i[\hat{L}_x\hat{L}_y] = \hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z$, and the presumed normalisation, $\langle a, b|a, b\rangle = 1$, one finds

$$\left|\left|\hat{L}_\pm|a,b\rangle\right|\right|^2 = \langle a, b|\left(\hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z\right)|a,b\rangle = a - b^2 \mp \hbar b \,. \tag{4.3}$$

As a represents the eigenvalue of a sum of squares of Hermitian operators, it is necessarily non-negative. Moreover, b is real. Therefore, for a given a, b must be bounded: there must be a $b_{\max}$ and a (negative or zero) $b_{\min}$. In particular,

$$\left|\left|\hat{L}_+|a, b_{\max}\rangle\right|\right|^2 = a - b_{\max}^2 - \hbar b_{\max}$$

$$\left|\left|\hat{L}_-|a, b_{\min}\rangle\right|\right|^2 = a - b_{\min}^2 + \hbar b_{\min} \,,$$

For a given a, $b_{\max}$ and $b_{\min}$ are determined uniquely — there cannot be two states with the same a but different b annihilated by $\hat{L}_+$. It also follows immediately that $a = b_{\max}(b_{\max}+\hbar)$ and $b_{\min} = -b_{\max}$. Furthermore, we know that if we keep operating on $|a, b_{\min}\rangle$ with $\hat{L}_+$, we generate a sequence of states with $\hat{L}_z$ eigenvalues $b_{\min} + \hbar$, $b_{\min} + 2\hbar$, $b_{\min} + 3\hbar$, $\cdots$. This series must terminate, and the only possible way for that to happen is for $b_{\max}$ to be equal to $b_{\min} + n\hbar$ with n integer, from which it follows that $b_{\max}$ is either an integer or half an odd integer times $\hbar$

At this point, we switch to the standard notation. We have established that the eigenvalues of $\hat{L}_z$ form a finite ladder, with spacing $\hbar$. We write them as $m\hbar$, and ℓ is used to denote the maximum value of m, so the eigenvalue of $\hat{\mathbf{L}}^2$, $a = \ell(\ell + 1)\hbar^2$. Both ℓ and m will be integers or half odd integers, but the spacing of the ladder of m values is always unity. Although we have been writing $|a, b\rangle$ with $a = \ell(\ell + 1)\hbar^2$, $b = m\hbar$ we shall henceforth follow convention and write $|\ell, m\rangle$.

In summary, the operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ have a common set of orthonormal eigenstates $|\ell, m\rangle$ with

Figure 4.1: The following is a schematic showing the angular momentum scheme for $\ell = 2$ with $\mathbf{L}^2 = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$ and the five possible values for the L_z projection.

$$\boxed{\hat{\mathbf{L}}^2|\ell, m\rangle = \ell(\ell + 1)\hbar^2|\ell, m\rangle, \qquad \hat{L}_z|\ell, m\rangle = m\hbar|\ell, m\rangle \,,} \tag{4.4}$$

where ℓ, m are integers or half-integers. The allowed quantum numbers m form a ladder with step spacing unity, the maximum value of m is ℓ, and the minimum value is $-\ell$. With these results, we may then return to the normalization of the raising and lowering operators. In particular, making use of Eq. (4.3), we have

$$\boxed{\begin{aligned}\hat{L}_+|\ell, m\rangle &= \sqrt{\ell(\ell + 1) - m(m + 1)}\hbar|\ell, m + 1\rangle \\ \hat{L}_-|\ell, m\rangle &= \sqrt{\ell(\ell + 1) - m(m - 1)}\hbar|\ell, m - 1\rangle\end{aligned}} \,. \tag{4.5}$$
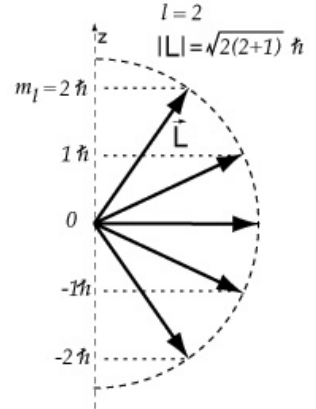
The use of m to denote the component of angular momentum in one direction came about because a Bohr-type electron in orbit is a current loop, with a magnetic moment parallel to its angular momentum. So the m measured the component of magnetic moment in a chosen direction, usually along an external magnetic field. For this reason, m is often termed the **magnetic quantum number**.

4.2.3 Representation of the angular momentum states

Having established expressions for the eigenvalues of the angular momentum operators, it is now necessary to establish (angular) coordinate representations for the corresponding eigenstates, $Y_{\ell m}(\theta, \phi) = \langle \theta, \phi | \ell, m \rangle$. Here the angles θ and ϕ denote the spherical coordinates parameterising the unit sphere (see figure). Previously, we obtained the eigenvalues of the angular momentum operator by making use of the raising and lowering operators in a manner that parallelled the study of the quantum harmonic oscillator. Similarly, to obtain explicit expressions for the eigenstates, we must make use of the coordinate representation of these operators. With $\mathbf{r} = r\hat{\mathbf{e}}_r$, the gradient operator can be written in spherical polar coordinates as

$$\nabla = \hat{\mathbf{e}}_r \partial_r + \hat{\mathbf{e}}_\theta \frac{1}{r} \partial_\theta + \hat{\mathbf{e}}_\phi \frac{1}{r \sin \theta} \partial_\phi \,.$$

From this result, we thus obtain

$$\boxed{\hat{L}_z = -i\hbar \partial_\phi, \qquad \hat{L}_\pm = \hbar e^{\pm i\phi} \left(\pm \partial_\theta + i \cot \theta \partial_\phi \right) \,,} \qquad (4.6)$$

and, at least formally,

$$\boxed{\hat{\mathbf{L}}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right] \,.}$$

Beginning with the eigenstates of $\hat{L}_z$, the eigenvalue equation (4.4), and making use of the expression above, we have

$$-i\hbar \partial_\phi Y_{\ell m}(\theta, \phi) = m\hbar Y_{\ell m}(\theta, \phi) \,.$$

Since the left hand side depends only on ϕ, the solution is separable and takes the form $Y_{\ell m}(\theta, \phi) = F(\theta) e^{im\phi}$. Note that, provided m is integer, the continuity of the wavefunction, $Y_{\ell m}(\theta, \phi + 2\pi) = Y_{\ell m}(\theta, \phi)$, is ensured. Thus, the condition that the co-ordinate representation of the wavefunction be single-valued requires m to be integer, and hence ℓ to be integer. (As discussed in Chapter 5, for "spin" angular momentum half-integer ℓ is possible.)

To determine the second component of the eigenstates, $F(\theta)$, we could immediately turn to the eigenvalue equation involving the differential operator for $\hat{\mathbf{L}}^2$,

$$\left[\frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) - \frac{m^2}{\sin^2 \theta} \right] F(\theta) = \ell(\ell + 1) F(\theta) \,.$$

However, to construct the states, it is easier to draw upon the properties of the angular momentum raising and lowering operators (much in the same way that the Hermite polynomials are generated by the action of ladder operators in the harmonic oscillator problem).
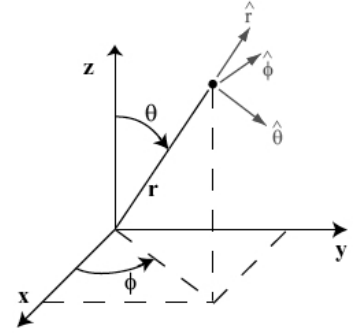
Consider then the state of maximal m, $|\ell, \ell\rangle$, for which $\hat{L}_+|\ell, \ell\rangle = 0$. Making use of the coordinate representation of the raising operator above together with the separability of the wavefunction, this relation implies that

$$0 = \langle\theta, \phi|\hat{L}_+|\ell, \ell\rangle = \hbar e^{i\phi}\left(\partial_\theta + i\cot\theta\partial_\phi\right)Y_{\ell\ell}(\theta, \phi) = \hbar e^{i(\ell+1)\phi}\left(\partial_\theta - \ell\cot\theta\right)F(\theta).$$

From this result it follows that $\partial_\theta F(\theta) = \ell\cot\theta F(\theta)$ with the solution $F(\theta) = C\sin^\ell\theta$, and C a constant of normalization. States with values of m lower than ℓ can then be obtained simply by repeated application of the angular momentum lowering operator $\hat{L}_-$ to the state $|\ell, \ell\rangle$. This amounts to the relation

$$Y_{\ell m}(\theta, \phi) = C(\hat{L}_-)^{\ell-m}\left[\sin^\ell\theta e^{i\ell\phi}\right]$$
$$= C\left(-\partial_\theta + i\cot\theta\partial_\phi\right)^{\ell-m}\left[\sin^\ell\theta e^{i\ell\phi}\right].$$

The eigenfunctions produced by this procedure are well known and referred to as the **spherical harmonics**. In particular, one finds that the normalized eigenstates take the form,

$$\boxed{Y_{\ell m}(\theta, \phi) = (-1)^{m+|m|}\left[\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2}P_\ell^{|m|}(\cos\theta)e^{im\phi},} \qquad (4.7)$$

where

$$P_\ell^m(\xi) = \frac{(1-\xi^2)^{m/2}}{2^\ell\ell!}\frac{d^{m+\ell}}{d\xi^{m+\ell}}(\xi^2-1)^\ell,$$

represent the **associated Legendre polynomials**. In particular, for the first few angular momentum states, we have

$Y_{00} = \frac{1}{\sqrt{4\pi}}$
$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad\qquad Y_{11} = -\sqrt{\frac{3}{8\pi}}e^{i\phi}\sin\theta$
$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \quad Y_{21} = -\sqrt{\frac{15}{8\pi}}e^{i\phi}\sin\theta\cos\theta, \quad Y_{22} = \sqrt{\frac{15}{32\pi}}e^{2i\phi}\sin^2\theta$

Figure 4.2 shows a graphical representation of the states for the lowest spherical harmonics.

As a complete basis set, the spherical harmonics can be used as a resolution of the identity

$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}|\ell, m\rangle\langle\ell, m| = \mathbb{I}.$$

In terms of the angular position eigenstates $|\theta, \phi\rangle$, we have

$$\int_0^\pi \sin\theta d\theta\int_0^{2\pi}d\phi\,|\theta, \phi\rangle\langle\theta, \phi| = \mathbb{I} \qquad\qquad (4.8)$$

where the integration measure $\sin\theta d\theta d\phi$ weights all directions equally. The normalization condition is

$$\langle\theta', \phi'|\theta, \phi\rangle = \frac{1}{\sin\theta}\delta(\theta - \theta')\delta(\phi - \phi')$$

as may be readily verified by requiring $\mathbb{I}^2 = \mathbb{I}$ from (4.8).
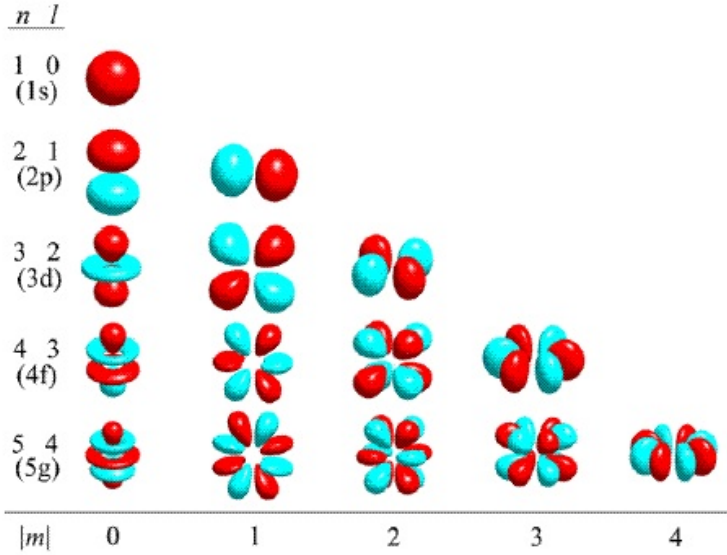
Figure 4.2: First four groups of spherical harmonics, $Y_{\ell m}(\theta, \phi)$ shown as a function of spherical angular coordinates. Specifically, the plots show the surface generated by $|\mathrm{Re}\, Y_{\ell m}(\theta, \phi)|$ to fix the radial coordinate and the colours indicate the relative sign of the real part.

Thus, expressing the angular momentum eigenstates in the coordinate basis, we have

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y_{\ell,m}^*(\theta', \phi') Y_{\ell,m}(\theta, \phi) = \frac{1}{\sin\theta} \delta(\theta - \theta') \delta(\phi - \phi'),$$

Similarly, we have the orthogonality condition,

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi Y_{\ell,m}^*(\theta, \phi) Y_{\ell',m'}(\theta, \phi) = \delta_{\ell\ell'} \delta_{mm'}.$$

After this lengthy digression, we may now return to the problem of the quantum mechanical rotor Hamiltonian and the rigid diatomic molecule. From the analysis above, we have found that the eigenstates of the Hamiltonian (4.1) are given by $\psi(\mathbf{R}, \mathbf{r}) = \frac{1}{\sqrt{2\pi}} e^{i\mathbf{K}\cdot\mathbf{R}} Y_{\ell,m}(\theta, \phi)$ with eigenvalues

$$E_{\mathbf{K},\ell} = \frac{\hbar^2 \mathbf{K}^2}{2M} + \frac{\hbar^2}{2I} \ell(\ell + 1),$$

where each $\mathbf{K}, \ell$ value has a $2\ell + 1$-fold degeneracy.

▷ EXERCISE. Using this result, determine the dependence of the heat capacity of a gas of rigid diatomic molecules on the angular degrees of freedom. How would this result change if the diatomic gas was constrained to just two spatial dimensions, i.e. the axis of rotation was always perpendicular to the plane in which the molecules can move?

Chapter 5

Spin

Until we have focussed on the quantum mechanics of particles which are "featureless", carrying no internal degrees of freedom. However, a relativistic formulation of quantum mechanics shows that particles can exhibit an intrinsic angular momentum component known as spin. However, the discovery of the spin degree of freedom marginally predates the development of relativistic quantum mechanics by Dirac and was achieved in a ground-breaking experiment by Stern and Gerlach (1922). In their experiment, they passed a well-collimated beam of silver atoms through a region of inhomogeneous field before allowing the particles to impact on a photographic plate (see figure). The magnetic field was directed perpendicular to the beam, and has a strong gradient, $\partial_z B_z \neq 0$ so that a beam comprised of atoms with a magnetic moment would be bent towards the z or -z axis. As the magnetic moment will be proportional to the total angular momentum, such an experiment can be thought of as a measurement of its projection along z.

At the time of the experiment, there was an expectation that the magnetic moment of the atom was generated in its entirety by the orbital angula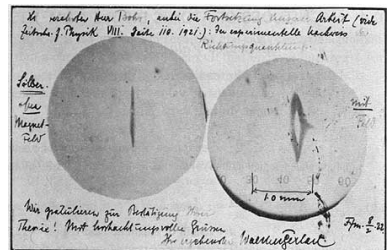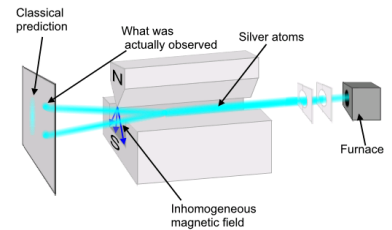r momentum. Within that expectation, the result was qualitatively consistent with the model of Bohr – that orbits of the electron are quantized. Hence the congratulations on the postcard. However, as we have seen, the full quantum theory (of Schrödinger, developed after 1922) leads one to expect that the angular momentum is $\ell = 0, 1, 2, \ldots$ so there should be a minimum of 3 possible values of l_z . As such, one would expect that there would be an *odd* number of possible z-components of angular momentum: $2\ell+1$ with ℓ integer. Curiously, Stern and Gerlach's experiment (right) showed that the beam of silver atoms split into *two*! This discovery, which caused great discussion and surprise in subsequent years, presented a puzzle.

Gerlach's postcard, dated 8th February 1922, to Niels Bohr. It shows a photograph of the beam splitting, with the message, in translation: "Attached [is] the experimental proof of directional quantization. We congratulate [you] on the confirmation of your theory." (Physics Today December 2003)

However, in our derivation of allowed angular momentum eigenvalues we found that, although for any system the allowed values of m form a ladder with spacing $\hbar$, we could not rule out half-integral values of m. The lowest such case, $\ell = 1/2$, would in fact have just two allowed m values: $m = \pm 1/2$. However, such an ℓ value could not translate to an orbital angular momentum because the z-component of the orbital wavefunction, ψ has a factor $e^{im\phi} = e^{\pm i\phi/2}$, and therefore acquires a factor -1 on rotating through 2π! This would imply that ψ is not single-valued, which doesn't make sense for a Schrödinger-type wavefunction.

Yet the experimental result was irrefutable. Therefore, this must be a new kind of non-orbital angular momentum – spin. Conceptually, just as the Earth has orbital angular momentum in its yearly circle around the sun, and also spin angular momentum from its daily turning, the electron has an analogous spin. But this analogy has obvious limitations: the Earth's spin is, after all,

made up of material orbiting around the axis through the poles. The electron spin cannot be imagined as arising from a rotating body, since orbital angular momenta always come in integral multiples of $\hbar$. Fortunately, this lack of a simple quasi-mechanical picture underlying electron spin doesn't prevent us from using the general angular momentum machinery developed earlier, which followed just from analyzing the effect of spatial rotation on a quantum mechanical system.

5.1 Spinors, spin operators, Pauli matrices

The Hilbert space of angular momentum states for spin $1/2$ is two-dimensional. Various notations are used: $|\ell, m\rangle$ becomes $|s, m\rangle$ or, more graphically,

$$\boxed{|1/2, 1/2\rangle = |\uparrow\rangle, \qquad |1/2, -1/2\rangle = |\downarrow\rangle.}$$

A general state of spin can be written as the linear combination,

$$\alpha|\uparrow\rangle + \beta|\downarrow\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

with the normalisation condition, $|\alpha|^2 + |\beta|^2 = 1$, and this two-dimensional ket is called a **spinor**. Operators acting on spinors are necessarily of the form of 2×2 matrices. We shall adopt the usual practice of denoting the angular momentum components L_i by S_i for spins. (Once again, for clarity, we also drop the hats on the angular momentum operators!)

From our definition of the spinor, it is evident that the z-component of the spin can be represented as the matrix,

$$S_z = \frac{\hbar}{2}\sigma_z, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Wolfgang Pauli and Niels Bohr demonstrating 'tippe top' toy at the inauguration of the new Institute of Physics at Lund, Sweden 1954.

From the general formulae (4.5) for raising and lowering operators $S_\pm = S_x \pm iS_y$, with $s = 1/2$, we have $S_+|1/2, -1/2\rangle = \hbar|1/2, 1/2\rangle$, $S_-|1/2, 1/2\rangle = \hbar|1/2, -1/2\rangle$, or, in matrix form,

$$S_x + iS_y = S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad S_x - iS_y = S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

It therefore follows that an appropriate matrix representation for spin $1/2$ is given by the **Pauli spin matrices**, $\mathbf{S} = \frac{\hbar}{2}\sigma$ where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5.1}$$

These matrices are Hermitian, traceless, and obey the relations $\sigma_i^2 = \mathbb{I}$, $\sigma_i\sigma_j = -\sigma_j\sigma_i$, and $\sigma_i\sigma_j = i\sigma_k$ for (i, j, k) a cyclic permutation of $(1, 2, 3)$. These relations can be summarised by the identity,

$$\boxed{\sigma_i\sigma_j = \mathbb{I}\delta_{ij} + i\epsilon_{ijk}\sigma_k.}$$

The total spin $\mathbf{S}^2 = \frac{\hbar^2}{4}\sigma^2 = \frac{3}{4}\hbar^2$, i.e. $s(s+1)\hbar^2$ for $s = 1/2$.

▷ EXERCISE. Explain why any 2×2 Hermitian matrix can be written in the form $\alpha_0\mathbb{I} + \sum_i \alpha_i\sigma_i$. Use your results to show that (a) $(\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})^2 = \mathbb{I}$ for any unit vector $\hat{\mathbf{n}}$, and (b) $(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = (\mathbf{A} \cdot \mathbf{B})\mathbb{I} + \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B})$.

5.2 Relating the spinor to the spin direction

For a general state $\alpha|\uparrow\rangle + \beta|\downarrow\rangle$, how do α, β relate to which way the spin is pointing? To find out, let us assume that it is pointing up along the unit vector $\hat{\mathbf{n}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, i.e. in the direction (θ, ϕ). In other words, the spin is an eigenstate of the operator $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}$ having eigenvalue unity:

$$\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

From this expression, we find that $\alpha/\beta = (n_x - in_y)/(1 - n_z) = e^{-i\phi}\cot(\theta/2)$ (exercise). Then, making use of the normalisation, $|\alpha|^2 + |\beta|^2 = 1$, we obtain (up to an arbitrary phase)

$$\boxed{\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\phi/2}\cos(\theta/2) \\ e^{i\phi/2}\sin(\theta/2) \end{pmatrix}.}$$

Since $e^{-i\phi}\cot(\theta/2)$ can be used to specify any complex number with $0 \leq \theta \leq \pi$, $0 \leq \phi < 2\pi$, so for any possible spinor, there is an associated direction along which the spin points up.

▷ INFO. **The spin rotation operator:** In general, the rotation operator for rotation through an angle θ about an axis in the direction of the unit vector $\hat{\mathbf{n}}$ is given by $e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}$ where $\mathbf{J}$ denotes the angular momentum operator. For spin, $\mathbf{J} = \mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$, and the rotation operator takes the form[1] $e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar} = e^{-i(\theta/2)(\hat{\mathbf{n}}\cdot\boldsymbol{\sigma})}$. Expanding the exponential, and making use of the Pauli matrix identities $((\mathbf{n}\cdot\boldsymbol{\sigma})^2 = \mathbb{I})$, one can show that (exercise)

$$e^{-i(\theta/2)(\mathbf{n}\cdot\boldsymbol{\sigma})} = \mathbb{I}\cos(\theta/2) - i\mathbf{n}\cdot\boldsymbol{\sigma}\sin(\theta/2).$$

The rotation operator is a 2×2 matrix operating on the ket space. The 2×2 rotation matrices are unitary and form a group known as SU(2); the 2 refers to the dimensionality, the U to their being unitary, and the S signifying determinant $+1$. Note that for rotation about the z-axis, $\hat{\mathbf{n}} = (0, 0, 1)$, it is more natural to replace θ with ϕ, and the rotation operator takes the form,

$$e^{-i(\theta/2)(\mathbf{n}\cdot\boldsymbol{\sigma})} = \begin{pmatrix} e^{-i\phi/2} & 0 \\ 0 & e^{i\phi/2} \end{pmatrix}.$$

In particular, the wavefunction is multiplied by -1 for a rotation of 2π. Since this is true for any initial wave function, it is clearly also true for rotation through 2π about any axis.

▷ EXERCISE. Construct the infinitesimal version of the rotation operator $e^{-i\delta\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}$ for spin 1/2, and prove that $e^{i\delta\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}\boldsymbol{\sigma}e^{-i\delta\theta\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar} = \boldsymbol{\sigma} + \delta\theta\hat{\mathbf{n}} \times \boldsymbol{\sigma}$, i.e. $\boldsymbol{\sigma}$ is rotated in the same way as an ordinary three-vector -— note particularly that the change depends on the angle rotated through (as opposed to the half-angle) so, reassuringly, there is no -1 for a complete rotation (as there cannot be -— the direction of the spin is a physical observable, and cannot be changed on rotating the measuring frame through 2π).

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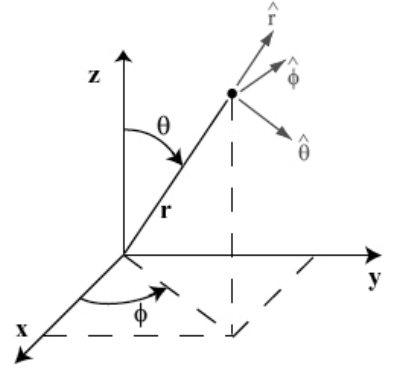
[1] Warning: do not confuse θ – the rotation angle —- with the spherical polar angle used to parameterise $\hat{\mathbf{n}}$.

5.3 Spin precession in a magnetic field

Consider a magnetized classical object spinning about its centre of mass, with angular momentum $\mathbf{L}$ and parallel magnetic moment $\boldsymbol{\mu}$, $\boldsymbol{\mu} = \gamma \mathbf{L}$. The constant γ is called the gyromagnetic ratio. Now suppose that we impose a magnetic field $\mathbf{B}$ along, say, the z-direction. This will exert a torque $\mathbf{T} = \boldsymbol{\mu} \times \mathbf{B} = \gamma \mathbf{L} \times \mathbf{B} = \frac{d\mathbf{L}}{dt}$. This equation is easily solved and shows that the angular momentum vector $\mathbf{L}$ precesses about the magnetic field direction with angular velocity of precession $\boldsymbol{\omega}_0 = -\gamma \mathbf{B}$.[2]

In the following, we will show that precisely the same result appears in the study of the quantum mechanics of an electron spin in a magnetic field. The electron has magnetic dipole moment $\boldsymbol{\mu} = \gamma \mathbf{S}$, where $\gamma = g\frac{-e}{2m_e}$ and the gyromagnetic ratio, g, is very close to 2.[3] The Hamiltonian for the interaction of the electron's dipole moment with the magnetic field is given by $\hat{H} = -\boldsymbol{\mu} \cdot \mathbf{B} = -\gamma \mathbf{S} \cdot \mathbf{B}$. Hence the time development is specified by the equation $|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$, with the time-evolution operator (or propagator), $\hat{U}(t) = e^{-i\hat{H}t/\hbar} = e^{i\gamma\sigma\cdot\mathbf{B}t/2}$. However, this is nothing but the rotation operator (as shown earlier) through an angle $-\gamma Bt$ about the direction of $\mathbf{B}$!

For an arbitrary initial spin orientation

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\phi/2}\cos(\theta/2) \\ e^{i\phi/2}\sin(\theta/2) \end{pmatrix},$$

the propagator for a magnetic field in the z-direction is given by

$$U(t) = e^{i\gamma\sigma\cdot\mathbf{B}t/2} = \begin{pmatrix} e^{-i\omega_0 t/2} & 0 \\ 0 & e^{i\omega_0 t/2} \end{pmatrix},$$

so the time-dependent spinor is set by

$$\begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} = \begin{pmatrix} e^{-i(\phi+\omega_0 t)/2}\cos(\theta/2) \\ e^{i(\phi+\omega_0 t)/2}\sin(\theta/2) \end{pmatrix}.$$

The angle θ between the spin and the field stays constant while the azimuthal angle around the field increases as $\phi = \phi_0 + \omega_0 t$, exactly as in the classical case. The frequency $\omega_0 = g\frac{|e|B}{2m_e}$ is the Larmor frequency for spin precession. For a magnetic field of $1\,\text{T}$, $\omega_0 \simeq 10^{11}\,\text{rads/s}$.

▷ EXERCISE. For a spin initially pointing along the x-axis, prove that $\langle S_x(t)\rangle = (\hbar/2)\cos(\omega_0 t)$.

5.4 Addition of angular momenta

In subsequent chapters, it will be necessary to add angular momentum, be it the addition of orbital and spin angular momenta, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, as with the study of spin-orbit coupling in atoms, or the addition of general angular momenta, $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ as occurs in the consideration of multi-electron atoms. In the

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[2]Proof: From the equation of motion, with $L_+ = L_x + iL_y$, $\frac{dL_+}{dt} = -i\gamma B L_+$, $L_+ = L_+^0 e^{-i\gamma Bt}$. Of course, $\frac{dL_z}{dt} = 0$, since $\frac{d\mathbf{L}}{dt} = \gamma \mathbf{L} \times \mathbf{B}$ is perpendicular to $\mathbf{B}$, which is in the z-direction.

[3]This g-factor terminology is used more widely. In general, the magnetic moment of an atom is written $\boldsymbol{\mu} = -g\mu_B(\hat{\mathbf{J}}/\hbar)$, where $\mu_B = \frac{e\hbar}{2m_e}$ is known as the **Bohr magneton**, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is the total (orbital and spin) angular momentum and g depends on the internal structure of the particular atom.

following section, we will explore three problems: The addition of two spin $1/2$ degrees of freedom; the addition of a general orbital angular momentum and spin; and the addition of spin $J = 1$ angular momenta. However, before addressing these examples in turn, let us first make some general remarks.

Without specifying any particular application, let us consider the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ where $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ correspond to distinct degrees of freedom, $[\hat{\mathbf{J}}_1, \hat{\mathbf{J}}_2] = 0$, and the individual operators obey angular momentum commutation relations. As a result, the total angular momentum also obeys angular momentum commutation relations,

$$[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k \,.$$

For each angular momentum component, the states $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ where $m_i = -j_i, \cdots j_i$, provide a basis of states of the total angular momentum operator, $\hat{\mathbf{J}}_i^2$ and the projection $\hat{J}_{iz}$. Together, they form a complete basis which can be used to span the states of the coupled spins,[4]

$$|j_1, m_1, j_2, m_2\rangle \equiv |j_1, m_1\rangle \otimes |j_2, m_2\rangle \,.$$

These product states are also eigenstates of $\hat{J}_z$ with eigenvalue $\hbar(m_1 + m_2)$, but not of $\hat{\mathbf{J}}^2$.

▷ EXERCISE. Show that $[\hat{\mathbf{J}}^2, \hat{J}_{iz}] \neq 0$.

However, for practical application, we require a basis in which the total angular momentum operator $\hat{\mathbf{J}}^2$ is also diagonal. That is, we must find eigenstates $|j, m_j, j_1, j_2\rangle$ of the four mutually commuting operators $\hat{\mathbf{J}}^2$, $\hat{J}_z$, $\hat{\mathbf{J}}_1^2$, and $\hat{\mathbf{J}}_2^2$.

In general, the relation between the two basis can be expressed as

$$|j, m_j, j_1, j_2\rangle = \sum_{m_1, m_2} |j_1, m_1, j_2, m_2\rangle\langle j_1, m_1, j_2, m_2|j, m_j, j_1, j_2\rangle \,,$$

where the matrix elements are known as **Clebsch-Gordan coefficients**. In general, the determination of these coefficients from first principles is a somewhat soul destroying exercise and one that we do not intend to pursue in great detail.[5] In any case, for practical purposes, such coefficients have been tabulated in the literature and can be readily obtained. However, in some simple cases, these matrix elements can be determined straightforwardly. Moreover, the algorithmic programme by which they are deduced offer some new conceptual insights.

Operationally, the mechanism for finding the basis states of the total angular momentum operator follow the strategy:

1. As a unique entry, the basis state with maximal $J_{\max}$ and $m_j = J_{\max}$ is easy to deduce from the original basis states since it involves the product of states of **highest weight**,

   $$|J_{\max}, m_j = J_{\max}, j_1, j_2\rangle = |j_1, m_1 = j_1\rangle \otimes |j_2, m_2 = j_2\rangle \,,$$

   where $J_{\max} = j_1 + j_2$.

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[4]Here $\otimes$ denotes the "direct product" and shows that the two constituent spin states access their own independent Hilbert space.

[5]In fact, one may show that the general matrix element is given by

$$\langle j_1, m_1, j_2, m_2|j, m_j, j_1, j_2\rangle = \delta_{m_j, m_1 + m_2}\sqrt{\frac{(j_1 + j_2 - j)!(j + j_1 - j_2)!(j + j_2 - j_1)!(2j + 1)}{(j + j_1 + j_2 + 1)!}}$$

$$\times \sum_k \frac{(-1)^k\sqrt{(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!(j + m)!(j - m)!}}{k!(j_1 + j_2 - j - k)!(j_1 - m_1 - k)!(j_2 + m_2 - k)!(j - j_2 + m_1 + k)!(j - j_1 - m_2 + k)!} \,.$$

2. From this state, we can use of the total spin lowering operator $\hat{J}_-$ to find all states with $J = J_{\max}$ and $m_j = -J_{\max} \cdots J_{\max}$.

3. From the state with $J = J_{\max}$ and $m_j = J_{\max} - 1$, one can then obtain the state with $J = J_{\max} - 1$ and $m_j = J_{\max} - 1$ by orthogonality.[6] Now one can return to the second step of the programme and repeat until $J = |j_1 - j_2|$ when all $(2j_1 + 1)(2j_2 + 1)$ basis states have been obtained.

5.4.1 Addition of two spin $1/2$ degrees of freedom

For two spin $1/2$ degrees of freedom, we could simply construct and diagonalize the complete 4×4 matrix elements of the total spin. However, to gain some intuition for the general case, let us consider the programme above. Firstly, the maximal total spin state is given by

$$|S = 1, m_S = 1, s_1 = 1/2, s_2 = 1/2\rangle = |s_1 = 1/2, m_{s_1} = 1/2\rangle \otimes |s_2 = 1/2, m_{s_2} = 1/2\rangle.$$

Now, since $s_1 = 1/2$ and $s = 1/2$ is implicit, we can rewrite this equation in a more colloquial form as

$$|S = 1, m_S = 1\rangle = |\uparrow_1\rangle \otimes |\uparrow_2\rangle.$$

We now follow step 2 of the programme and subject the maximal spin state to the total spin lowering operator, $\hat{S}_- = \hat{S}_1^- + \hat{S}_2^-$. In doing so, making use of Eq. (4.5), we find

$$\hat{S}_-|S = 1, m_S = 1\rangle = \sqrt{2}\hbar|S = 1, m_S = 0\rangle = \hbar\left(|\downarrow_1\rangle \otimes |\uparrow_2\rangle + |\uparrow_1\rangle \otimes |\downarrow_2\rangle\right),$$

i.e. $|S = 1, m_S = 0\rangle = \frac{1}{\sqrt{2}}(|\downarrow_1\rangle \otimes |\uparrow_2\rangle + |\uparrow_1\rangle \otimes |\downarrow_2\rangle)$. Similarly,

$$\hat{S}_-|S = 1, m_S = 0\rangle = \sqrt{2}\hbar|S = 1, m_S = -1\rangle = \sqrt{2}\hbar|\downarrow_1\rangle \otimes |\downarrow_2\rangle,$$

i.e. $|S = 1, m_S = -1\rangle = |\downarrow_1\rangle \otimes |\downarrow_2\rangle$. This completes the construction of the manifold of spin $S = 1$ states – the **spin triplet** states. Following the programme, we must now consider the lower spin state.

In this case, the next multiplet is the unique total **spin singlet** state $|S = 0, m_S = 0\rangle$. The latter must be orthogonal to the spin triplet state $|S = 1, m_S = 0\rangle$. As a result, we can deduce that

$$|S = 0, m_S = 0\rangle = \frac{1}{\sqrt{2}}\left(|\downarrow_1\rangle \otimes |\uparrow_2\rangle - |\uparrow_1\rangle \otimes |\downarrow_2\rangle\right).$$

5.4.2 Addition of angular momentum and spin

We now turn to the problem of the addition of angular momentum and spin, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. In the original basis, for a given angular momentum ℓ, one can identify $2 \times (2\ell + 1)$ product states $|\ell, m_\ell\rangle \otimes |\uparrow\rangle$ and $|\ell, m_\ell\rangle \otimes |\downarrow\rangle$, with $m_\ell = -\ell, \cdots \ell$, involving eigenstates of $\hat{\mathbf{L}}^2$, $\hat{L}_z$, $\hat{\mathbf{S}}^2$ and $\hat{S}_z$, but not $\hat{\mathbf{J}}^2$. From these basis states, we are looking for eigenstates of $\hat{\mathbf{J}}^2$, $\hat{J}_z$, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$. To undertake this programme, it is helpful to recall the action of the angular momentum raising and lower operators,

$$\hat{L}_\pm|\ell, m_\ell\rangle = ((\ell \pm m_\ell + 1)(\ell \mp m_\ell))^{1/2}\hbar|\ell, m_\ell \pm 1\rangle,$$

---

[6]Alternatively, as a maximal spin state, $|J = J_{\max} - 1, m_j = J_{\max} - 1, j_1, j_2\rangle$ can be identified by the "killing" action of the raising operator, $\hat{J}_+$.

as well as the identity

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + \overbrace{2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{S}_+\hat{L}_-}^{2\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}} \ .$$

For the eigenstates of $\hat{\mathbf{J}}^2$, $\hat{J}_z$, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ we will adopt the notation $|j, m_j, \ell\rangle$ leaving the spin $S = 1/2$ implicit. The maximal spin state is given by[7]

$$|\ell + 1/2, \ell + 1/2, \ell\rangle = |\ell, \ell\rangle \otimes |\uparrow\rangle \, .$$

To obtain the remaining states in the multiplet, $|j = \ell + 1/2, m_{j=\ell+1/2}, \ell\rangle$, we may simply apply the total spin lowering operator $\hat{J}_-$,

$$\hat{J}_- |\ell, \ell\rangle \otimes |\uparrow\rangle = \hbar(2\ell)^{1/2}|\ell, \ell - 1\rangle \otimes |\uparrow\rangle + \hbar|\ell, \ell\rangle \otimes |\downarrow\rangle \, .$$

Normalising the right-hand side of this expression, one obtains the spin state,

$$|\ell + 1/2, \ell - 1/2, \ell\rangle = \sqrt{\frac{2\ell}{2\ell + 1}}|\ell, \ell - 1\rangle \otimes |\uparrow\rangle + \sqrt{\frac{1}{2\ell + 1}}|\ell, \ell\rangle \otimes |\downarrow\rangle \, .$$

By repeating this programme, one can develop an expression for the full set of basis states,

$$|j = \ell + 1/2, m_j, \ell\rangle = \sqrt{\frac{\ell + m_j + 1/2}{2\ell + 1}}|\ell, m_j - 1/2\rangle \otimes |\uparrow\rangle$$
$$+ \sqrt{\frac{\ell - m_j + 1/2}{2\ell + 1}}|\ell, m_j + 1/2\rangle \otimes |\downarrow\rangle \, ,$$

with $m_j = \ell + 1/2, \cdots, -(\ell + 1/2)$. In order to obtain the remaining states with $j = \ell - 1/2$, we may look for states with $m_j = \ell - 1/2, \cdots, -(\ell - 1/2)$ which are orthogonal to $|\ell + 1/2, m_j, \ell\rangle$. Doing so, we obtain

$$|\ell - 1/2, m_j, \ell\rangle = -\sqrt{\frac{\ell - m_j + 1/2}{2\ell + 1}}|\ell, m_j - 1/2\rangle \otimes |\uparrow\rangle$$
$$+ \sqrt{\frac{\ell + m_j + 1/2}{2\ell + 1}}|\ell, m_j + 1/2\rangle \otimes |\downarrow\rangle \, .$$

Finally, these states can be cast in a compact form by setting

$$\boxed{|j = \ell \pm 1/2, m_j, \ell\rangle = \alpha_\pm|\ell, m_j - 1/2\rangle \otimes |\uparrow\rangle + \beta_\pm|\ell, m_j + 1/2\rangle \otimes |\downarrow\rangle \, ,} \quad (5.2)$$

where $\alpha_\pm = \pm\sqrt{\frac{\ell \pm m_j + 1/2}{2\ell + 1}} = \pm\beta_\mp$.

---

[7]The proof runs as follows:

$$\hat{J}_z|\ell, \ell\rangle \otimes |\uparrow\rangle = (\hat{L}_z + \hat{S}_z)|\ell, \ell\rangle \otimes |\uparrow\rangle = (\ell + 1/2)\hbar|\ell, \ell\rangle \otimes |\uparrow\rangle \, ,$$

and

$$\hat{\mathbf{J}}^2|\ell, \ell\rangle \otimes |\uparrow\rangle = \hbar^2(\ell(\ell + 1) + 1/2(1/2 + 1) + 2\ell\frac{1}{2})|\ell, \ell\rangle \otimes |\uparrow\rangle$$
$$= \hbar^2(\ell + 1/2)(\ell + 3/2)|\ell, \ell\rangle \otimes |\uparrow\rangle \, .$$

5.4.3 Addition of two angular momenta $J = 1$

As mentioned above, for the general case the programme is algebraically technical and unrewarding. However, for completeness, we consider here the explicit example of the addition of two spin 1 degrees of freedom. Once again, the maximal spin state is given by

$$|J = 2, m_J = 2, j_1 = 1, j_2 = 1\rangle = |j_1 = 1, m_1 = 1\rangle \otimes |j_2 = 1, m_2 = 1\rangle \,,$$

or, more concisely, $|2, 2\rangle = |1\rangle \otimes |1\rangle$, where we leave j_1 and j_2 implicit. Once again, making use of Eq. (4.5) and an economy of notation, we find (exercise)

$$\begin{cases} |2, 2\rangle = |1\rangle \otimes |1\rangle \\ |2, 1\rangle = \frac{1}{\sqrt{2}} \left(|0\rangle \otimes |1\rangle + |1\rangle \otimes |0\rangle\right) \\ |2, 0\rangle = \frac{1}{\sqrt{6}} \left(|-1\rangle \otimes |1\rangle + 2|0\rangle \otimes |0\rangle + |1\rangle \otimes |-1\rangle\right) \\ |2, -1\rangle = \frac{1}{\sqrt{2}} \left(|0\rangle \otimes |-1\rangle + |-1\rangle \otimes |0\rangle\right) \\ |2, -2\rangle = |-1\rangle \otimes |-1\rangle \end{cases} .$$

Then, from the expression for $|2, 1\rangle$, we can construct the next maximal spin state $|1, 1\rangle = \frac{1}{\sqrt{2}}(|0\rangle \otimes |1\rangle - |1\rangle \otimes |0\rangle)$, from the orthogonality condition. Once again, acting on this state with the total spin lowering operator, we obtain the remaining members of the multiplet,

$$\begin{cases} |1, 1\rangle = \frac{1}{\sqrt{2}} \left(|0\rangle \otimes |1\rangle - |1\rangle \otimes |0\rangle\right) \\ |1, 0\rangle = \frac{1}{\sqrt{2}} \left(|-1\rangle \otimes |1\rangle - |1\rangle \otimes |-1\rangle\right) \\ |1, -1\rangle = \frac{1}{\sqrt{2}} \left(|-1\rangle \otimes |0\rangle - |0\rangle \otimes |-1\rangle\right) \end{cases} .$$

Finally, finding the state orthogonal to $|1, 0\rangle$ and $|2, 0\rangle$, we obtain the final state,

$$|0, 0\rangle = \frac{1}{\sqrt{3}} \left(|-1\rangle \otimes |1\rangle - |0\rangle \otimes |0\rangle + |1\rangle \otimes |-1\rangle\right) \,.$$

Chapter 6

Motion of a charged particle in a magnetic field

Hitherto, we have focussed on applications of quantum mechanics to free particles or particles confined by scalar potentials. In the following, we will address the influence of a magnetic field on a charged particle. Classically, the force on a charged particle in an electric and magnetic field is specified by the **Lorentz force law**:

$$\mathbf{F} = q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right),$$

where q denotes the charge and $\mathbf{v}$ the velocity. (Here we will adopt a convention in which q denotes the charge (which may be positive or negative) and $e \equiv |e|$ denotes the *modulus* of the electron charge, i.e. for an electron, the charge $q = -e = -1.602176487 \times 10^{-19}$ C.) The velocity-dependent force associated with the magnetic field is quite different from the conservative forces associated with scalar potentials, and the programme for transferring from classical to quantum mechanics --— replacing momenta with the appropriate operators --— has to be carried out with more care. As preparation, it is helpful to revise how the Lorentz force arises in the Lagrangian formulation of classical mechanics.

6.1 INFO: Classical mechanics of a particle in a field

For a system with m degrees of freedom specified by coordinates $q_1, \cdots q_m$, the classical action is determined from the Lagrangian $L(q_i, \dot{q}_i)$ by

$$\boxed{S[q_i] = \int dt\, L(q_i, \dot{q}_i).}$$

The action is said to be a **functional** of the coordinates $q_i(t)$. According to **Hamilton's extremal principle** (also known as the **principle of least action**), the dynamics of a classical system is described by the equations that minimize the action. These equations of motion can be expressed through the classical Lagrangian in the form of the Euler-Lagrange equations,

$$\boxed{\frac{d}{dt}\left(\partial_{\dot{q}_i} L(q_i, \dot{q}_i)\right) - \partial_{q_i} L(q_i, \dot{q}_i) = 0.} \tag{6.1}$$

▷ INFO. **Euler-Lagrange equations:** According to Hamilton's extremal principle, for any smooth set of curves $w_i(t)$, the variation of the action around the classical solution $q_i(t)$ is zero, i.e. $\lim_{\epsilon \to 0} \frac{1}{\epsilon}(S[q_i + \epsilon w_i] - S[q_i]) = 0$. Applied to the action,
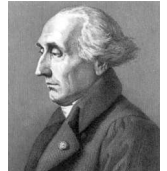
the variation implies that, for any i, $\int dt\, (w_i \partial_{q_i} L(q_i, \dot{q}_i) + \dot{w}_i \partial_{\dot{q}_i} L(q_i, \dot{q}_i)) = 0$. Then, integrating the second term by parts, and dropping the boundary term, one obtains

$$\int dt\, w_i \left(\partial_{q_i} L(q_i, \dot{q}_i) - \frac{d}{dt} \partial_{\dot{q}_i} L(q_i, \dot{q}_i) \right) = 0\,.$$

Since this equality must follow for any function $w_i(t)$, the term in parentheses in the integrand must vanish leading to the Euler-Lagrange equation (6.1).

The **canonical momentum** is specified by the equation $p_i = \partial_{\dot{q}_i} L$, and the classical Hamiltonian is defined by the Legendre transform,

$$H(q_i, p_i) = \sum_i p_i \dot{q}_i - L(q_i, \dot{q}_i)\,. \tag{6.2}$$

It is straightforward to check that the equations of motion can be written in the form of Hamilton's equations of motion,

$$\dot{q}_i = \partial_{p_i} H, \qquad \dot{p}_i = -\partial_{q_i} H\,.$$

From these equations it follows that, if the Hamiltonian is independent of a particular coordinate q_i, the corresponding momentum p_i remains constant. For **conservative forces**,[1] the classical Lagrangian and Hamiltonian can be written as $L = T - V$, $H = T + V$, with T the kinetic energy and V the potential energy.

▷ INFO. **Poisson brackets:** Any dynamical variable f in the system is some function of the phase space coordinates, the q_is and p_is, and (assuming it does not depend explicitly on time) its time-development is given by:

$$\frac{d}{dt} f(q_i, p_i) = \partial_{q_i} f\, \dot{q}_i + \partial_{p_i} f\, \dot{p}_i = \partial_{q_i} f\, \partial_{p_i} H - \partial_{p_i} f\, \partial_{q_i} H \equiv \{f, H\}.$$

The curly brackets are known as Poisson brackets, and are defined for any dynamical variables as $\{A, B\} = \partial_{q_i} A\, \partial_{p_i} B - \partial_{p_i} A\, \partial_{q_i} B$. From Hamilton's equations, we have shown that for any variable, $\dot{f} = \{f, H\}$. It is easy to check that, for the coordinates and canonical momenta, $\{q_i, q_j\} = 0 = \{p_i, p_j\}$, $\{q_i, p_j\} = \delta_{ij}$. This was the classical mathematical structure that led Dirac to link up classical and quantum mechanics: He realized that the Poisson brackets were the classical version of the commutators, so a classical canonical momentum must correspond to the quantum differential operator in the corresponding coordinate.[2]

With these foundations revised, we now return to the problem at hand; the influence of an electromagnetic field on the dynamics of the charged particle.

As the Lorentz force is velocity dependent, it can not be expressed simply as the gradient of some potential. Nevertheless, the classical path traversed by a charged particle is still specified by the principle of least action. The electric and magnetic fields can be written in terms of a scalar and a vector potential as $\mathbf{B} = \nabla \times \mathbf{A}$, $\mathbf{E} = -\nabla \phi - \dot{\mathbf{A}}$. The corresponding Lagrangian takes the form:[3]

$$L = \frac{1}{2} m \mathbf{v}^2 - q\phi + q\mathbf{v} \cdot \mathbf{A}.$$

Siméon Denis Poisson 1781-1840
A French mathematician, geometer, and physicist whose mathematical skills enabled him to compute the distribution of electrical charges on the surface of conductors. He extended the work of his mentors, Pierre Simon Laplace and Joseph Louis Lagrange, in celestial mechanics by taking their results to a higher order of accuracy. He was also known for his work in probability.

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[1] i.e. forces that conserve mechanical energy.

[2] For a detailed discussion, we refer to Paul A. M. Dirac, *Lectures on Quantum Mechanics*, Belfer Graduate School of Science Monographs Series Number 2, 1964.

[3] In a relativistic formulation, the interaction term here looks less arbitrary: the relativistic version would have the relativistically invariant $q \int A^\mu dx_\mu$ added to the action integral, where the four-potential $A_\mu = (\phi, \mathbf{A})$ and $dx_\mu = (ct, dx_1, dx_2, dx_3)$. This is the simplest possible invariant interaction between the electromagnetic field and the particle's four-velocity. Then, in the non-relativistic limit, $q \int A^\mu dx_\mu$ just becomes $q \int (\mathbf{v} \cdot \mathbf{A} - \phi) dt$.

In this case, the general coordinates $q_i \equiv x_i = (x_1, x_2, x_3)$ are just the Cartesian coordinates specifying the position of the particle, and the $\dot{q}_i$ are the three components $\dot{x}_i = (\dot{x}_1, \dot{x}_2, \dot{x}_3)$ of the particle velocities. The important point is that the *canonical* momentum

$$p_i = \partial_{\dot{x}_i} L = mv_i + qA_i \,,$$

is no longer simply given by the mass $\times$ velocity – there is an extra term!

Making use of the definition (6.2), the corresponding Hamiltonian is given by

$$H(q_i, p_i) = \sum_i \left(mv_i + qA_i\right) v_i - \frac{1}{2}m\mathbf{v}^2 + q\phi - q\mathbf{v} \cdot \mathbf{A} = \frac{1}{2}m\mathbf{v}^2 + q\phi \,.$$

Reassuringly, the Hamiltonian just has the familiar form of the sum of the kinetic and potential energy. However, to get Hamilton's equations of motion, the Hamiltonian has to be expressed solely in terms of the coordinates and canonical momenta, i.e.

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A}(\mathbf{r}, t))^2 + q\phi(\mathbf{r}, t) \,.$$

Let us now consider Hamilton's equations of motion, $\dot{x}_i = \partial_{p_i} H$ and $\dot{p}_i = -\partial_{x_i} H$. The first equation recovers the expression for the canonical momentum while second equation yields the Lorentz force law. To understand how, we must first keep in mind that dp/dt is not the acceleration: The A-dependent term also varies in time, and in a quite complicated way, since it is the field at a point moving with the particle. More precisely,

$$\dot{p}_i = m\ddot{x}_i + q\dot{A}_i = m\ddot{x}_i + q\left(\partial_t A_i + v_j \partial_{x_j} A_i\right) \,,$$

where we have assumed a summation over repeated indices. The right-hand side of the second of Hamilton's equation, $\dot{p}_i = -\frac{\partial H}{\partial x_i}$, is given by

$$-\partial_{x_i} H = \frac{1}{m}(\mathbf{p} - q\mathbf{A}(\mathbf{r}, t))q\partial_{x_i}\mathbf{A} - q\partial_{x_i}\phi(\mathbf{r}, t) = qv_j \partial_{x_i} A_j - q\partial_{x_i}\phi \,.$$

Together, we obtain the equation of motion, $m\ddot{x}_i = -q\left(\partial_t A_i + v_j \partial_{x_j} A_i\right) + qv_j\partial_{x_i} A_j - q\partial_{x_i}\phi$. Using the identity, $\mathbf{v} \times (\nabla \times \mathbf{A}) = \nabla(\mathbf{v} \cdot \mathbf{A}) - (\mathbf{v} \cdot \nabla)\mathbf{A}$, and the expressions for the electric and magnetic fields in terms of the potentials, one recovers the Lorentz equations

$$m\ddot{x} = \mathbf{F} = q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right) \,.$$

With these preliminary discussions of the classical system in place, we are now in a position to turn to the quantum mechanics.

6.2 Quantum mechanics of a particle in a field

To transfer to the quantum mechanical regime, we must implement the canonical quantization procedure setting $\hat{\mathbf{p}} = -i\hbar\nabla$, so that $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$. However, in this case, $\hat{p}_i \neq m\hat{v}_i$. This leads to the novel situation that the velocities in different directions do not commute.[4] To explore influence of the magnetic field on the particle dynamics, it is helpful to assess the relative weight of the $\mathbf{A}$-dependent contributions to the quantum Hamiltonian,

$$\hat{H} = \frac{1}{2m}(\hat{\mathbf{p}} - q\mathbf{A}(\mathbf{r}, t))^2 + q\phi(\mathbf{r}, t) \,.$$

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[4]With $m\hat{v}_i = -i\hbar\partial_{x_i} - qA_i$, it is easy (and instructive) to verify that $[\hat{v}_x, \hat{v}_y] = \frac{i\hbar q}{m^2}B$.

Advanced Quantum Physics
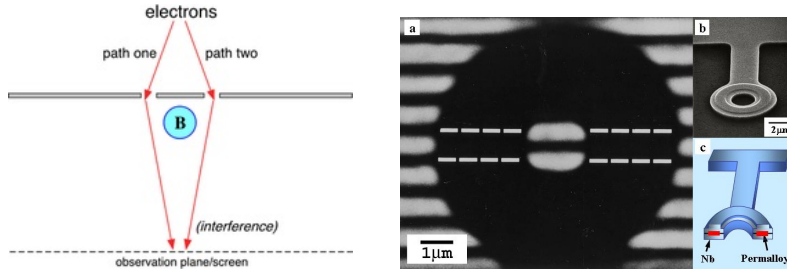
Figure 6.1: (Left) Schematic showing the geometry of an experiment to observe the Aharonov-Bohm effect. Electrons from a coherent source can follow two paths which encircle a region where the magnetic field is non-zero. (Right) Interference fringes for electron beams passing near a toroidal magnet from the experiment by Tonomura and collaborators in 1986. The electron beam passing through the center of the torus acquires an additional phase, resulting in fringes that are shifted with respect to those outside the torus, demonstrating the Aharonov-Bohm effect. For details see the original paper from which this image was borrowed see Tonomura *et al.*, *Evidence for Aharonov-Bohm effect with magnetic field completely shielded from electron wave*, Phys. Rev. Lett. **56**, 792 (1986).

6.3 Gauge invariance and the Aharonov-Bohm effect

Our derivation above shows that the quantum mechanical Hamiltonian of a charged particle is defined in terms of the vector potential, $\mathbf{A}$. Since the latter is defined only up to some gauge choice, this suggests that the wavefunction is not a gauge invariant object. Indeed, it is only the observables associated with the wavefunction which must be gauge invariant. To explore this gauge freedom, let us consider the influence of the **gauge transformation**,

$$\mathbf{A} \mapsto \mathbf{A}' = \mathbf{A} + \nabla\Lambda, \qquad \phi \mapsto \phi' = \phi - \partial_t\Lambda \,,$$

where $\Lambda(\mathbf{r}, t)$ denotes a scalar function. Under the gauge transformation, one may show that the corresponding wavefunction gets transformed as

$$\psi'(\mathbf{r}, t) = \exp\left[i\frac{q}{\hbar}\Lambda(\mathbf{r}, t)\right]\psi(\mathbf{r}, t)\,. \tag{6.3}$$

▷ EXERCISE. If wavefunction $\psi(\mathbf{r}, t)$ obeys the time-dependent Schrödinger equation, $i\hbar\partial_t\psi = \hat{H}[\mathbf{A}, \phi]\psi$, show that $\psi'(\mathbf{r}, t)$ as defined by (6.3) obeys the equation $i\hbar\partial_t\psi' = \hat{H}[\mathbf{A}', \phi']\psi'$.

The gauge transformation introduces an additional space and time-dependent phase factor into the wavefunction. However, since the observable translates to the probability density, $|\psi|^2$, this phase dependence seems invisible.

One physical manifestation of the gauge invariance of the wavefunction is found in the **Aharonov-Bohm effect**. Consider a particle with charge q travelling along a path, P, in which the magnetic field, $\mathbf{B} = 0$ is identically zero. However, a vanishing of the magnetic field does not imply that the vector potential, $\mathbf{A}$ is zero. Indeed, as we have seen, any $\Lambda(\mathbf{r})$ such that $\mathbf{A} = \nabla\Lambda$ will translate to this condition. In traversing the path, the wavefunction of the particle will acquire the phase factor $\varphi = \frac{q}{\hbar}\int_P \mathbf{A} \cdot d\mathbf{r}$, where the line integral runs along the path.

If we consider now two separate paths P and P' which share the same initial and final points, the relative phase of the wavefunction will be set by

$$\Delta\varphi = \frac{q}{\hbar}\int_P \mathbf{A} \cdot d\mathbf{r} - \frac{q}{\hbar}\int_{P'} \mathbf{A} \cdot d\mathbf{r} = \frac{q}{\hbar}\oint \mathbf{A} \cdot d\mathbf{r} = \frac{q}{\hbar}\int_A \mathbf{B} \cdot d^2\mathbf{r}\,,$$

where the line integral $\oint$ runs over the loop involving paths P and P', and $\int_A$ runs over the area enclosed by the loop. The last relation follows from the application of Stokes' theorem. This result shows that the relative phase $\Delta\varphi$ is fixed by the factor $q/\hbar$ multiplied by the magnetic flux $\Phi = \int_A \mathbf{B} \cdot d^2\mathbf{r}$ enclosed by the loop.[5] In the absence of a magnetic field, the flux vanishes, and there is no additional phase.

However, if we allow the paths to enclose a region of non-vanishing magnetic field (see figure 6.1(left)), *even if the field is identically zero on the paths P and P'*, the wavefunction will acquire a non-vanishing relative phase. This flux-dependent phase difference translates to an observable shift of interference fringes when on an observation plane. Since the original proposal,[6] the Aharonov-Bohm effect has been studied in several experimental contexts. Of these, the most rigorous study was undertaken by Tonomura in 1986. Tonomura fabricated a doughnut-shaped (toroidal) ferromagnet six micrometers in diameter (see figure 6.1b), and covered it with a niobium superconductor to completely confine the magnetic field within the doughnut, in accordance with the Meissner effect.[7] With the magnet maintained at $5\,\mathrm{K}$, they measured the phase difference from the interference fringes between one electron beam passing though the hole in the doughnut and the other passing on the outside of the doughnut. The results are shown in figure 6.1(right,a). Interference fringes are displaced with just half a fringe of spacing inside and outside of the doughnut, indicating the existence of the Aharonov-Bohm effect. Although electrons pass through regions free of any electromagnetic field, an observable effect was produced due to the existence of vector potentials.

The observation of the half-fringe spacing reflects the constraints imposed by the superconducting toroidal shield. When a superconductor completely surrounds a magnetic flux, the flux is quantized to an integral multiple of quantized flux $h/2e$, the factor of two reflecting that fact that the superconductor involves a condensate of electron *pairs*. When an odd number of vortices are enclosed inside the superconductor, the relative phase shift becomes π (mod. 2π) – half-spacing! For an even number of vortices, the phase shift is zero.[8]

6.4 Free electron in a magnetic field

Finally, to complete our survey of the influence of a uniform magnetic field on the dynamics of charged particles, let us consider the problem of a free quantum particle. In this case, the classical electron orbits can be macroscopic and there is no reason to neglect the diamagnetic contribution to the Hamiltonian. Previously, we have worked with a gauge in which $\mathbf{A} = (-y, x, 0)B/2$, giving a constant field B in the z-direction. However, to address the Schrödinger equation for a particle in a uniform perpendicular magnetic field, it is convenient to adopt the **Landau gauge**, $\mathbf{A}(\mathbf{r}) = (-By, 0, 0)$.

▷ EXERCISE. Construct the gauge transformation, $\Lambda(\mathbf{r})$ which connects these two representations of the vector potential.

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[5]Note that the phase difference depends on the magnetic flux, a function of the magnetic field, and is therefore a gauge invariant quantity.

[6]Y. Aharonov and D. Bohm, *Significance of electromagnetic potentials in quantum theory*, Phys. Rev. **115**, 485 (1959).

[7]Perfect diamagnetism, a hallmark of superconductivity, leads to the complete expulsion of magnetic fields – a phenomenon known as the Meissner effect.

[8]The superconducting flux quantum was actually predicted prior to Aharonov and Bohm, by Fritz London in 1948 using a phenomenological theory.

Sir George Gabriel Stokes, 1st Baronet 1819-1903
A mathematician and physicist, who at Cambridge made important contributions to fluid dynamics (including the Navier–Stokes equations), optics, and mathematical physics (including Stokes' theorem). He was secretary, and then president, of the Royal Society.
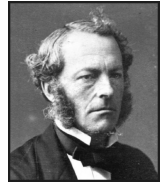
Lev Davidovich Landau 1908-1968
A prominent Soviet physicist who made fundamental contributions to many areas of theoretical physics. His accomplishments include the co-discovery of the density matrix method in quantum mechanics, the quantum mechanical theory of diamagnetism, the theory of superfluidity, the theory of second order phase transitions, the Ginzburg-Landau theory of superconductivity, the explanation of Landau damping in plasma physics, the Landau pole in quantum electrodynamics, and the two-component theory of neutrinos. He received the 1962 Nobel Prize in Physics for his development of a mathematical theory of superfluidity that accounts for the properties of liquid helium II at a temperature below 2.17K.
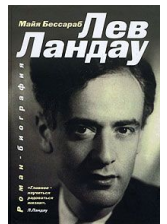
In this case, the stationary form of the Schrödinger equation is given by

$$\hat{H}\psi(\mathbf{r}) = \frac{1}{2m}\left[(\hat{p}_x + qBy)^2 + \hat{p}_y^2 + \hat{p}_z^2\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

Since $\hat{H}$ commutes with both $\hat{p}_x$ and $\hat{p}_z$, both operators have a common set of eigenstates reflecting the fact that p_x and p_z are conserved by the dynamics. The wavefunction must therefore take the form, $\psi(\mathbf{r}) = e^{i(p_x x + p_z z)/\hbar}\chi(y)$, with $\chi(y)$ defined by the equation,

$$\left[\frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega_c^2(y - y_0)^2\right]\chi(y) = \left(E - \frac{p_z^2}{2m}\right)\chi(y).$$

Here $y_0 = -p_x/qB$ and $\omega_c = |q|B/m$ coincides with the **cyclotron frequency** of the classical charged particle (exercise). We now see that the conserved canonical momentum p_x in the x-direction is in fact the coordinate of the centre of a simple harmonic oscillator potential in the y-direction with frequency ω_c. As a result, we can immediately infer that the eigenvalues of the Hamiltonian are comprised of a free particle component associated with motion parallel to the field, and a set of harmonic oscillator states,

$$E_{n,p_z} = (n + 1/2)\hbar\omega_c + \frac{p_z^2}{2m}.$$

The quantum numbers, n, specify states known as **Landau levels**.

Let us confine our attention to states corresponding to the lowest oscillator (Landau level) state, (and, for simplicity, $p_z = 0$), $E_0 = \hbar\omega_c/2$. What is the degeneracy of this Landau level? Consider a rectangular geometry of area $A = L_x \times L_y$ and, for simplicity, take the boundary conditions to be periodic. The centre of the oscillator wavefunction, $y_0 = -p_x/qB$, must lie between 0 and L_y. With periodic boundary conditions $e^{ip_x L_x/\hbar} = 1$, so that $p_x = n2\pi\hbar/L_x$. This means that y_0 takes a series of evenly-spaced discrete values, separated by $\Delta y_0 = h/qBL_x$. So, for electron degrees of freedom, $q = -e$, the total number of states $N_{\text{states}} = L_y/|\Delta y_0|$, i.e.

$$N_{\text{states}} = \frac{L_x L_y}{h/eB} = A\frac{B}{\Phi_0}, \tag{6.4}$$

where $\Phi_0 = h/e$ denotes the "flux quantum". So the total number of states in the lowest energy level coincides with the total number of flux quanta making up the field B penetrating the area A.

The Landau level degeneracy, N_{states}, depends on field; the larger the field, the more electrons can be fit into each Landau level. In the physical system, each Landau level is spin split by the Zeeman coupling, with (6.4) applying to one spin only. Finally, although we treated x and y in an asymmetric manner, this was merely for convenience of calculation; no physical quantity should differentiate between the two due to the symmetry of the original problem.

▷ EXERCISE. Consider the solution of the Schrödinger equation when working in the symmetric gauge with $\mathbf{A} = -\mathbf{r} \times \mathbf{B}/2$. Hint: consider the commutation relations for the velocities, $[\hat{v}_x, \hat{v}_y]$, and how these might be deployed as conjugate variables.

▷ INFO. **Integer quantum Hall effect:** Until now, we have considered the impact of just a magnetic field. Consider now the Hall effect geometry in which

Klaus von Klitzing, 1943-
German physicist who was awarded the Nobel Prize for Physics in 1985 for his discovery that under appropriate conditions the resistance offered by an electrical conductor is quantized. The work was first reported in the following reference, K. v. Klitzing, G. Dorda, and M. Pepper, *New method for high-accuracy determination of the fine-structure constant based on quantized Hall resistance*, Phys. Rev. Lett. **45**, 494 (1980).
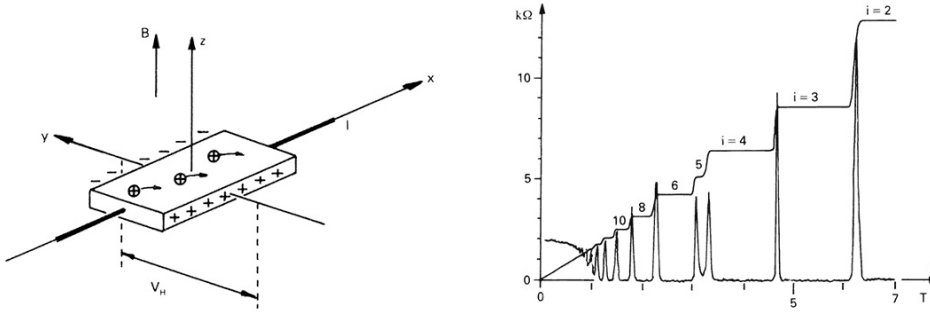
Figure 6.2: (Left) A voltage V drives a current I in the positive x direction. Normal Ohmic resistance is V/I. A magnetic field in the positive z direction shifts positive charge carriers in the negative y direction. This generates a Hall potential and a Hall resistance (VH/I) in the y direction. (Right) The Hall resistance varies stepwise with changes in magnetic field B. Step height is given by the physical constant h/e^2 (value approximately $25\,\mathrm{k\Omega}$) divided¡ by an integer i. The figure shows steps for $i = 2, 3, 4, 5, 6, 8$ and 10. The effect has given rise to a new international standard for resistance. Since 1990 this has been represented by the unit 1 klitzing, defined as the Hall resistance at the fourth step ($h/4e^2$). The lower peaked curve represents the Ohmic resistance, which disappears at each step.

we apply a crossed electric, $\mathbf{E}$ and magnetic field, $\mathbf{B}$. Taking into account both contributions, the total current flow is given by

$$\mathbf{j} = \sigma_0 \left(\mathbf{E} - \frac{\mathbf{j} \times \mathbf{B}}{ne} \right),$$

where σ_0 denotes the conductivity, and n is the electron density. With the electric field oriented along y, and the magnetic field along z, the latter equation may be rewritten as

$$\begin{pmatrix} 1 & \frac{\sigma_0 B}{ne} \\ -\frac{\sigma_0 B}{ne} & 1 \end{pmatrix} \begin{pmatrix} j_x \\ j_y \end{pmatrix} = \sigma_0 \begin{pmatrix} 0 \\ E_y \end{pmatrix}.$$

Inverting these equations, one finds that

$$j_x = \underbrace{\frac{-\sigma_0^2 B/ne}{1 + (\sigma_0 B/ne)^2}}_{\sigma_{xy}} E_y, \qquad j_y = \underbrace{\frac{\sigma_0}{1 + (\sigma_0 B/ne)^2}}_{\sigma_{yy}} E_y.$$

These provide the classical expressions for the longitudinal and Hall conductivities, σ_{yy} and σ_{xy} in the crossed field. Note that, for these classical expressions, σ_{xy} is proportional to B.

How does quantum mechanics revise this picture? For the classical model – **Drude theory**, the random elastic scattering of electrons impurities leads to a constant drift velocity in the presence of a constant electric field, $\sigma_0 = \frac{ne^2 \tau}{m_e}$, where τ denotes the mean time between collisions. Now let us suppose the magnetic field is chosen so that the electrons exactly fill all of the states in the first ν Landau levels, i.e. the total number of electrons nL_xLy is

$$nL_xL_y = \nu N_{\text{states}} \Rightarrow n = \nu \frac{eB}{h}.$$

The scattering of electrons must lead to a transfer between quantum states. However, if all states of the same energy are filled,[9] elastic (energy conserving) scattering becomes impossible. Moreover, since the next accessible Landau level energy is a distance $\hbar \omega_c$ away, at low enough temperatures, inelastic scattering becomes frozen

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[9]Note that electrons are subject to Pauli's exclusion principle restricting the occupancy of each state to unity.

out. As a result, the scattering rate $1/\tau$ vanishes at special values of the field, i.e. $\sigma_{yy} \to 0$ and

$$\sigma_{xy} \to \frac{ne}{B} = \nu \frac{e^2}{h}.$$

At critical values of the field, the Hall conductivity is quantized in units of e^2/h. Inverting the conductivity tensor, one obtains the resistivity tensor,

$$\begin{pmatrix} \rho_{xx} & \rho_{xy} \\ -\rho_{xy} & \rho_{xx} \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ -\sigma_{xy} & \sigma_{xx} \end{pmatrix}^{-1},$$

where

$$\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2}, \qquad \rho_{xy} = -\frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2},$$

So, when $\sigma_{xx} = 0$ and $\sigma_{xy} = \nu e^2/h$, $\rho_{xx} = 0$ and $\rho_{xy} = h/\nu e^2$. The quantum Hall state describes dissipationless current flow in which the Hall conductance σ_{xy} is quantized in units of e^2/h. Experimental measurements of these values provides the best determination of fundamental ratio e^2/h, better than 1 part in 10^7.

Chapter 7

Approximation methods for stationary states

7.1 Time-independent perturbation theory

While we have succeeded in deriving formal analytical solutions for stationary states of the Schrödinger operator in a variety of settings, in the majority of practical applications, *exact* solutions are inaccessible.[1] For example, if an atom is placed in an external electric field, the energy levels shift, and the wavefunctions become distorted — the Stark effect. The new energy levels and wavefunctions could in principle be obtained by writing down a complete Hamiltonian, including the external field. Indeed, such a programme may be achieved for the hydrogen atom. But even there, if the external field is small compared with the electric field inside the atom (which is billions of volts per metre) it is easier to compute the changes in the energy levels and wavefunctions within a scheme of successive corrections to the zero-field values. This method, termed perturbation theory, is the single most important method for solving problems in quantum mechanics, and is widely used in atomic physics, condensed matter and particle physics.

▷ INFO. It should be acknowledged that there are – typically very interesting – problems which cannot be solved using perturbation theory, even when the perturbation is very weak; although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localized potential of strength λ. As we found earlier in chapter 2, switching on an arbitrarily weak attractive potential causes the $k = 0$ free particle wavefunction to drop below the continuum of plane wave energies and become a localized bound state with binding energy of order λ^2. However, on changing the sign of λ to give a repulsive potential, there is no bound state; the lowest energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation cannot be represented as a power series in λ, the strength of the perturbation. This particular difficulty does not typically occur in three dimensions, where arbitrarily weak potentials do not in general lead to bound states.

▷ EXERCISE. Focusing on the problem of bound state formation in one dimension described above, explore the dependence of the ground state energy on λ. Consider why a perturbative expansion in λ is infeasible.

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[1]Indeed, even if such a solution is formally accessible, its complexity may render it of no practical benefit.

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7.1.1 The perturbation series

Let us then consider an unperturbed Hamiltonian, $\hat{H}^{(0)}$, having known (orthonormal) eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$,

$$\hat{H}^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle . \tag{7.1}$$

In the following we will address the question of how the eigenstates and eigenenergies are modified by the imposition of a small perturbation, $\hat{H}^{(1)}$ (such as that imposed by an external electric or magnetic field on a charged particle, or the deformation of some other external potential). In short, we are interested in the solution of the Schrödinger equation,

$$(\hat{H}^{(0)} + \hat{H}^{(1)})|n\rangle = E_n|n\rangle . \tag{7.2}$$

If the perturbation is small, $\langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \ll E_n^{(0)}$, it seems natural to suppose that, on turning on $\hat{H}^{(1)}$, the eigenfunctions and eigenvalues will change adiabatically from their unperturbed to their perturbed values, a situation described formally as "adiabatic continuity",

$$|n^{(0)}\rangle \longmapsto |n\rangle, \qquad E_n^{(0)} \longmapsto E_n .$$

However, note that this is not always the case. For example, as mentioned above, an infinitesimal perturbation has the capacity to develop a bound state not present in the unperturbed system. For now, let us proceed with the perturbative expansion and return later to discuss its potential range of validity.

The basic assumption that underpins the perturbation theory is that, for $\hat{H}^{(1)}$ small, the leading corrections are of the same order of magnitude as $\hat{H}^{(1)}$ itself. The perturbed eigenenergies and eigenvectors can then be obtained to a greater accuracy by a successive series of corrections, each of order $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$ compared with the previous. To identify terms of the same order in $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$, it is convenient to extract from $\hat{H}^{(1)}$ a dimensionless parameter λ, characterising the relative magnitude of the perturbation against $\hat{H}^{(0)}$, and then expand $|n\rangle$ and E_n as a power series in λ, i.e.

$$|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots = \sum_{m=0}^{\infty} \lambda^m |n^{(m)}\rangle,$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots = \sum_{m=0}^{\infty} \lambda^m E_n^{(m)} .$$

One may think of the parameter λ as an artificial book-keeping device to organize the perturbative expansion, and which is eventually set to unity at the end of the calculation.

Applied to the stationary form of the Schrödinger equation (7.2), an expansion of this sort leads to the relation

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots)$$
$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots) \tag{7.3}$$

From this equation, we must relate terms of equal order in λ. At the lowest order, $O(\lambda^0)$, we simply recover the unperturbed equation (7.1). In practical applications, one is usually interested in determining the first non-zero perturbative correction. In the following, we will explore the form of the first and second order perturbative corrections.

7.1.2 First order perturbation theory

Isolating terms from (7.3) which are first order in λ,

$$\hat{H}^{(0)}|n^{(1)}\rangle + \hat{H}^{(1)}|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle. \tag{7.4}$$

and taking the inner product with the unperturbed states $\langle n^{(0)}|$, one obtains

$$\langle n^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle + \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle = \langle n^{(0)}|E_n^{(0)}|n^{(1)}\rangle + \langle n^{(0)}|E_n^{(1)}|n^{(0)}\rangle.$$

Noting that $\langle n^{(0)}|\hat{H}^{(0)} = \langle n^{(0)}|E_n^{(0)}$, and exploiting the normalization $\langle n^{(0)}|n^{(0)}\rangle = 1$, one finds that the first order shift in energy is given simply by the expectation value of the perturbation taken with respect to the unperturbed eigenfunctions,

$$\boxed{E_n^{(1)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle.} \tag{7.5}$$

Turning to the wavefunction, if we instead take the inner product of (7.4) with $\langle m^{(0)}|$ (with $m \neq n$), we obtain

$$\langle m^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle + \langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle = \langle m^{(0)}|E_n^{(0)}|n^{(1)}\rangle + \langle m^{(0)}|E_n^{(1)}|n^{(0)}\rangle.$$

Once again, with $\langle m^{(0)}|\hat{H}^{(0)} = \langle m^{(0)}|E_m^{(0)}$ and the orthogonality condition on the wavefunctions, $\langle m^{(0)}|n^{(0)}\rangle = 0$, one obtains an expression for the first order shift of the wavefunction expressed in the unperturbed basis,

$$\boxed{\langle m^{(0)}|n^{(1)}\rangle = \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}.} \tag{7.6}$$

In summary, setting $\lambda = 1$, to first order in perturbation theory, we have the eigenvalues and eigenfunctions,

$$E_n \simeq E_n^{(0)} + \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle$$

$$|n\rangle \simeq |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}.$$

Before turning to the second order of perturbation theory, let us first consider a simple application of the method.

▷ EXAMPLE: **Ground state energy of the Helium atom:** For the Helium atom, two electrons are bound to a nucleus of two protons and two neutrons. If one neglects altogether the Coulomb interaction between the electrons, in the ground state, both electrons would occupy the ground state hydrogenic wavefunction (scaled appropriately to accommodate the doubling of the nuclear charge) and have opposite spin. Treating the Coulomb interaction between electrons as a perturbation, one may then use the basis above to estimate the shift in the ground state energy with

$$\hat{H}^{(1)} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

The hydrogenic wave functions are specified by three quantum numbers, n, ℓ, and m. In the ground state, the corresponding wavefunction takes the spatially isotropic form,

$$\langle \mathbf{r}|n=1, \ell=0, m=0\rangle = \psi_{100}(\mathbf{r}) = \left(\frac{1}{\pi a^3}\right)^{1/2} e^{-r/a}, \tag{7.7}$$
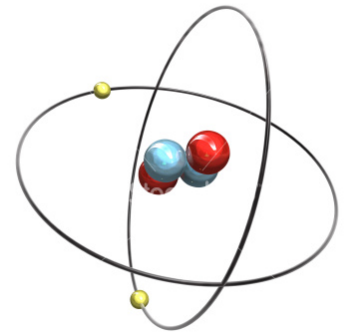
where $a = \frac{4\pi\epsilon_0}{Ze^2} \frac{\hbar^2}{m_e} = \frac{a_0}{Z}$ denotes the atomic Bohr radius for a nuclear charge Z. For the Helium atom ($Z = 2$), the symmetrized ground state of the unperturbed Hamiltonian is given by the spin singlet ($S = 0$) electron wavefunction,

$$|\text{g.s.}^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|100,\uparrow\rangle \otimes |100,\downarrow\rangle - |100,\downarrow\rangle \otimes |100,\uparrow\rangle\right).$$

Here we have used the **direct product** $\otimes$ to discriminate between the two electrons. Then, applying the perturbation theory formula above (7.5), to first order in the Coulomb interaction, the energy shift is given by

$$E_n^{(1)} = \langle \text{g.s.}^{(0)}|\hat{H}^{(1)}|\text{g.s.}^{(0)}\rangle = \frac{e^2}{4\pi\epsilon_0}\frac{1}{(\pi a^3)^2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^{-2(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{e^2}{4\pi\epsilon_0}\frac{C_0}{2a},$$

where we have defined the dimensionless constant $C_0 = \frac{1}{(4\pi)^2}\int d\mathbf{z}_1 d\mathbf{z}_1 \frac{e^{-(z_1+z_2)}}{|\mathbf{z}_1 - \mathbf{z}_2|}$. Then, making use of the identity,

$$\frac{1}{(4\pi)^2}\int d\Omega_1 d\Omega_2 \frac{1}{|\mathbf{z}_1 - \mathbf{z}_2|} = \frac{1}{\max(z_1, z_2)},$$

where the integrations runs over the angular coordinates of the vectors $\mathbf{z}_1$ and $\mathbf{z}_2$, and $z_{1,2} = |\mathbf{z}_{1,2}|$, one finds that $C_0 = 2\int_0^\infty dz_1 z_1^2 e^{-z_1}\int_{z_1}^\infty dz_2 z_2 e^{-z_2} = 5/4$. As a result, noting that the Rydberg energy, $\text{Ry} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{2a_0}$, we obtain the first order energy shift $\Delta E = \frac{5}{4}Z\text{Ry} \simeq 34\text{eV}$ for $Z = 2$. This leads to a total ground state energy of $(2Z^2 - \frac{5}{4}Z)\,\text{Ry} = -5.5\text{Ry} \simeq -74.8\text{eV}$ compared to the experimental value of -5.807Ry.

7.1.3 Second order perturbation theory

With the first order of perturbation theory in place, we now turn to consider the influence of the second order terms in the perturbative expansion (7.3). Isolating terms of order λ^2, we have

$$\hat{H}^{(0)}|n^{(2)}\rangle + \hat{H}^{(1)}|n^{(1)}\rangle = E_n^{(0)}|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle.$$

As before, taking the inner product with $\langle n^{(0)}|$, one obtains

$$\langle n^{(0)}|\hat{H}^{(0)}|n^{(2)}\rangle + \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle$$
$$= \langle n^{(0)}|E_n^{(0)}|n^{(2)}\rangle + \langle n^{(0)}|E_n^{(1)}|n^{(1)}\rangle + \langle n^{(0)}|E_n^{(2)}|n^{(0)}\rangle.$$

Noting that the first two terms on the left and right hand sides cancel, we are left with the result

$$E_n^{(2)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle - E_n^{(1)}\langle n^{(0)}|n^{(1)}\rangle.$$

Previously, we have made use of the normalization of the basis states, $|n^{(0)}\rangle$. We have said nothing so far about the normalization of the exact eigenstates, $|n\rangle$. Of course, eventually, we would like to ensure normalization of these states too. However, to facilitate the perturbative expansion, it is operationally more convenient to impose a normalization on $|n\rangle$ through the condition $\langle n^{(0)}|n\rangle = 1$. Substituting the λ expansion for $|n\rangle$, we thus have

$$\langle n^{(0)}|n\rangle = 1 = \langle n^{(0)}|n^{(0)}\rangle + \lambda\langle n^{(0)}|n^{(1)}\rangle + \lambda^2\langle n^{(0)}|n^{(2)}\rangle + \cdots.$$

From this relation, it follows that $\langle n^{(0)}|n^{(1)}\rangle = \langle n^{(0)}|n^{(2)}\rangle = \cdots = 0$.[2] We can therefore drop the term $E_n^{(1)}\langle n^{(0)}|n^{(1)}\rangle$ from consideration. As a result, we

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[2]Alternatively, would we suppose that $|n\rangle$ and $|n^{(0)}\rangle$ were both normalised to unity, to leading order, $|n\rangle = |n^{(0)}\rangle + |n^{(1)}\rangle$, and $\langle n^{(0)}|n^{(1)}\rangle + \langle n^{(1)}|n^{(0)}\rangle = 0$, i.e. $\langle n^{(0)}|n^{(1)}\rangle$ is pure imaginary. This means that if, to first order, $|n\rangle$ has a component parallel to $|n^{(0)}\rangle$, that component has a small imaginary amplitude allowing us to define $|n\rangle = e^{i\phi}|n^{(0)}\rangle$+orthog. components. However, the corresponding phase factor ϕ can be eliminated by redefining the phase of $|n\rangle$. Once again, we can conclude that the term $E_n^{(1)}\langle n^{(0)}|n^{(1)}\rangle$ can be eliminated from consideration.

obtain

$$E_n^{(2)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle = \langle n^{(0)}|\hat{H}^{(1)} \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}},$$

i.e.

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}. \tag{7.8}$$

From this result, we can conclude that,

▷ for the ground state, the second order shift in energy is always negative;

▷ if the matrix elements of $\hat{H}^{(1)}$ are of comparable magnitude, neighbouring levels make a larger contribution than distant levels;

▷ Levels that lie in close proximity tend to be **repelled**;

▷ If a fraction of the states belong to a continuum, the sum in Eq. (7.8) should be replaced by an integral.

Once again, to illustrate the utility of the perturbative expansion, let us consider a concrete physical example.

▷ EXAMPLE: **The Quadratic Stark Effect:** Consider the influence of an external electric field on the ground state of the hydrogen atom. As the composite electron and proton are drawn in different directions by the field, the relative displacement of the electron cloud and nucleus results in the formation of a dipole which serves to lower the overall energy. In this case, the perturbation due to the external field takes the form

$$\hat{H}^{(1)} = -q\mathcal{E}z = e\mathcal{E}r\cos\theta,$$

where $q = -e$ denotes the electron charge, and the electric field, $\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{e}_z$ is oriented along the z-axis. With the non-perturbed energy spectrum given by $E_{n\ell m}^{(0)} \equiv E_n^{(0)} = -\text{Ry}/n^2$, the ground state energy is given by $E^{(0)} \equiv E_{100}^{(0)} = -\text{Ry}$. At first order in the electric field strength, $\mathcal{E}$, the shift in the ground state energy is given by $E^{(1)} = \langle 100|e\mathcal{E}z|100\rangle$ where the ground state wavefunction was defined above (7.7). Since the potential perturbation is antisymmetric in z, it is easy to see that the energy shift vanishes at this order.

We are therefore led to consider the contribution second order in the field strength. Making use of Eq. (7.8), and neglecting the contribution to the energy shift from the continuum of unbound positive energy states, we have

$$E^{(2)} = \sum_{n \neq 1, \ell, m} \frac{|\langle n\ell m|e\mathcal{E}z|100\rangle|^2}{E_1^{(0)} - E_n^{(0)}},$$

where $|n\ell m\rangle$ denote the set of bound state hydrogenic wavefunctions. Although the expression for $E^{(2)}$ can be computed exactly, the programme is somewhat tedious. However, we can place a strong bound on the energy shift through the following argument: Since, for $n > 2$, $|E_1^{(0)} - E_n^{(0)}| > |E_1^{(0)} - E_2^{(0)}|$, we have

$$|E^{(2)}| < \frac{1}{E_2^{(0)} - E_1^{(0)}} \sum_{n \neq 1, \ell, m} \langle 100|e\mathcal{E}z|n\ell m\rangle\langle n\ell m|e\mathcal{E}z|100\rangle.$$

Since $\sum_{n,\ell,m} |n\ell m\rangle\langle n\ell m| = \hat{I}$, we have $\sum_{n \neq 1, \ell, m} |n\ell m\rangle\langle n\ell m| = \hat{I} - |100\rangle\langle 100|$. Finally, since $\langle 100|z|100\rangle = 0$, we can conclude that $|E^{(2)}| < \frac{1}{E_2^{(0)} - E_1^{(0)}} \langle 100|(e\mathcal{E}z)^2|100\rangle$. With $\langle 100|z^2|100\rangle = a_0^2$, $E_1^{(0)} = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{2a_0} = -\text{Ry}$, and $E_2^{(0)} = E_1^{(0)}/4$, we have

$$|E^{(2)}| < \frac{1}{\frac{3}{4}e^2/8\pi\epsilon_0 a_0}(e\mathcal{E})^2 a_0^2 = \frac{8}{3}4\pi\epsilon_0\mathcal{E}^2 a_0^3.$$

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Furthermore, since all terms in the perturbation series for $E^{(2)}$ are negative, the first term in the series sets a lower bound, $|E^{(2)}| > \frac{|\langle 210|e\mathcal{E}z|100\rangle|^2}{E_2^{(0)} - E_1^{(0)}}$. From this result, one can show that $0.55 \times \frac{8}{3} 4\pi\epsilon_0 \mathcal{E}^2 a_0^3 < |E^{(2)}| < \frac{8}{3} 4\pi\epsilon_0 \mathcal{E}^2 a_0^3$ (exercise).[3]

7.2 Degenerate perturbation theory

The perturbative analysis above is reliable providing that the successive terms in the expansion form a convergent series. A necessary condition is that the matrix elements of the perturbing Hamiltonian must be smaller than the corresponding energy level differences of the original Hamiltonian. If it has different states with the same energy (i.e. degeneracies), and the perturbation has non-zero matrix elements between these degenerate levels, then clearly the theory breaks down. However, the problem is easily fixed. To understand how, let us consider a particular example.

Recall that, for the simple harmonic oscillator, $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$, the ground state wavefunction is given by $\langle x|0\rangle = (\frac{m\omega}{\pi\hbar})^{1/4} e^{-\xi^2/2}$, where $\xi = x\sqrt{m\omega/\hbar}$ and the first excited state by $\langle x|1\rangle = (\frac{4m\omega}{\pi\hbar})^{1/4}\xi e^{-\xi^2/2}$. The wavefunctions for the two-dimensional harmonic oscillator,

$$\hat{H}^{(0)} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2).$$

are given simply by the product of two one-dimensional oscillators. So, setting $\eta = y\sqrt{m\omega/\hbar}$, the ground state is given by $\langle x, y|0,0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(\xi^2+\eta^2)/2}$, and the two *degenerate* first excited states, an energy $\hbar\omega$ above the ground state, are given by,

$$\left\{ \begin{array}{l} \langle x, y|1,0\rangle \\ \langle x, y|0,1\rangle \end{array} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(\xi^2+\eta^2)/2} \left\{ \begin{array}{l} \xi \\ \eta \end{array} \right. \right..$$

Suppose now we add to the Hamiltonian a perturbation,

$$\hat{H}^{(1)} = \alpha m\omega^2 xy = \alpha\hbar\omega\xi\eta,$$

controlled by a small parameter α. Notice that, by symmetry, the following matrix elements all vanish, $\langle 0,0|\hat{H}^{(1)}|0,0\rangle = \langle 1,0|\hat{H}^{(1)}|1,0\rangle = \langle 0,1|\hat{H}^{(1)}|0,1\rangle = 0$. Therefore, according to a naïve perturbation theory, there is no first-order correction to the energies of these states. However, on proceeding to consider the second-order correction to the energy, the theory breaks down. The off-diagonal matrix element $\langle 1,0|\hat{H}^{(1)}|0,1\rangle$ is non-zero, but the two states $|0,1\rangle$ and $|1,0\rangle$ have the same energy! This gives an infinite term in the series for $E_{n=1}^{(2)}$.

Yet we know that a small perturbation of this type will not wreck a two-dimensional simple harmonic oscillator – so what is wrong with our approach? To understand the origin of the problem and its fix, it is helpful to plot the original harmonic oscillator potential $\frac{1}{2}m\omega^2(x^2 + y^2)$ together with the perturbing potential $\alpha m\omega^2 xy$. The first of course has circular symmetry, the second has two symmetry axes oriented in the directions $x = \pm y$, climbing most steeply from the origin along $x = y$, falling most rapidly in the directions $x = -y$. If we combine the two potentials into a single quadratic form,

$$\frac{1}{2}m\omega^2(x^2 + y^2) + \alpha m\omega^2 xy = \frac{1}{2}m\omega^2\left[(1+\alpha)\left(\frac{x+y}{\sqrt{2}}\right)^2 + (1-\alpha)\left(\frac{x-y}{\sqrt{2}}\right)^2\right].$$

---

[3]Energetic readers might like to contemplate how the exact answer of $|E^{(2)}| = \frac{9}{4}(4\pi\epsilon_0)\mathcal{E}^2 a_0^3$ can be found exactly. The method can be found in the text by Shankar.
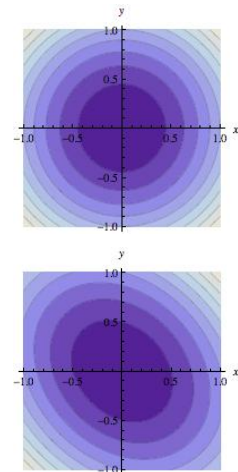
the original circles of constant potential become ellipses, with their axes aligned along $x = \pm y$.

As soon as the perturbation is introduced, the eigenstates lie in the direction of the new elliptic axes. This is a large change from the original x and y bases, which is not proportional to the small parameter α. But the original unperturbed problem had circular symmetry, and there was no particular reason to choose the x and y axes as we did. If we had instead chosen as our original axes the lines $x = \pm y$, the basis states would not have undergone large changes on switching on the perturbation. The resolution of the problem is now clear: *Before* switching on the perturbation, *one must choose a set of basis states in a degenerate subspace in which the perturbation is diagonal.*

In fact, for the simple harmonic oscillator example above, the problem can of course be solved exactly by rearranging the coordinates to lie along the symmetry axes, $(x \pm y)/\sqrt{2}$. It is then clear that, despite the results of naïve first order perturbation theory, there is indeed *a first order shift* in the energy levels, $\hbar\omega \to \hbar\omega\sqrt{1 \pm \alpha} \approx \hbar\omega(1 \pm \alpha/2)$.

▷ EXAMPLE: **Linear Stark Effect:** As with the two-dimensional harmonic oscillator discussed above, the hydrogen atom has a non-degenerate ground state, but degeneracy in its lowest excited states. Specifically, there are four $n = 2$ states, all having energy $-\frac{1}{4}$Ry. In spherical coordinates, these wavefunctions are given by

$$\left\{ \begin{array}{l} \psi_{200}(\mathbf{r}) \\ \psi_{210}(\mathbf{r}) \\ \psi_{21,\pm1}(\mathbf{r}) \end{array} \right. = \left(\frac{1}{32\pi a_0^3} \right)^{1/2} e^{-r/2a_0} \left\{ \begin{array}{l} \left(2 - \frac{r}{a_0}\right) \\ \frac{r}{a_0}\cos\theta \\ \frac{r}{a_0}e^{\pm i\phi}\sin\theta \end{array} \right. .$$

When perturbing this system with an electric field oriented in the z-direction, $\hat{H}^{(1)} = e\mathcal{E}r\cos\theta$, a naïve application of perturbation theory predicts no first-order shift in any of these energy levels. However, to first order in $\mathcal{E}$ there is a non-zero matrix element between two degenerate levels $\Delta = \langle 200|\hat{H}^{(1)}|210\rangle$. All the other matrix elements between these basis states in the four-dimensional degenerate subspace are zero. So the only diagonalization necessary is within the *two*-dimensional degenerate subspace spanned by $|200\rangle$ and $|210\rangle$, i.e.

$$\hat{H}^{(1)} = \left(\begin{array}{cc} 0 & \Delta \\ \Delta & 0 \end{array} \right),$$

with $\Delta = e\mathcal{E} \left(\frac{1}{32\pi a_0^3} \right) \int \left(2 - \frac{r}{a_0}\right) \frac{(r\cos\theta)^2}{a_0} e^{-r/a_0} r^2 dr \sin\theta \, d\theta \, d\phi = -3e\mathcal{E}a_0$.

Diagonalizing $\hat{H}^{(1)}$ within this sub-space, the new basis states are given by the symmetric and antisymmetric combinations, $(|200\rangle \pm |210\rangle)/\sqrt{2}$ with energy shifts $\pm\Delta$, *linear* in the perturbing electric field. The states $|2\ell, \pm1\rangle$ are not changed by the presence of the field to this level of approximation, so the complete energy map of the $n = 2$ states in the electric field has two states at the original energy of $-$Ry$/4$, one state moved up from that energy by Δ, and one down by Δ. Notice that the new eigenstates $(|200\rangle \pm |210\rangle)/\sqrt{2}$ are *not* eigenstates of the parity operator – a sketch of their wavefunctions reveals that, in fact, they have non-vanishing electric dipole moment $\mathbf{p}$. Indeed this is the reason for the energy shift, $\pm\Delta = \mp 2e\mathcal{E}a_0 = \mp\mathbf{p}\cdot\mathcal{E}$.

▷ EXAMPLE: As a second and important example of the degenerate perturbation theory, let us consider the problem of a particle moving in one dimension and subject to a weak periodic potential, $V(x) = 2V\cos(2\pi x/a)$ – the **nearly free electron model**. This problem provides a caricature of a simple crystalline solid in which (free) conduction electrons propagate in the presence of a periodic background lattice potential. Here we suppose that the strength of the potential V is small as compared to the typical energy scale of the particle so that it may be treated as a small pertur-

bation. In the following, we will suppose that the total one-dimensional system is of length $L = Na$, with periodic boundary conditions.

For the unperturbed free particle system, the eigenstates are simply plane waves $\psi_k(x) = \langle x|k \rangle = \frac{1}{\sqrt{L}}e^{ikx}$ indexed by the wavenumber $k = 2\pi n/L$, n integer, and the unperturbed spectrum is given by $E_k^{(0)} = \hbar^2 k^2/2m$. The matrix elements of the perturbation between states of different wavevector are given by

$$\langle k|V|k' \rangle = \frac{1}{L} \int_0^L dx e^{i(k'-k)x} 2V \cos(2\pi x/a)$$

$$= \frac{V}{L} \int_0^L \left(e^{i(k'-k+2\pi/a)x} + e^{i(k'-k-2\pi/a)x} \right) = V\delta_{k'-k, \pm 2\pi/a} .$$

Note that all diagonal matrix elements of the perturbation are identically zero. In general, for wavevectors k and k' separated by $G = 2\pi/a$, the unperturbed states are non-degenerate. For these states one can compute the relative energy shift within the framework of second order perturbation theory. However, for states $k = -k' = G/2 \equiv \pi/a$, the unperturbed free particle spectrum is degenerate. Here, and in the neighbourhood of these k values, we must implement a degenerate perturbation theory.

For the sinusoidal potential considered here, only states separated by $G = 2\pi/a$ are coupled by the perturbation. We may therefore consider matrix elements of the full Hamiltonian between pairs of coupled states, $|k = G/2 + q\rangle$ and $|k = -G/2 + q\rangle$

$$H = \begin{pmatrix} E_{G/2+q}^{(0)} & V \\ V & E_{-G/2+q}^{(0)} \end{pmatrix} .$$

As a result, to leading order in V, we obtain the eigenvalues,

$$E_q = \frac{\hbar^2}{2m}(q^2 + (\pi/a)^2) \pm \left(V^2 + \frac{\pi^2 \hbar^4 q^2}{4m^2 a^2} \right)^{1/2} .$$

In particular, this result shows that, for $k = \pm G/2$, the degeneracy of the free particle system is lifted by the potential. In the vicinity, $|q| \ll G$, the spectrum of eigenvalues is separated by a gap of size $2V$. The appearance of the gap mirrors the behaviour found in our study of the Kronig-Penney model of a crystal studied in section 2.2.3.

The appearance of the gap has important consequences in theory of solids. Electrons are fermions and have to obey Pauli's exclusion principle. In a metal, at low temperatures, electrons occupy the free particle-like states up to some (Fermi) energy which lies away from gap. Here, the accessibility of very low-energy excitations due to the continuum of nearby states allows current to flow when a small electric field is applied. However, when the Fermi energy lies in the gap created by the lattice potential, an electric field is unable to create excitations and induce current flow. Such systems are described as **(band) insulators**.
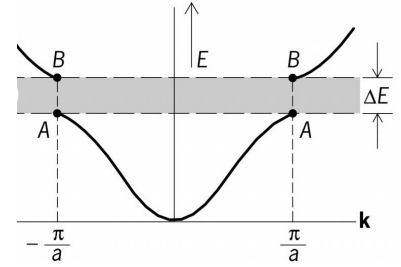
7.3 Variational method

So far, in devising approximation methods for quantum mechanics, we have focused on the development of a perturbative expansion scheme in which the states of the non-perturbed system provided a suitable platform. Here, by "suitable" we refer to situations in which the states of the unperturbed system mirror those of the full system – adiabatic continuity. For example, the states of the harmonic oscillator potential with a small perturbation will mirror those of the unperturbed Hamiltonian: The ground state will be nodeless, the first excited state will be antisymmetric having one node, and so on. However, often we working with systems where the true eigenstates of the problem may not be adiabatically connected to some simple unperturbed reference state. This

situation is particularly significant in strongly interacting quantum systems where many-particle correlations can effect phase transitions to new states of matter – e.g. the development of superfluid condensates, or the fractional quantum Hall fluid. To address such systems if it is often extremely effective to "guess" and then optimize a trial wavefunction. The method of optimization relies upon a simple theoretical framework known as the variational approach. For reasons that will become clear, the variational method is particularly well-suited to addressing the ground state.

The variational method involves the optimization of some trial wavefunction on the basis of one or more adjustable parameters. The optimization is achieved by minimizing the expectation value of the energy on the trial function, and thereby finding the best approximation to the true ground state wave function. This seemingly crude approach can, in fact, give a surprisingly good approximation to the ground state energy but, it is usually not so good for the wavefunction, as will become clear. However, as mentioned above, the real strength of the variational method arises in the study of many-body quantum systems, where states are more strongly constrained by fundamental symmetries such as "exclusion statistics".

To develop the method, we'll begin with the problem of a single quantum particle confined to a potential, $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r})$. If the particle is restricted to one dimension, and we're looking for the ground state in any fairly localized potential well, it makes sense to start with a trial wavefunction which belongs to the family of normalized Gaussians, $\langle x|\psi(\alpha)\rangle = (\alpha/\pi)^{1/4}e^{-\alpha x^2/2}$. Such a trial state fulfils the criterion of being nodeless, and is exponentially localized to the region of the binding potential. It also has the feature that it includes the exact ground states of the harmonic binding potential.

The variation approach involves simply minimizing the expectation value of the energy, $E = \langle \psi(\alpha)|\hat{H}|\psi(\alpha)\rangle$, with respect to variations of the **variational parameter**, α. (Of course, as with any minimization, one must check that the variation does not lead to a maximum of the energy!) Not surprisingly, this programme leads to the exact ground state for the simple harmonic oscillator potential, while it serves only as an approximation for other potentials. What is perhaps surprising is that the result is only off by only ca. 30% or so for the attractive δ-function potential, even though the wavefunction looks substantially different. The Gaussian family cannot be used if there is an infinite wall anywhere: since the wavefunction must vanish where the potential is infinite, one must find a family of wavefunctions that vanishes at such a boundary.

▷ EXERCISE. Using the Gaussian trial state, find the optimal value of the variational state energy, E, for an attractive δ-function potential and compare it with the exact result.

To gain some further insight into the approach, suppose the Hamiltonian $\hat{H}$ has a set of eigenstates, $\hat{H}|n\rangle = E_n|n\rangle$. Since the Hamiltonian is Hermitian, these states span the space of possible wave functions, including our variational family of Gaussians, so we can write, $|\psi(\alpha)\rangle = \sum_n a_n(\alpha)|n\rangle$. From this expansion, we have

$$\boxed{\frac{\langle \psi(\alpha)|\hat{H}|\psi(\alpha)\rangle}{\langle \psi(\alpha)|\psi(\alpha)\rangle} = \sum_n |a_n|^2 E_n \geq E_0\,,}$$

for *any* $|\psi(\alpha)\rangle$. (We don't need the denominator if we've chosen a family of normalized wavefunctions, as we did with the Gaussians above.) Evidently,

minimizing the left hand side of this equation as function of α provides an **upper bound** on the ground state energy.

We can see immediately that this will probably be better for finding the ground state energy than for the wavefunction: Suppose the optimum state in our family is given by, say, $|\alpha_{\min}\rangle = N(|0\rangle + 0.2|1\rangle)$ with the normalization $N \simeq 0.98$, i.e. a 20% admixture of the first excited state. Then the wavefunction is off by ca. 20%, but the energy estimate will be too high by only $0.04(E_1 - E_0)$, usually a much smaller error.

▷ EXAMPLE: To get some idea of of how well the variational approach works, consider its application to the ground state of the hydrogen atom. Taking into account the spherical symmetry of the ground state, we may focus on the one-dimensional radial component of the wavefunction. Defining the trial radial wavefunction $u(\rho)$ (presumed real), where $\rho = r/a_0$, the variational energy is given by

$$E(u) = -\mathrm{Ry} \frac{\int_0^\infty d\rho\, u(\rho) \left(\frac{d^2}{d\rho^2} + \frac{2}{\rho} \right) u(\rho)}{\int_0^\infty d\rho\, u^2(\rho)}\,.$$

For the three families of trial functions,

$$u_1(\rho) = \rho e^{-\alpha\rho}, \qquad u_2(\rho) = \frac{\rho}{\alpha^2 + \rho^2}, \qquad u_3(\rho) = \rho^2 e^{-\alpha\rho},$$

and finds $\alpha_{\min} = 1$, $\pi/4$, and $3/2$ respectively (exercise). The first family, u_1, includes the exact result, and the minimization procedure correctly finds it. For the three families, the predicted energy of the optimal state is off by 0, 25%, and 21% respectively.

The corresponding error in the wavefunction is defined by how far the square of the overlap with the true ground state wavefunction falls short of unity. For the three families, $\varepsilon = 1 - |\langle \psi_0 | \psi_{\mathrm{var}} \rangle|^2 = 0$, 0.21, and 0.05. Notice here that our handwaving argument that the energies would be found much more accurately than the wavefunctions seems to come unstuck. The third family has far better wavefunction overlap than the second, but only a slightly better energy estimate. Why? A key point is that the potential is singular at the origin; there is a big contribution to the potential energy from a rather small region, and the third family of trial states is the least accurate of the three there. The second family of functions are very inaccurate at large distances: the expectation value $\langle r \rangle = 1.5a_0$, ∞, $1.66a_0$ for the three families. But at large distances, both kinetic and potential energies are small, so the result can still look reasonable. These examples reinforce the point that the variational method should be implemented with some caution.

In some cases, one can exploit symmetry to address the properties of higher-lying states. For example, if the one-dimensional attractive potential is symmetric about the origin, and has more than one bound state, the ground state will be even, the first excited state odd. Therefore, we can estimate the energy of the first excited state by minimizing a family of odd functions, such as $\psi(x, \alpha) = (\frac{\sqrt{\pi}}{2\alpha^{3/2}})^{1/2} x e^{-\alpha x^2/2}$.

▷ EXAMPLE: **Helium atom addressed by the variational approach:** For the hydrogen atom, we know that the ground state energy is $-1\,\mathrm{Ry}$, or $-13.6\,\mathrm{eV}$. The He$^+$ ion (with just a single electron) has a nuclear charge of $Z = 2$, so the ground state energy of the electron, being proportional to Z^2, will now be equal to $-4\,\mathrm{Ry}$. Therefore, for the He atom, if we neglect their mutual interaction, the electrons will occupy the ground state wavefunction having opposite spin, leading to a total ground state energy of $-8\,\mathrm{Ry}$ or $-109\,\mathrm{eV}$. In practice, as we have seen earlier, the repulsion between the electrons raises the ground state energy to $-79\,\mathrm{eV}$ (see page 61).

To get a better estimate for the ground state energy, one can retain the form of the ionic wavefunction, $(\frac{\mathcal{Z}^3}{\pi a_0^3})^{1/2} e^{-\mathcal{Z} r/a_0}$, but now with $\mathcal{Z}$ a variational parameter, rather

than setting it equal to the nuclear charge $Z = 2$. In other words, let us accommodate the effects of electron-electron repulsion, which must "push" the wavefunctions to larger radii, by keeping exactly the same wavefunction profile but lessening the effective nuclear charge as reflected in the spread of the wavefunction from $\mathcal{Z} = 2$ to $\mathcal{Z} < 2$. The precise value will be set by varying it to find the minimum total energy, including the term from electron-electron repulsion.

To find the potential energy from the nuclear-electron interactions, we of course must use the actual nuclear charge $Z = 2$, but impose a variable $\mathcal{Z}$ for the wavefunction, so the nuclear potential energy for the two electrons is given by,

$$\text{p.e.} = -2 \times \frac{2e^2}{4\pi\epsilon_0} \int_0^\infty 4\pi r^2 dr \frac{\mathcal{Z}^3}{\pi a_0^3} \frac{e^{-2\mathcal{Z}r/a_0}}{r} = -\mathcal{Z}\frac{e^2}{\pi\epsilon_0 a_0} = -8\mathcal{Z}\,\text{Ry.}$$

This could have been inferred from the formula for the one electron ion of charge Z, where the potential energy for the one electron is $-2Z^2\,\text{Ry}$, one factor of Z being from the nuclear charge, the other from the consequent shrinking of the orbit. The kinetic energy is even easier to determine: it depends entirely on the form of the wavefunction, and not on the actual nuclear charge. So for our trial wavefunction it has to be $\mathcal{Z}^2\,\text{Ry}$ per electron. Finally, making use of our calculation on page 61, we can immediately write down the positive contribution to the energy expectation value from the electron-electron interaction,

$$\frac{e^2}{4\pi\epsilon_0} \frac{\mathcal{Z}^3}{(\pi a_0^3)^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^{-2\mathcal{Z}(r_1+r_2)/a_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{5}{4}\frac{e^2}{4\pi\epsilon_0}\frac{\mathcal{Z}}{2a_0} = \frac{5}{4}\mathcal{Z}\,\text{Ry}\,.$$

Collecting all of the terms, the total variational state energy is given by:

$$E = -2\left(4\mathcal{Z} - \mathcal{Z}^2 - \frac{5}{8}\mathcal{Z}\right)\,\text{Ry}\,.$$

Minimization of this energy with respect to $\mathcal{Z}$ obtains the minimum at $\mathcal{Z} = 2 - \frac{5}{16}$, leading to an energy of $-77.5\,\text{eV}$. This result departs from the true value by about $1\,\text{eV}$. So, indeed, the presence of the other electron leads effectively to a shielding of the nuclear charge by an amount of ca. $(5/16)e$.

This completes our discussion of the principles of the variational approach. However, later in the course, we will find the variational methods appearing in several important applications.

Léon Nicolas Brillouin 1889-1969
A French physicist, his father, Marcel Brillouin, grandfather, Éleuthère Mascart, and great-grandfather, Charles Briot, were physicists as well. He made contributions to quantum mechanics, radio wave propagation in the atmosphere, solid state physics, and information theory.

Hendrik Anthony "Hans" Kramers 1894-1952
A Dutch physicist who conducted early and important work in quantum theory and electromagnetic dispersion relations, solid-state physics, and statistical mechanics. He was a long-time assistant and friend to Niels Bohr, and collaborated with him on a 1924 paper contending that light consists of probability waves, which became a foundation of quantum mechanics. He introduced the idea of renormalization, a cornerstone of modern field theory, and determined the dispersion formulae that led to Werner Heisenberg's matrix mechanics. He is not as well known as some of his contemporaries (primarily because his work was not widely translated into English), but his name is still invoked by physicists as they discuss Kramers dispersion theory, Kramers-Heisenberg dispersion formulae, Kramers opacity formula, Kramers degeneracy, or Kramers-Kronig relations.