Quantum Mechanics 3 2001–2002

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http://www.roe.ac.uk/japwww/teaching/qm3.html

Synopsis

This course covers non-relativistic quantum mechanics, supplying the basic concepts and tools needed to understand the physics of atoms, molecules, and the solid state. The calculational rules of quantum mechanics are introduced and motivated, including Dirac notation. Angular momentum and spin are shown to be quantized, and the corresponding wave-function symmetries are discussed. The Schrödinger equation is solved for a number of important cases, including the harmonic oscillator and the Hydrogen atom. Approximate methods of solution are studied, including time-independent perturbation theory.

Recommended books

Davies & Betts: Quantum mechanics (Chapman & Hall) A short and admirably focused book, at about the level of this course. A very clear exposition of the core material, although less useful if you want to dig deeper into the subject.

Griffiths: Introduction to quantum mechanics (Prentice Hall) The strength of this book is its many detailed problems (without solutions, unfortunately), which encourage you to think carefully about many of the subtleties of the subject. The chapter on the mathematical basis of the subject is unnecessarily abstract, but this level of formality does not carry over to the actual applications.

Park: Introduction to the quantum theory (McGraw-Hill) Goes beyond the level of this course, but is very clear in its arguments. A nice balance of mathematical elegance without excessive formality. Will be useful next year, and is a bargain. Alas, the idiots at McGraw-Hill have recently decided to withdraw this book from print; it can only be hoped that this is a temporary aberration. In the meantime, buy it while you can.

Syllabus

(1) Basics revision; de Broglie; Bohr atom; Matter waves

(2) Schrödinger equation; stationary states; probability density and current

(3) Examples; Square well(s); Bound states and tunnelling; Delta potential

(4) Harmonic oscillator in 1D and 3;. Degeneracy; Wave functions

(5) Rules of QM I: Complete sets; Eigenfunctions, eigenvalues and Hermitian operators

(6) Rules of QM II: Measurements; expectation values; classical limit

(7) Momentum space; uncertainty principle for wavepackets

(8) Dirac notation; generalized uncertainty principle

(9) Angular momentum: Operators; commutation relations; vector model

(10) Ladder operators: Angular momentum; harmonic oscillator; occupation numbers

(11) Hydrogen atom I

(12) Hydrogen atom II

(13) Spin; Stern-Gerlach

(14) Addition of angular momentum; Fine structure

(15) Many-particle systems; identical particles

(16) Spin & symmetry; spin wavefunctions

(17) Time-independent perturbation theory.

(18) Perturbation theory in action: atomic structure

1 Evidence for a quantum world

Quantum mechanics is the closest we have come to a description of the 'true' nature of physical reality. It is a difficult body of knowledge to understand, since the physics of the everyday world is only an approximate limit of the quantum theory. The actual tools and concepts that have to be used in the subatomic world are utterly different to the familiar ideas of classical physics, and seem alien and intimidating at first sight. Given this failure of our existing intuition, mathematical reasoning is often the only way to make progress, and this can make quantum mechanics seem offputtingly abstract. The main solution to this is practice: as experience with applying the quantum method grows, it all starts to make sense. It should help to have had some brief exposure to the main issues in second year, but we start by going back over the basics.

Quantum mechanics began with the observed quantization of light. Energy is not transmitted continuously, but arrives in discrete packets of energy, or **photons**:

$$\boxed{E = \hbar\omega.} \tag{1}$$

Here, ω is angular frequency ($\omega = 2\pi\nu$). The term **Planck's constant** can unfortunately apply either to the number $\hbar = 1.055 \times 10^{-34}\,\mathrm{Js}$, or to $h = 2\pi\hbar$ (so $E = h\nu$). We will almost always use angular frequency. There were several pieces of evidence leading to this conclusion:

BLACK-BODY RADIATION Planck formula for thermal energy density (1901):

$$\frac{dU}{d\omega} = \frac{\hbar\omega^3/\pi^2c^3}{e^{\hbar\omega/kT} - 1} \tag{2}$$

where **Boltzmann's constant** is $k = 1.381 \times 10^{-23}\,\mathrm{JK}^{-1}$. Initially, this was just a fitting formula, but later came the interpretation that each mode of the electromagnetic field was an oscillator for which the energy was quantized: $E = n\hbar\omega$. There's no need to remember the details of this formula, but note that the energy density is proportional to $(kT) \times \omega^2 d\omega$ for low energies (where the photon energy is much less than kT). This is of the form of the number of electromagnetic wave modes with frequency in the range $d\omega$ (as we will show), times the typical equipartition energy kT. Only discreteness of photon energy cuts this off, and stops the energy density being infinite.

PHOTOELECTRIC EFFECT Light ejects electrons from metals, but only for light above some minimum frequency. Einstein (1905) used this fact plus Planck's quantization of energy to predict that the energy of the electrons would increase with frequency of light:

$$mv_{\mathrm{max}}^2/2 = \hbar\omega - W \tag{3}$$

The constant is the same $\hbar$ as in the Planck formula. This is a much more direct indication that light energy is transmitted as individual photon particles. This was exactly the view that Newton held in the mid-1600s, but interference experiments carried out by Huygens appeared to prove that light was a wave phenomenon. In reality, we have to face the concept of **wave-particle duality**: light can behave at different times as though it is either a continuous wave disturbance, or a particle phenomenon.

YOUNG'S SLITS Of course, there are not two different kinds of light. To try to understand what is going on, consider the basic two-slit interference experiment. The detector can be made very sensitive, and detectors are routinely used in astronomy that can register the arrival of individual photons. When the experiment is run at high light levels, it appears to be a standard piece of wave physics, and a normal interference fringe pattern is observed. However, when the experiment is run at low light levels, it is possible to see the photons arriving one at a time on the detector. For very low light intensities, there can be minutes between photons, so that there is only one in the apparatus at any one time. You might then think the photons would behave like little balls: they would travel through only one slit or the other, and the interference fringes would disappear. In fact, over time, the interference pattern still builds up. It's as if the wave field is still there, but what it does is give the photons information as to the probability that they should arrive at a given spot. It is therefore wrong to think of the photon as travelling like a classical particle: it is not clear where it is until it is detected, and where a given photon does actually arrive appears to be unpredictable. This **randomness** is one of the most disturbing features of the quantum world.

SPECTROSCOPY AND MATTER QUANTIZATION Since wave-particle duality is observed in light, it is tempting to believe that it may also exist in matter: is it possible that particles like electrons may also have a wave phenomenon underlying them?

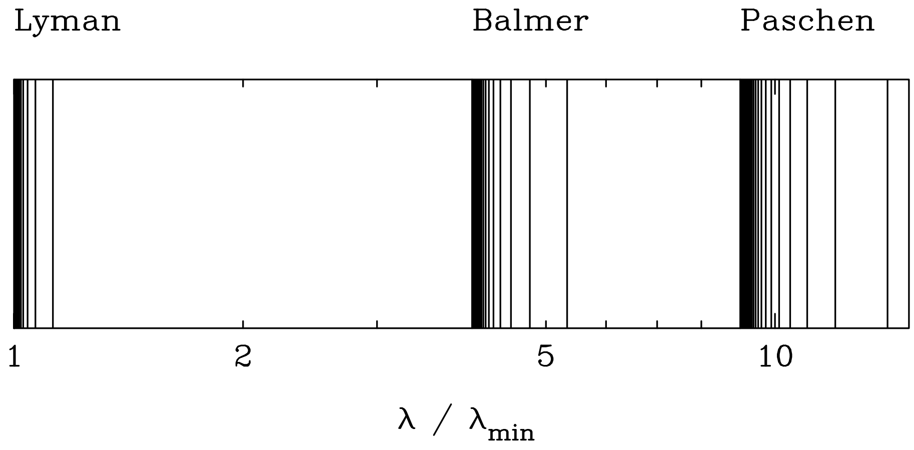

Figure 1 The line spectrum of atomic Hydrogen consists of various distinct series. Each series has a maximum wavelength, and a series limit at some minimum wavelength, with progressively more finely spaced lines as the series limit is approached.

Evidence for odd behaviour of matter at the atomic scale emerged quite early on from atomic spectroscopy. The **Balmer-Rydberg formula** (1885 – 1889) fits regularities in Hydrogen emission and absorption spectra:

$$\nu = \nu_{\rm max} \left[\frac{1}{n^2} - \frac{1}{m^2} \right] \tag{4}$$

where $\nu_{\rm max} = 3.29 \times 10^{15}$ Hz (a wavelength of 91.2 nm). Furthermore, there is **fine structure**: at high resolution, lines split up into multiplets with a fractional splitting of $\delta\nu/\nu \sim 10^{-4}$.

Classically, this makes no sense. Viewing an atom as a miniature 'solar system' of an electron orbiting a nucleus, we expect that the accelerating electron should radiate energy at a frequency equal to its orbital frequency. This just depends on the energy of the electron, which should be able to take any value. In fact, knowing about energy quantization for photons, we can see that the electrons must have only a few special allowed values of orbital energy, with the difference in these energies governing the frequency of the emitted photon via $\hbar\omega = \Delta E$. Furthermore, the existence of these special allowed energy levels is essential for the existence of atoms: if orbital energies could take any value, electrons would radiate away energy continuously, and spiral in to the nucleus.

As with the Planck formula, the Balmer-Rydberg formula was just a piece of numerology, but one that cried out for explanation. The theoretical developments of quantum mechanics in the 1920s were driven by the need to explain the huge body of accurate data on atomic spectroscopy.

2 The wave nature of matter

DE BROGLIE'S HYPOTHESIS Consider the experimental quantization relations for the energy and momentum of photons, in terms of angular frequency ω and wave vector $\mathbf{k}$ (the wavenumber is related to wavelength by $k = 2\pi/\lambda$; k can be made into a vector by defining it to point in the direction of wave propagation):

$$\boxed{E = \hbar\omega \quad \Rightarrow \quad \mathbf{p} = \hbar\mathbf{k}} \tag{5}$$

(because $E = mc^2$, $p = mc$, and $k = 2\pi/\lambda = \omega/c$). Although this course will stick strictly to non-relativistic quantum mechanics, the relativistically-minded will note that de Broglie's hypothesis can be written as a single 4-vector relation between 4-momentum and 4-wavevector: $P^\mu = \hbar k^\mu$. It is the inevitable relativistic generalization of $E = \hbar\omega$.

It was proposed (in 1923) by Louis de Broglie that any wave-like behaviour of matter might display the same energy–frequency and momentum–wavenumber relations as are observed for photons. Since wave-like behaviour in electrons had not been noticed before de Broglie's suggestion, the wavelength must be short in normal circumstances. For nonrelativistic electrons of energy E, the relation to momentum is $E = p^2/(2m)$, so that

$$\lambda = \frac{2\pi}{k} = \frac{2\pi\hbar}{p} = \frac{2\pi\hbar}{(2mE)^{1/2}} = 10^{-10.41}\ \mathrm{m}\ (E/\mathrm{keV})^{-1/2}. \tag{6}$$

Electrons accelerated to moderate energies are thus expected to show diffraction effects from the finite lattice spacing in solids. By a nice irony, this wave nature of electrons was first demonstrated experimentally (in 1925) by G.P. Thomson – the son of J.J. Thomson, who discovered the electron and 'proved' that it was a particle.

BOHR ATOM Given de Broglie's hypothesis, the idea of electron waves can be applied to give a preliminary model of the atom. In fact, this model was invented by Niels Bohr in 1913, but the key idea can be motivated more easily using the later concepts. Classical electron orbits need to be replaced with the idea that electrons form something like standing waves. If a travelling wave packet is to reinforce itself after travelling round a circular orbit of radius r, then the circumference must be a whole number of wavelengths: $2\pi r = n\lambda$, where $n = 1, 2, \ldots$. Since $\lambda = 2\pi\hbar/p$, this suggests that angular momentum must be quantized:

$$\boxed{L \equiv pr = n\hbar; \quad n = 1, 2, \ldots} \tag{7}$$

Bohr made this guess, but assumed that all other classical relations still held. The orbital energy comes from kinetic energy plus the nuclear potential:

$$E = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} \tag{8}$$

In equilibrium, centripetal force ($mv^2/r = p^2/[rm]$) must balance electrostatic force, so the kinetic energy is half the magnitude of the potential, and $E = -p^2/2m = -e^2/(8\pi\epsilon_0 r)$. We eliminate p in terms of L in the last equation:

$$L = pr = n\hbar \quad \Rightarrow \quad \frac{(n\hbar)^2}{2m} = \frac{e^2}{8\pi\epsilon_0 r}. \tag{9}$$

The orbital radius can thus be deduced, which then gives the energy:

$$r = \frac{4\pi\epsilon_0\hbar^2}{e^2 m}\, n^2 \quad \Rightarrow \quad E = -\frac{m}{2}\left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2 \frac{1}{n^2}. \tag{10}$$

This model reproduces the Balmer-Rydberg formula successfully, both in the n dependence, and in predicting the coefficient governing the level spacing. However, the Bohr model failed to describe the **fine structure** of the lines, and turned out to be a dead end. As we will see, it gets some of the physics of Hydrogen badly wrong (e.g. the **ground state** with $n = 1$ actually has zero angular momentum, not $L = \hbar$ as predicted by Bohr).

BASIC WAVE MATHEMATICS We now need to assemble some of the machinery needed for a mathematical treatment of quantum waves. A key element is the complex representation of plane waves. It is common to write $V = Ae^{i\omega t}$ to represent a quantity V that oscillates as a function of time. Normally, it is implicitly assumed that you take the real part, to get $V = |A|\cos(\omega t + \phi)$, where ϕ is the phase of A: $A = |A|e^{i\phi}$. In fact, one of the most radical features of quantum mechanics is that we will not take this step: it is necessary to accept the use of i as a part of physics, not just a useful mathematical trick.

For propagating waves, the phase depends linearly on distance, and we would distinguish right- and left-moving waves:

$$V \propto \begin{cases} \cos(\omega t - kx + \phi) & \text{(right)} \\ \cos(\omega t + kx + \phi) & \text{(left)} \end{cases} \tag{11}$$

Here, k and ω are both assumed to be positive numbers. Alternatively, these expressions can be combined into just $V \propto \cos(\omega t - kx + \phi)$, where ω is still positive, but k can now take *either* sign; the sign governs the direction of propagation. This makes sense when we generalize to 3D: $V \propto \cos(\omega t - \mathbf{k}\cdot\mathbf{x} + \phi)$ describes a wave that propagates in the $\mathbf{k}$ direction.

Now, because $\cos(-y) = \cos(y)$, we could equally well have written $V \propto \cos(\mathbf{k}\cdot\mathbf{x} - \omega t - \phi)$. These two expressions describe the same wave, and it is an arbitrary choice whether we want to see the time dependence written with a $+$ sign or a $-$ sign. Similarly, there is a choice of conventions for the complex representation of travelling waves. A complex disturbance, ψ, can be written either as

$$\psi \propto e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)} \qquad \text{or} \qquad \psi \propto e^{i(\omega t-\mathbf{k}\cdot\mathbf{x})}. \tag{12}$$

Both the real and imaginary parts of these expressions represent waves moving in the direction of $\mathbf{k}$; the real parts are identical, and the imaginary parts just have a relative phase shift of π. Again, therefore, these are physically identical expressions, and we have to decide which to adopt. Fortunately, there is a single agreed convention used in all quantum mechanics books:

$$\boxed{\psi \propto e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}.} \tag{13}$$

This means that a wave with a spatial dependence $\psi \propto e^{i(\mathbf{k}\cdot\mathbf{x})}$ can be assumed to move in the $\mathbf{k}$ direction, without explicitly worrying about the time dependence.

All this discussion assumes $\omega > 0$, and we are used to the idea that frequencies are automatically positive. This is less obvious in quantum mechanics, since $\omega = E/\hbar$ and E will be *negative* for a bound particle. We have to hope that a choice of formalism that works for plane waves will give sensible results when applied to the unknown territory of bound matter waves.

PHASE AND GROUP VELOCITIES The **phase velocity** of a single wave is clearly

$$v_p = \frac{\omega}{|k|}. \tag{14}$$

In general, this velocity will not be a constant, but will depend on wavenumber. A wave packet defined by a range of waves around some central k then moves at a different speed: the **group velocity**

$$v_g = \frac{d\omega}{d|k|}. \tag{15}$$

The proof of this is not examinable in this course, but suppose we write ψ as a superposition of waves: $\psi = \int f(k)\ \exp[i(kx - \omega t)]\, dk$. This is a form of the **Fourier transform** that was studied in Physical Mathematics; there will be more about Fourier methods later. If $f(k)$ peaks about some mean wavenumber $\bar{k}$, the wave packet can be written as a product of mean wave and modulation:

$$\psi = \exp[i(\bar{k}x - \bar{\omega}t)] \int f(k)\ \exp[i(\delta k\, x - \delta\omega\, t)]\, dk. \tag{16}$$

The final intergral defines where the wave has significant amplitude, and this clearly moves at speed $\delta\omega/\delta|k|$. If the packet is narrow enough in k space, we can treat this speed as independent of k and approximate the group velocity by using the derivative $d\omega/d|k|$ (formally, expand $\delta\omega$ an a Taylor series in δk).

The de Broglie relations predict a group velocity $d\omega/dk = dE/dp$ equal to the particle velocity (because $E = p^2/2m$ nonrelativistically; the relativistic relation $E^2 = p^2c^2 + m^2c^4$ gives the same answer because $p = Mv$, where $Mc^2 = E$ defines the relativistic mass), so this procedure makes some physical sense if particles are thought of as wave packets.

WAVE EQUATIONS A one-dimensional disturbance $\psi(x)$ (e.g. transverse displacement on a string) satisfies a second-order partial differential equation:

$$\frac{\partial^2}{\partial x^2}\psi - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi = 0, \tag{17}$$

where c is the speed of propagation. From MP2h, you should know that this equation has solutions that travel in either direction without changing shape: $\psi(x,t) = g(x \pm ct)$, where g is any function.

Here, we will often need to consider 3D situations, which require the differential 'del' operator:

$$\boldsymbol{\nabla} = \begin{pmatrix} \partial/\partial x \\ \partial/\partial y \\ \partial/\partial z \end{pmatrix}. \tag{18}$$

In 1D situations, one can loosely think of $\boldsymbol{\nabla}$ as being $\partial/\partial x$ in a particular direction, but we often need to be more careful.

A 3D disturbance propagating with a speed c (e.g. a pressure fluctuation in the atmosphere) satisfies the **3D wave equation**:

$$\boxed{\nabla^2\psi - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi = 0.} \tag{19}$$

As in 1D, solutions of this equation propagate without changing shape. However, there are other partial differential equations that do not have this property, and yet are still called wave equations. A good example is the **diffusion equation** $D\nabla^2\psi + \partial\psi/\partial t = 0$, where D is the diffusion coefficient. This equation describes the flow of heat, and it has wave-like solutions. If we try a 1D solution $\psi \propto e^{i(kx-\omega t)}$, then the equation requires $-Dk^2 = i\omega$. This means that k has an imaginary component, and this causes the waves to be damped as they propagate.

3 Schrödinger's equation

Since so many classical physical phenomena satisfy a wave equation of some form, it is a reasonable guess that matter waves also satisfy some unknown partial differential equation. All we know about this equation is that, for free particles, it must have de Broglie waves as its solutions. For a single plane wave, we can extract the energy and momentum by the following **operator substitutions**:

$$\boxed{\psi \propto e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} \quad \Rightarrow \quad \left\{ \begin{array}{l} \mathbf{p} \to -i\hbar\,\boldsymbol{\nabla} \\ E \to i\hbar\,\partial/\partial t \end{array} \right. .} \tag{20}$$

In other words, $\mathbf{p}\psi = (-i\hbar\boldsymbol{\nabla})\psi$. We use this to deduce the momentum vector $\mathbf{p}$: operate on ψ with $(-i\hbar\boldsymbol{\nabla})$ and then divide by ψ. Similarly, $i\hbar\,\partial/\partial t$ operates on ψ to bring the energy 'downstairs'. Now, we know a relation between energy and momentum for a free particle, which is just $E = p^2/2m$. If we want this relation to be satisfied for all possible plane waves, the same relation must be satisfied by the operator forms of energy and momentum. Inserting these substitutions into the energy–momentum relation, gives the **free-particle Schrödinger equation**:

$$\frac{p^2}{2m} = E \quad \Rightarrow \quad \frac{p^2}{2m}\psi = E\psi \quad \Rightarrow \quad \frac{-\hbar^2}{2m}\nabla^2\psi = i\hbar\dot{\psi}. \tag{21}$$

Like the classical wave equation, the free-particle Schrödinger equation is linear and therefore satisfys **superposition**: a sum of different solutions of the wave equation is also a solution. The Schrödinger equation will therefore apply to a wave function which is a sum of different plane waves, so it is a candidate for a general wave equation.

However, the equation needs extending if we consider particles moving in potentials. The wave function will then no longer be a simple plane wave, so what do we do? The free-particle equation was just a relation between kinetic and total energies: $K\psi = E\psi$, so the simplest possibility is that we should now write $(K+V)\psi = E\psi$. In the absence of any other idea, we guess that the K and E terms are as before, giving the full **time-dependent Schrödinger equation**:

$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\dot{\psi}.} \tag{22}$$

Note that the wave function *must* be a complex quantity in this equation, because the differential operator involved is a mixture of real spatial derivatives and an imaginary time derivative.

STATIONARY STATES The puzzling need for a complex wave function can be avoided to some extent if we assume that the wave function has a simple time dependence (corresponding to a state of definite energy):

$$\psi = u(\mathbf{x})\, e^{-iEt/\hbar}. \tag{23}$$

This is called a **stationary state**. To prove that this simple time behaviour is allowed, suppose we try something more general and just guess that the wave function may sometimes factorize: $\psi = X(\mathbf{x})T(t)$. Putting this form in the full Schrödinger equation gives

$$\frac{1}{X}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)X = \frac{i\hbar\dot{T}}{T}. \tag{24}$$

The lhs is just a function of x and the rhs is just a function of t. Since these are independent, they can only be equal if each side is a constant. This is the method of **separation of variables**, which is a powerful general way of solving partial differential equations. Solving the simple time equation shows that the wave function can have the oscillatory time dependence of a free-particle plane wave, and yet have a more complicated spatial behaviour. We then get the **time-independent Schrödinger equation**:

$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + [V-E]\right)u = 0.} \tag{25}$$

Historically, Schrödinger first obtained the time-independent equation, for which the wave function can be real, and only reluctantly moved to a complex ψ in the time-dependent case (see the biography by Moore 1992 for many interesting insights on the development of Schrödinger's ideas).

BOUNDARY CONDITIONS An important aspect of quantum mechanics is the relation between the wave functions in different regions of space. Since the Schrödinger equation is of the form $(\nabla^2+k^2)\psi=0$, this will only have a solution for finite ψ and k if both ψ and its first derivatives match at a boundary. A discontinuity in first derivative of ψ will give an infinite spike in $\nabla^2\psi$; discontinuities in ψ are even worse. However, if the potential becomes infinite, ψ must still be continuous, but there can be a discontinuity in the first derivatives. In practice, we will mainly be interested in applying these boundary conditions to one-dimensional problems, where we want to join together forms of solution that work in different ranges of the x coordinate.

4 Probability density and current

Born showed how to interpret the Schrödinger equation. If we use the shorthand $S\psi = i\hbar\dot{\psi}$, then write $\psi^* S\psi - \psi S^*\psi^* = i\hbar(\partial/\partial t)[\psi^*\psi]$. This can be written as

$$\boldsymbol{\nabla}\cdot\mathbf{j}+\dot{\rho}=0, \tag{26}$$

where

$$\begin{aligned}\rho &= |\psi|^2\\ \mathbf{j} &= \frac{i\hbar}{2m}(\psi\boldsymbol{\nabla}\psi^* - \psi^*\boldsymbol{\nabla}\psi)\end{aligned} \tag{27}$$

The first equation always arises when something is being conserved: ρ is a density and $\mathbf{j}$ is a current density. Note that both are real, even if ψ is complex. The most sensible interpretation is that ρ is the probability density of finding a particle.

To convince yourself about the above reasoning, the **divergence theorem** is needed:

$$\int \mathbf{u}\cdot\mathbf{dA} = \int \boldsymbol{\nabla}\cdot\mathbf{u}\,dV, \tag{28}$$

where $\mathbf{u}$ is any vector and $\mathbf{dA}$ is an element of area on a surface. This says that the total 'flow' of $\mathbf{u}$ through a closed surface is equal to the volume integral of $\boldsymbol{\nabla}\cdot\mathbf{u}$ within the surface. If we choose $\mathbf{u}$ as the current density $\mathbf{j}$, then $\int\mathbf{j}\cdot\mathbf{dA}$ should give (minus) the time derivative of the total quantity of charge, mass etc. inside the volume:

$$\int \mathbf{j}\cdot\mathbf{dA} = -\frac{d}{dt}\int\rho\,dV = -\int\dot{\rho}\,dV. \tag{29}$$

The divergence theorem then says

$$\int(\dot{\rho}+\boldsymbol{\nabla}\cdot\mathbf{j})\,dV=0. \tag{30}$$

Of course, we can't just divide by $\int dV$, but it is possible to argue that, since the volume is arbitrary, the only way the integral can always vanish is if $\dot{\rho}+\boldsymbol{\nabla}\cdot\mathbf{j}=0$, which is called the **continuity equation**.

The wave function should therefore be **normalized** so that the total probability is unity:

$$\boxed{\int|\psi|^2\,dV=1.} \tag{31}$$

This is impossible in the case of a plane wave if the integration extends to infinity, so the best we can do is to impose a **box normalization** in a volume V. The idea would be that the plane wave represents the probability of finding a number of particles, at a density of one per volume V.

5 Square potential wells

Before pressing on with quantum formalism, it is a good idea to give some concrete illustrations of Schrödinger's equation in action. Generally, we will stick to states of fixed energy, so we can ignore the time dependence and just solve for $\psi(x)$.

1D INFINITE WELL Just about the simplest problem to solve is the single 1D square well of infinite depth:

$$V = \begin{cases} 0 & \text{for } |x| < L \\ \infty & \text{for } |x| > L \end{cases} \tag{32}$$

The wave equation to solve is just $\psi'' + k^2\psi = 0$, where $k = (2mE)^{1/2}/\hbar$. The solution is

$$\psi = A\sin kx + B\cos kx. \tag{33}$$

The boundary conditions are $\psi(\pm L) = 0$ (since the probability of being outside the well must vanish), implying

$$A\sin kL = B\cos kL = 0. \tag{34}$$

There are therefore two families of solutions: either $A = 0$ or $B = 0$. Either way, we get linearly spaced wavenumbers, and hence quadratic energies:

$$k = n\frac{\pi}{2L} \quad \Rightarrow \quad E = n^2\frac{\pi^2\hbar^2}{8mL^2}; \quad n = 1, 2, 3, \ldots \tag{35}$$

The boundary conditions have forced **quantization of energy**. Notice that there is a **ground state**: the lowest allowed energy is non-zero. This reflects the confinement of the particle: zero energy implies zero momentum, so that the wavelength would have to go to infinity; ψ would then extend beyond the box walls, which is forbidden.

The above solutions are cosine-like if n is odd and sine-like if n is even. The former are symmetric (**even wavefunctions**) about $x = 0$, whereas the latter are antisymmetric (**odd wavefunctions**). In other words, we can write

$$\boxed{\psi(-x) = \pm\psi(x).} \tag{36}$$

This symmetry arises from the symmetry of the potential (see below).

3D INFINITE WELL AND DEGENERACY Life is messier if the well is a 3D box, with (x, y, z) dimensions (L_1, L_2, L_3). The Schrödinger equation is a sum of parts that just depend on (x, y, z) individually, so we try separation of variables: $\psi = X(x)Y(y)Z(z)$. This gives

$$\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} = -\frac{2mE}{\hbar^2}, \tag{37}$$

and the usual argument shows that each of the X etc. functions are mixtures of sine and cosine, with some wavenumber k_x. Applying the boundary conditions gives $k_x = n_x\pi/2L_1$ etc., and the energy depends on three quantum numbers:

$$E = \frac{\pi^2\hbar^2}{8m}\left(\frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2} + \frac{n_z^2}{L_3^2}\right). \tag{38}$$

If the well is symmetric, $L_1 = L_2 = L_3$, the states are **degenerate**. If $(n_1, n_2, n_3) = (1, 1, 2)$, there are two other ways of getting the same energy. Similarly, the $(1, 2, 2)$ state is also three-fold degenerate, and the $(1, 2, 3)$ state is six-fold degenerate.

1D FINITE WELL Consider now a square potential of finite range:

$$V = \begin{cases} V_0 & \text{for } |x| < L \\ 0 & \text{for } |x| > L \end{cases} \tag{39}$$

Depending on the sign of V_0, this can either be a **potential well** that will tend to confine particles, or a **potential barrier**, which will tend to scatter them. The wave functions are of exponential form inside and outside the well: $\psi \propto \exp[ikx]$, where

$$k^2 = \begin{cases} 2m(E - V_0)/\hbar^2 & \text{for } |x| < L \\ 2mE/\hbar^2 & \text{for } |x| > L \end{cases} \tag{40}$$

There are three cases to consider:

(1) Propagating plane waves everywhere; the well acts like a slab of dielectric in electromagnetism. This happens if $E > 0$ and $E > V_0$ – i.e. for shallow wells of either sign.

(2) If $V_0 > 0$ and $0 < E < V_0$, we have propagating plane waves outside the well, but the wavenumber is imaginary inside the well (an **evanescent wave function**). Propagating waves cannot penetrate a sufficiently high potential barrier.

(3) If E is negative, we have a **bound state**; the external wavefunctions are exponentially damped at large $|x|$. It turns out that this is only possible if V_0 is negative (which is intuitively reasonable); the wave functions inside the well can then be plane waves.

Consider case (3) first. Inside, we have $\psi = A\sin\alpha x + B\cos\alpha x$. As before, the symmetry of the situation ($|\psi|^2$ should be unchanged under reflection) suggests we set either A or B to zero. This has to match to $\psi = Ce^{-\beta x}$ at $x > L$, where α and β are $|k|$ in the relevant regions, as above. The matching conditions at $x = L$ are

$$\begin{aligned} A\sin\alpha L &= Ce^{-\beta L} \\ \alpha A\cos\alpha L &= -\beta Ce^{-\beta L} \end{aligned} \tag{41}$$

for odd solutions and

$$\begin{aligned} B\cos\alpha L &= Ce^{-\beta L} \\ -\alpha B\sin\alpha L &= -\beta Ce^{-\beta L} \end{aligned} \tag{42}$$

for even ones. These imply $\tan\alpha L = \beta/\alpha$ (even) or $-\alpha/\beta$ (odd). Unfortunately, these equations can't be solved; even this simple case is a little messy, and the details are left as a problem. The main features of the solution depend on the depth of the well, expressed as

$$\gamma = \sqrt{2m|V_0|L^2/\hbar^2}. \tag{43}$$

For $\gamma < \pi/2$, there is only one bound solution, which is the even state. As γ increases, alternate odd and even states become accessible, and there are $n = 1 + \mathrm{int}(\gamma/[\pi/2])$ bound states in general.

Notice that the case where $V_0 \to -\infty$ is the same as the infinite well considered above, where we took $V = 0$ *inside* the well. The internal wavefunctions only depend on the kinetic energy $E - V$; changing the mean value of V alters how strongly an external observer thinks the particle is bound, but this has no effect on the wavefunction.

The treatment for unbound states is similar mathematically, but distinct physically. In this case, the matter waves must arrive from ∞, and we have to choose whether they are incident from L or R. If we choose the former, then there will also be a reflected component to the L, so the wave function is

$$\psi = \begin{cases} Ae^{i\beta x} + Be^{-i\beta x} & x < -L \\ Ce^{i\alpha x} + De^{-i\alpha x} & -L < x < L \\ Fe^{i\beta x} & x > L \end{cases} \tag{44}$$

Note that this is asymmetric, unlike the bound case. We broke the symmetry by injecting waves from a particular direction. We now have four equations from the boundary conditions at $x = \pm L$. These can be manipulated to get the transmission coefficient:

$$T \equiv \frac{|F|^2}{|A|^2} = \left[1 + \frac{\sin^2(2\alpha L)}{4(E/V_0)(E/V_0 - 1)}\right]^{-1}. \tag{45}$$

This tends to unity as $E \to \infty$, but suffers resonant oscillations as E approaches V_0.

This analysis also applies to the case of a potential barrier, provided $V_0 < E$. However, for higher barriers, the internal waves are evanescent. The transmission coefficient can pretty well be guessed immediately, since it mainly replaces sin by sinh:

$$T = \left[1 + \frac{\sinh^2(2\alpha L)}{4(E/V_0)(1 - E/V_0)}\right]^{-1}. \tag{46}$$

Even though classical penetration of the barrier is impossible when $V_0 > E$, the quantum waves get through. In the limit of a thick barrier, the main effect is an exponential suppression from the sinh term:

$$T \sim \exp[-4\alpha L], \tag{47}$$

which is as expected: the internal wave function is dominated by the declining term $\psi \propto \exp[-\alpha x]$, so the above expression is the factor by which the probability density declines from one side of the barrier to the other.

THE DELTA-POTENTIAL An interesting limit of all this is to make the barrier very thin, in the sense $L \ll 2\pi/\beta$. It may seem that, in the limit $L \to 0$, the effect of the well would vanish, but this need not be so. Consider the 1D Schrödinger equation: $(-\hbar^2/2m)\psi'' + (V - E)\psi = 0$. By integrating this, we can find the change in gradient of ψ from one side of the well to the other:

$$[-\hbar^2/2m]\Delta(\psi') = \int_{-L}^{L} (V - E)\,\psi\,dx \tag{48}$$

As $L \to 0$, the rhs will tend to zero, but not if we let the depth of the well go to ∞ at the same time. In this case, we get

$$[-\hbar^2/2m]\Delta(\psi') \to \psi \int_{-L}^{L} V\,dx = \psi A, \tag{49}$$

where A is the 'area' of the potential well. We can now ignore the internal structure of the well, and treat it as a single object of infinitesimal size. In deriving this expression, we have treated ψ as though it was a constant inside the well. This will be justified properly in the problems class.

Mathematically, this infinitesimally thin square well of finite area is one representation of Dirac's **delta function**. This is written as $\delta(x)$, and has the following property:

$$\boxed{\int f(x)\, \delta(x - x_0)\, dx = f(x_0).} \tag{50}$$

A square well of unit area, centred at x_0, will clearly play this role for any reasonable continuous function $f(x)$; when the well is thin enough, $f(x)$ is very nearly a constant, and can be taken outside the integral. Although mathematicians didn't like this beast when Dirac (a physicist) introduced it, it is a very useful tool. Many physical systems can be thought of as being sums of delta functions (e.g. a charge distribution is really a set of electrons, which are delta-functions of charge density). It is clearly possible to extend this definition to more than one dimension by considering an infinitesimal 'pulse' of finite volume:

$$\int f(\mathbf{x})\, \delta^{(3)}(\mathbf{x} - \mathbf{x}_0)\, d^3x = f(\mathbf{x}_0). \tag{51}$$

TUNNELLING IN GENERAL The simple square well is not a potential ever likely to be found in nature. With realistic potentials, the Schrödinger equation usually cannot be solved exactly; however, we can get an approximate feel for the general form of the solution to the 1D equation. The wave equation is

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V(x)\psi = E\psi, \tag{52}$$

which takes the simple form

$$\psi'' + k^2(x)\psi = 0, \tag{53}$$

where $k^2 = 2m(E - V)/\hbar^2$. If $k(x)$ is a constant, the solution is easy: $\psi = A\exp[\pm ikx]$. This is a plane wave with wavelength $\lambda = 2\pi/k$.

Now suppose that k changes slowly with x, so that fractional change in k per wavelength is small: $\lambda k' \ll k \Rightarrow k'/k^2 \ll 1$. Intuitively, it then seems reasonable that the wavefunction will behave locally rather like a plane wave, whose wavenumber is the local value of $k(x)$. We could could consider the wavefunction $\psi \propto \exp[\pm ik(x)x]$, but a better choice is

$$\boxed{\psi(x) = A(x)\exp\left[\pm i \int k(x)\, dx\right],} \tag{54}$$

since k represents $d(\text{phase})/dx$. The advantage of writing the wavefunction in this form is that the amplitude $A(x)$ often varies slowly with x, and the main behaviour is controlled by the exponential term. In particular, we can divide the potential into two distinct regions according to whether k^2 is positive or negative:

$k^2 > 0$ This is the classically allowed region, and the wavefunction takes the form of travelling waves.

$k^2 < 0$ This is the classically forbidden region, in which $V > E$. The wavefunctions are exponential-like (**evanescent waves**)

The transition between these two zones occurs at **turning points**, where k vanishes.

So, inside the forbidden region, we have solutions that grow or decay in an exponential-like manner: $\psi \propto \exp(\pm \int |k(x)|\, dx)$. However, for sufficiently 'thick' barriers, it turns out that we only need one sign of the exponential, and the tunnelling probability is approximately

$$\boxed{P(\text{tunnel}) \sim \exp\left(-2\int_a^b |k(x)|\, dx\right),} \tag{55}$$

where a and b are the turning points, and the incident wave is supposed to be travelling in the positive x direction.

We now give a loose justification of this statement, assuming for the moment that the wave amplitude can be treated as a constant. Inside the barrier, we write

$$\psi = C\exp\left(-\int_a^x |k(x)|\, dx\right) + D\exp\left(+\int_a^x |k(x)|\, dx\right), \tag{56}$$

and we consider this expression as we reach the second turning point, b. If the barrier is thick in the sense $\int_a^b |k(x)|\, dx \gg 1$, then the tunnelling probability will be very small, so that $\psi(b)$ must almost vanish, requiring $D/C \simeq -\exp(-2\int_a^b |k(x)|\, dx)$ This means that both terms are of equal importance at the end of the barrier, but only the first is significant at the start of the barrier, $x = a$, and indeed it is only the declining wave that matters at almost all places inside the barrier. This is why, to within factors of order unity, we get the correct tunnelling probability if we just ignore the growing wave altogether.

NUCLEAR REACTIONS IN STARS Nuclear reactions have a range $\sim 10^{-15}$, m – can charged particles get this close, in order to allow nuclear reactions in stars? Classically, we need $e^2/4\pi\epsilon_0 r \sim kT$, implying $T \simeq 10^{10.2}$ K for $r = 10^{-15}$ m. In practice, in the Sun fusion occurs at temperatures 100 times smaller. The classical barrier is penetrated by quantum tunnelling.

For two ions of charge $Z_1 e$ and $Z_2 e$, the wavenumber is

$$k^2 = \frac{2m}{\hbar^2}\left[E - \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}\right] = \frac{2mE}{\hbar^2}[1 - 1/y], \tag{57}$$

and the tunnelling probability is

$$\begin{aligned} P &= \exp\left(-2\int_{r_{\rm min}}^{r_{\rm turn}} |k|\, dr\right) \\ &= \exp\left(-2\sqrt{\frac{2mE}{\hbar^2}}\,\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 E}\int_{y_{\rm min}}^1 \sqrt{1/y - 1}\, dy\right). \end{aligned} \tag{58}$$

The integral is dominated by $y \sim 1$, so the scale at which nuclear reactions operate is irrelevant. We get

$$\boxed{P(\text{tunnel}) = \exp[-(E_{\rm G}/E)^{1/2}],} \tag{59}$$

where the **Gamow energy** is

$$E_{\rm G} = (\pi\alpha Z_1 Z_2)^2\, 2mc^2, \tag{60}$$

($\alpha \simeq 1/137$), which is 493 keV for pp fusion.

The actual reaction rate will depend on the balance between this suppression probability and the thermal energy distribution, for which the probability of exceeding an energy E is mainly governed by the Boltzmann factor $\exp(-E/kT)$. The product of these factors has a **Gamow peak** at $E = [(kT)^2 E_{\rm G}/4]^{1/3}$, giving a peak probability of

$$P_{\rm max} = \exp\left[-\frac{3}{2^{2/3}}\left(\frac{E_{\rm G}}{kT}\right)^{1/3}\right], \tag{61}$$

and the overall fusion rate scales with this factor times powers of E and kT. For pp fusion in the Sun, typically $kT \simeq 2\,\text{keV}$, so that $d\ln P/d\ln T \simeq 3.9$, and the fusion rate scales roughly as T^4. Energy generation by fusion thus 'switches on' very abruptly as the forming Sun collapses and heats up. A lot of energy is generated when quantum barrier penetration is still very rare, halting the collapse well before the typical thermal energy reaches the Gamow energy.

6 The harmonic oscillator

Armed with some technology, we now look at a more realistic quantum model than the square well. This is where a particle sits in a potential that varies quadratically with position from the origin. Since almost any potential will have a Taylor expansion about its minimum that is quadratic in lowest order, this is a pretty general model. The classical equation of motion would be

$$m\frac{d^2\mathbf{r}}{dt^2} = -K\mathbf{r} = -\boldsymbol{\nabla}[Kr^2/2], \tag{62}$$

where K is the 'spring constant' and the potential is thus $V = Kr^2/2$. Since both sides of the equation depend linearly on $\mathbf{r}$, taking the dot product with a unit vector in a given direction shows that the 3D motion can be decomposed into independent motions in three orthogonal 1D directions, each satisfying **simple harmonic motion**:

$$\ddot{x} + \omega^2 x = 0; \quad \omega = \sqrt{K/m} \tag{63}$$

to which the solution is of course $x = A\sin(\omega t + \phi)$. At maximum extent ($x = A$), the energy is all potential, so $E = KA^2/2$, or $A = \sqrt{2E/K}$. From this, we get the probability distribution for the position of the particle, which will be interesting to compare with the quantum result:

$$\begin{aligned} dp &= dt/(\text{period}/2) = \mathrm{dt}/(\pi/\omega) = \mathrm{dx}/(\dot{\mathrm{x}})/(\pi/\omega) \\ &= \frac{dx}{\pi A\cos(\omega t + \phi)} \\ &= \frac{dx}{\pi\sqrt{A^2 - x^2}}. \end{aligned} \tag{64}$$

(half a period, because the particle covers the ground from $-A$ to $+A$ twice in one period). The particle spends most of its time near $x = \pm A$, and the probability density has an (integrable) singularity there.

THE 1D OSCILLATOR Now for the quantum problem, starting with the 1D case. The Schrödinger equation is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (Kx^2/2 - E)\psi = 0. \tag{65}$$

This is better rewritten as

$$\frac{d^2\psi}{dz^2} + (2\epsilon - z^2)\psi = 0, \tag{66}$$

where dimensionless versions of the position and energy are

$$z \equiv x/\sqrt{\hbar/m\omega}; \quad \epsilon \equiv E/\hbar\omega. \tag{67}$$

This is an eigenvalue equation: $(z^2/2)\psi - \psi''/2 = \epsilon\psi$. The eigenvalues will determine the allowed values of the energy.

The main general procedure for dealing with nonlinear differential equations like this is power-law solution (see Physical Mathematics). First, however, think about the large-x behaviour. The potential is large here, so experience with square wells suggests ψ will be exponentially damped. For large z, we have $\psi'' = z^2\psi$, and it is not to hard to see that $\psi = \exp(-z^2/2)$ is a solution in this limit, since it has $\psi'' = (z^2 - 1)\exp(-z^2/2)$. As a bonus, we see that this is in fact an exact solution of the equation, with $\epsilon = 1/2$. This turns out to be the ground state. For the general case, it therefore makes sense to take out this factor, and try

$$\psi(z) = F(z)\exp(-z^2/2). \tag{68}$$

The wave equation is now $F'' - 2zF' + (2\epsilon - 1)F = 0$.

To solve this equation, try a power-law series $F = \sum a_i z^i$: the coefficients for powers that differ by 2 are related:

$$(n+2)(n+1)a_{n+2} + (2\epsilon - 2n - 1)a_n = 0. \tag{69}$$

We can construct two independent families of solutions, odd and even, by specifying a_0 and a_1. Notice that these solutions can be finite polynomials (the **Hermite polynomials**) if we make the factor multiplying a_n vanish; this requires $2\epsilon = 2n + 1$, i.e.

$$\boxed{E = (n + 1/2)\hbar\omega.} \tag{70}$$

What's wrong with the non-terminating solutions? The coefficients a_n don't fall off all that fast with n, and in fact $F(z)$ ends up blowing up like $\exp(z^2)$. This overwhelms the previous damping factor, so ψ can't be normalized.

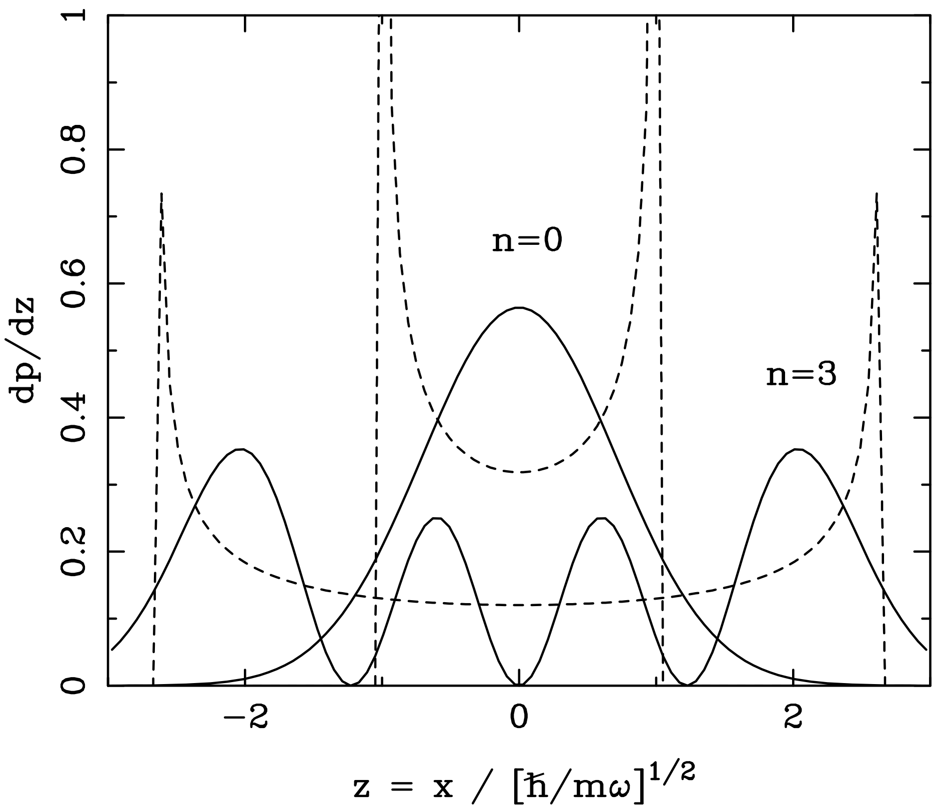

Figure 2 The probability density for various states of the 1D harmonic oscillator. The classical probability density is shown dotted, and this is approached for large n.

The energy is quantized, which we might have expected by comparison with the square well. However, the energy levels are *linearly* spaced, rather than quadratically. The ground-state energy, or **zero-point energy** is half the level spacing. This feature is important when we consider electromagnetism, for which each wave mode in a box can be thought of as an oscillator. From the photoelectric effect, we might have expected to find $E = \hbar\omega$ without the zero-point offset. However, all that is measured by the photoelectric effect is the difference in energy caused by adding or removing one quantum. The existence of some energy even with no quanta is not so surprising in retrospect, because of the uncertainty principle. For the case we have been considering (a ball in a 1D potential), the energy cannot be zero: this would correspond to zero momentum, and so the positional uncertainty would be infinite. However, this is nonsensical, since the potential must confine the ball. If the uncertainty in position is δx, this generates a potential energy of order $K(\delta x)^2$. To this must be added a kinetic energy $(\delta p)^2/2m \sim (\hbar/\delta x)^2/2m$. The minimum value of the total energy is when $(\delta x)^2 = [\hbar^2/2mK]^{1/2}$, at which point the energy is of order $\hbar\omega$. The same argument says that the electromagnetic field must always have a minimum level of fluctuations.

THE 3D OSCILLATOR AND DEGENERACY Moving to 3D, the wave function factorizes. The potential does not even need to be spherically symmetric: the classical oscillation frequencies along each of the three axes can be different. The energy is the sum:

$$E = (n_x + 1/2)\hbar\omega_x + (n_y + 1/2)\hbar\omega_y + (n_z + 1/2)\hbar\omega_z. \tag{71}$$

If the potential is symmetric, then we get degeneracy, as with the square well: $E = (n+3/2)\hbar\omega$, where now n is the sum of three integers. The level n has a degeneracy factor of $(n+1)(n+2)/2$.

7 The rules of quantum mechanics

Having revised wave mechanics, we now discuss a general set of rules for doing quantum-mechanical calculations. These are partly a clear restatement of some of the principles we have used so far, but some of the rules go further. They are really just guesswork – making a plausible generalization of the principles at work in wave mechanics. Since the quantum world is remote from our intuition and experience, it is hardly surprising that a watertight proof of these rules cannot be given: they can only really be justified by the fact that they work when applied to real quantum problems. The rules may be summarized as follows:

(1) The wave function is all there is.

(2) Physical observables correspond to Hermitian operators.

(3) The possible results of any observation are the eigenvalues of the corresponding operators.

(4) The effect of an observation is to leave a system in one of the eigenstates of the corresponding operator.

Now we have to explain what these mean, justify them, and introduce various important new concepts.

THE WAVE FUNCTION To say the wave function is all there is implies that nature is **probabilistic**: we may learn from $|\psi|^2$ the probability of finding a particle at a given position, but we cannot predict exactly where it will appear, nor where it is before it appears. This is familiar from the case of Young's slits, where a pattern of interference fringes forms even where the light intensity is very low. Photons can be detected one at a time, arriving apparently at random, but over time they build up the fringe pattern. Note that the interference fringes are a nonlinear function of the wavefunction. Although the wave equation is linear and allows superposition, the superimposed waves interact when it comes to the probability of detecting a particle:

$$|\psi|^2 = |\psi_1 + \psi_2|^2 = |\psi_1|^2 + |\psi_2|^2 + \psi_1^*\psi_2 + \psi_2^*\psi_1, \tag{72}$$

where ψ_1 and ψ_2 are the waves due to the two slits.

A better name for ψ is the **state function**, since it encodes all information about a system. This can include internal degrees of freedom, such as spin, as well as external ones, such as position.

OPERATORS AND OBSERVABLES The de Broglie substitution $\mathbf{p} \to -i\hbar\boldsymbol{\nabla}$ is one example where a physical observable (momentum) is replaced by a differential operator. This suggests that all observables might need to be treated in this way. In other words, we guess that we should always write

$$\boxed{O\psi \to \hat{O}\psi,} \tag{73}$$

where O is any observable, and $\hat{O}$ is the corresponding differential operator. This says that, in order to extract information about O from the wave function, we need to operate on it.

Notice the distinction between O and $\hat{O}$. It is quite common to use this explicit 'hat' notation whenever an operator is involved. However, we will not do this, for several reasons: (i) in some cases, O and $\hat{O}$ are the same (e.g. position $\mathbf{x}$); (ii) not all books make the distinction; (iii) the relation $O\psi \to \hat{O}\psi$ applies for any ψ, so in a sense $\hat{O}$ *is* the observable – the classical quantity O is really only defined as a limit of the quantum quantity.

This doesn't say how to get the O operator for a given case, so we assume the **correspondence principle**, which is that the relations between operators are the same as in the classical case. Simple functions of position are unchanged as operators, whereas the momentum operator takes the de Broglie form. This means that the total energy (known as the **Hamiltonian operator**, and normally written as H) is

$$H = \frac{p^2}{2m} + V(\mathbf{x}). \tag{74}$$

The time-dependent Schrödinger equation is then $H\psi = i\hbar\dot{\psi}$.

The key difference between classical and quantum observables is that, in the quantum world, the order of the observations matters. The **commutator** of two operators is

$$\boxed{[A, B] \equiv AB - BA.} \tag{75}$$

This is often non-zero, reflecting the fact that the observation of quantity A affects the system, thus influencing the observation of quantity B. For example, consider the position and momentum operators in 1D:

$$p_x x\psi = p_x(x\psi) = \frac{\hbar}{i}\frac{\partial}{\partial x}(x\psi) = \frac{\hbar}{i}\psi + x\,\frac{\hbar}{i}\frac{\partial}{\partial x}\psi. \tag{76}$$

This says that $[p_x, x] = \hbar/i$. Position and momentum do not commute, so it is impossible to measure one without influencing the other. This is the basis of the **uncertainty principle**, to be studied later.

EXPECTATION VALUES Since quantum mechanics is probabilistic, the classical limit should be approached through average values. Since $|\psi|^2$ is a probability density, the mean value of any function of position, $f(\mathbf{x})$, is

$$\langle f\rangle = \int f\,|\psi|^2\,dV = \int \psi^*\,f\,\psi\,dV. \tag{77}$$

We generalize this to the assumption that the expectation value of an operator is always given by

$$\boxed{\langle O\rangle = \int \psi^*\,O\,\psi\,dV.} \tag{78}$$

To make physical sense in the classical limit, the expectation value of an operator had better be real. We can see how this can be arranged by introducing a more general concept about operators.

HERMITIAN OPERATORS The **Hermitian conjugate**, $O^\dagger$ of an operator O is defined to be

$$\boxed{\left(\int \psi_1^* \, O \, \psi_2 \; dV\right)^* \equiv \int \psi_2^* \, O^\dagger \, \psi_1 \; dV.} \tag{79}$$

In words, swap $1 \leftrightarrow 2$, replace O by $O^\dagger$, and you get the complex conjugate of the integral you started with.

Clearly, a **Hermitian operator**, which is equal to its own conjugate, will have real expectation values as a special case of the above equation. All physical observables are assumed to correspond to Hermitian operators. As a 1D example, consider the operator d/dx, and suppose we want the integral $\int \psi_1^* \, (d/dx) \, \psi_2 \; dx$. Integration by parts says

$$\int u \, v' \; dx = [uv] - \int v \, u' \; dx. \tag{80}$$

If ψ_1 and ψ_2 vanish on the boundary, this gives

$$\int \psi_1^* \, (d/dx) \, \psi_2 \; dx = -\int \psi_2 \, (d/dx) \, \psi_1^* \; dx = -\left(\int \psi_2^* \, (d/dx) \, \psi_1 \; dx\right)^* . \tag{81}$$

So, $(d/dx)^\dagger = -(d/dx)$, and (d/dx) is not Hermitian. Multiplying by i cures this, so the momentum operator is Hermitian.

EIGENVALUES AND EIGENVECTORS Each Hermitian operator comes with a special set of wavefunctions, for which operating on ψ gives a result 'parallel' to ψ:

$$\boxed{O\psi_n = o_n \psi_n .} \tag{82}$$

The number o_n is the **eigenvalue** associated with the **eigenvector** ψ_n (with a label n because in general there will be a whole family of them). The term comes from the German for 'self'; literally, the meaning is 'self-value', 'self-vector', etc. Perhaps more memorably, 'eigen' alone means 'selfish'! The eigenvectors of Hermitian operators have two important properties:

(1) The eigenvalues are real.

(2) The eigenvectors are orthogonal.

Property (1) is proved by considering

$$\int \psi_m^* O \psi_n \; dV = o_n \int \psi_m^* \psi_n \; dV = o_m^* \int \psi_n \psi_m^* \; dV \tag{83}$$

(if ψ_n is normalized). So, if $m = n$, the eigenvalues are real. If $m \neq n$ *and* the eigenvalues o_m and o_n are different, then $\int \psi_m^* \psi_n \; dV$ vanishes. We can sum this up by writing

$$\boxed{\int \psi_m^* \psi_n \; dV = \delta_{mn},} \tag{84}$$

where δ_{mn} is the **Kroneker delta**. The eigenfunctions are **orthonormal** (i.e. orthogonal and normalized).

Even if the eigenvalues are degenerate, it is still possible to make the eigenvectors orthonormal, by choosing new linear combinations. For example, given two functions ψ_a and ψ_b that are not orthogonal, then choose $\psi'_a = \psi_a$ and $\psi'_b = \psi_b - \psi_a \int \psi_a^* \psi_b \, dV$ (i.e. subtract from b the component 'parallel' to a).

COMPLETE SETS These properties of Hermitian operators suggest that it will often be a good idea to think of wavefunctions that are a sum of different eigenfunctions, with some expansion coefficients a_n:

$$\psi = \sum_n a_n \psi_n. \tag{85}$$

Because of the orthonormality property of the eigenfunctions, this then gives a very simple form for the expectation value of O:

$$\langle O \rangle = \sum_n |a_n|^2 o_n. \tag{86}$$

Moreover, the expectation of the square of the operator is

$$\langle O^2 \rangle = \sum_n |a_n|^2 o_n^2. \tag{87}$$

Given these two numbers, we can work out something very important: the uncertainty in the quantity O introduced by the probabilistic nature of quantum mechanics.

The **variance** in a quantity is the mean-squared dispersion about the mean:

$$\boxed{\sigma^2(O) \equiv \left\langle (O - \langle O \rangle)^2 \right\rangle = \langle O^2 \rangle - \langle O \rangle^2,} \tag{88}$$

where the second form follows by expanding the square in the first definition. Looking at the above expressions for $\langle O \rangle$ and $\langle O^2 \rangle$, we see that the variance in O vanishes if only one expansion coefficient, a_i, is non-zero: the observation returns exactly $O = o_i$ with no scatter. In general, the variance is non-zero: the value of an observable is only well-defined when the system is in an eigenstate of that observable.

Now, the description of a wavefunction as the sum of a set of eigenfunctions looks very attractive, but so far we haven't proved a critical fact – which is that *any* wavefunction can be expanded in this way. A set of orthonormal functions that can expand any arbitrary function is called a **complete set**. The eigenfunctions of Hermitian operators are indeed complete, but proving this is a bit tricky. Seek enlightenment in Physical Mathematics. Given a complete set, we can always find the expansion coefficients by using orthonormality to 'project' out the required component (to find a_m, multiply by ψ_m^* and integrate):

$$\boxed{a_m = \int \psi_m^* \psi \, dV.} \tag{89}$$

This is one of the most important concepts in this course, and it will be used in many quantum applications.

MATRIX ELEMENTS If we expand a wave function in terms of some complete set, $\psi = \sum_n a_n \psi_n$, then the effect of an operator must also be expressible in terms of that set

$$O\psi = \sum_n a_n O\psi_n = \sum_n b_n \psi_n. \tag{90}$$

The relation between the coefficients is found by multiplying through by ψ_m^* and integrating:

$$b_m = \sum_n a_n \int \psi_m^* \, O\psi_n \, dV \tag{91}$$

This is an equation in matrix algebra: the vector $\mathbf{b}$ is the result of operating on $\mathbf{a}$ with a matrix:

$$\boxed{\mathbf{b} = \mathbf{M} \cdot \mathbf{a}; \quad M_{ij} = \int \psi_i^* \, O\psi_j \, dV \equiv O_{ij}.} \tag{92}$$

The integral $\int \psi_i^* O\psi_j \, dV$ is therefore called the **matrix element** of O. This shows that there is a close relation between quantum mechanics and vector algebra. A vector can be expressed as a sum over some **basis vectors**: $\mathbf{v} = \sum_i a_i \mathbf{e}_i$, and the vector can be thought of either as the 'directed number' $\mathbf{v}$, or as the list of coefficients (a_i). In the same way, a complete set of states can be called **basis functions**, and we can think of a wave function as being characterized by its expansion coefficients. This means that the operator O really *is* just the matrix of coefficients O_{ij}.

An advantage of having quantum mechanics in matrix form is that it is then possible to use standard tools to solve quantum-mechanical problems. For example, to find the eigenvalues and eigenvectors of an operator supplied as a matrix $\mathbf{O}$, we have to solve the determinant equation $|\mathbf{O} - \lambda \mathbf{I}|$, where I is the identity matrix. This yields a polynomial equation whose roots are the eigenvalues λ_i. If we use the eigenvectors as the basis, the orthonormality of the vectors means that the operator matrix is **diagonalized**: it has zero everywhere except $\lambda_1, \lambda_2, \ldots$ down the leading diagonal.

This matrix analogy can also provide a helpful concrete means of understanding quantum-mechanical concepts. For example, it is well-known that matrix multiplication is not commutative, so non-commuting operators are not a surprise. The Hermitian conjugate is particularly easy to visualize in the matrix representation:

$$O_{ij}^\dagger = O_{ji}^*. \tag{93}$$

This is also a simple way of proving an important relation between Hermitian conjugates:

$$\boxed{(AB)^\dagger = B^\dagger A^\dagger.} \tag{94}$$

To prove this, write AB in components, and just use the above expression for $O_{ij}^\dagger$.

Historically, Heisenberg came up with **matrix mechanics** before Schrödinger produced his wave equation. Heisenberg's work represented a radical break with classical physics, and he was most unhappy when Schrödinger tried to re-introduce classical ideas by thinking of particles as wave packets.

WAVE-FUNCTION COLLAPSE The most radical law of quantum mechanics is left for last, and it is the aspect which really is hard to find in Schrödinger's apparatus. Suppose we measure a system and get a value o for an observable whose operator is O. Suppose further that o is one of the eigenvalues of O: o_n. We know from above that this is what we would find if ψ was the ψ_n eigenstate. It might seem that we could tell whether or not the initial state was an eigenstate by repeated measurement: for an eigenstate, we will keep getting o_n, whereas a mixed state will give a variety of answers.

However, this is not what happens: we cannot observe a quantum-mechanical system without perturbing its wavefunction. Once we have obtained a value o_n for some observable, that fixes its value, and forces the wavefunction to be the corresponding eigenstate. This suggests that the eigenvalues o_n are the *only* possible results of the measurement process – if we got any other number, it could not leave the system in a definite state. To sum up:

(1) For a **mixed state** $\psi = \sum_n a_n \psi_n$, the possible results of an observation are o_n, the eigenvalues of the observable: $O\psi_n = o_n \psi_n$.

(2) The probability of getting a result o_i is $|a_i|^2$.

(3) After observing o_i, the system is left in the ψ_i eigenstate.

This process of **wave-function collapse** is a subtle business. It is not so controversial for a classical system like a human observing an atom, but the process of collapse is less easy to understand when one quantum system observes another. Some of the frontiers of research are concerned with processes of this sort.

COMPATIBLE OBSERVATIONS Wave-function collapse shows how two observations interfere with each other. Suppose we observe quantity O_1 and get the eigenvalue a, leaving the state as ψ_a. If this isn't an eigenstate of some other O_2, we have to expand ψ_a in the eigenfunctions of the O_2 operator, and observations of O_2 will give a dispersion of results. However, sometimes ψ_a will be an eigenvector of both O_1 and O_1. The condition for this is that the operators should commute:

$$\boxed{[O_1, O_2] = 0.} \tag{95}$$

Clearly, for a common eigenstate, $O_1 O_2 \psi_a = O_2 O_1 \psi_a$. If this is true for all eigenstates, then it must be true for *any* ψ, since the eigenstates are complete. This is what we mean when we write $O_1 O_2 = O_2 O_1$. The converse is also true: commuting operators have common eigenstates, although the proof is a little more involved if the eigenvalues are degenerate.

One example of this is **parity**. We saw above that the eigenstates of the square well are either odd or even; here is a general explanation of this fact. Let P be the parity operator, whose effect is **spatial inversion**: it replaces $\mathbf{x}$ by $-\mathbf{x}$. Like any operator, this must have eigenstates $P\psi = p\psi$. Since double inversion puts us back where we started, we need $p^2 = 1 \Rightarrow p = \pm 1$. The eigenstates of P are therefore either odd or even. Now, for a symmetric system, the Hamiltonian is unaffected by P, so $[H, P] = 0$. This says that the eigenstates of H can also be eigenstates of P. Take a given eigenstate, $H\psi_i = E_i \psi_i$, and apply P:

$$H(P\psi_i) = PH\psi_i = E_i(P\psi_i). \tag{96}$$

This says that $P\psi_i$ is an eigenstate of H, with energy E_i. If the energy states are non-degenerate, this says that $P\psi_i$ must be the same as ψ_i, to within a constant – i.e. it is a parity eigenstate.

This argument fails if there is degeneracy, but in this case we can define explicit odd and even states that still have the same energy eigenvalue:

$$\psi_\pm = \frac{1}{2}[\psi(x) \pm \psi(-x)]. \tag{97}$$

The energy eigenstates can thus always be *chosen* to be odd or even if the potential is symmetric.

8 Fourier analysis and momentum space

A plane wave has a well-defined momentum – i.e. it is an eigenstate of the momentum operator:

$$\mathbf{p}\left(e^{i(\mathbf{k}_n\cdot\mathbf{x}-\omega_n t)}\right) = \hbar\mathbf{k}_n\left(e^{i(\mathbf{k}_n\cdot\mathbf{x}-\omega_n t)}\right). \tag{98}$$

Suppose we have a wavefunction that is a sum of different plane waves:

$$\psi = \sum_n a_n\, e^{i(\mathbf{k}_n\cdot\mathbf{x}-\omega_n t)} \tag{99}$$

The rules of quantum mechanics say that the probability of measuring momentum $\mathbf{p} = \hbar\mathbf{k}$ is $\propto |a_n|^2$. The set of plane waves is the simplest and most natural complete set in which we can choose to expand a wavefunction, but it is given added physical importance by the connection to momentum.

THE FOURIER SERIES The description of a function in terms of a set of plane waves is very common in physics, and was invented by Fourier. **Fourier methods** are discussed in detail in Physical Mathematics, but it will do no harm to revise the main features here. The first problem to face is normalization: $|\psi|^2$ is a constant for a plane wave, so $\int |\psi|^2\, dV$ diverges. The way to deal with this is via a finite **normalization volume**, which we take to be a cube of side L. We expand ψ in terms of the eigenstates in the box, and later take the limit $L \to \infty$. For a single plane wave, this may seem to give nonsensical results. If $\psi = Ae^{i(\mathbf{k}\cdot\mathbf{x})}$, then normalization requires $A = 1/\sqrt{L^3}$ and the probability density goes to zero as $L \to \infty$. There are two ways to make sense of this:

(1) A plane wave of finite amplitude may represent, not one particle, but a beam of many particles, with a number density of one per volume $1/|A|^2$. This is the correct interpretation in scattering problems.

(2) The alternative solution is to see what happens when we expand a fixed wavefunction of finite range in terms of the eigenfunctions inside the normalization box. We have already met one set of eigenfunctions, in the case of the infinite square well. The states factorize into functions of x, y, z, so it will do to consider just the 1D case.

The boundary conditions are $\psi = 0$ at the box edge, so we have either $\psi \propto \cos k_x x$ or $\sin k_x x$, with

$$k_x = n\,\frac{\pi}{L} \tag{100}$$

as before (actually, previously the box was $2L$ long, whereas now it is simpler to call the side L). It's not so clear that this goes over to free waves as $L \to \infty$, however, because the waves always feel the effect of the box near the edge. A common alternative is to take **periodic boundary conditions**. Here, the idea is that a wave (or particle) that exits from one side of the box should re-emerge from the other: the opposite sides of the box are identified, and there is no physical effect of the box. However, this trick only works for waves where there are a whole number of wavelengths across the box:

$$k_x = n\,\frac{2\pi}{L} \tag{101}$$

The difference with the previous case arises because now we use $\psi \propto e^{ik_x x}$ as the wavefunction. We can therefore now also consider states where k_x is *negative*: these are distinct waves, that propagate in the opposite direction to states with $k_x > 0$. For the previous case, ψ consists of standing waves, and $k_x < 0$ is never considered: the physical content is the same as $k_x > 0$. Either way, then, there are the same number of modes in a given range of $|k_x|$.

The same thing applies for k_y and k_z, so allowed states lie on a 3D grid of points in (k_x, k_y, k_z)-space (also known as **k space** or **momentum space**), with a mesh spacing of $\Delta k = 2\pi/L$. The **density of states** is thus $L^3/(2\pi)^3$:

$$\boxed{\text{Number of modes} = \frac{L^3}{(2\pi)^3}\,d^3k.} \tag{102}$$

This is an important concept which is used in many areas of physics.

THE FOURIER TRANSFORM To complete the story, we need to be able to extract a given Fourier coefficient. We do this by using orthonormality over the box:

$$\begin{aligned} \psi(\mathbf{r}) &= \sum_i \tilde{\psi}(\mathbf{k}_i)\, e^{i\mathbf{k}\cdot\mathbf{r}} \\ \tilde{\psi}(\mathbf{k}) &= \frac{1}{V}\int \psi(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, d^3r \end{aligned} \tag{103}$$

(where $V = L^3$). The sum is over wavenumbers lying on a 3D grid of points in (k_x, k_y, k_z)-space (also known as **k space** or **momentum space**), with a mesh spacing of $\Delta k = 2\pi/L$. Now we can let $L \to \infty$, because the k-space sum can be replaced by an integral in the limit that the k-space mesh becomes very fine. The number of modes in a volume of k-space d^3k is just this volume multiplied by the **density of states**, $V/(2\pi)^3$. We can now write

$$\begin{aligned} \psi(\mathbf{r}) &= \frac{V}{(2\pi)^3}\int \tilde{\psi}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d^3k \\ \tilde{\psi}(\mathbf{k}) &= \frac{1}{V}\int \psi(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, d^3r \end{aligned} \tag{104}$$

This treats real space and k-space asymmetrically, but this is easily amended by defining a new $\tilde{\psi}$ as the old $\tilde{\psi}V/(2\pi)^{3/2}$:

$$\boxed{\begin{aligned} \psi(\mathbf{r}) &= \frac{1}{(2\pi)^{3/2}}\int \tilde{\psi}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d^3k \\ \tilde{\psi}(\mathbf{k}) &= \frac{1}{(2\pi)^{3/2}}\int \psi(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, d^3r \end{aligned}} \tag{105}$$

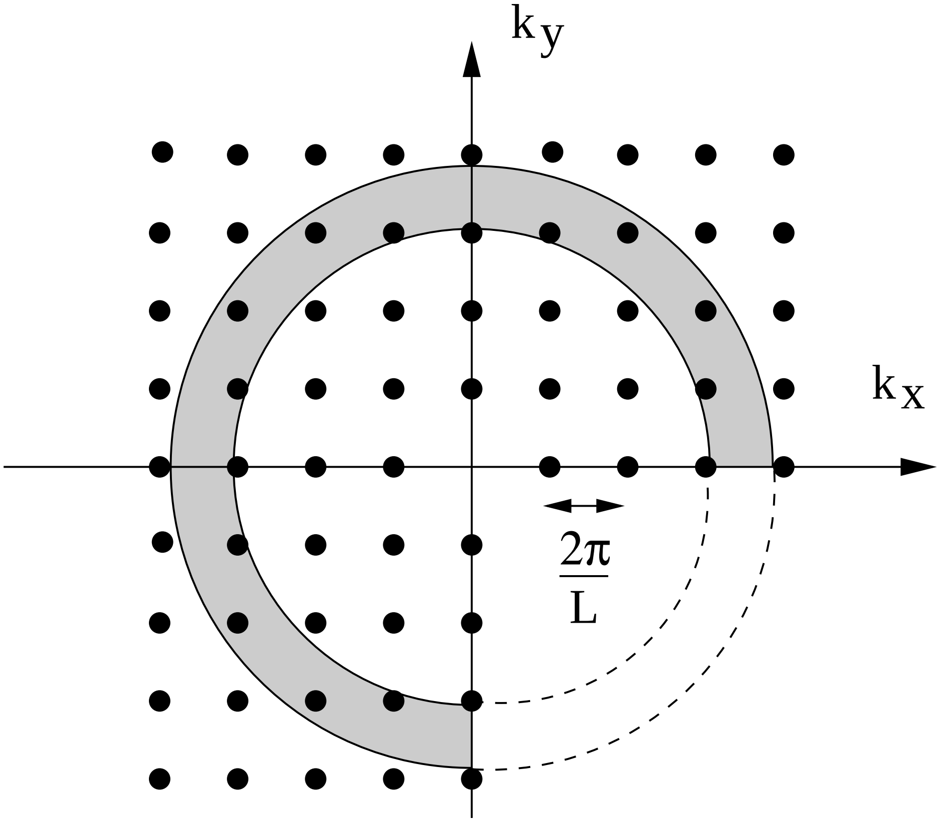

Figure 3 Illustrating the origin of the density of states in 2D. The allowed modes are shown as points, with a separation in k_x and k_y of $2\pi/L$, where L is the side of the box. The number of modes between $|k|$ and $|k|+d|k|$ (i.e. inside the shaded annulus) is well approximated by $(L/2\pi)^2$ times the area of the annulus, as $L \to \infty$, and the mode spacing tends to zero. Clearly, in n dimensions, the mode density is just $(L/2\pi)^n$.

This would have the 1D analogue

$$\begin{aligned} \psi(x) &= \frac{1}{(2\pi)^{1/2}} \int \tilde{\psi}(k)\, e^{ikx}\, dk \\ \tilde{\psi}(k) &= \frac{1}{(2\pi)^{1/2}} \int \psi(x)\, e^{-ikx}\, dx \end{aligned} \tag{106}$$

Unfortunately, both the symmetrical and unsymmetrical definitions are used in practice. The main thing is not to mix the conventions. One thing to note is that, for a **real wave function**, the Fourier coefficients must satisfy a reflection symmetry: $\tilde{\psi}(-k) = \tilde{\psi}^*(k)$.

THE DELTA-FUNCTION AGAIN As an application of this, we can get the Fourier representation of the delta-function:

$$\boxed{\delta(x - x_0) = \frac{1}{2\pi} \int e^{ik(x-x_0)}\, dk.} \tag{107}$$

UNCERTAINTY PRINCIPLE The Fourier transform shows how to express a non-periodic wavefunction as an integral over k-space. By analogy with the discrete case, we see that $|\tilde{\psi}|^2\ dk$ is proportional to the probability that the particle's momentum will be found to lie in a momentum range $dp = \hbar dk$. It is interesting to illustrate this in the case of a **Gaussian** wavefunction:

$$|\psi|^2 = \frac{1}{\sqrt{2\pi}\sigma_x} \exp\left[-\frac{(x-\mu)^2}{2\sigma_x^2}\right]. \tag{108}$$

This 'bell-shaped' curve is also known as the **normal distribution**, and is important in probability theory. It defines a mean of μ and an rms in position of σ_x. If the wavefunction has a fixed phase, then it is not too hard to find the corresponding momentum distribution:

$$\tilde{\psi}(k) = \frac{1}{(2\pi)^{1/2}} \frac{1}{(2\pi)^{1/4}\sigma_x^{1/2}} \int \exp\left[-ikx - \frac{(x-\mu)^2}{4\sigma_x^2}\right].\ dx. \tag{109}$$

Completing the square shows that the momentum distribution is also Gaussian:

$$|\tilde{\psi}|^2 = \frac{1}{\sqrt{2\pi}\sigma_k} \exp\left[-\frac{k^2}{2\sigma_k^2}\right]. \tag{110}$$

and $\sigma_k = 1/(2\sigma_x)$, independent of μ. This says that the spatial and momentum dispersions obey the following relation:

$$\sigma_x \sigma_p = \hbar/2. \tag{111}$$

The narrower the spatial distribution, the broader the distribution of momentum, and vice-versa. This is not surprising: given a wavefunction of a width σ_x, one clearly requires waves down to a minimum wavelength of $\sim 1/\sigma_x$ in order to Fourier analyze it. In fact, this relation for Gaussian wave functions turns out to be the best one can do. For any other distribution, the dispersions in position and momentum satisfy the inequality

$$\boxed{\langle(\Delta x)^2\rangle\langle(\Delta p)^2\rangle \geq \hbar^2/4.} \tag{112}$$

The proof of this is left for later.

MEASUREMENT UNCERTAINTY This is Heisenberg's famous **uncertainty principle**. It says that the position and momentum of a particle cannot be specified simultaneously to arbitrary accuracy. Normally, though, we think of uncertainty in e.g. position as being something that affect a *measurement*, whereas the uncertainty principle concerns the properties of the particle before any measurement has happened. Nevertheless, the process of quantum-mechanical measurement fits in well with the idea of uncertainty. For example, if we measure the momentum of a particle with perfect accuracy, the rules of quantum mechanics say that the state becomes an eigenstate of momentum, which is a plane wave: the position of the particle becomes infinitely uncertain. Similarly, a perfect measurement of position must leave the wave function as a delta function, for which the momentum distribution is infinitely broad.

ENERGY-TIME UNCERTAINTY PRINCIPLE Viewing the uncertainty principle as being just a property of Fourier transforms suggests another form, where we Fourier-transform with respect to time. Oscillations $\exp(i\omega t)$ are eigenstates of energy, so the same algebra as before now ought to give

$$\boxed{\langle(\Delta E)^2\rangle\langle(\Delta t)^2\rangle \geq \hbar^2/4.} \tag{113}$$

In other words, a system that only exists for a finite period must have a dispersion in energy.

One example of this is the natural width of atomic emission lines. Atomic transitions occur between different energy levels, emitting photons of angular frequency $\hbar\omega = E_1 - E_2$. Now, we will see later that a given excited state has some finite lifetime τ before it undergoes **spontaneous decay**. The energy-time uncertainty relation therefore says that the emitted photons will have a spread of frequencies $\delta\omega \sim 1/\tau$: atomic spectral lines will be resolved at this resolution.

A more striking example is provided by **Yukawa's argument** about inter-nuclear forces. Rutherford's experiments on alpha-particle scattering proved that the forces that bind the nucleus are of very short range, $\sim 10^{-15}$ m. Now, all forces are the result of the interchange of some particle – the photon in the case of electromagnetism. Yukawa's insight was that the short range of nuclear forces would arise if the particle involved was massive. One way of interpreting the energy-time relation is that it is possible to violate conservation of energy, at least for a short time. If we want to create a particle of mass m, we can only 'borrow' enough energy to do this for a time $\hbar/E = \hbar/(mc^2)$. In this time the **virtual particle** thus created can travel no further than ct before it has to be reabsorbed. The range of the interaction is therefore $\lesssim \hbar/(mc)$. In this way, Yukawa predicted the existence of the pion, which is a particle about 15% of the mass of the proton.

9 Dirac notation

For practical quantum-mechanical calculations, the notation derived by Dirac is invaluable. The use of this notation is not fully examinable in third year: you will be expected to recognize expressions in Dirac notation, and know what they mean, but the calculations you will have to do can always be tackled without using Dirac's machinery. This is because Dirac notation can make things seem a little abstract for some tastes, and it can make more sense if things are written out in a bit more detail.

The wave function is replaced by the more general notion of the **state function**, written $|\psi\rangle$. This encodes all the information about the quantum state, including internal degrees of freedom, such as spin. States of particular interest are the **eigenfunctions** of operators: $A\,|i\rangle = a_i|i\rangle$.

The most common calculation in quantum mechanics is to evaluate some matrix element for an operator, and the Dirac notation for this is particularly simple, emphasizing the similarity to an inner product:

$$\int \psi_1^*(\mathbf{x})\, A\, \psi_2(\mathbf{x})\; d^3x \quad \longrightarrow \quad \langle 1|A|2\rangle. \tag{114}$$

This is a simple extension of the notation for an expectation value. For $A = 1$, this becomes just $\langle 1|2\rangle$. Dirac split this expression up:

$$\boxed{\langle 1|2\rangle = \langle 1| \quad |2\rangle;} \tag{115}$$

i.e. a **bracket** is made from a **bra** $\langle\psi|$ and a **ket** $|\psi\rangle$. This is like a scalar product of a row vector and a column vector: the bra and ket are alternative and equally valid representations of the same state vector.

A crucial definition is the **Hermitian conjugate** of an operator:

$$\boxed{\langle\phi|A|\psi\rangle^* \equiv \langle\psi|A^\dagger|\phi\rangle.} \tag{116}$$

Using this relation twice shows that we can think of a bracket as arising either through A operating to the right, or $A^\dagger$ to the left: $\langle\phi|A|\psi\rangle = \langle\phi|A\psi\rangle$, so we can write

$$\boxed{\langle\phi|A|\psi\rangle = \langle\psi|A^\dagger|\phi\rangle^* = \langle A^\dagger\phi|\psi\rangle.} \tag{117}$$

This trick of thinking of an operator A interchangably either as A acting to the right or $A^\dagger$ acting to the left is an important results that we will keep using. It is something that you should be capable of proving without using Dirac notation, starting from the definition of a Hermitian operator in terms of integrals.

A Hermitian operator has $A^\dagger = A$, and so $\langle n|A|n\rangle^* = \langle n|A|n\rangle \Rightarrow a_n^* = a_n$: the eigenvalues are real. Similarly,

$$\langle n|A|m\rangle^* = \langle m|A|n\rangle \quad \Rightarrow \quad a_m^*\langle m|n\rangle = a_n\langle m|n\rangle; \tag{118}$$

if the eigenvalues are non-degenerate, the eigenfunctions are therefore orthogonal, and can thus be defined to be orthonormal: $\langle i|j\rangle = \delta_{ij}$. Such a set of eigenfunctions is called a **complete set**, since any other state function can be expanded in terms of them:

$$\begin{aligned} |\psi\rangle &= \sum_i c_i|i\rangle \\ \langle\psi| &= \sum_i c_i^*\langle i| \\ c_i &= \langle i|\psi\rangle. \end{aligned} \tag{119}$$

The coefficient c_i can be extracted by operating on the first sum with a bra; this proves that the coefficients in the analogous series for $\langle\psi|$ are c_i^*.

GENERALIZED UNCERTAINTY PRINCIPLE As an illustration of the power of Dirac notation, let us look at the uncertainty principle again. Consider the following expression:

$$\langle\psi|(A + i\lambda B)^\dagger(A + i\lambda B)|\psi\rangle. \tag{120}$$

Since operators act to the left by taking the Hermitian conjugate, we see that

$$\langle\psi|O^\dagger O|\psi\rangle = \langle O\psi|O\psi\rangle = \langle|O\psi|^2\rangle \geq 0. \tag{121}$$

Now, $(i\lambda B)^\dagger = -i\lambda B^\dagger$; if A and B are Hermitian, then the overall bracket is

$$\langle A^2\rangle + \lambda^2\langle B^2\rangle + \lambda(i\langle[A,B]\rangle) \geq 0. \tag{122}$$

Now find the minimum of the lhs as a function of λ. This minimum is still ≥ 0, and so

$$\boxed{\langle A^2\rangle\langle B^2\rangle \geq -\langle[A,B]\rangle^2/4.} \tag{123}$$

If we take $A = x - \langle x\rangle$ and $B = p - \langle p\rangle$, $[A,B] = i\hbar$, and we get the normal Heisenberg relation.

10 Angular momentum

Although we have set up the general machinery of quantum mechanics, so far the only observables it has actually been applied to are the two basic de Broglie operators x and p. Next to these, the most important quantity in dynamics is angular momentum:

$$\boxed{\mathbf{L} = \mathbf{r} \wedge \mathbf{p}.} \tag{124}$$

The quantum properties of angular momentum are crucial in determining atomic structure, so we should look at these in general before embarking on the Hydrogen atom.

Written explicitly in components,

$$L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right), \tag{125}$$

and the same for other components, cyclically permuting x, y, z. This can be made to look a bit simpler in terms of spherical polars:

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta. \end{aligned} \tag{126}$$

The partial derivative with respect to ϕ is

$$\frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\phi}\frac{\partial}{\partial z} = x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \tag{127}$$

which gives the simple relation

$$\boxed{L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}.} \tag{128}$$

This is clearly the direct angular counterpart of the correspondence between linear momentum and $\boldsymbol{\nabla}$. The expressions for L_x and L_y are less illuminating, but this is to do with the choice of polar axis. What this shows, however, is the important fact that the $\mathbf{L}$ operator is independent of radius – the eigenfunctions of angular momentum will be functions of angle *only*.

COMMUTATORS There are two important commutation relations for angular momentum, which come from putting in the Cartesian components and grinding away:

$$\boxed{[L_x, L_y] = i\hbar L_z,} \tag{129}$$

and cyclic permutations of x, y, z.

$$\boxed{[L^2, L_z] = 0,} \tag{130}$$

and the same for x & y. The second relation says that L^2 and L_z are compatible: a state can have a well-defined total angular momentum and z component at the same time. However, the values of the x and y components are then not definite.

Also, for a system with a spherically symmetric potential, it is easily seen that

$$[L_x, H] = 0 \quad \text{etc.} \tag{131}$$

States in which both energy and angular momentum have well-defined values are thus possible. This will be important when we come to the Hydrogen atom.

EIGENVALUES The eigenvalue equation for L_z is easy:

$$\frac{\hbar}{i}\frac{\partial}{\partial \phi}\psi = \ell_z \psi \quad \Rightarrow \quad \psi = f(\theta)\exp(i\ell_z\phi/\hbar). \tag{132}$$

In order for ψ to be single valued, we see that

$$\boxed{\ell_z = m\hbar, \quad m = 0, \pm 1, \pm 2, \ldots} \tag{133}$$

is required. For reasons explained below, m is known as the **magnetic quantum number**.

VECTOR MODEL The quantization of total angular momentum is less easily dealt with. We will give a detailed treatment later, but first it is worth taking a more intuitive approach that both derives the answer and gives a good feel for what it means. This is based on the idea that there must still be an angular momentum vector, even if quantum uncertainty may mean that we can never discover exactly where it is pointing.

Start by noting that it is possible to have a simultaneous eigenstate of L^2 and L_z, because these operators commute. Assume that we are in such a state, for which the L_z eigenvalue is $m\hbar$. There must be some limit to m, since the z component of angular momentum cannot exceed the total. Call this maximum value of m by the symbol ℓ. Our first guess is that it might be possible to point $\mathbf{L}$ directly along the z axis, so that the eigenvalue of L^2 would be $\ell^2\hbar^2$. However, a little thought shows that this is impossible, because of the uncertainty principle. In order for $\mathbf{L}$ to point 'straight up', both L_x and L_y would have to be zero simultaneously; however, since these operators don't commute, it is impossible to have perfect knowledge of both these quantities at once. The commutator is $[L_x, L_y] = i\hbar L_z$, and if we insert this in the general form of the uncertainty principle, we get

$$\langle L_x^2\rangle \, \langle L_y^2\rangle \geq \frac{\hbar^2}{4}\,\langle L_z^2\rangle. \tag{134}$$

How do we interpret this uncertainty? If we choose the $m = 0$ eigenstate, then $\mathbf{L}$ is confined to the xy plane, but it could point in any direction in that plane, so both $\langle L_x^2\rangle$ and $\langle L_y^2\rangle$ are substantial, so their product is > 0 and the uncertainly principle is amply satisfied in this case. What about the state of *minimum* uncertainty, in which the uncertainty relation is an equality, rather than an inequality? Clearly, as we increase m, the x and y components must fall. The minimum uncertainty state is therefore when $m = \ell$, its maximum value, so that

$$\langle L_x^2\rangle \, \langle L_y^2\rangle = \ell^2\hbar^4/4. \tag{135}$$

Now, we have said nothing that distinguishes x from y, so the uncertainties in these components must be equal, implying

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \ell\hbar^2/2. \tag{136}$$

This is all we need, because the total angular momentum is

$$\langle L^2 \rangle = \langle L_x^2 + L_y^2 + L_z^2 \rangle \tag{137}$$

We know the expectation values of the three terms on the rhs in the minimum-variance case, so the eigenvalue of L^2 is determined by the quantum number ℓ, which we know is an integer:

$$\boxed{\langle L^2 \rangle = \ell(\ell+1)\hbar^2; \quad \ell = 0, 1, 2, \ldots} \tag{138}$$

In summary, the angular momentum vector is not allowed to point in any old direction. If the total quantum number is ℓ, it can point so that the z component is

$$m = -\ell, -(\ell-1), \ldots, 0, \ldots, (\ell-1), \ell, \tag{139}$$

i.e. a total of $2\ell+1$ distinct states. However, $\ell(\ell+1)$ is always greater than m^2, so $\mathbf{L}$ can never point entirely along one axis.

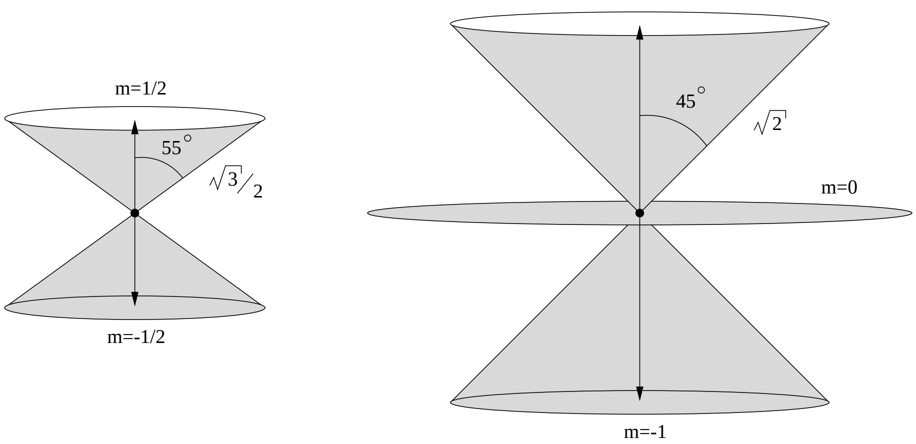
(a) $\ell = 1/2$ (b) $\ell = 1$

Figure 4 The vector model of angular momentum illustrated for $\ell = 1/2$ and $\ell = 1$. The 'length' of the $\mathbf{L}$ vector is $\sqrt{\ell(\ell+1)}$ (in units of $\hbar$), but its maximum component along the z axis is $m = \pm\ell$. The vector is constrained to lie along cones such that the z components differ by integer multiples of $\hbar$.

Lastly, note that angular momentum is unaffected by parity, because both x and $\partial/\partial x$ change sign under P. The angular momentum eigenstates are therefore eigenstates of parity. For now, we just quote the actual result:

$$\boxed{P = (-1)^{\ell}.} \tag{140}$$

11 Ladder operators

There is an alternative way of deducing the eigenvalues of angular momentum, which is much more general than the method used above. The angular momentum operators are

$$L_x = -i\hbar(y\,\partial/\partial z - z\,\partial/\partial y) \tag{141}$$

etc., from which the Hermitian conjugate ladder operators are defined:

$$\begin{aligned} u &= L_x + iL_y \\ d &= L_x - iL_y. \end{aligned} \tag{142}$$

These commute with total angular momentum L^2, but not with L_z: if $L_z\psi = b\psi$, $L_z(u\psi) = (b+\hbar)u\psi$, so u is a **raising operator** (this requires the commutator $[u, L_z] = -\hbar u$, which is easily proved from the basic commutators $[L_x, L_y] = i\hbar L_z$ etc.).

Similarly, d lowers the eigenvalue of L_z by $\hbar$. Now suppose there is a highest eigenstate of L_z, with eigenvalue c, such that $u\psi = 0$. Not only is this intuitively reasonable, but $du = L^2 - L_z^2 - \hbar L_z$ and $\langle u\psi \mid u\psi\rangle = \langle\psi|du|\psi\rangle$, so the wavefunction cannot be normalized if L_z is too big. Now, use the equation for du plus $du\psi = 0$, to show that the eigenvalue of L^2 is $L^2 = c(c+\hbar)$. It is usual to write $c = \ell\hbar$, so that

$$\boxed{L^2 = \ell(\ell+1)\hbar^2.} \tag{143}$$

Now do the same trick with the lowest eigenstate: the eigenvalue here must be $c - n\hbar$, where n is an integral number of lowerings from the top state. In this case, we have $ud\psi = 0$, where $ud = L^2 - L_z^2 + \hbar L_z$, which gives $L^2 = (c-n\hbar)^2 - (c-n\hbar)$; together with the previous equation, this gives $c = n\hbar/2$. The fundamental quantum of angular momentum is therefore $\hbar/2$, even though successive L_z states are separated by twice this amount. The half-integral states correspond to **spin**, which is the intrinsic angular momentum carried by particles; as shown above, orbital angular momentum is quantized in unit steps.

LADDER OPERATORS AND OSCILLATORS The use of ladder operators is an important general method. As a further illustration of its power, we revisit the case of the harmonic oscillator, for which the Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}. \tag{144}$$

Define the operator a, and its conjugate, $a^\dagger$:

$$\begin{aligned} a &= \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(x + \frac{i}{m\omega}p\right) \\ a^\dagger &= \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(x - \frac{i}{m\omega}p\right) \end{aligned} \tag{145}$$

Since $[p, x] = -i\hbar$, these have the commutator $[a, a^\dagger] = 1$. In these terms, the Hamiltonian is

$$H = \frac{\hbar\omega}{2}\left(a^\dagger a + a a^\dagger\right) = \hbar\omega(N + 1/2); \quad N = a^\dagger a. \tag{146}$$

The number operator $N \equiv a^\dagger a$ is Hermitian, because $(AB)^\dagger = B^\dagger A^\dagger$, so that we can label states by the real eigenvalues of N:

$$N\psi_n = n\psi_n. \tag{147}$$

Using the commutator of a and $a^\dagger$ gives the commutators

$$\begin{aligned} [a, N] &= a \\ [a^\dagger, N] &= -a^\dagger; \end{aligned} \tag{148}$$

this shows that a and $a^\dagger$ are the **annihilation** and **creation** operators, which respectively lower or raise n by one unit:

$$\begin{aligned} N a^\dagger\psi_n &= (n+1)\, a^\dagger\psi_n \quad \Rightarrow \quad a^\dagger\psi_n \propto \psi_{n+1} \\ N a\psi_n &= (n-1)\, a\psi_n \quad \Rightarrow \quad a\psi_n \propto \psi_{n-1}. \end{aligned} \tag{149}$$

Now, eigenstates of N are also energy eigenstates, since $H \propto N + 1/2$. However, the energy eigenvalue cannot be negative, since this would mean that there existed a state with the expectation value $\langle H \rangle < 0$. Because H is a sum of quadratic terms in x and p, this cannot be. There must therefore be a lowest state, for which $a\psi_{\rm low} = 0$. This in turn implies $a^\dagger a\psi_{\rm low} = 0$, so that $(H - \hbar\omega/2)\psi_{\rm low} = 0$. This shows that the lowest state has $E = \hbar\omega/2$, or $n = 0$. The energy eigenvalues are therefore $E = (n + 1/2)\hbar\omega$, $n = 0, 1, 2, \ldots$, as before.

LADDER OPERATORS IN DIRAC NOTATION It is a valuable exercise to recast this algebra of oscillator ladder operators in Dirac notation. We label states by the real eigenvalues of $N = a^\dagger a$:

$$N|n\rangle = n|n\rangle. \tag{150}$$

Using the commutators $[a, N] = a$ and $[a^\dagger, N] = -a^\dagger$ gives

$$\begin{aligned} N a^\dagger|n\rangle &= (n+1)\, a^\dagger|n\rangle \quad \Rightarrow \quad a^\dagger|n\rangle \propto |n+1\rangle \\ N a|n\rangle &= (n-1)\, a|n\rangle \quad \Rightarrow \quad a|n\rangle \propto |n-1\rangle. \end{aligned} \tag{151}$$

Finally, consider the normalization of the wave function, $\langle an|an\rangle = 1 = \langle n|N|n\rangle$ (where $|an\rangle$ stands for $a|n\rangle$). The last step follows from the above idea of operators operating to the left: $\langle O^\dagger m|n\rangle = \langle m|O|n\rangle$. This gives the relations

$$\boxed{\begin{aligned} a|n\rangle &= \sqrt{n}\;|n-1\rangle \\ a^\dagger|n\rangle &= \sqrt{n+1}\;|n+1\rangle. \end{aligned}} \tag{152}$$

This shows us that there must be a ground state at $n = 0$: $a|0\rangle$ produces the empty set, and n cannot be lowered further.

BLACK-BODY RADIATION Having solved the harmonic oscillator fully, it is interesting to return to one of the subjects that started the quantum revolution. Although we won't prove it here, it should be intuitively reasonable that a single mode of the electromagnetic waves inside a cavity may be treated as an oscillator: classically, a given mode oscillates with a fixed frequency, and can have any amplitude. In the quantum treatment, the energy of the mode will be $E = (n + 1/2)\hbar\omega$. In this context, the number n is called the **occupation number**, as it counts how many photons are occupying each mode. Notice that the photons are not treated at all as particles: nothing says where the photons actually *are*: we just know they are in the cavity somewhere.

The number n is set by thermodynamics. The probability of a given n is proportional to the **Boltzmann factor** $\exp(-E/kT)$ (where k is not wavenumber). The mean n is evaluated by summing all the possibilities:

$$\bar{n} = \frac{0 + 1P(1) + 2P(2) + \cdots}{P(0) + P(1) + P(2) + \cdots} \tag{153}$$

Since we have P's top and bottom, only relative probabilities matter, so we can take $P(n) = F^n$, where $F = \exp(-\hbar\omega/kT)$. The top line is related to d/dF of the bottom line, which is just a geometric series, so we get

$$\boxed{\bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1}.} \tag{154}$$

For very small T, the expected occupation number is exponentially small: the gap between oscillator energy levels is too large for thermal fluctuations to have much chance of exciting even a single quantum of oscillation. For large T, conversely, $\bar{n} \gg 1$, which is the classical limit. $\bar{n}$ tends to $kT/\hbar\omega$, so the mean energy per mode, $\bar{n}\hbar\omega$, tends to the equipartition value of kT. Multiplying this mean energy per mode times the number of modes in a given frequency range gives Planck's formula for the energy density of black-body radiation, as we saw in the first lecture.

Actually, the story is not quite over, because of the extra 1/2 in $E = (n + 1/2)\hbar\omega$. This means that, even for $n = 0$, each mode has a fixed **zero-point energy**. Even as $\bar{n}$ tends to zero for the high-ω modes, this energy is still there, and apparently gives an infinite total, since the number of modes is $\propto \omega^2\, d\omega$. The conclusion is that the **quantum vacuum** (defined as the state with $n = 0$ for every mode) should have infinite energy density. This sounds like we have made a silly mistake, but no-one properly understands how to fix matters. The best that can be said is that it is possible to find other quantum contributions to the energy density of the vacuum that are infinitely negative – so the sum could be anything. In recent years, cosmologists appear to have measured the energy density of the vacuum, obtaining the energy equivalent of about $10^{-26}\mathrm{kg\,m^{-3}}$. How this number can be so small, but non-zero, is one of the biggest open questions in physics.

12 The Hydrogen atom

The Hydrogen atom is one of the simplest realistic quantum problems. However, given that even the 1D square well turned out to evade analytic treatment, you will not be surprised to find that the Hydrogen atom has one or two nasty moments. It would be nice to pretend that this is all simple and elegant, but in truth some of the analysis is a bit tedious. Therefore, the full solution of the Hydrogen atom is not examinable. The main thing is to understand the general approach and key concepts, and to have a physical understanding of the final answer. We will skip over many of the details, but these are given in an appendix at the end of the notes, for those who want to see what is involved.

REDUCED MASS The Hamiltonian for the electron requires the electrostatic potential due to the nuclear proton charge:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}. \tag{155}$$

Actually, even this needs amending, since it assumes that the proton is fixed at $r = 0$, whereas really the proton and electron are orbiting each other. The classical solution of this problem is as follows: The equations of motion are

$$\begin{aligned} m_e\ddot{\mathbf{r}}_e &= -\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_e - \mathbf{r}_p|^3}(\mathbf{r}_e - \mathbf{r}_p) \\ m_p\ddot{\mathbf{r}}_p &= -\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_e - \mathbf{r}_p|^3}(\mathbf{r}_p - \mathbf{r}_e) \end{aligned} \tag{156}$$

Differencing these equations shows that $(\mathbf{r}_e - \mathbf{r}_p)$ obeys an equation of the same form, but incorporating a **reduced mass**, μ:

$$\mu^{-1} = m_e^{-1} + m_p^{-1} \quad\Rightarrow\quad \mu = \frac{m_e m_p}{m_e + m_p}. \tag{157}$$

The same things applies quantum-mechanically, since we have to add the electron and proton kinetic energies:

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|). \tag{158}$$

The two spatial coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ can be replaced by a centre-of-mass coordinate and a coordinate difference:

$$\begin{aligned} m\mathbf{R} &= m_1\mathbf{r}_1 + m_2\mathbf{r}_2 \\ \mathbf{r} &= \mathbf{r}_2 - \mathbf{r}_1 \end{aligned} \tag{159}$$

where total mass is $m = m_1 + m_2$ and $\mathbf{R} = (X, Y, Z)$ are the centre-of-mass coordinates. Derivatives look like

$$\frac{\partial}{\partial x_2} = \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_2}\frac{\partial}{\partial X} = \frac{\partial}{\partial x} + \frac{m_2}{m}\frac{\partial}{\partial X}. \tag{160}$$

We can then easily enough get

$$\frac{1}{m_1}\nabla_1^2 + \frac{1}{m_2}\nabla_2^2 = \frac{1}{\mu}\nabla_r^2 + \frac{1}{m}\nabla_R^2, \tag{161}$$

so the relative momentum separates out, at the price of using the reduced electron mass.

SPHERICAL POLARS The radial nature of the potential implies that it may make sense to use a spherical polar coordinate system. In Physical Mathematics, you learned that ∇^2 in spherical polars is

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}. \tag{162}$$

This looks quite a mess, and it may help to have an alternative derivation of this important expression (but this is just for illumination, and is not examinable). Write

$$\boldsymbol{\nabla} = \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \left(\frac{1}{r}\right) \frac{\partial}{\partial \theta} + \mathbf{e}_\phi \left(\frac{1}{r\sin\theta}\right) \frac{\partial}{\partial \phi}, \tag{163}$$

where $\mathbf{e}_r$ etc. are unit vectors in the directions of increasing r, θ, ϕ. Squaring this expression to get ∇^2 is more complicated than in Cartesian coordinates. First, there are the factors like $(1/r)$; second, we may have to differentiate some of the unit vectors (which would be constant in a Cartesian coordinate system). However, most of the terms produced by differentiation don't matter, because we always have to take the dot product at the end. For example, consider $(\mathbf{e}_r \partial/\partial r) \cdot \mathbf{T}$, where $\mathbf{T}$ is any term. This will only be non-zero if differentiation of $\mathbf{T}$ yields a component in the direction of $\mathbf{e}_r$. The only chance of doing this is through differentiating the basis vectors.

A little thought gives the following relations:

$$\begin{aligned}
\frac{\partial}{\partial\theta}\mathbf{e}_r &= \mathbf{e}_\theta \\
\frac{\partial}{\partial\theta}\mathbf{e}_\theta &= -\mathbf{e}_r \\
\frac{\partial}{\partial\phi}\mathbf{e}_r &= \sin\theta\,\mathbf{e}_\phi \\
\frac{\partial}{\partial\phi}\mathbf{e}_\theta &= \cos\theta\,\mathbf{e}_\phi \\
\frac{\partial}{\partial\phi}\mathbf{e}_\phi &= -\mathbf{e}_\rho
\end{aligned} \tag{164}$$

where $\mathbf{e}_\rho$ is a unit vector perpendicular to the z axis, which satisfies

$$\begin{aligned}
\mathbf{e}_\rho\cdot\mathbf{e}_r &= \sin\theta \\
\mathbf{e}_\rho\cdot\mathbf{e}_\theta &= \cos\theta \\
\mathbf{e}_\rho\cdot\mathbf{e}_\phi &= 0
\end{aligned} \tag{165}$$

We can now take the full dot product $\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}$. This gives the three obvious terms:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}, \tag{166}$$

plus extra terms from differentiating basis vectors. Since only $\partial/\partial\theta$ and $\partial/\partial\phi$ have any effect, we only care about cases where $\partial/\partial\theta$ gives a result proportional to $\mathbf{e}_\theta$ or $\partial/\partial\phi$ gives a result proportional to $\mathbf{e}_\phi$. From the above, there are three such cases: (i) $\partial\mathbf{e}_r/\partial\theta$; (ii) $\partial\mathbf{e}_r/\partial\phi$; (iii) $\partial\mathbf{e}_\theta/\partial\phi$. These give additional terms that are respectively (i) $(1/r)\partial/\partial r$; (ii) $(1/r)\partial/\partial r$; (iii) $(\cot\theta/r^2)\partial/\partial\theta$. That completes this derivation of ∇^2 in spherical polars; Physical Mathematics gave a more general method (see section 8.10 of Riley, Hobson & Bence).

SEPARATION OF VARIABLES We now look for a solution

$$\psi = R(r)Y(\theta,\phi). \tag{167}$$

The angular part must be expandable in terms of the eigenfunctions of the angular momentum operator. In fact, with some effort, it can be shown that

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{1}{\hbar^2 r^2}L^2, \tag{168}$$

so the angular momentum operator commutes with the Hamiltonian, and the energy eigenfunctions can also be angular momentum eigenstates.

Separation of variables gives the equation

$$-\frac{\hbar^2}{2\mu}\left[Y\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\right] + R\frac{1}{2\mu r^2}L^2 Y = (E-V)RY. \tag{169}$$

Multiplying through by $r^2/(RY)$ gives

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\right] - (E-V)r^2 = \frac{1}{2\mu Y}L^2 Y \tag{170}$$

As usual, both sides of this equation must be constants, and we can use our knowledge of angular momentum to identify the rhs as $\ell(\ell+1)\hbar^2/2\mu$.

SPHERICAL HARMONICS This separation of variables approach is very similar to the route that is followed for other 3D wave equations, including the simple non-dispersive case $(\nabla^2 + k^2)\psi = 0$. The angular eigenfunctions are the same in this case. We know that states of given ℓ split into $2\ell+1$ states with different values of m, where the ϕ dependence is $\propto \exp(im\phi)$. The dependence on θ is not so straightforward; it is obtained by performing separation of variables again, and writing $Y(\theta,\phi) = \Theta(\theta)\exp(im\phi)$, and converting the eigenvalue equation for L^2 into an equation for $\Theta(\theta)$. The desired solutions are standard functions called the **associated Legendre functions**, $P_\ell^m(\cos\theta)$:

$$P_\ell^m(z) = (1-z^2)^{|m|/2}\frac{d^{|m|}}{dz^{|m|}}P_\ell(z), \tag{171}$$

where $P_\ell(z)$ are the ordinary **Legendre polynomials**. These are specified up to an overall normalization, which is taken to be $P_\ell(1) = 1$; the $P_\ell(z)$ are thus orthogonal over the range $-1 < z < 1$, but are not orthonormal. The first few Legendre polynomials are:

$$\begin{aligned} P_0(x) &= 1 \\ P_1(x) &= x \\ P_2(x) &= (3x^2-1)/2 \\ P_3(x) &= (5x^3-3x)/2 \end{aligned} \tag{172}$$

A general expression for these functions is given by **Rodrigues' formula**:

$$P_\ell(x) = \frac{1}{2\ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell \tag{173}$$

(see e.g. p453 of Riley, Hobson & Bence).

In summary, the overall angular solutions are the **spherical harmonics**:

$$\boxed{Y_\ell^m(\theta,\phi) \propto P_\ell^m(\cos\theta)e^{im\phi};} \tag{174}$$

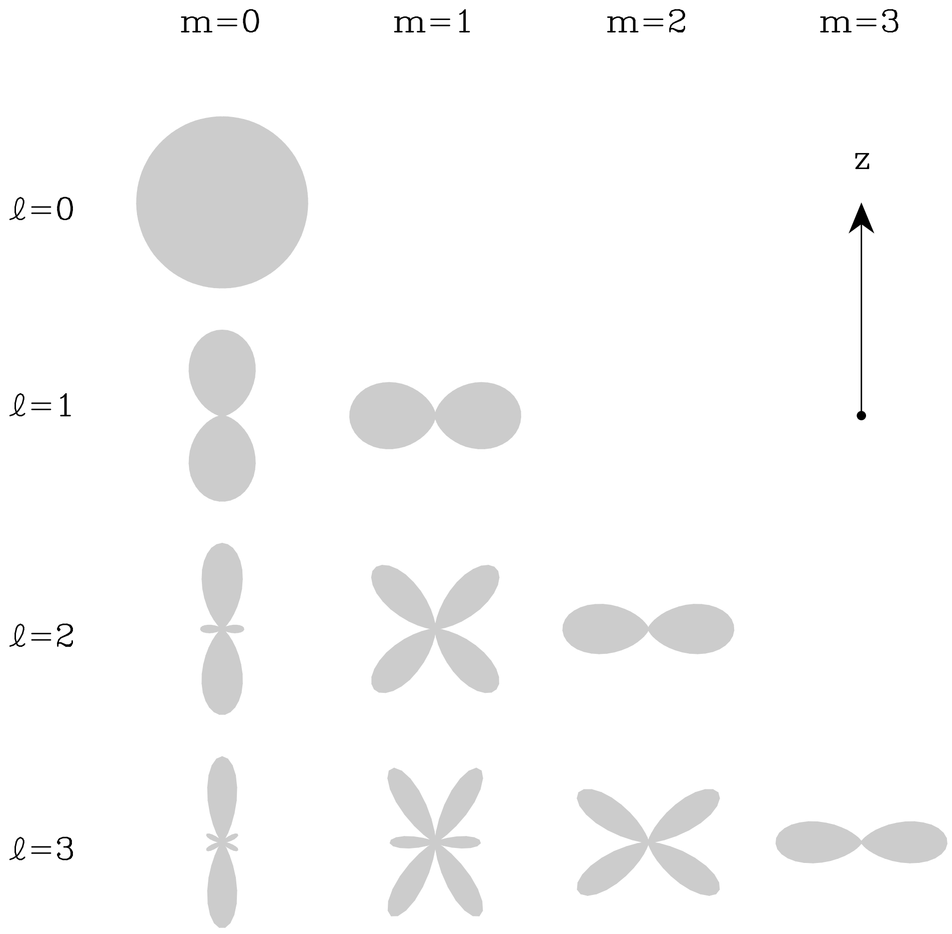

Figure 5 The low-order angular eigenfunctions of the angular momentum operator. The radius of these 'polar-diagram' patterns is proportional to $|Y_\ell^m|^2$

The shapes of some of these functions are illustrated in figure 5; these are the familiar atomic orbitals.

RADIAL EQUATION Return now to the radial equation, which will determine the energy levels of the atom:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{\ell(\ell+1)}{r^2}\right]R=(E-V)R \tag{175}$$

Notice that the effect of angular momentum is to add a term that looks like another contribution to $V(r)$: this is known as the **centrifugal potential**:

$$V\to V+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} \tag{176}$$

We might have expected such a term classically. The equation for conservation of energy in a classical orbit is

$$m\dot{r}^2/2+m(r\dot{\phi})^2/2+mV(r)=E, \tag{177}$$

where ϕ is the polar angle, and we choose $\theta = \pi/2$ as the orbital plane. Since $L = mr^2\dot{\phi}$ is also a constant, this gives the radial equation of motion

$$m\dot{r}^2/2 + m[V(r) + L^2/(2mr^2)] = E. \tag{178}$$

This contains an effective potential with a centrifugal term, and Schrödinger's equation contains the quantum analogue of such a term. This potential reduces the binding effect (since V is negative), so we can see intuitively that the ground state of the system will be $\ell = 0$.

The solution of the radial equation is conceptually identical to what was done in the case of the harmonic oscillator: we argue that the main behaviour of the wavefunction at large r should be an exponential decline, and we look for a solution in which the full wavefunction is some new function times this exponential. Trying a series solution for the new function, we conclude that it must be a finite polynomial, otherwise it blows up at large r and spoils the normalizability of the wavefunction. To express the answer, we use the following notation:

$$\begin{aligned} \rho &\equiv \alpha r \\ \alpha^2 &\equiv 8\mu|E|/\hbar^2 \\ \lambda &\equiv 2\mu e^2/(4\pi\epsilon_0\alpha\hbar^2) = \frac{e^2}{4\pi\epsilon_0\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2}, \end{aligned} \tag{179}$$

so ρ is a dimensionless radius, and λ is the dimensionless measure of the energy. Sadly, this is not standard, and is different in various books (Griffiths, for example).

In this notation, an evanescent wave at large r (where the potential is negligible) would be $R \propto \exp(-|k|r)$, where where $k^2 = 2\mu E/\hbar^2$, so that $R \propto \exp(-\rho/2)$. We now guess that the full solution is $R = F(\rho)\exp(-\rho/2)$, and the resulting equation for F is

$$F'' + \left(\frac{2}{\rho} - 1\right)F' + \left(\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)F = 0 \tag{180}$$

This equation has simple enough coefficients that a power-law solution looks attractive. We will skip the details, since there is no new principle involved. The main thing to remember is that the lowest power of ρ in the series expansion turns out to be ρ^ℓ. If the series terminates at power $\rho^{\ell+k}$, then this requires the condition

$$\lambda = n = k + \ell + 1; \quad k = 0, 1, \ldots, \tag{181}$$

where n is the **principal quantum number**. This is the sum of unity plus two integers (k & ℓ), each of which can be zero. Thus, n is also an integer, with lowest value $n = 1$. For given n, ℓ can be any integer between 0 and $n - 1$.

ENERGY LEVELS AND ORBITALS Since $\lambda \propto 1/|E|^{1/2}$, this says

$$\boxed{|E| = \frac{\mu e^4}{2\hbar^2(4\pi\epsilon_0)^2}\,\frac{1}{n^2} = \mu c^2\,\frac{\alpha^2}{2n^2},} \tag{182}$$

where the **fine-structure constant** is

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}. \tag{183}$$

The energy levels of the Hydrogen atom according to the Schrödinger equation are thus identical to what is obtained in the Bohr treatment of the atom. This has to be seen as just a lucky coincidence, since the essential physics differs in many ways. The Bohr analysis assumed classical circular orbits, introducing quantization via $L_z = n\hbar$, where $n = 1, 2, \ldots$ In fact, the true ground state has zero angular momentum. The Bohr analysis also provides the radii of the electron orbits:

$$r = a_0 n^2; \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}, \tag{184}$$

where a_0 is the **Bohr radius**. In terms of this unit, our variable ρ is $2r/(na_0)$.

Lastly, note that another way of writing the bohr radius is

$$a_0 = \alpha^{-1}\frac{\hbar}{\mu c}. \tag{185}$$

Since the uncertainty principle suggests that this should be of order $\hbar/mv$, we see that the effective orbital speed in the ground state is about $c/137$. This is small enough that the nonrelativistic quantum mechanics used here is not a bad approximation.

In summary, the full hydrogen wavefunctions are written as

$$\boxed{\psi_{\ell mn} \propto Y_\ell^m(\theta,\phi)\, e^{im\phi}\rho^\ell G_n^\ell(\rho)e^{-\rho/2},} \tag{186}$$

where $\rho = 2r/(na_0)$. The polynomials $G_n^\ell(\rho)$ can be written in terms of standard functions called **associated Laguerre polynomials**; we will not need to be familiar with these in too much detail. It will suffice to look at the form of the lowest few wavefunctions:

$$\begin{aligned} G_1^0(z) &= 1 \\ G_2^1(z) &= 1 \\ G_2^0(z) &= 1 - z/2 \\ G_3^2(z) &= 1 \\ G_3^1(z) &= 1 - z/4 \\ G_3^0(z) &= 1 - z + z^2/6 \end{aligned} \tag{187}$$

Some plots of these functions are shown below, in the form of the radial probability distribution ($dp/dr \propto \pi r^2|\psi|^2$). In order not to over-interpret these plots, remember that ψ is non-zero at the origin for all $\ell = 0$ states. Nevertheless, for large n, the electron spends almost all its time at increasing distances from the nucleus, in qualitative accord with the expectation of the Bohr theory. As expected, the $n = 3$ states have typical radii about 9 times that for $n = 1$.

TERM DIAGRAM The states of a given energy have the same **principal quantum number**, n, but these are degenerate in two ways, because $n = k + \ell + 1$. Since k cannot be negative, the largest value of ℓ for a given n is

$$\ell_{\max} = n - 1. \tag{188}$$

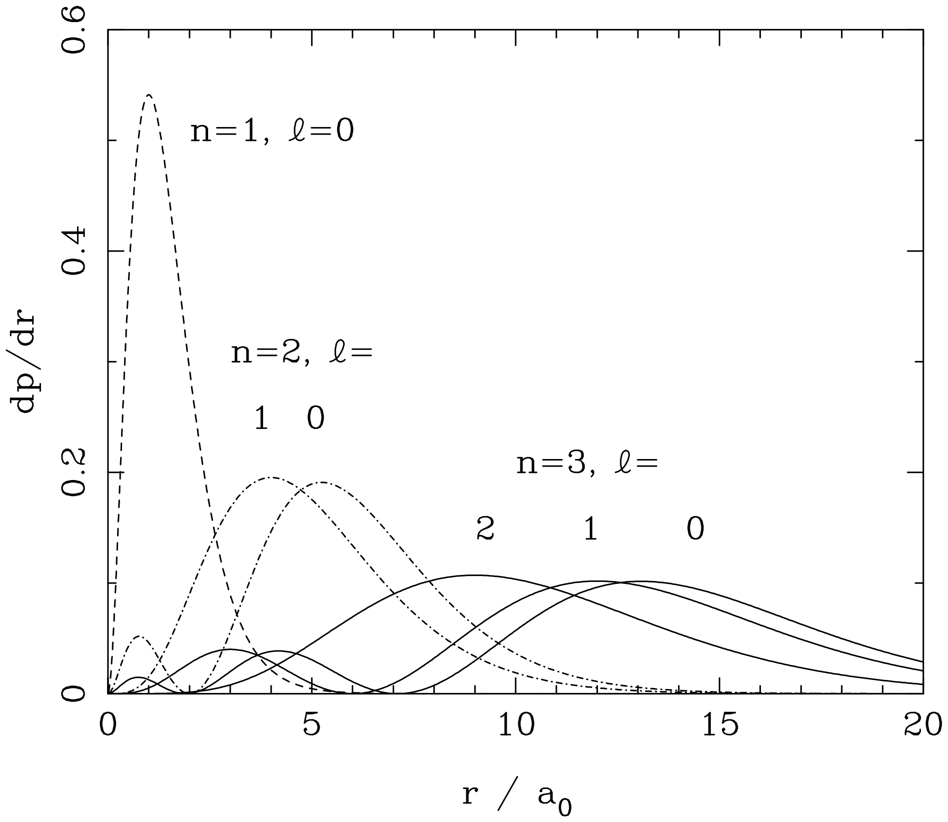

Figure 6 Plots of the radial probability distribution ($dp/dr \propto \pi r^2|\psi|^2$) for the lowest three energy levels of the Hydrogen atom. Note that, for a given n, states with larger ℓ are pushed to smaller radii on average.

Each state of given (n, ℓ) has a further degeneracy, since there are $2\ell + 1$ different L_z-states. The total degeneracy is therefore

$$\text{degeneracy} = \sum_{\ell=0}^{n-1}(2\ell + 1) = n^2. \tag{189}$$

The energy levels may be illustrated in a **term diagram**. Spectroscopic notation labels each level by its value of n, and a letter to denote ℓ:

$$\begin{array}{rccccc} & s & p & d & f & \dots \\ \ell = & 0 & 1 & 2 & 3 & \dots \end{array} \tag{190}$$

The ground state is 1s; the first excited states are 2s and 2p etc. The value of this notation is that n and ℓ together specify the spatial dependence of $|\psi|^2$ – i.e. what kind of **orbital** the electron inhabits.

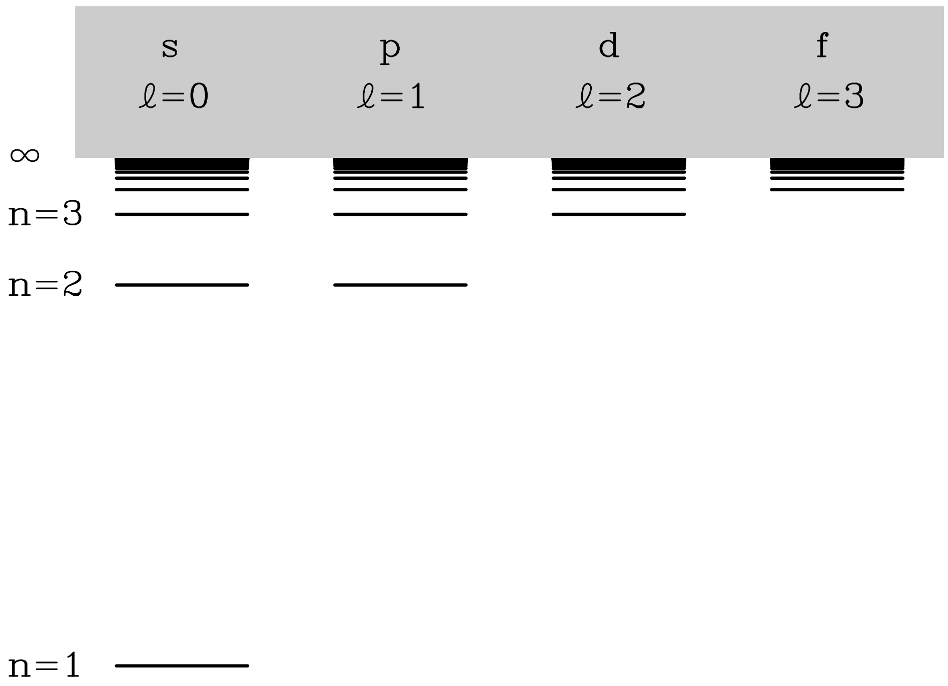

Figure 7 The energy levels of Hydrogen. Energy runs vertically, and levels of different ℓ are displaced to the right. As $n \to \infty$, the levels become progressively more closely spaced, and the binding energy approaches zero. For positive energy, there is a continuum of states, represented by the shaded bar.

13 Spin

The degeneracy of different ℓ, m states in the Hydrogen atom is easily broken. The simplest way is to apply a magnetic field along the z direction. Classically, an electron in a circular orbit of radius r looks like a magnetic dipole. The dipole moment of a current loop is $\mathbf{M} = I\,\mathbf{A}$, where $\mathbf{A}$ is the vector area of the loop. For an electron orbiting with angular frequency ω, the effective current is $I = e/(2\pi/\omega)$, and the area is πr^2. So, for an orbit in the xy plane, the magnitude of the dipole moment is

$$M_z = \frac{er^2\omega}{2} = \frac{e}{2m}\,L_z = \frac{e\hbar}{2m}\,(L_z/\hbar). \tag{191}$$

The magnetic moment is quantized in units of the **Bohr magneton**: $\mu_{\rm B} = e\hbar/2m$.

This magnetic moment causes states of different angular momentum to have a different energy in the presence of a magnetic field $\mathbf{B}$:

$$\Delta E = -\mathbf{M} \cdot \mathbf{B}. \tag{192}$$

In other words, on the basis of the theory of Hydrogen just expounded, each energy level of given n should split into distinct levels, according to their value of the m quantum number. Since $\ell_{\rm max} = n - 1$ and m ranges between $\pm\ell$, there should be $2\ell_{\rm max} + 1 = 2n - 1$ sub-levels. In particular, the $n = 1$ ground state should not split.

This prediction of an odd number of sub-levels fails by comparison with the observed **Zeeman effect**. For example, the ground state of Hydrogen splits into two levels when a magnetic field is applied – although this is not so easy to see directly; in practice, the first evidence for half-integral quantum numbers was found in heavier atoms. The idea that something in atoms was contributing half-integral angular momentum was first proposed by Goudsmidt & Uhlenbeck in 1925.

STERN-GERLACH EXPERIMENT A more direct piece of evidence for half-integral angular momentum was provided in 1922. The experiment is based on the fact that an inhomogeneous magnetic field generates a force on a dipole. This is easily seen by differentiating the expression for the magnetic energy:

$$\mathbf{F} = -\boldsymbol{\nabla}(-\mathbf{M} \cdot \mathbf{B}). \tag{193}$$

So, if B_z varies with z, then $F_z = M_z dB_z/dz$. A beam of atoms sent through such a field will split spatially according to the value of L_z, thus giving an experimental measurement of the m quantum number. The surprising fact (first demonstrated with beams of silver atoms) was that sometimes only two beams were produced. Since the number of angular momentum states should be $2\ell + 1$, this result requires $\ell = 1/2$.

INTRINSIC SPIN Goudsmidt & Uhlenbeck's proposal for resolving these problems was that the electron should generate angular momentum not only through its orbital motion, but also *internally* by having angular momentum $\hbar/2$ even when stationary. This suggests perhaps a picture of an electron as a little spinning sphere, but attempts to get too concrete a picture of the origin of spin can lead you into trouble. The deepest difficulty concerns the argument we have made so far for single-valuedness of the wave function. For *orbital* angular momentum this argument gives the correct answer:

$$\boxed{\psi \propto e^{im\phi} \quad \Rightarrow \quad m = 0, 1, 2, \ldots} \tag{194}$$

Allowing $m = 1/2$ apparently makes no sense, since $\psi \to -\psi$ on rotation by 2π and the system only returns to its starting point after a rotation of 4π. However, it turns out that our intuition is wrong when it says 'rotation by 2π is equivalent to no rotation'. This is true for simple systems, but even classically there are cases where it takes a rotation of 4π to return to your starting point. The general algebra of angular momentum told us that examples of such complicated systems must exist in quantum mechanics: experimentally, the electron is one.

Because total angular momentum is integral for orbital angular momentum, the quantum number ℓ is used only for the orbital case. For spin, we denote the angular momentum vector by $\mathbf{S}$, not $\mathbf{L}$. We also express the eigenvalues of S^2 via the **total spin quantum number**, s:

$$\boxed{\langle S^2 \rangle = s(s+1)\hbar^2,} \tag{195}$$

so that $s = 1/2$ for the electron. However, the quantum number $m = s, s-1, \ldots$ is still used to denote the z component of angular momentum.

SPIN WAVE FUNCTIONS A particle with spin 1/2 is about the simplest quantum-mechanical system possible. If there is no spin-dependent term in the Hamiltonian, we can factorize the wavefunction into $\psi(\mathbf{x}, \mathbf{S}) = u(\mathbf{x})v(\mathbf{S})$, then the spin part $v(\mathbf{S})$ contains only two distinct states: 'spin up' and 'spin down'. We can represent these either as Dirac kets, or as column vectors:

$$|\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}; \quad |\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}. \tag{196}$$

These spin wavefunctions are known as **spinors**.

PAULI MATRICES Using the vector representation, the algebra of the $m = \pm\hbar/2$ angular momentum operator can be represented by the **Pauli spin matrices**:

$$\boxed{\sigma_1 = \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}, \quad \sigma_2 = \begin{pmatrix}0 & -i\\i & 0\end{pmatrix}, \quad \sigma_3 = \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}.} \tag{197}$$

For convenience, $\hbar/2$ is factored out: $L_x = (\hbar/2)\sigma_1$ etc. The Pauli matrices therefore obey the **commutation relation** $[\sigma_i, \sigma_j] = 2i\sigma_k$, where (i, j, k) is a cyclic permutation of $(1, 2, 3)$.

The simple form of these matrices makes it easy to deduce the eigenfunctions. We have already written these for L_z. For L_x, they are

$$|x\uparrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}; \quad |x\downarrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}, \tag{198}$$

and for L_y

$$|y\uparrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix}; \quad |y\downarrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-i\end{pmatrix}. \tag{199}$$

The factor $1/\sqrt{2}$ ensures normalization. These results are very useful. Suppose we want the probability of getting $m = -1$ for L_z, given a system in an $m = +1$ eigenstate of L_x. The required probability is

$$|\langle\downarrow|x\uparrow\rangle|^2 = \left|(0,1)\cdot\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}\right|^2 = \frac{1}{2}. \tag{200}$$

More impressively, suppose we start with a beam of 'spin up' particles in state $|\uparrow\rangle$. If we pass this beam (which contains no 'spin down' particles) through a Stern-Gerlach apparatus orientated along the x axis, the beam will split into two equal parts, corresponding to x spin $\pm\hbar/2$. If we take the beam with positive x spin, we can now pass it through a Stern-Gerlach apparatus orientated along the z axis. The first experiment placed the particles in the state $|x\uparrow\rangle$, so the above calculation tells us that half the particles will be found to have z spin down, even though they all started with z spin up:

$$|\uparrow\rangle \to \begin{cases}|x\uparrow\rangle\\|x\downarrow\rangle\end{cases} \quad |x\uparrow\rangle \to \begin{cases}|\uparrow\rangle\\|\downarrow\rangle\end{cases} \tag{201}$$

This is a classic illustration of the scrambling effect that measurement of non-commuting quantities can have on quantum systems.

The same experiment can be used to prove experimentally that the act of measurement forces an eigenstate. Take the beam of particles with positive x spin and pass it through a second Stern-Gerlach apparatus – but this time also orientated along the x axis. Here, the beam does not split: all particles still have x spin up. The first measurement has removed the randomness in S_x that originated by starting in an eigenstate of L_z:

$$|\uparrow\rangle \to \left\{ \begin{array}{l} |x\uparrow\rangle \\ |x\downarrow\rangle \end{array} \right. \qquad |x\uparrow\rangle \to |x\uparrow\rangle \tag{202}$$

14 Addition of angular momentum

The existence of spin has a complicating effect on atomic structure, since the overall angular momentum is the sum of the orbital angular momentum and the spin. Usually, the total angular momentum operator is denoted by **J**:

$$\boxed{\mathbf{J} = \mathbf{L} + \mathbf{S}.} \tag{203}$$

The general theory still applies: there will be a quantum number j, such that the eigenvalues of J^2 are $\hbar^2 j(j+1)$ and the eigenvalues of $J_z/\hbar$ are $m = j, j-1, \ldots$

In the simplest cases, spin and angular momentum will be independent variables; the overall state of the system will then be characterized by four quantum numbers: ℓ and s for the total orbital and spin momenta, plus m_1 and m_2 for their two z components. Moreover, the wavefunction will factorize:

$$\psi_{\ell,s,m_1,m_2} = \psi^L_{\ell,m_1}\psi^S_{s,m_2}. \tag{204}$$

Is this system also characterised by quantum numbers for the total angular momentum, j & m? The total z component is well-defined, since $J_z = L_z + S_z$; this operators commutes with L_z, S_z, L^2 and S^2, so there must be a simultaneous eigenvalue of J_z. From the factorized form of the wavefunction, the eigenvalue is easily seen to be

$$m = m_1 + m_2. \tag{205}$$

However, the total quantum number j is not well defined. This is easily seen from the vector model: we are adding two vectors constrained to lie on cones, so the length of the resultant depends on their relative orientations. More formally,

$$J^2 = L^2 + S^2 + 2\mathbf{L}\cdot\mathbf{S}. \tag{206}$$

This operator commutes with L^2 and S^2: the first two terms on the rhs are trivial, and the third gives no commutator because $[L^2, L_z] = 0$ etc. However, this third term is linear in L_x, L_y, etc., so it does not commute with L_z (or with S_z). Therefore, the eigenvalue j cannot be well-defined for a system in an eigenstate of L_z and S_z.

Alternatively, a system for which j and m are specified will not have well-defined values of m_1 and m_2. There are two different sets of basis vectors for a system with spin and orbital angular momentum, each characterized by four quantum numbers:

$$\boxed{|\ell, s, m_1, m_2\rangle \quad \text{or} \quad |\ell, s, j, m\rangle.} \tag{207}$$

Clearly, it should be possible to write one eigenstate as a superposition of the other states:

$$|\ell, s, m_1, m_2\rangle = \sum_{j,m} a_{j,m}|\ell, s, j, m\rangle \quad \Rightarrow \quad a_{j,m} = \langle \ell, s, j, m|\ell, s, m_1, m_2\rangle. \tag{208}$$

The expansion coefficients $a_{j,m}$ are known as the **Clebsch-Gordan coefficients**.

Most of the Clebsch-Gordan coefficients are zero. The non-zero ones must satisfy $m = m_1 + m_2$. Similarly, only certain values of j are allowed. If m_1 and m_2 take their maximum values (ℓ and s), then the maximum value of m is $\ell + s$. For a given j, the maximum value of m is j; therefore, the expansion of $|\ell, s, m_1, m_2\rangle$ cannot involve states higher than $j = \ell + s$. A more subtle argument is needed to show that the minimum value of j is $|\ell - s|$:

$$\boxed{|\ell - s| \le j \le \ell + s.} \tag{209}$$

The simplest justification for this is to count states:

$$\sum_{j=|\ell-s|}^{j=\ell+s} (2j+1) = (2\ell+1)(2s+1). \tag{210}$$

To summarize: the allowed values of total angular momentum from the addition of angular momentum ℓ and spin s range between $|\ell - s|$ and $\ell + s$. The total angular momentum is not well defined, but measurement of j will give one of these states, with a probability controlled by the square of the Clebsch-Gordan coefficients. Although we have discussed it in the context of the addition of spin and orbital angular momentum, the result is general for the addition of any two angular momenta, j_1 and j_2, of any type.

FINE STRUCTURE The addition of angular momentum is important in the effects that split the degeneracy of the levels in the Hydrogen atom. We have seen that the energy of the levels is $E = -\alpha^2 \mu c^2 / 2n^2$, where $\alpha \simeq 1/137$ is the **fine-structure constant**. The reason for this name is that there are corrections to the main expression for the energy, which are of order $\alpha^4 \mu c^2$, so the fractional perturbation to the energy is of order $\alpha^2 \simeq 10^{-4}$. The causes of the splitting are:

(1) Relativistic effects. The effective velocity of the electron is $\sim \alpha c$, so we should consider a second-order correction to the kinetic energy:

$$K = \sqrt{p^2c^2 + m^2c^4} - mc^2 \simeq \frac{p^2}{2m} + \frac{p^4}{8m^3c^2}, \tag{211}$$

using the relativistic energy-momentum relation.

(2) Spin-orbit effects. We already saw the idea that a magnetic moment $\mathbf{M}$ in a magnetic field $\mathbf{B}$ has an energy $-\mathbf{M} \cdot \mathbf{B}$, and we showed that orbital angular momentum generates a moment according to the relation $M_z = \mu_{\rm B}(L_z/\hbar)$, where $\mu_{\rm B}$ is the Bohr magneton. Interaction with external B field gives $\Delta E = -\mathbf{M} \cdot \mathbf{B}$.

Orbiting electron sees orbiting proton in its rest frame, which gives a B field. Biot-Savart:

$$\mathbf{B} = \frac{\mu_0}{4\pi r^2} I \mathbf{dx} \wedge \hat{\mathbf{r}}. \tag{212}$$

Effective current is $I = e/(2\pi/\omega)$; integrate round loop of circumference $2\pi r$.

$$B = \frac{\mu_0 e \omega}{4\pi r} = \frac{\mu_0 e}{4\pi m r^3} L. \tag{213}$$

This field acts on the electron. We might expect a moment $M = \mu_{\rm B}/2$ for $s = 1/2$, but in fact $M = \mu_{\rm B}$. Write

$$\boxed{\mathbf{M} = -g\frac{\mu_{\rm B}}{\hbar}\mathbf{J}.} \tag{214}$$

So $g = 1$ for orbits, $g = 2$ for spin. Using $g = 2$, the **Spin-orbit energy** is $-\mathbf{M}\cdot\mathbf{B}$, or

$$\boxed{\Delta E = \frac{\mu_0\mu_{\rm B}e}{2\pi m\hbar r^3}\,\mathbf{L}\cdot\mathbf{S}.} \tag{215}$$

In fact, this expression is twice the correct answer (the **Thomas effect**: the electron is in a non-inertial frame).

LEVEL SPLITTING Since $\mathbf{J} = \mathbf{L} + \mathbf{S}$, $2\mathbf{L}\cdot\mathbf{S} = J^2 - L^2 - S^2$, the spin-orbit energy can be written as

$$\Delta E = \frac{\hbar^3\alpha}{4m^2cr^3}[j(j+1) - \ell(\ell+1) - s(s+1)] \tag{216}$$

(for states where j, ℓ, s are all well-defined). Since radii are of order the **Bohr radius** $r \sim a_0 = \hbar/(\alpha mc)$, the spin-orbit energy is of order $\alpha^4 mc^2$. The full relativistic effect for the energy shift in Hydrogen is

$$\langle\delta E\rangle = -\frac{\alpha^4 mc^2}{4n^3}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right), \tag{217}$$

i.e. low j is more bound.

The allowed j is either $j = 1/2$ if $\ell = 0$ or $j = \ell \pm 1/2$ if $\ell \neq 0$.

$$\boxed{\text{splitting at fixed } n = 0 \ (\ell = 0) \text{ or } \propto \frac{1}{\ell(\ell+1)}.} \tag{218}$$

For given n, max $0 \leq \ell \leq n-1$, so $1/2 \leq j \leq n - 1/2$ and there are n sublevels.

15 Many-particle systems

The course so far has concentrated on the quantum mechanics of a single particle. If we have N particles, with coordinates $\mathbf{x}_i$, there will be a multi-particle wavefunction, $\psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots)$, such that $|\psi|^2$ is probability of finding particle 1 at $\mathbf{x}_1$, particle 2 at $\mathbf{x}_2$, etc. By analogy with the single-particle case, we expect that ψ will satisfy the **many-particle Schrödinger equation**:

$$H(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots)\psi = i\hbar\dot{\psi}, \tag{219}$$

where $H = \sum_i (p_i^2/2m_i) + V(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots)$.

INDEPENDENT PARTICLES If there are no interactions, then $H = H_1(\mathbf{x}_1) + H_2(\mathbf{x}_2) + \ldots$, and the wave-function factorizes: $\psi = \psi_1(\mathbf{x}_1) \times \psi_2(\mathbf{x}_2) \times \ldots$ – this is similar to when we factorized the single-particle ψ into $u(\text{space}) \times v(\text{spin})$. Putting this form into the many-particle Schrödinger equation gives $(H_1\psi_1 - i\hbar\dot{\psi}_1)/\psi_1 + (H_2\psi_2 - i\hbar\dot{\psi}_2)/\psi_2 + \ldots = 0$. The usual separation of variables argument says $(H_1\psi_1 - i\hbar\dot{\psi}_1)/\psi_1 = A$ etc. The constant can be absorbed by changing the global zero point of energy: $H_1 \rightarrow H_1 - A$, giving the usual one-particle equation.

CENTRE OF MASS If there is interaction in the form of a **central force**, with $V(\mathbf{x}_1, \mathbf{x}_2) = f(|\mathbf{x}_1 - \mathbf{x}_2|)$, we saw earlier that can still factorize the wavefunction, by defining centre-of-mass coordinates and relative coordinates $\mathbf{X} = (m_1\mathbf{x}_1 + m_2\mathbf{x}_2)/(m_1 + m_2)$ and $\mathbf{x} = \mathbf{x}_1 - \mathbf{x}_2$:

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_1(\mathbf{X}) \times \psi_2(\mathbf{x}). \tag{220}$$

This procedure can in fact can be extended to > 2 particles.

IDENTICAL PARTICLES How do we tell the difference between two electrons? Unlike vaguely similar objects such as Mars bars, electrons appear to be truly indistinguishable. They have intrinsic properties of charge and spin, but apparently there is no other way of labelling them other than by their coordinates – so it should make no detectable difference if we swap positions of any two particles:

$$\boxed{\mathbf{x}_1 \leftrightarrow \mathbf{x}_2 \quad \Rightarrow \quad |\psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \text{ unchanged.}} \tag{221}$$

This is similar to the argument we made over parity, where again we wanted $|\psi|^2$ not to change under coordinate inversion. The most effect swapping can have is therefore a phase factor: $\psi(\mathbf{x}_2, \mathbf{x}_1) = C\psi(\mathbf{x}_1, \mathbf{x}_2)$, with $|C| = 1$. Double swapping restores the original situation, so $C^2 = 1$, implying $C = \pm 1$. One of the most important results in physics is that the number C depends on the spin of the particle:

$$\boxed{\begin{array}{rl} \textbf{bosons}\ (s = 0, 1, \ldots): & C = +1 \\ \textbf{fermions}\ (s = \frac{1}{2}, \frac{3}{2}, \ldots): & C = -1. \end{array}} \tag{222}$$

This is the **Spin–statistics theorem**. No-one has ever produced a simple proof of the result – which is a great pity given its importance. It is perhaps easiest to be convinced by looking at the experimental consequences, which are profound.

SPIN AND SYMMETRY The spin–statistics theorem says that particles like electrons have **antisymmetric** wavefunctions, whereas particles with integral spin have **symmetric** wavefunctions.

Consider particles with no interaction, and take two single-particle eigenfunctions u and v. We cannot write the usual factorization

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = u(\mathbf{x}_1)v(\mathbf{x}_2), \tag{223}$$

because this is not symmetric. The (normalized) possibilities for $\psi(\mathbf{x}_1, \mathbf{x}_2)$ are

$$\boxed{\begin{array}{ll} \frac{1}{\sqrt{2}}\left[u(\mathbf{x}_1)v(\mathbf{x}_2) + u(\mathbf{x}_2)v(\mathbf{x}_1)\right] & \text{(symm.)} \\ \frac{1}{\sqrt{2}}\left[u(\mathbf{x}_1)v(\mathbf{x}_2) - u(\mathbf{x}_2)v(\mathbf{x}_1)\right] & \text{(antisymm.)} \end{array}} \tag{224}$$

These don't look so different, but try to put both particles in the same state: for the symmetric case $\psi \propto u(\mathbf{x}_1)u(\mathbf{x}_2)$, but $\psi = 0$ in the antisymmetric case. It is impossible to have two fermions in the same state. This is the **Pauli exclusion principle**. The existence of exclusion was first deduced empirically as a means of explaining the electronic structure of atoms; the connection to the idea of symmetry of the wavefunction came later.

SPATIAL CORRELATIONS One of the odd consequences of the spin-statistics theorem is that two identical particles are 'aware' of each others presence, even if they don't interact. For two distinguishable particles, we can have $\psi = u(\mathbf{x}_1)v(\mathbf{x}_2)$; otherwise we have the symmetric or antisymmetric states given above. The probability density for finding both particles at the same position is

$$|\psi(\mathbf{x}, \mathbf{x})|^2 = \begin{cases} |u(\mathbf{x})v(\mathbf{x})|^2 & \text{(distinguishable)} \\ 2|u(\mathbf{x})v(\mathbf{x})|^2 & \text{(bosons)} \\ 0 & \text{(fermions)} \end{cases} \tag{225}$$

In short, bosons like to clump, but fermions avoid each other.

It may help to illustrate this pictorially with a concrete example. Consider two identical particles in our familiar 1D well with infinitely high walls, and consider ways of constructing two-particle states from the two lowest one-particle states:

$$\begin{aligned} A(x) &= 2^{1/2} \sin \pi x \\ B(x) &= 2^{1/2} \sin 2\pi x, \end{aligned} \tag{226}$$

where the well is taken to run from $x = 0$ to $x = 1$. We can construct 4 valid 2-particle states from these: 3 symmetric and one antisymmetric. The joint probability distributions for the positions of the two particles are shown in figure 8. Notice how the antisymmetric case alone leads to avoidance: zero probability along the leading diagonal where the positions of the two particles would be equal.

MANY IDENTICAL PARTICLES This procedure extends to more than two particles. Suppose we are given some energy eigenstate of a multi-particle Hamiltonian, $\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots)$. We can always construct from this a special state that is totally symmetric or totally antisymmetric:

$$\psi_+ = \frac{1}{\sqrt{N!}} \sum_{\text{perm. } i,j,k} \psi(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k, \ldots) \tag{227}$$

or

$$\psi_- = \frac{1}{\sqrt{N!}} \sum_{\text{perm. } i,j,k} \epsilon_{ijk\ldots} \psi(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k, \ldots). \tag{228}$$

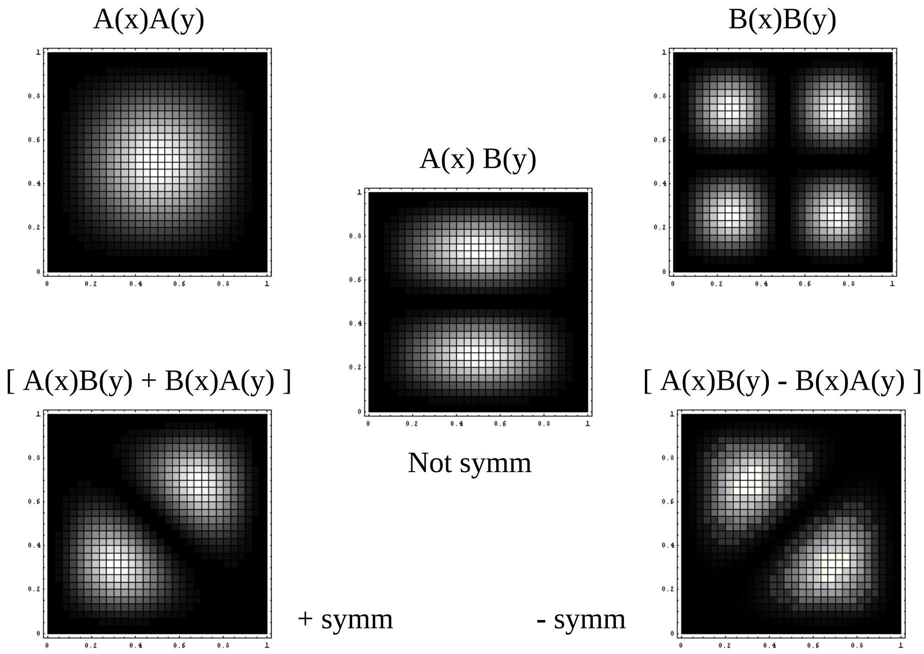

Figure 8 Plots of the joint probability density for finding particle 1 at position x and particle 2 at position y. The (un-normalized) forms of the wavefunctions are given above each panel in terms of single-particle eigenstates A and B. The central panel shows the case $\psi = A(x)B(y)$. This would be a valid wavefunction for a pair of distinguishable particles, but it clearly is not acceptable for indistinguishable particles (probability density should have a mirror symmetry for reflection in $x = y$). The other 4 panels show the acceptable states for identical particles. The probability tends to cluster along the leading diagonal for the symmetric case, but the particles clearly avoid each other in the antisymmetric state.

In other words, we sum over all possible permutations of $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots)$, inserting a minus sign for odd permutations in the antisymmetric case.

The simplest example of this is the non-interacting case, where the multi-particle eigenstate is just a product of single-particle eigenstates: $\psi(\mathbf{x}_1, \mathbf{x}_2) = u(\mathbf{x}_1)v(\mathbf{x}_2)$ in the two-particle case; $\psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = u(\mathbf{x}_1)v(\mathbf{x}_2)w(\mathbf{x}_3)$ etc. It should be clear that antisymmetric combinations of such states will only exist when each of u, v, etc. are different states. If they are not, the combinations $u(\mathbf{x}_1)v(\mathbf{x}_2)$ and $u(\mathbf{x}_2)v(\mathbf{x}_1)$ will enter with opposite signs, and the wavefunction becomes identically zero..

16 Identical particles and spin

SPIN WAVEFUNCTIONS There is in fact a way out of the exclusion principle, which allows two electrons to occupy the same state. This is to realise that the spin-statistics theorem applies only when we swap space and spin coordinates at the same time: $\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{S}_1, \mathbf{S}_2, \ldots) = \pm\psi(\mathbf{x}_2, \mathbf{x}_1, \ldots, \mathbf{S}_2, \mathbf{S}_1, \ldots)$. This makes sense, since spin is the only label that we can tie to an electron. If I have two electrons, spin up and spin down, I can tell if their positions have been swapped by looking at the spin values; however, if the spin values are also swapped, I have no way of telling whether anything has changed.

In the absence of spin-dependent interactions, we factorize the single-particle wavefunctions into **product states**, $\psi(\mathbf{x}, \mathbf{S}) = \psi_{\text{space}}(\mathbf{x}) \times \psi_{\text{spin}}(\mathbf{S})$. If the particles do not interact amongst themselves, we can produce multi-particle states by multiplying product states for each particle, and then taking combinations of the appropriate symmetry. Consider how this works for two particles, where there are two single-particle spatial states A and B, and the two spin states α and β. A typical product state might be written in the following shorthand:

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{S}_1, \mathbf{S}_2) = A(\mathbf{x}_1)\alpha(\mathbf{S}_1)B(\mathbf{x}_2)\beta(\mathbf{S}_2) \equiv A(1)\alpha(1)B(2)\beta(2), \tag{229}$$

i.e. particle 1 is in state A with spin up; particle 2 is in state B with spin down.

There are 4 single-particle states ($A\alpha$, $A\beta$, $B\alpha$, $B\beta$), so there are ${}^4C_2 = 6$ distinct pairs to combine into 2-particle states (the exclusion principle says that the two states must be different). Written explicitly, the antisymmetric combinations are

$$\begin{aligned}
\psi_a &= [A(1)\alpha(1)A(2)\beta(2) - A(2)\alpha(2)A(1)\beta(1)]/\sqrt{2} \\
\psi_b &= [B(1)\alpha(1)B(2)\beta(2) - B(2)\alpha(2)B(1)\beta(1)]/\sqrt{2} \\
\psi_c &= [A(1)\alpha(1)B(2)\alpha(2) - A(2)\alpha(2)B(1)\alpha(1)]/\sqrt{2} \\
\psi_d &= [A(1)\beta(1)B(2)\beta(2) - A(2)\beta(2)B(1)\beta(1)]/\sqrt{2} \\
\psi_e &= [A(1)\alpha(1)B(2)\beta(2) - A(2)\alpha(2)B(1)\beta(1)]/\sqrt{2} \\
\psi_f &= [A(1)\beta(1)B(2)\alpha(2) - A(2)\beta(2)B(1)\alpha(1)]/\sqrt{2}.
\end{aligned} \tag{230}$$

The interesting thing to note is that linear combinations of these states can be rewritten as a product of a space wavefunction and a spin wavefunction, each with a definite symmetry:

$$\begin{aligned}
\psi_a &= [A(1)A(2)] \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)]/\sqrt{2} \\
\psi_b &= [B(1)B(2)] \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)]/\sqrt{2} \\
\psi_c &= [A(1)B(2) - A(2)B(1)]/\sqrt{2} \times [\alpha(1)\alpha(2)] \\
\psi_d &= [A(1)B(2) - A(2)B(1)]/\sqrt{2} \times [\beta(1)\beta(2)] \\
(\psi_e + \psi_f)/\sqrt{2} &= [A(1)B(2) - A(2)B(1)]/\sqrt{2} \times [\alpha(1)\beta(2) + \alpha(2)\beta(1)]/\sqrt{2} \\
(\psi_f - \psi_e)/\sqrt{2} &= [A(1)B(2) + A(2)B(1)]/\sqrt{2} \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)]/\sqrt{2}
\end{aligned} \tag{231}$$

In short,

$$\boxed{\psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{S}_1, \mathbf{S}_2) = \psi_{\text{space}}(\mathbf{x}_1, \mathbf{x}_2) \times \psi_{\text{spin}}(\mathbf{S}_1, \mathbf{S}_2),} \tag{232}$$

where each of the space and spin wavefunctions has a distinct symmetry. In order that the overall wavefunction be antisymmetric (for **fermions**) under exchange of space and spin labels, the symmetries of these two parts must be **opposite**, i.e. $(-) = (+)(-)$ or $(-) = (-)(+)$. For a **boson**, the wavefunction can be decomposed in the same way, but now the symmetries of ψ_{space} and ψ_{spin} must the **same**.

Lastly, note that this factorization only works for two-particle systems; for 3 or more, we have to consider just the combination of product states. To prove this, it is enough to consider the spin wavefunction: for 3 particles, at least 2 must be either both spin-up or spin-down.

There is therefore no antisymmetric spin wavefunction for three fermions. If factorization always applied, this says that the spatial wavefunction would have to be antisymmetric, so that all three particles would need to be in different states. However, we can put two particles in state A with spins up and down, and a third particle in state B with e.g spin up. The wavefunction is the antisymmetrized version of $A(1)\alpha(1)A(2)\beta(2)B(3)\alpha(3)$, which does not factorize, by the above argument.

SINGLET AND TRIPLET STATES So, a state with two electrons in the same spatial eigenstate requires a symmetric spatial wavefunction, and hence an antisymmetric spin wavefunction. For the addition of two spins, there are the following possible combinations of single spin wavefunctions (α is short for $|\uparrow\rangle$, β stands for $|\downarrow\rangle$):

$$\boxed{\begin{aligned} \chi_{0,0} &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ \chi_{1,1} &= \alpha(1)\alpha(2) \\ \chi_{1,0} &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \chi_{1,-1} &= \beta(1)\beta(2) \end{aligned}} \tag{233}$$

The index on the states denotes total angular momentum: $\chi_{j,m}$ is a state of total angular momentum j and z quantum number m. The interpretations of $\chi_{1,1}$ and $\chi_{1,-1}$ are pretty obvious, since these need either both spins up or both down. The distinction between $\chi_{0,0}$ and $\chi_{1,0}$ is more subtle (see the problem sheets).

For obvious reasons, the $j = 0$ state is called a **singlet state**, whereas $j = 1$ is called a **triplet state**. Since only singlets are antisymmetric, we see that the ground state of a two-electron system must be have $j = 0$.

To illustrate these principles, consider the following problem: an infinitely deep one-dimensional potential well runs from $x = 0$ to $x = L$; the normalized energy eigenstates are $u_n(x) = (2/L)^{1/2}\sin(n\pi x/L)$. Two identical non-interacting spin-1/2 particles are placed in the well. What is the ground-state energy of the 2-particle system, and how does it depend on the overall spin state? If we take $V = 0$ inside the well, the energy eigenvalue corresponding to u_n is $E_n = n^2\pi^2\hbar^2/(2mL^2)$. The possible spin states are $j = 0$ or $j = 1$; the former is antisymmetric, so we need a symmetric spatial wavefunction, which can be achieved by placing both particles in the $n = 1$ state. The total energy is thus $(1+1) \times \pi^2\hbar^2/(2mL^2)$. Conversely, $j = 1$ is symmetric, so we need an antisymmetric spatial wavefunction; only one particle can occupy $n = 1$, so the lowest total energy comes from placing the second particle in $n = 2$. The total energy is thus $(1^2 + 2^2)/(1^2 + 1^2) = 5/2$ times larger than in the $j = 0$ case.

17 Time-independent perturbation theory

We need to solve $H\psi = E\psi$, but this is often impossible, even for quite simple Hamiltonians. An alternative is to solve a simpler problem $H^{(0)}\psi = E^{(0)}\psi$, where $H^{(0)}$ is 'close' to H. Having done this, write the full Hamiltonian of interest as $H = H^{(0)} + \delta H$; we now need to solve

$$\left(H^{(0)} + \delta H\right)\psi = \left(E^{(0)} + \delta E\right)\psi. \tag{234}$$

ROUGH APPROACH At first sight, this looks easy to handle. Multiply by ψ^* on the left and integrate to take expectation values. This gives

$$E^{(0)} + \delta E = \langle\psi|H^{(0)}|\psi\rangle + \langle\psi|\delta H|\psi\rangle. \tag{235}$$

It looks tempting to say that $\langle\psi|H^{(0)}|\psi\rangle = E^{(0)}$, which would imply

$$\boxed{\delta E = \langle\psi|\delta H|\psi\rangle.} \tag{236}$$

This is in fact one of the key formulae in quantum mechanics; it allows us to estimate the shift in energy levels that arises when an extra term is added to the Hamiltonian.

The trouble is, this 'derivation' is completely bogus, since we have ignored the fact that the presence of the perturbation alters the wavefunction. The state ψ is an eigenfunction of the new Hamiltonian, whereas all we know is the **unperturbed** eigenstate $H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$. Being a little more careful, we write $\psi = \psi^{(0)} + \delta\psi$, so that

$$(H^{(0)} + \delta H)(\psi^{(0)} + \delta\psi) = (E^{(0)} + \delta E)(\psi_n + \delta\psi). \tag{237}$$

Now, a very common technique in dealing with equations of this sort is **linearization**: we assume that we can ignore the second-order terms like $\delta H\delta\psi$ if δH is 'small'. This gives an equation containing only first-order terms:

$$H^{(0)}\psi^{(0)} + H^{(0)}\delta\psi + \delta H\psi^{(0)} \simeq E^{(0)}(\psi^{(0)} + \delta\psi) + \delta E\psi^{(0)}. \tag{238}$$

Now multiply by $\psi^{(0)*}$ on the left and integrate. This gives a messier equation:

$$\delta E = \langle\psi^{(0)}|\delta H|\psi^{(0)}\rangle + \langle\psi^{(0)}|H^{(0)}|\delta\psi\rangle - E^{(0)}\langle\psi^{(0)}|\delta\psi\rangle, \tag{239}$$

but the last two terms cancel because $H^{(0)}$ is Hermitian: $H^{(0)}$ acts to the left on $\psi^{(0)}$ to give $E^{(0)}\psi^{(0)}$.

This gives the proper justification of the basic result: the energy eigenvalue of an eigenstate is the expectation value of the Hamiltonian, but we can get away with using the old wavefunctions to take the expectation value. We have already implicitly used this result when discussing spin-orbit coupling and the fine structure of the Hydrogen atom.

FORMAL APPROACH To set the above analysis on a firmer footing, label the perturbation: $\delta H = \lambda H^{(1)}$. We assume that all quantities in the problem can be expanded as a series solution in λ:

$$\begin{aligned} \psi_n &= \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \end{aligned} \tag{240}$$

Notice that this assumes a 1-to-1 correspondence between states in the initial and final problems: if the perturbation changes the energy by an amount that exceeds the separation of the initial states, this approach will be invalid.

Now we need to solve

$$\left(H^{(0)} + \lambda H^{(1)}\right)\sum_i \lambda^i\psi_n^{(i)} = \sum_i \lambda^i E_n^{(i)} \times \sum_i \lambda^i\psi_n^{(i)}, \tag{241}$$

By equating coefficients for each power of λ, a series of equations is obtained:

$$\begin{aligned} &\lambda^0 : H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \\ &\lambda^1 : H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \\ &\lambda^2 : \text{etc.} \end{aligned} \tag{242}$$

The first equation is the unperturbed problem. The second is the key: it gives the first main correction to ψ_n and E_n.

PERTURBED ENERGY   Multiply the first-order equation by $\psi_n^{(0)*}$ on the left and integrate:

$$\langle\psi_n^{(0)}|H^{(0)} - E_n^{(0)}|\psi_n^{(1)}\rangle = \langle\psi_n^{(0)}|E_n^{(1)} - H^{(1)}|\psi_n^{(0)}\rangle. \tag{243}$$

The key term, as before, is $\langle\psi_n^{(0)}|H^{(0)}|\psi_n^{(1)}\rangle$. Being explicit, the Hermitian property of $H^{(0)}$ says

$$\begin{aligned} \langle\psi_n^{(0)}|H^{(0)}|\psi_n^{(1)}\rangle &= \langle\psi_n^{(1)}|H^{(0)}|\psi_n^{(0)}\rangle^* \\ &= \langle\psi_n^{(1)}|E_n^{(0)}\psi_n^{(0)}\rangle^* \\ &= E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle. \end{aligned} \tag{244}$$

So, $\langle\psi_n^{(0)}|H^{(0)} - E_n^{(0)}|\psi_n^{(1)}\rangle = 0$, giving

$$\boxed{E_n^{(1)} = \langle\psi_n^{(0)}|H^{(1)}|\psi_n^{(0)}\rangle.} \tag{245}$$

This has rederived, in a slightly more satisfactory way, the formula we had before: $\delta E_n = \lambda E_n^{(1)} = \langle\psi_n^{(0)}|\delta H|\psi_n^{(0)}\rangle$. We can now set $\lambda = 1$ and have $\delta H = H^{(1)}$. This may seem a bit odd – how can we have a series expansion in λ if $\lambda = 1$? It is the product of λ and $H^{(1)}$ that matters, so terms with a given power of λ will also be of higher order in $H^{(1)}$. We can write a given δH either as $\lambda H^{(1)}$ where $\lambda = 1$ and $H^{(1)} \ll H^{(0)}$, or have $H^{(1)} \sim H^{(0)}$, in which case $\lambda \ll 1$ is needed for perturbation theory to apply. The label λ is just a convenient way of picking out the terms that are higher order in $H^{(1)}$ and therefore (we assume) less important.

PERTURBED WAVEFUNCTION   To get the correction to the nth eigenstate, $\psi_n^{(1)}$, expand it in the initial eigenstates:

$$\psi_n^{(1)} = \sum_i a_i\psi_i^{(0)}. \tag{246}$$

Now we have

$$(E_n^{(0)} - H^{(0)})\sum_i a_i\psi_i^{(0)} = (H^{(1)} - E_n^{(1)})\psi_n^{(0)}, \tag{247}$$

so multiply by $\psi_j^{(0)*}$ on the left:

$$\sum_i a_i(E_n^{(0)} - E_i^{(0)})\langle j|i\rangle = \langle j|(H^{(1)} - E_n^{(1)})|n\rangle, \tag{248}$$

using $|i\rangle$ to stand for $\psi_i^{(0)}$. If $j = n$ then both sides of this equation vanish. If $j \neq n$,

$$\boxed{a_j = \frac{\langle j|H^{(1)}|n\rangle}{E_n^{(0)} - E_j^{(0)}}.} \tag{249}$$

The missing coefficient is a_n, and we can learn about it via normalization: $\langle\psi_n^{(0)} + \psi_n^{(1)}|\psi_n^{(0)} + \psi_n^{(1)}\rangle = 1$. To first order, this gives

$$\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(1)}|\psi_n^{(0)}\rangle = 0, \tag{250}$$

or $a_n + a_n^* = 0$; a_n is pure imaginary. We are looking for a first-order term, so we can write $a_n = i\lambda\gamma$. We don't know how to calculate γ, but this doesn't matter, because a global phase change, $\psi_n \to \exp(i\lambda\gamma)\psi_n$, is unobservable. This is $\psi_n \to (1 + i\lambda\gamma)\psi_n$ to first order, so can always choose $\gamma = 0$.

SECOND-ORDER ENERGY The first-order correction to the energy often vanishes by symmetry, so the second-order term can be the main effect. The order-λ^2 equation from the series expansion was:

$$H^{(0)}\psi_n^{(2)} + H^{(1)}\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}. \tag{251}$$

The same trick as for the first-order equation gives

$$\langle\psi_n^{(0)}|H^{(1)}|\psi_n^{(1)}\rangle = E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(2)}. \tag{252}$$

Now use the expansion for $\psi_n^{(1)}$:

$$E_n^{(2)} = \sum_i a_i\langle\psi_n^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle - E_n^{(1)}a_n. \tag{253}$$

If we define the shorthand $H'_{ij} = \langle\psi_i^{(0)}|H^{(1)}|\psi_j^{(0)}\rangle$, and use $E_n^{(1)} = H'_{nn}$, it is easily seen that the effect of a_n cancels exactly – we don't need to assume it to be zero.

The previous expression for a_i was $H'_{in}/(E_n^{(0)} - E_i^{(0)})$, so

$$\boxed{E_n^{(2)} = \sum_{i\neq n} \frac{|H'_{ni}|^2}{E_n^{(0)} - E_i^{(0)}}.} \tag{254}$$

This is the second-order correction to the energy eigenvalue of state $|n\rangle$.

18 Applications of perturbation theory

PERTURBED OSCILLATOR A good example of perturbation theory is to apply the formalism to a problem that can be solved exactly, such as the one-dimensional harmonic oscillator: $H^{(0)} = p^2/2m + m\omega^2 x^2/2$. Consider $H^{(1)} = m\alpha^2 x^2/2$, for which it is very easy to get the exact energies:

$$E_n = (n+1/2)\hbar(\omega^2+\alpha^2)^{1/2} \quad n = 0, 1, \ldots \tag{255}$$

The first-order expansion of this is:

$$\begin{aligned} E_n^{(0)} &= (n+1/2)\hbar\omega \\ E_n^{(1)} &= (n+1/2)\hbar\omega\,(\alpha^2/2\omega^2) \end{aligned} \tag{256}$$

and perturbation theory says that

$$E_n^{(1)} = \langle n|m\alpha^2 x^2/2|n\rangle, \tag{257}$$

so we need $\langle x^2\rangle$. To work out this matrix element, it is easiest to use ladder operators:

$$\begin{aligned} a &= \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(x + \frac{i}{m\omega}p\right) \\ a^\dagger &= \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(x - \frac{i}{m\omega}p\right). \end{aligned} \tag{258}$$

These satisfy

$$\begin{aligned} a|n\rangle &= \sqrt{n}\,|n-1\rangle \\ a^\dagger|n\rangle &= \sqrt{n+1}\,|n+1\rangle. \end{aligned} \tag{259}$$

So, $x = (\hbar/2m\omega)^{1/2}(a+a^\dagger)$. Only cross terms in the matrix element of x^2 survive (raise once, lower once):

$$\langle x^2\rangle = \frac{\hbar}{2m\omega}\left[\langle n|aa^\dagger|n\rangle + \langle n|a^\dagger a|n\rangle\right] = \frac{\hbar}{2m\omega}(2n+1). \tag{260}$$

So, the first-order perturbation to the energy is

$$E_n^{(1)} = \left(\frac{m\alpha^2}{2}\right)\left(\frac{\hbar}{2m\omega}\right)(2n+1) = (n+1/2)\frac{\hbar\alpha^2}{2\omega}, \tag{261}$$

as required.

19 Multi-electron atoms

The tools of perturbation theory find one of their most important applications in atomic physics. To appreciate the problem to be solved, consider the Hamiltonian for a multielectron atom:

$$\begin{aligned} H = &\sum_i \frac{-\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \\ &+\sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} \\ &+\sum_i f(r_i)(\mathbf{L}\cdot\mathbf{S})_i, \end{aligned} \tag{262}$$

i.e. the sum of kinetic terms for each of the electrons, together with the electrostatic interaction with the nucleus (of charge $Z|e|$) and with each other, plus spin-orbit terms.

The simplest perturbation scheme is to ignore all electron-electron interactions, and the spin-orbit terms. We therefore get single-particle eigenstates like those for the Hydrogen atom:

$$u(\mathbf{r}) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi). \tag{263}$$

A given state is labelled by quantum numbers (n, ℓ, m); because of the larger nuclear charge, all lengths in the radial wavefunction will be smaller by a factor Z, and the binding energy of a given level will be larger by a factor Z^2. To get a first estimate of the ground state, we use the **aufbau principle** (from the German for 'building up'): put electrons in energy eigenstates in ascending order of binding energy, with no more than 2 electrons per state.

CENTRAL FIELD AND ELECTRON SHELLS Even before starting perturbation theory, this is a bad approximation, for the following reason: if all $2\ell + 1$ states of different m are filled for a given n & ℓ, the electron charge distribution is spherically symmetric. This can be regarded as intuitively obvious, since the z axis is arbitrary. It is obvious for $n = 1$, since $\ell = 0$ and the wavefunction is symmetric. Now, we know that a spherically symmetric charge distribution acts identically to a charge at the origin, so far as particles outside the distribution are concerned (just like a spherical mass distribution in gravity). Since electrons have a typical distance from the nucleus that scales as n^2, it will be a good approximation to say that all electrons in states of lower n simply act to **screen** the nuclear charge. Consider Lithium ($3e$): the first 2 electrons populate the 1s level, and see the nuclear charge ($q = 3|e|$). The third electron goes in the $2s$ level, but the inner electrons shield the nucleus, so the third electron only sees $q = |e|$.

A more sensible unperturbed state is therefore to give each electron a different apparent electron charge, according to which level it is in: we can still label states with (n, ℓ, m), but now the effective nuclear charge depends on the number of electrons in lower levels. Starting with this Hydrogen-like ψ for each electron, we can average $|\psi|^2$ over angles to get the mean charge density at each radius. As a first estimate of the perturbation to the Hydrogenic states, we can now assume that each electron sees $V(r)$ = nucleus + mean of all other electrons in interior shells, and use this spherically symmetric potential to refine the solution (the **Hartree method**). Already, this approach requires numerical solution of the Schrödinger equation for each electron.

An important point to note is that the result of the central-field approximation is to break the degeneracy of the Hydrogenic energy levels; because the potential is no longer Coulomb, $E = E(n, \ell)$. It is easy enough to see that, for a given n, states of lower ℓ will be more strongly bound. This may at first seem puzzling, given that we showed in studying the Hydrogen atom that dp/dr peaks *closer* to the nucleus for large ℓ. However, the biggest effects on the energy come from the parts of the electron orbit that penetrate close to the nucleus, and these effects are strongest for small ℓ (remember the wavefunction scales as $\psi \propto r^\ell$ near the origin).

This introduces the concept of an **electron shell**, which is a set of states of given n and ℓ (in the central-field model, different values of m are still degenerate). The order of filling of shells may be calculated as:

$$\begin{aligned} 1s, 2s, 2p, 3s, 3p,&[4s, 3d], 4p, [5s, 4d], 5p, \\ &[6s, 4f, 5d], 6p, [7s, 5f, 6d]. \end{aligned} \tag{264}$$

For [states], the order varies from atom to atom. This is the basis of the periodic table and of chemistry.

Finally, we need to add the effects of $e - e$ forces (not generally treatable as a central field) and $\mathbf{L} \cdot \mathbf{S}$ as perturbations. The reason $e - e$ forces are not too big a problem in practice is explained by the symmetry of the wavefunction, as follows.

EXCHANGE FORCE We saw that, for a spatially antisymmetric 2-particle state, prob$(x_1 = x_2) = 0$. Fermions tend to avoid each other, provided the spin wavefunction is symmetric (i.e. the spins are parallel). It is therefore clear that the electrostatic interaction energy of two electrons will be reduced if they are in a spatially antisymmetric state, and raised if they are in a spatially symmetric state. In other words, the interaction energy is reduced for the case of parallel spins. This is roughly equivalent to the appearance of an interaction $\propto -\mathbf{S}_1 \cdot \mathbf{S}_2$.

This non-classical spin-spin **exchange interaction** is responsible for ferromagnetism. It also leads to **Hund's rule**: for filling states of the same energy (i.e. in one shell), set spins parallel as far as possible (i.e. maximise $\mathbf{S}$).

20 Appendix: the Hydrogen atom

This appendix contains the full gory details of the solution of the Hydrogen atom, for the sake of curiosity. As emphasized previously, these details are not examinable. We need to solve

$$\frac{-\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0}\psi = E\psi, \tag{265}$$

where

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}. \tag{266}$$

We look for a separable solution

$$\psi = R(r)Y(\theta,\phi). \tag{267}$$

The angular part must be expandable in terms of the eigenfunctions of the angular momentum operator. In fact,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{1}{\hbar^2 r^2}L^2, \tag{268}$$

so the angular eigenfunctions are exactly the angular momentum eigenstates.

Separation of variables gives the equation

$$-\frac{\hbar^2}{2\mu}\left[Y\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\right] + R\frac{1}{2\mu r^2}L^2Y = (E-V)RY. \tag{269}$$

Multiplying through by $r^2/(RY)$ gives

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\right] - (E-V)r^2 = \frac{1}{2\mu Y}L^2Y \tag{270}$$

As usual, both sides of this equation must be constants, and we can use our knowledge of angular momentum to identify the rhs as $\ell(\ell+1)\hbar^2/2\mu$

SPHERICAL HARMONICS If we didn't want to assume that ℓ was an integer, we would need to apply separation of variables further, and split the angular function into $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$. The angular eigenvalue equation is

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Theta(\theta)\Phi(\phi) = -\ell(\ell+1)\Theta(\theta)\Phi(\phi). \tag{271}$$

Multiplying through by $\sin^2\theta/(\Theta\Phi)$ gives

$$-\frac{1}{\Phi}\frac{\partial^2}{\partial\phi^2}\Phi = \frac{1}{\Theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\Theta + \ell(\ell+1)\sin^2\theta. \tag{272}$$

Yet again, we say that both sides must be constant, which we call m^2. From the previous argument about L_z, we know that m will be an integer, and $\Phi \propto \exp(im\phi)$. This leaves one nasty equation for $\Theta(\theta)$:

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right]\Theta(\theta) = 0. \tag{273}$$

It is normal to rewrite this in terms of $z \equiv \cos\theta$, to get

$$\frac{d}{dz}\left[(1-z^2)\frac{d\Theta}{dz}\right] + \left(\ell(\ell+1) - \frac{m^2}{1-z^2}\right)\Theta = 0. \tag{274}$$

This is a standard equation, whose solutions are the **associated Legendre functions**, P_ℓ^m. We will not need too many detailed properties of these functions, but it is worth summarizing a few properties, without much proof. The equation with $m = 0$ can be solved by the usual technique of power-law solution, since the nasty $1/(1-z^2)$ term is removed:

$$\Theta(z) = \sum_{k=0}^{\infty} a_k z^k. \tag{275}$$

The resulting recurrence relation is

$$(k+1)(k+2)a_{k+2} = [k(k+1) - \ell(\ell+1)]a_k, \tag{276}$$

so the solution splits into two independent series, odd and even; one of these terminates at $k = k_{\rm max}$ if ℓ is chosen to be an integer $\ell = k_{\rm max}$, and the other series is set to zero. The solutions are then the **Legendre polynomials**, $P_\ell(z)$. These are specified up to an overall normalization, which is taken to be $P_\ell(1) = 1$. This means that the spatial wavefunctions are *not* normalized. The first few Legendre polynomials are:

$$\begin{aligned} P_0(x) &= 1 \\ P_1(x) &= x \\ P_2(x) &= (3x^2-1)/2 \\ P_3(x) &= (5x^3-3x)/2 \end{aligned} \tag{277}$$

A general expression for these functions is given by **Rodrigues' formula**:

$$P_\ell(x) = \frac{1}{2\ell!}\,\frac{d^\ell}{dx^\ell}\,(x^2-1)^\ell \tag{278}$$

(see e.g. p453 of Riley, Hobson & Bence). For the full solution, it can be shown that the following modifications of the Legendre polynomials work:

$$P_\ell^m(z) = (1-z^2)^{|m|/2}\frac{d^{|m|}}{dz^{|m|}}P_\ell(z). \tag{279}$$

This defines the associated Legendre polynomials.

In summary, the overall angular solutions are the **spherical harmonics**. With the correct normalization, these are defined for $m \geq 0$ as

$$Y_\ell^m = (-1)^m\sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}}P_\ell^m(\cos\theta)e^{im\phi}; \tag{280}$$

For negative m, $Y_\ell^{-|m|} = (-1)^{|m|}(Y_\ell^{|m|})^*$, so harmonics with positive and negative m are identical apart from a (conventional) overall sign and the sign of the $e^{im\phi}$ term. No-one with any sense would try to remember the exact coefficient here. The main thing is that the spherical harmonics are orthonormal over the unit sphere:

$$\int Y_\ell^{m*}Y_{\ell'}^{m'}\,d\Omega = \delta_{\ell\ell'}\delta_{mm'} \tag{281}$$

($d\Omega$ being an element of solid angle).

RADIAL EQUATION Return now to the radial equation, which will determine the energy levels of the atom:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{\ell(\ell+1)}{r^2}\right]R=(E-V)R \tag{282}$$

The radial equation can be simplified by using

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)=\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR)\,. \tag{283}$$

If we put $R=u/r$, then

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2}-\frac{\ell(\ell+1)}{r^2}\right]u=(E-V)u. \tag{284}$$

This is valid for any spherically-symmetric potential, not just the hydrogen atom.

Notice that the effect of angular momentum is to add a term that looks like another contribution to $V(r)$: this is known as the **centrifugal potential**:

$$V\rightarrow V+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} \tag{285}$$

This potential reduces the binding effect (since V is negative), so we can see intuitively that the ground state of the system will be $\ell=0$.

As an example of this, consider the spherical 'square well', where $V=-|V_0|$ for $r<a$, but is zero at larger r. For $\ell=0$, the radial equation for u is identical to the case of the 1D well, so the solutions are either $u=\cos kr$ or $u=\sin kr$. However, there is a critical difference from the 1D case, which is that now the even solutions are disallowed. This is because the wave function near the origin would otherwise be $\psi\propto(\cos kr)/r\rightarrow 1/r$. This infinite spike is unphysical if V is finite; the way to avoid it is to take the odd solution, since $(\sin kr)/r\rightarrow k$ as $r\rightarrow 0$. In the 1D case, we saw that there was only one solution (the even wavefunction) when

$$\gamma=\sqrt{2m|V_0|a^2/\hbar^2}<\pi/2. \tag{286}$$

In the 3D case, this is disallowed, and no bound state exists for wells that are too shallow.

COULOMB POTENTIAL It is now time to complete the Hydrogen problem, and this needs a little work. To start, it is a good idea to put the problem in dimensionless form. Define

$$\begin{aligned}\rho &\equiv \alpha r\\ \alpha^2 &\equiv 8\mu|E|/\hbar^2\\ \lambda &\equiv 2\mu e^2/(4\pi\epsilon_0\alpha\hbar^2)=\frac{e^2}{4\pi\epsilon_0\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2},\end{aligned} \tag{287}$$

so λ is the dimensionless measure of the energy.

We can also use intuition to realise that the Coulomb potential is negligible at large r, so the eigenfunctions must go over to simple evanescent waves there: $R \propto \exp(ikr)$, where $k^2 = 2\mu E/\hbar^2$. Since E is negative, we have the choice of decaying or growing exponentials, and choose the former, which is

$$R \propto \exp(-\rho/2). \tag{288}$$

More formally, the dimensionless radial equation is

$$R'' + \frac{2}{\rho}R' + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\right] R = 0. \tag{289}$$

As $\rho \to \infty$, we get $R'' - R/4 = 0$, and $\exp(-\rho/2)$ times any power of ρ is a solution in this limit.

As usual, having the asymptotic behaviour, we try a correction factor: $R = F(\rho)\exp(-\rho/2)$. The equation for F is

$$F'' + \left(\frac{2}{\rho} - 1\right) F' + \left(\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) F = 0 \tag{290}$$

and, once again, we try power-law solution. This is a little messy, and it helps to start by thinking about the solution close to the origin, where the centrifugal potential dominates unless $\ell = 0$. It is easy to see by substitution that a power-law solution works as $\rho \to 0$:

$$F \propto \rho^\ell \quad \text{or} \quad \rho^{-(\ell+1)}. \tag{291}$$

The second of these is unphysical: it cannot be normalized. We are therefore led to try a solution

$$R = \rho^\ell G(\rho)\exp(-\rho/2); \quad G = \sum_{i=0}^{\infty} a_i \rho^i, \tag{292}$$

where the unknown factor G is expressed as a power series. This yields yet another differential equation for the functions G:

$$\rho G'' + (2\ell + 2 - \rho)G' + (\lambda - \ell - 1)G = 0. \tag{293}$$

The details now follow the pattern familiar from the Legendre polynomials. There is a recurrence relation for the coefficients a_i:

$$a_{i+1} = \frac{i + \ell + 1 - \lambda}{(i+1)(i + 2\ell + 2)}\, a_i; \tag{294}$$

it is argued that the G functions must be finite polynomials, otherwise the series blows up too badly at large ρ. If the largest non-zero coefficient is a_k, then

$$\lambda = n = k + \ell + 1; \quad k = 0, 1, \ldots, \tag{295}$$

where n is the **principal quantum number** Since $\lambda \propto 1/|E|^{1/2}$, this says

$$|E| = \frac{\mu e^4}{2\hbar^2(4\pi\epsilon_0)^2}\,\frac{1}{n^2} = \mu c^2\,\frac{\alpha^2}{2n^2}, \tag{296}$$

where the **fine-structure constant** is

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}. \tag{297}$$

The details of the wavefunctions can be expressed in terms of the **Laguerre polynomials**:

$$L_n(x) = e^x \frac{d^n}{dx^n} x^n e^{-x}. \tag{298}$$

These solve the differential equation $xL_n'' + (1-x)L_n' + nL_n = 0$. Last of all, the **associated Laguerre polynomials** are

$$L_n^m(x) = \frac{d^m}{dx^m} L_n(x). \tag{299}$$

Working out the differential equation they obey and comparing to the one for the radial function G, it can be seen that the polynomials we need are $G(\rho) = L_{n+\ell}^{2\ell+1}(\rho)$.

In summary, the hydrogen wavefunctions are thus

$$\psi_{\ell m n} \propto Y_\ell^m(\theta, \phi)\, e^{im\phi} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho) e^{-\rho/2}. \tag{300}$$