Part A Quantum Theory

Prof. Luis Fernando Alday, Michaelmas Term 2018

(Largely based on the previous lecture notes by profs. Hodges, Tod and Sparks)

Synopsis

- Wave-particle duality; Schrödinger's equation; stationary states; quantum states of a particle in a box (infinite square-well potential).

- Interpretation of the wave function; boundary conditions; probability density and conservation of current; parity.

- The one-dimensional harmonic oscillator; higher-dimensional oscillators and normal modes; degeneracy. The rotationally symmetric states of the hydrogen atom with fixed nucleus.

- The mathematical structure of quantum mechanics and the postulates of quantum mechanics.

- Commutation relations. Heisenberg's uncertainty principle.

- Creation and annihilation operators for the harmonic oscillator. Measurements and the collapse of the wave function.

- Schrödinger's cat. Angular momentum in quantum mechanics. The particular case of spin-1/2. Particle in a central potential. General states of the hydrogen atom.

Preamble

Classical physics — Newton's laws of mechanics and the theory of electromagnetism developed in the 19th century — fails at the atomic scale. From the beginning of the 20th century, mounting experimental evidence pointed towards the existence of a radically different theory of physics that governs the properties of atoms and their constituent particles. The deterministic and continuous nature of classical physics was replaced by a new *quantum theory*, with probability and discreteness at its heart. The theory of quantum mechanics developed in the 20th century not only successfully describes the structure of atoms and molecules, but also nuclear physics, particle physics (such as in particle accelerators like the LHC), chemistry (such as chemical bonding), the structure of solids, superconductors, *etc.* Quantum theory also underpinned many important technological advances in the 20th century, such as the laser, the microchip (hence computers and mobile phones), and the electron microscope. Future applications may include quantum cryptography and the quantum computer.

In this course we begin with an overview of some key physical ideas and formulae. These developed from experiments that demonstrate the failure of classical physics at the atomic scale. An important concept here is *wave-particle duality*. This, together with some intuition from classical physics, will lead us to the *Schrödinger equation* that governs such *matter-waves*. We discuss general properties of the Schrödinger equation, and interpret the wave function in terms of a probability distribution. We also study in detail some of the simplest, and most important, solutions: a particle confined to a box, the harmonic oscillator (which universally describes small oscillations of any quantum system), and, after an interlude of mathematical formalism, the hydrogen atom. In particular, we will derive the observed emission/absorption spectrum of the hydrogen atom, a computation that was in Schrödinger's original 1926 paper.

0 Classical particles and waves

Before starting the course proper, we begin with a brief review of classical point particles and waves. This is to remind you of some concepts and formulae learned at school or in Prelims, and to set notation used later in the text.

0.1 Point particles

A point particle is an idealized object that, at any given instant of time, is located at a point in space, and the position of the particle is governed by Newton's second law: if the particle has constant mass m and is acted on by a force $\mathbf{F}$, then $\mathbf{r}(t)$ obeys

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \mathbf{F}.$$

In principle here $\mathbf{F}$ could depend on time, but in this course we shall only consider *conservative forces* where $\mathbf{F} = -\nabla V$, for some function $V = V(\mathbf{r})$ called the *potential* and independent of time (or *static*).

In this case, the *total energy* of the particle

$$E = \frac{1}{2}m|\dot{\mathbf{r}}|^2 + V$$

is *conserved*, where we shall sometimes denote $\dot{\mathbf{r}} \equiv \mathrm{d}\mathbf{r}/\mathrm{d}t$. That is, E is independent of time:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = m\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} \cdot \frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} + \nabla V \cdot \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} \cdot \left(m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} - \mathbf{F} \right) = 0 \ .$$

Here the particle has *kinetic energy* $\frac{1}{2}m|\dot{\mathbf{r}}|^2$, *potential energy* $V = V(\mathbf{r}(t))$, and *momentum* $\mathbf{p} = m\dot{\mathbf{r}}$. We may also write the kinetic energy as

$$E_{\text{kinetic}} = \frac{|\mathbf{p}|^2}{2m} \ .$$

A particle that is subjected to no forces is called a *free particle*.

* The above formulae are true (to a very good approximation) for a *non-relativistic* point particle, which means its speed $u = |\dot{\mathbf{r}}|$ is much less than the speed of light, $u \ll c =$ speed of light. For example, a *massless* particle, with $m = 0$, necessarily moves at speed c and has energy $E = c|\mathbf{p}|$, where $\mathbf{p}$ is its momentum. This will be treated in the Special Relativity option course.

0.2   Waves

Recall the classical *wave equation*

$$\frac{1}{v^2}\frac{\partial^2\phi}{\partial t^2} = \nabla^2\phi \ ,$$

where v is the constant speed of the wave. This linear equation governs, for example, the propagation of sound or light. As basic solution we have the *complex plane wave*

$$\phi(\mathbf{r}, t) = A \exp\left[\mathrm{i}(\mathbf{k} \cdot \mathbf{r} - \omega t)\right] \ ,$$

where we have the constant *wave vector* $\mathbf{k}$, *angular frequency* ω, and (possibly complex) *amplitude* A. Substituting into the wave equation gives $-\omega^2/v^2 = -|\mathbf{k}|^2$, or equivalently the relation

$$v = \frac{\omega}{|\mathbf{k}|} \ . \tag{0.1}$$

Both the real and imaginary parts of ϕ separately satisfy the wave equation, giving real solutions that are linear combinations of sines and cosines of $(\mathbf{k} \cdot \mathbf{r} - \omega t)$. In fact it is a result of Fourier analysis that *every* solution to the wave equation is a linear combination (in general involving an integral) of these plane waves.

The *wave frequency* is $\nu = \omega/2\pi$, while the *wavelength* is $\lambda = 2\pi/|\mathbf{k}|$, so that (0.1) is equivalent to saying that the wave speed is $v = \nu\lambda =$ frequency $\times$ wavelength.

1 Physical background and wave-particle duality

1.1 The photoelectric effect: waves as particles

In the mid 19th century Maxwell successfully described light as a *wave* propagating in the *electromagnetic field*. We shall not need to know anything about electromagnetic theory in this course. Nevertheless, we note in passing that, in Maxwell's theory, light propagating through a vacuum is described by two vector fields $\mathbf{E}(\mathbf{r}, t)$, $\mathbf{B}(\mathbf{r}, t)$, called the *electric* and *magnetic* fields, respectively, each Cartesian component of which satisfies the wave equation, with $v = c$ being the speed of light in vacuum. This theory of electromagnetism unified the theories of electricity, magnetism and radiation, and explained wave-like properties of light such as reflection, polarization and diffraction. However, by the beginning of the 20th century it was becoming clear that Maxwell's theory could not explain experiments at the *atomic* scale.

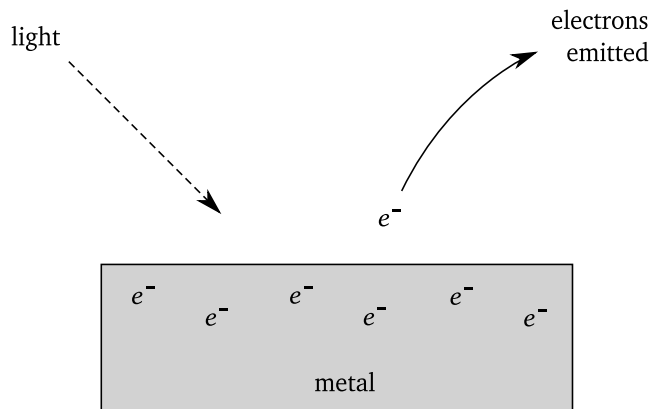A clear and simple experiment that demonstrates this is the *photoelectric effect*, shown in Figure 1.

Figure 1: To observe the photoelectric effect, light is shone on a metal plate in vacuum. Electrons e^- are emitted from the surface of the metal, and their kinetic energy E_{kinetic} is measured.

Light of angular frequency ω is shone on a metal plate in vacuum. Electrons e^-, which are only weakly bound to the metal, are emitted from the surface. One measures their kinetic energy and discovers the formula

$$E_{\text{kinetic}} = -E_0 + \hbar\omega \ . \tag{1.1}$$

- $E_0 > 0$ is a constant energy which depends only on the particular metal used.

- The constant of proportionality $\hbar$ (usually read as "h bar") is a constant of Nature that is fundamental to Quantum Theory. From (1.1) we see that it has dimensions $[\hbar] = \text{energy} \times \text{time}$, or equivalently $[\hbar] = M(LT^{-1})^2 \times T = MLT^{-1} \times L = \text{dimensions of } angular\ momentum$, where M, L and T denote dimensions of mass, length and time, respectively. Numerically, $\hbar \simeq 1.05 \times 10^{-34}\,\text{J s}$. The combination $2\pi\hbar \equiv h$ is called *Planck's constant*, while $\hbar$ is sometimes referred to as the *reduced Planck's constant*.

- If the angular frequency $\omega < E_0/\hbar$, *no e^- are emitted.*

- The formula (1.1) is independent of the *intensity* (brightness) of the light, but as the latter is increased the *number* of e^- emitted increases.

The classical theory of Maxwell does not explain these observations. Instead Einstein made the following remarkable hypothesis:

Light of angular frequency ω exists in small packets, or "quanta", of energy $E = \hbar\omega$, a relation we call the *Einstein-Planck relation*.

These packets of light are known as *photons*, and are massless particles ($m = 0$) that travel at the speed of light c (*cf.* the starred remark at the end of section 0.1). In Einstein's interpretation of the photoelectric effect, each electron e^- absorbs one photon of energy $\hbar\omega$ (very occasionally more than one). Part of this photon energy goes into overcoming the "binding energy" E_0 of the electron to the metal; the remainder is then converted into the observed kinetic energy of e^- when it is emitted. Increasing the intensity of the light simply increases the *number* of photons.[1]

1.2   Emission/absorption spectra of atoms

Atoms emit and absorb light at very particular frequencies. The simplest atom is the hydrogen atom, which we shall study in more detail at the end of this course. For hydrogen these frequencies were discovered experimentally in the 19th century, and are given by the formula

$$\omega_{n_1,n_2} \;\; = \;\; 2\pi R_0 c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \; . \tag{1.2}$$

Here $n_1 < n_2$ are positive *integers*, and $R_0 \simeq 1.10 \times 10^7 \, \mathrm{m}^{-1}$ is *Rydberg's constant*, named after the discoverer of the empirical formula (1.2).

From Einstein's description of light in terms of photons, this implies that a hydrogen atom emits and absorbs photons of particular *energies* $\hbar\omega_{n_1,n_2}$. By conservation of energy, the energy of the hydrogen atom itself must then be changing by these amounts when a photon is emitted/absorbed. This strongly suggests that the energies of the hydrogen atom must be given by

$$E_n \;\; = \;\; -\frac{2\pi R_0 \hbar c}{n^2} \; , \tag{1.3}$$

where n is an integer, so that *e.g.* for $n_1 < n_2$ the energy of the atom can change from E_{n_2} to E_{n_1} by emitting a photon of frequency ω_{n_1,n_2}. That the hydrogen atom energies are indeed *quantized* in this way – that is, taking particular discrete values, rather than being continuous – has been confirmed in many other experiments. At the end of this course we will derive (1.3) theoretically.

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[1]* Planck had introduced the constant $h = 2\pi\hbar$ in earlier work on radiation emitted from certain idealized hot objects, called *black bodies*.

1.3 The double slit experiment: particles as waves

The photoelectric effect implies that light, described classically by waves satisfying the wave equation with speed $v = c$, is sometimes better described as a beam of particles, namely photons.

Similarly, particles, such as the electron e^-, can display wave-like characteristics. Perhaps the best experiment that demonstrates this is the famous *double slit experiment*, performed with electrons. This is shown in Figures 2 and 3. A beam of electrons is fired at a double slit configuration, with a detector screen on the other side. An electron hitting the screen appears as a bright spot, and over time one can plot this as a distribution. The latter exhibits a familiar diffraction pattern, similar to that seen in the corresponding experiment with the beam of electrons replaced by a beam of light. Such diffraction patterns are explained by the interference of waves: two waves that travel through each of the slits and arrive at the same point on the detector screen have travelled different distances. These waves then either constructively or destructively interfere with each other, depending on whether the difference in these distances is an even or odd number of wavelengths, respectively. This is perhaps familiar to those who have done A-level physics.
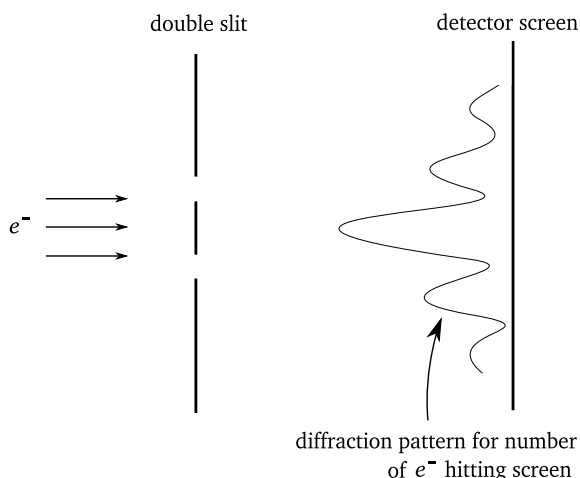

Figure 2: The double slit experiment, performed with a beam of electrons.

A remarkable point here is that the diffraction pattern is still observed even when only a *single* electron is passing through the slits at a time. In fact this is the case in the Hitachi experimental results shown in Figure 3 (the time lapse up to picture (iv) is 20 minutes). This implies that the electrons are not interfering with each other to cause the diffraction pattern, but rather a *single* electron is behaving like a wave. Or, more precisely, the detected distribution of electron particles is characteristic of a wave passing between the slits. Notice that we may also interpret this distribution as a *probability distribution* for where any single electron will hit the screen. In this viewpoint, it is the *probability* that displays wave-like characteristics, while the electrons themselves are always detected on the screen as localized particles. These remarks are absolutely central to wave-particle duality.

The double slit experiment (and variants of it) is extremely interesting and subtle, and we refer the interested reader to the references (especially the Feynman lectures) for further discussion
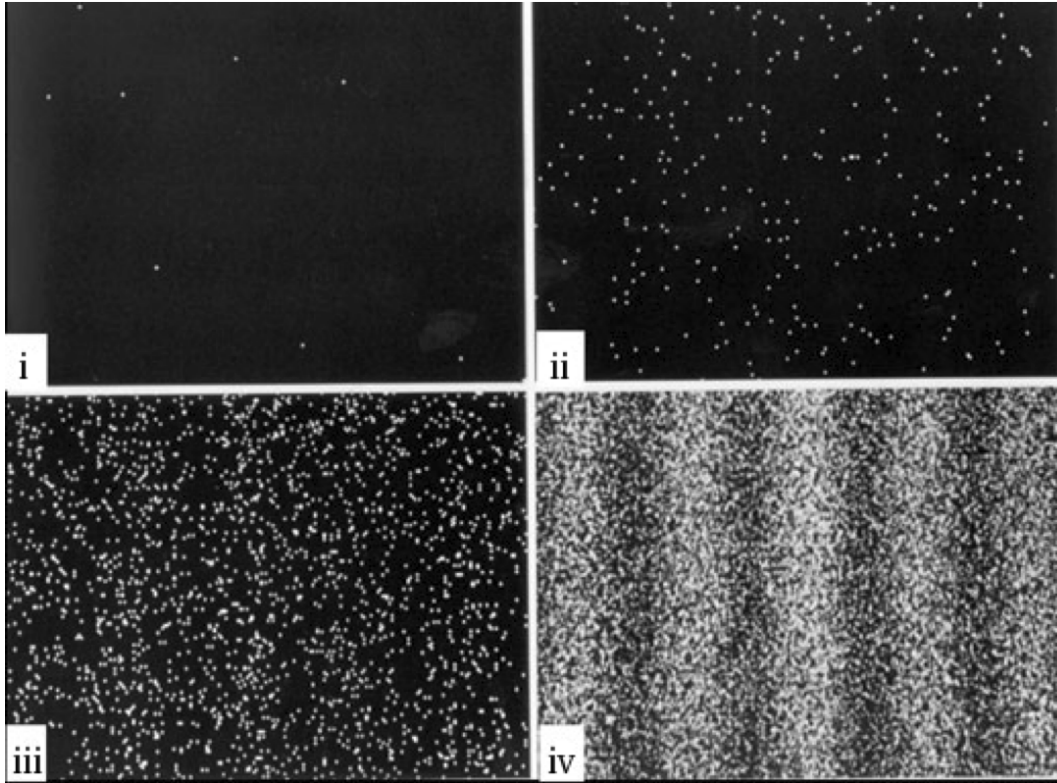
Figure 3: Actual electron hits in an experiment by a group at Hitachi (© Hitachi, Ltd): (i) 8 e^-, (ii) 270 e^-, (iii) 2,000 e^-, (iv) 160,000 e^-.

of its role in understanding wave-particle duality.

1.4   De Broglie's matter-waves

The experiment we have just described suggests that particles, such as electrons, are also associated with waves. De Broglie made this more precise with the claim:

> A free particle of energy E and momentum $\mathbf{p}$ is associated with a *wave* of angular frequency ω and wave vector $\mathbf{k}$ via
>
> $$\begin{aligned} E &= \hbar\omega \,, \\ \mathbf{p} &= \hbar\mathbf{k} \qquad \text{(de Broglie relations) .} \end{aligned} \qquad (1.4)$$

Since the wavelength is $\lambda = 2\pi/|\mathbf{k}|$, we may also write the latter relation as $\lambda = 2\pi\hbar/|\mathbf{p}| = h/|\mathbf{p}|$. De Broglie's insight was that these relations should apply to *all* particles, not just massless photons. In this context, $E = \hbar\omega$ is usually referred to as a de Broglie relation, rather than the Einstein-Planck relation.

* We note that for a photon, the second relation in (1.4) is implied by the first relation $E = \hbar\omega$. This follows from the starred comment at the end of section 0.1: for a photon $E = c|\mathbf{p}|$, so that $E = \hbar\omega$ together with $c = \omega/|\mathbf{k}|$ implies that $|\mathbf{p}| = \hbar|\mathbf{k}|$. In the Special Relativity option you can learn that $(E, \mathbf{p})$ and $(\omega, \mathbf{k})$ are both 4-vectors, and indeed this was part of de Broglie's reasoning.

2   Wave mechanics

2.1   The Schrödinger equation

De Broglie had hypothesized that particles, such as the electron e^-, are associated with waves. Schrödinger set out to discover the equation that governs these *matter-waves*. He began by considering the plane wave, reviewed in section 0.2,

$$\Psi(\mathbf{r}, t) = A \exp\left[i(\mathbf{k} \cdot \mathbf{r} - \omega t)\right] .$$

This of course satisfies the wave equation, with ϕ replaced by Ψ; the change of notation is meant to emphasize that we now wish to reinterpret this plane wave as a de Broglie matter-wave. Making use of the de Broglie relations (1.4), we notice

$$
\begin{aligned}
i\hbar\frac{\partial \Psi}{\partial t} &= \hbar\omega\Psi = E\Psi , \\
-i\hbar\nabla\Psi &= \hbar\mathbf{k}\Psi = \mathbf{p}\Psi .
\end{aligned}
$$

In particular, taking the divergence of the second equation implies that $-\hbar^2\nabla^2\Psi = |\mathbf{p}|^2\Psi$, where ∇^2 is the Laplacian.

The de Broglie relations apply to a free particle, for which the particle's energy is equal to its kinetic energy (since $\mathbf{F} = \mathbf{0}$ the potential is constant, and we take this constant to be zero). If the particle has mass m, then $E = E_{\text{kinetic}} = |\mathbf{p}|^2/2m$. Using the de Broglie relations (1.4) then implies

$$\omega = \frac{E}{\hbar} = \frac{\hbar|\mathbf{k}|^2}{2m} . \tag{2.1}$$

Putting everything together, we have

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi = \frac{|\mathbf{p}|^2}{2m}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi . \tag{2.2}$$

Thus we may associate to a free particle of mass m a plane wave $\Psi(\mathbf{r}, t)$, using the de Broglie relations, which then satisfies the equation

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi . \tag{2.3}$$

This is essentially expressing the relation (2.1), which is simply the relation between energy and momentum for a free particle.

More generally, a particle of mass m moving in a potential $V = V(\mathbf{r})$ has energy

$$E = \frac{|\mathbf{p}|^2}{2m} + V . \tag{2.4}$$

This led Schrödinger to

Definition / postulate A single, non-relativistic particle of mass m moving in a potential $V(\mathbf{r})$ is described by a *wave function* $\Psi(\mathbf{r}, t)$ that is governed by the *Schrödinger equation*

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \ . \tag{2.5}$$

The wave function $\Psi(\mathbf{r}, t)$ is precisely de Broglie's matter-wave.

Let us make some remarks about what we have done above, which is deceptively straightforward, and about the Schrödinger equation itself:

1. It is important to realize that we have not *derived* the Schrödinger equation, in any rigorous sense. In particular, in the last step we have taken formulae that apply to free particles, that have been suggested by a combination of experiments and theoretical arguments, and extrapolated this, using the classical formula (2.4) for energy, to an equation governing the matter-wave of a particle moving in a general potential. It turns out this equation is indeed correct, but nothing in the rather naive argument we gave really guarantees this. The real test of the Schrödinger equation is that it agrees with experiments.

2. The Schrödinger equation is a *linear* partial differential equation for a *complex-valued* function $\Psi(\mathbf{r}, t)$. Thus if Ψ_1, Ψ_2 are solutions, then so is $\alpha_1\Psi_1 + \alpha_2\Psi_2$, for any complex constants $\alpha_1, \alpha_2 \in \mathbb{C}$. This implies that solutions form a (usually infinite-dimensional) *vector space* over $\mathbb{C}$. It is precisely this superposition of wave functions that leads to interference effects, as in the double slit experiment with electrons. Notice that, in contrast with the classical wave equation, the Schrödinger equation (2.5) is complex, due to the $i = \sqrt{-1}$ on the left hand side.

3. Although we began our exposition by discussing photons, it is important to remark that the photon is a *massless*, *relativistic* particle, and as such is **not** governed by the Schrödinger equation. The quantum theory of photons is a much more involved theory, known as *quantum electrodynamics*, that requires a thorough understanding of both classical electromagnetism and Special Relativity, as well as quantum ideas. We shall only refer to the photon again in the context of emission/absorption in atoms, for which we need only the Einstein-Planck relation.

Before continuing to discuss some basic mathematical properties of the Schrödinger equation, and looking at our first example, let us pause to comment on the change of viewpoint that is already implicit in what we have said so far. Consider the classical problem of a point particle of mass m moving in a potential V. The dynamics is governed by Newton's law with $\mathbf{F} = -\nabla V$, the solutions of which give the particle's trajectory $\mathbf{r}(t)$. For given initial conditions, say the particle's position $\mathbf{r}$ and momentum $\mathbf{p} = m\dot{\mathbf{r}}$ at time $t = t_0$, one solves for the trajectory $\mathbf{r}(t)$, which gives the particle's location and momentum at any subsequent time.

The corresponding quantum mechanical problem is very different. Given a quantum point particle of mass m moving in a potential V, we should instead solve the Schrödinger equation

(2.5). We shall discuss the boundary conditions involved later, but notice immediately that the result will be some complex-valued function $\Psi(\mathbf{r}, t)$. You might immediately wonder what this function has to do with the particle's position at some time t. Again, we shall address this shortly.

2.2 Stationary states

It is natural to seek separable solutions to the Schrödinger equation. Thus we write $\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) T(t)$, so that the Schrödinger equation (2.5) becomes

$$\frac{i\hbar \frac{dT}{dt}}{T} = \frac{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi}{\psi} . \tag{2.6}$$

Since the left hand side depends only on t, while the right hand side depends only on $\mathbf{r}$, both sides must be constant. If we call this constant E (anticipating that this will be the energy of the particle), then in particular we have

$$i\hbar \frac{dT}{dt} = ET , \tag{2.7}$$

which immediately integrates to

$$T(t) = e^{-iEt/\hbar} . \tag{2.8}$$

Here we have absorbed the overall multiplicative integration constant into ψ. The full wave function is thus

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar} . \tag{2.9}$$

That E is then indeed the energy of the particle follows from the de Broglie relation between energy and angular frequency for matter-waves: for this wave function the angular frequency is $\omega = E/\hbar$, or equivalently $E = \hbar\omega$. The function ψ then satisfies

Definition The *time-independent*, or *stationary state*, *Schrödinger equation* for a particle of mass m and energy E moving in a potential $V = V(\mathbf{r})$ is

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi . \tag{2.10}$$

The wave function $\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar}$ is then called a *stationary state wave function* of energy E, although in a common abuse of language the function ψ is also often referred to as the stationary state wave function.

2.3 One-dimensional equations

Although ultimately we are interested in studying particles moving in the three spatial dimensions that we observe, it is often technically more straightforward to study the *one-dimensional Schrödinger equation*

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi , \tag{2.11}$$

with corresponding stationary state equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi , \tag{2.12}$$

and

$$\Psi(x,t) = \psi(x)\, e^{-iEt/\hbar} . \tag{2.13}$$

Here we have replaced the Laplacian ∇^2 by the corresponding one-dimensional operator, which is simply $\partial^2/\partial x^2$. Equations (2.11), (2.12) govern a particle propagating on the x-axis with potential $V = V(x)$. Similar remarks apply in two dimensions. Although the one-dimensional equation looks somewhat unphysical, in fact sometimes a three-dimensional problem effectively reduces to a lower-dimensional Schrödinger equation; for example, due to symmetry reduction (see section 8), or because the particle is constrained to lie in some subspace.

2.4 Particle in a box

Consider a particle inside a "box" on the x-axis. This means that the particle moves freely inside some interval $[0, a] \subset \mathbb{R}$, but cannot leave this region. One can model this by a potential function $V = V(x)$ that is zero inside the interval/box, and infinite outside:

$$V(x) = \begin{cases} 0 , & 0 < x < a , \\ +\infty , & \text{otherwise} . \end{cases} \tag{2.14}$$

This is also sometimes referred to as the *infinite square well potential*. See Figure 4.

Before discussing the quantum problem, let us briefly comment on the classical problem. Since $V = 0$ inside the box, the classical particle moves at some constant velocity, or equivalently constant momentum p. Since the energy $E = p^2/2m$ is conserved when the particle hits the edge of the box, after the collision p is replaced by $-p$ and the particle heads towards the other edge of the box. Classically, notice that E may take any non-negative value.

Now let us consider the quantum particle. The stationary state Schrödinger equation (2.12) *inside the box* is
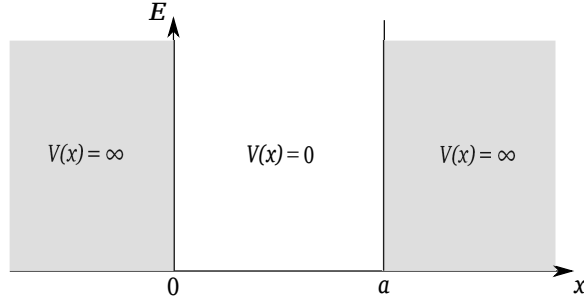
Figure 4: A particle in box $[0, a]$ on the x-axis.

$$\frac{\mathrm{d}^2 \psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2} \psi \,, \tag{2.15}$$

for $x \in (0, a)$. We shall discuss boundary conditions more systematically in section 3.2, but here we note that since $V = \infty$ outside the box, the Schrödinger equation will make sense only if $\psi = 0$ there.[2] When we come to discuss the physical meaning of the wave function, we shall see that this assertion is very well justified physically. If we also assume that ψ is *continuous*, then we must solve (2.15) subject to the *boundary condition* $\psi(0) = \psi(a) = 0$.

The general solution to (2.15) is

$$\psi(x) = \begin{cases} A\cos\frac{\sqrt{2mE}}{\hbar}x + B\sin\frac{\sqrt{2mE}}{\hbar}x \,, & E > 0 \,, \\ A + Bx \,, & E = 0 \,, \\ A\cosh\frac{\sqrt{-2mE}}{\hbar}x + B\sinh\frac{\sqrt{-2mE}}{\hbar}x \,, & E < 0 \,. \end{cases} \tag{2.16}$$

In all cases the boundary condition $\psi(0) = 0$ implies $A = 0$. When $E \leq 0$, $\psi(a) = 0$ implies also $B = 0$. Thus the only solution is $\psi \equiv 0$, which is always a physically meaningless solution to the Schrödinger equation (again, we shall discuss this more later). On the other hand, for $E > 0$ the boundary condition $\psi(a) = 0$ implies that (either $B = 0$ and $\psi \equiv 0$ or)

$$\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a} \,, \tag{2.17}$$

for some *integer* $n \in \mathbb{Z}$. Thus the solutions

$$\psi(x) = \psi_n(x) = \begin{cases} B\sin\frac{n\pi x}{a} \,, & 0 < x < a \,, \\ 0 \,, & \text{otherwise} \,, \end{cases} \tag{2.18}$$

are labelled by n. Notice that, without loss of generality, we may take $n > 0$. The first three wave functions, for $n = 1, 2, 3$, are shown in Figure 5.

The associated energies are, from (2.17),

$$E = E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \,. \tag{2.19}$$

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[2]This is not a very rigorous statement. We can make the discussion rigorous by simply declaring that a particle in a box by definition has $\psi = 0$ outside the box and that ψ is everywhere continuous. See also section 3.2.
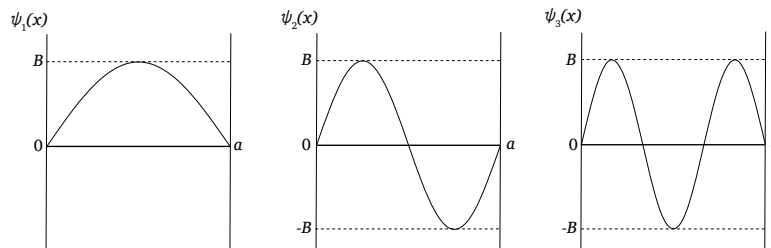
Figure 5: Wave functions for the first three states of a particle in a box. $\psi_1(x)$ is the ground state wave function.

We see immediately that the energy is *quantized, i.e.* it takes values in a discrete set, here labelled by a positive integer. This is in stark contrast with the energy of the classical particle, which may take any real non-negative value. There is also a lowest energy, given by setting $n = 1$.

Definition When the possible energies of a quantum system are discrete and bounded below, the lowest possible energy is called the *ground state energy* (also sometimes called the *zero point energy*). The higher energies are, in increasing order, the *first excited state energy, second excited state energy, etc.* The corresponding wave functions are called the *ground state wave function, kth excited state wave function.*

* Are these values of energy reasonable?
For the particle in a box the ground state energy is $E_1 = \pi^2 \hbar^2 / 2ma^2$, while $E_n = n^2 E_1$. Of course, we precisely wanted a theoretical understanding of such quantized energies in order to explain the energy levels of the hydrogen atom, determined empirically as (1.3). For the particle in a box, if we take $m = m_{e^-} \simeq 9.11 \times 10^{-31}$ kg to be the mass of an electron and $a = 10^{-10}$ m to be the approximate size of an atom, we obtain

$$E_n \quad \simeq \quad 5.97 \times 10^{-18}\, n^2 \text{ J} . \qquad (2.20)$$

In particular, the difference in energies between the ground state and first excited state is $E_2 - E_1 \simeq 1.79 \times 10^{-17}$ J. A photon that is emitted in a transition between these energy levels then has a wavelength $\lambda \simeq 1.12 \times 10^{-8}$ m (on the boundary between the ultraviolet and X-ray parts of the electromagnetic spectrum), which is indeed the correct order of magnitude observed in atomic transitions! Here we are effectively modelling a hydrogen atom as an electron confined to an atom-sized box, which is very crude; we shall treat the hydrogen atom more precisely in section 8. Nevertheless, the above computation is encouraging.

The full time-dependent wave functions (2.13) are

$$\Psi_n(x,t) \quad = \quad \begin{cases} B \sin \frac{n\pi x}{a}\, \mathrm{e}^{-in^2\pi^2\hbar t/2ma^2} , & 0 < x < a , \\ 0 , & \text{otherwise} . \end{cases} \qquad (2.21)$$

Any linear combination of such wave functions satisfies the time-dependent Schrödinger equation (2.11); in particular, the space of solutions, or possible wave functions, is *infinite dimensional.* In this example the energy levels E_n, and associated stationary state wave functions ψ_n,

are labelled naturally by a (positive) integer n. As we shall see throughout the course, such integers arise in many important solutions to the Schrödinger equation, and they are generally known as *quantum numbers* (although it is difficult to give a precise general definition).

2.5 Degeneracy

Having studied a particle in a one-dimensional box, it is now straightforward to extend this to a three-dimensional box.

Consider a particle confined to the box region given by $\{(x, y, z) \in \mathbb{R}^3 \mid 0 \le x \le a, 0 \le y \le b, 0 \le z \le c\} \subset \mathbb{R}^3$, where the potential is zero inside the box. In other words,

$$V(x, y, z) = \begin{cases} 0, & 0 < x < a, \ 0 < y < b, \ 0 < z < c, \\ +\infty, & \text{otherwise}. \end{cases} \tag{2.22}$$

As before, the stationary state wave function $\psi(\mathbf{r}) = \psi(x, y, z)$ is taken to be zero on, and outside, the boundary of the box region. Inside the box the stationary state Schrödinger equation (2.10) reduces to

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{2mE}{\hbar^2} \psi. \tag{2.23}$$

This may be solved by separation of variables. Equation (2.23) essentially reduces to three copies of the one-dimensional equation, with the wave functions labelled by three quantum numbers $n_1, n_2, n_3 \in \mathbb{Z}_{>0}$. Explicitly, inside the box these are given by

$$\psi_{n_1, n_2, n_3}(x, y, z) = B \sin \frac{n_1 \pi x}{a} \sin \frac{n_2 \pi y}{b} \sin \frac{n_3 \pi z}{c}, \tag{2.24}$$

with B again an arbitrary constant, and the corresponding energies are

$$E_{n_1, n_2, n_3} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right). \tag{2.25}$$

Exercise (Problem Sheet 1) Derive the wave functions (2.24) and energies (2.25) by solving (2.23) by separation of variables.

Definition If the space of solutions to the stationary state Schrödinger equation with energy E has dimension $d > 1$, we say this energy level is *d-fold degenerate*; if it is one-dimensional we say E is a *non-degenerate* energy level.

For the one-dimensional particle in a box all the energy levels are non-degenerate. However, consider now the three-dimensional box with equal length sides $a = b = c$, so that

$$E_{n_1, n_2, n_3} = \frac{\pi^2 \hbar^2}{2ma^2} \left(n_1^2 + n_2^2 + n_3^2 \right). \tag{2.26}$$

In this case there are *linearly independent* wave functions with the *same* energy. For example, we may take (n_1, n_2, n_3) to be any of $(2, 1, 1)$, $(1, 2, 1)$, $(1, 1, 2)$, all of which have the *same* energy $E = 6\pi^2 \hbar^2 / 2ma^2$. There is thus a three-fold degeneracy in the number of quantum stationary states with this energy. The degeneracy in this case is related to the *symmetry* of the potential. We shall see other examples of this later.

3 The Born interpretation

We have now met the Schrödinger equation and solved it in the simplest interesting example, namely a particle confined to a box. We have seen that this leads to quantized energy levels, and that by crudely modelling a hydrogen atom as an electron confined to an atom-sized box, we obtain energies of the correct order of magnitude seen in atomic transitions.

An immediate question is: *what is the physical meaning of the wave function* $\Psi(\mathbf{r}, t)$ *that we are solving for?* Comparing to the corresponding classical problem, described at the end of section 2.1, we may also ask: where is the particle at time t? In this section we shall answer these questions.

3.1 Probability density

In order to motivate the interpretation that follows, we begin by going back to the double slit experiment in section 1.3. In fact let us begin by discussing the corresponding experiment with light (also called *Young's experiment*). In this case the *intensity* of the light hitting the detector screen forms an interference pattern, and in classical electromagnetic theory this intensity is proportional to the *absolute value squared of the amplitude of the wave.* Unfortunately we won't have time to explain this in detail here, but this fact would have been well-known to the pioneers of quantum theory in the early 20th century. In the double slit experiment with electrons, we instead plot the spatial distribution of electrons hitting the detector screen over some long period of time, and then reinterpret this as a *probability distribution* for where any given electron will hit the screen.

If we now conflate these observations, we are led to the hypothesis that the *probability density function* for an electron hitting the detector screen is given by the *absolute value squared of the de Broglie wave* associated to the electron. Of course, the detector screen could be anywhere, and the de Broglie wave is precisely the wave function $\Psi(\mathbf{r}, t)$ appearing in the Schrödinger equation. Hence we arrive at:

Definition / postulate The function

$$\rho(\mathbf{r}, t) \equiv |\Psi(\mathbf{r}, t)|^2 , \tag{3.1}$$

is a *probability density function* for the position of the particle, where $\Psi(\mathbf{r}, t)$ is the particle's wave function.

This interpretation of Schrödinger's wave function is due to Born.

The assertion (3.1) is equivalent to the statement that the probability of finding the particle in a volume $D \subset \mathbb{R}^3$ is given by

$$P_\Psi(D) = \int_D |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x . \tag{3.2}$$

This probability depends both on the region D, and also on the wave function $\Psi(\mathbf{r}, t)$ satisfying the Schrödinger equation. We have already seen for the particle in a box that the space of

solutions to the Schrödinger equation is an infinite-dimensional vector space, with basis (2.21). A given solution is said to describe the *state* of the particle, so that the probabilities (3.2) depend on the state. Notice $P_\Psi(D)$ also depends in general on time t, although this is suppressed in the notation.

Of course, the above assertions immediately raise some issues. In particular, the probability of finding the particle *somewhere* in $\mathbb{R}^3$ should equal 1, at any time. Thus for (3.1), or equivalently (3.2), to make sense, the wave function must be *normalized* in the following sense:

Definition A wave function Ψ is said to be *normalizable* if

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \quad < \quad \infty \,, \qquad \forall \text{ time } t \,. \tag{3.3}$$

Moreover, if

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \quad = \quad 1 \,, \qquad \forall \text{ time } t \,, \tag{3.4}$$

then Ψ is said to be a *normalized wave function.*

Similar definitions apply in one dimension. For example, the normalized condition (3.4) becomes

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 \, \mathrm{d}x \quad = \quad 1 \,. \tag{3.5}$$

Let us make some remarks:

1. The normalized condition (3.4) fixes the freedom to multiply a given solution to the Schrödinger equation by a complex constant, up to a constant *phase* $\mathrm{e}^{\mathrm{i}\varphi}$. The latter is in fact not physical, so that wave functions differing by a constant phase are physically equivalent. Notice also that the normalized condition rules out the *trivial solution* $\Psi \equiv 0$.

2. For the particle in a box, the wave functions (2.21) are normalizable:

$$\int_{-\infty}^{\infty} |\Psi_n(x, t)|^2 \, \mathrm{d}x \quad = \quad |B|^2 \int_0^a \sin^2 \frac{n\pi x}{a} \, \mathrm{d}x \quad = \quad \frac{1}{2} a |B|^2 \,. \tag{3.6}$$

   The total wave functions

$$\Psi_n(x, t) \quad = \quad \begin{cases} \sqrt{\frac{2}{a}} \, \sin \frac{n\pi x}{a} \, \mathrm{e}^{-\mathrm{i}n^2\pi^2 \hbar t / 2ma^2} \,, & 0 < x < a \,, \\ 0 \,, & \text{otherwise} \,, \end{cases} \tag{3.7}$$

   with $B = \sqrt{2/a}$, are then *normalized.* Note that a particle being "confined to a box" may be interpreted as saying that there is *zero probability* of finding it anywhere outside the box, or in other words that the wave function is identically zero outside the box.

3. More generally, notice that for a stationary state of energy E, we have

$$\rho(\mathbf{r}, t) \quad = \quad |\Psi(\mathbf{r}, t)|^2 \quad = \quad \left| \psi(\mathbf{r}) \, \mathrm{e}^{-\mathrm{i}Et/\hbar} \right|^2 \quad = \quad |\psi(\mathbf{r})|^2 \,. \tag{3.8}$$

   Thus $\Psi(\mathbf{r}, t)$ is normalized for all time provided $\psi(\mathbf{r})$ is normalized, *i.e.*

$$\int_{\mathbb{R}^3} |\psi(\mathbf{r})|^2 \, \mathrm{d}^3 x \quad = \quad 1 \,. \tag{3.9}$$

4. Recall that the plane wave

$$\Psi(\mathbf{r}, t) \;=\; A \exp\left[\mathrm{i} \left(\mathbf{k} \cdot \mathbf{r} - \frac{\hbar |\mathbf{k}|^2 t}{2m} \right) \right] \;, \tag{3.10}$$

satisfies the free Schrödinger equation ($V = 0$), and was interpreted as describing a free particle of mass m and momentum $\mathbf{p} = \hbar \mathbf{k}$ – see the discussion around equation (2.1). However, clearly $|\Psi(\mathbf{r}, t)|^2 = |A|^2$ is not integrable over $\mathbb{R}^3$, and thus the plane wave is *not* normalizable! In fact the plane wave is better interpreted as a *beam* of particles of mass m and momentum $\mathbf{p}$.

Example (Particle in a box) Let us apply the above ideas to the particle in a one-dimensional box. The normalized wave functions are (3.7). The corresponding probability density functions are then, for $x \in [0, a]$, given by

$$\rho_n(x) \;=\; \frac{2}{a} \sin^2 \frac{n\pi x}{a} \;=\; \frac{1}{a} \left(1 - \cos \frac{2n\pi x}{a} \right) \;, \tag{3.11}$$

and identically zero outside the box. Plots of the probability density functions for the ground state and first two excited states are shown in Figure 6.
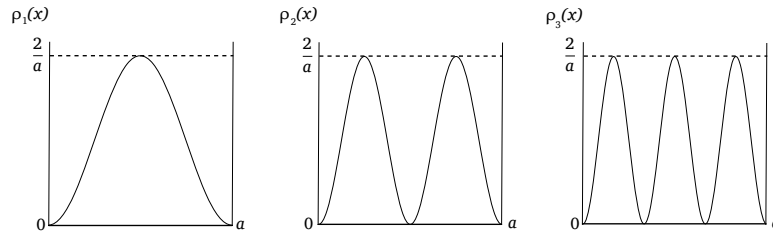

Figure 6: Probability density functions for the first three states of a particle in a box.

As usual in probability theory, we may define the *distribution function* as

$$F_n(x) \;\equiv\; \int_0^x \rho_n(y) \, \mathrm{d}y \;=\; \frac{x}{a} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{a} \;. \tag{3.12}$$

Notice in particular that the first term, $\frac{x}{a}$, is the result for the *uniform distribution*, where the particle is equally likely to be found anywhere in $[0, a]$. This is interpreted as the *classical result*. By this we mean that if we are ignorant of the state of the classical particle before we observe its position, then because it moves at constant velocity back and forth across the box, it is equally likely to be found anywhere. The second, oscillatory term in (3.12) is then a *quantum contribution*, or *quantum correction*, to the classical result.

Let us compute some example probabilities using these formulae. The probability that the particle is within $\frac{a}{4}$ distance from the centre of the box is given by

$$
\begin{aligned}
\int_{\frac{a}{4}}^{\frac{3a}{4}} |\psi_n(x)|^2 \, \mathrm{d}x &\;=\; F_n\left(\frac{3a}{4} \right) - F_n\left(\frac{a}{4} \right) \;, \\
&\;=\; \frac{1}{2} + \frac{1}{n\pi} \sin \frac{n\pi}{2} \;, \\
&\;=\; \begin{cases} \frac{1}{2} \;, & n \text{ even} \;, \\ \frac{1}{2} + \frac{(-1)^{(n-1)/2}}{n\pi} \;, & n \text{ odd} \;. \end{cases}
\end{aligned} \tag{3.13}
$$

In particular, we see that this *approaches the classical result* of $\frac{1}{2}$, for the uniform distribution, as $n \to \infty$. The tendancy of quantum results to approach those of the corresponding classical theory for large quantum numbers is called the *correspondence principle*.

We may similarly use the probability density ρ to compute *expectation values*:

Definition In quantum mechanics the *expectation value of a function of position $f(\mathbf{r})$* is denoted

$$\mathbb{E}_\Psi(f(\mathbf{r})) \equiv \int_{\mathbb{R}^3} f(\mathbf{r}) \, |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3x \; . \tag{3.14}$$

Notice that this expectation value depends on the wave function/state Ψ, and in general is a function of time t.

Example For the particle in a box we compute the expected value of its position

$$
\begin{aligned}
\mathbb{E}_{\Psi_n}(x) &= \int_0^a x \, \rho_n(x) \, \mathrm{d}x \; , \\
&= [x \, F_n(x)]_0^a - \int_0^a F_n(x) \, \mathrm{d}x \; , \\
&= a - \left[\frac{x^2}{2a} + \frac{a}{4n^2\pi^2} \cos\frac{2n\pi x}{a} \right]_0^a \; , \\
&= \frac{1}{2}a \; ,
\end{aligned}
\tag{3.15}
$$

agreeing with the classical result for the uniform distribution.

3.2 The continuity equation and boundary conditions

In this section we consider more carefully the *boundary conditions* involved in the Schrödinger equation.

Proposition 3.1 *The Schrödinger equation implies the* continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \; , \tag{3.16}$$

where $\rho(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2$ is the probability density we have already met, and the vector field

$$\mathbf{j}(\mathbf{r}, t) \equiv \frac{i\hbar}{2m} \left(\Psi(\mathbf{r}, t) \overline{(\nabla\Psi)(\mathbf{r}, t)} - \overline{\Psi(\mathbf{r}, t)}(\nabla\Psi)(\mathbf{r}, t) \right) \; , \tag{3.17}$$

is the probability current $\mathbf{j}$.

Proof This is a direct computation:

$$
\begin{aligned}
\frac{\partial}{\partial t} |\Psi(\mathbf{r}, t)|^2 &= \left(\frac{\partial}{\partial t} \overline{\Psi(\mathbf{r}, t)} \right) \Psi(\mathbf{r}, t) + \overline{\Psi(\mathbf{r}, t)} \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) \, , \\
&= \overline{\left[-\frac{i}{\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2\Psi + V\Psi \right) \right]} \Psi + \overline{\Psi} \left[-\frac{i}{\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2\Psi + V\Psi \right) \right] , \text{(Schrödinger)} \\
&= \frac{i}{\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2\overline{\Psi} + V\overline{\Psi} \right) \Psi - \overline{\Psi} \frac{i}{\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2\Psi + V\Psi \right) , \quad (V \text{ is real}) \\
&= \frac{i\hbar}{2m} \left(\overline{\Psi} \, \nabla^2\Psi - \Psi \, \nabla^2\overline{\Psi} \right) \, , \\
&= \frac{i\hbar}{2m} \nabla \cdot \left(\overline{\Psi} \, \nabla\Psi - \Psi \, \nabla\overline{\Psi} \right) = -\nabla \cdot \mathbf{j} \, . \quad \blacksquare
\end{aligned}
\tag{3.18}
$$

This leads to the following result:

Proposition 3.2 *Suppose that $\forall$ time t, $\mathbf{j}(\mathbf{r}, t)$ satisfies the boundary condition that it tends to zero faster than $1/|\mathbf{r}|^2$ as $|\mathbf{r}| = r \to \infty$. Then*

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \tag{3.19}$$

is independent of t. In particular, if Ψ is normalized at some time $t = t_*$, it is normalized $\forall t$.

Proof Let S be a closed surface that encloses a region $D \subset \mathbb{R}^3$. Then

$$\frac{\partial}{\partial t} \int_D |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \;=\; \int_D \frac{\partial \rho}{\partial t} \, \mathrm{d}^3 x \;, \quad \text{(derivative through the integral)}$$

$$=\; \int_D (-\nabla \cdot \mathbf{j}) \, \mathrm{d}^3 x \;, \quad \text{(continuity equation)}$$

$$=\; -\int_S \mathbf{j} \cdot \mathrm{d}\mathbf{S} \;, \quad \text{(Divergence Theorem)} \;. \tag{3.20}$$

Now take S to be a sphere of radius $r > 0$, centred on the origin, so that D is a ball. Then $\mathbf{n} = \dfrac{\mathbf{r}}{r}$ and hence

$$\mathbf{j} \cdot \mathrm{d}\mathbf{S} \;=\; \mathbf{j} \cdot \mathbf{n} \; r^2 \, \mathrm{d}S_{\text{unit}} \;, \tag{3.21}$$

where $\mathrm{d}S_{\text{unit}}$ is the area element on a *unit* radius sphere. In general, the function $\mathbf{j} \cdot \mathbf{n}$ will depend on r and the angular variables θ, ϕ on the sphere (and on time t). Provided $\mathbf{j} \cdot \mathbf{n} = o(1/r^2)$, uniformly in the angular coordinates, then using (3.21) the surface integral in (3.20) tends to zero as $r \to \infty$, and hence

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \;=\; 0 \;, \tag{3.22}$$

which implies that the expression in (3.19) is independent of t. ∎

We now state more formally the conditions that solutions to the Schrödinger equation should satisfy:

1. *The wave function $\Psi(\mathbf{r}, t)$ should be a continuous, single-valued function.* This condition ensures that the probability density $\rho = |\Psi|^2$ is single-valued and has no discontinuities. We already imposed the continuity property for the particle in a box.

2. *Ψ should be normalizable, i.e. the integral of $|\Psi|^2$ over all space should be finite.* Proposition 3.2 ensures that if the probability current $\mathbf{j}$ in (3.17) tends to zero fast enough at infinity, then this integral is independent of time t. Then if Ψ is normalizable, we may normalize it for all time. Without this condition, the probabilistic interpretation of the wave function is not possible. As already mentioned, this condition may be relaxed for free particles and scattering problems.

3. *$\nabla\Psi$ should be continuous everywhere, except where there is an infinite discontinuity in the potential V.* This condition follows since a finite discontinuity in $\nabla\Psi$ implies an infinite discontinuity in $\nabla^2\Psi$, and thus from the Schrödinger equation an infinite discontinuity in V. Again, we encountered precisely this behaviour for the particle in a box.

3.3 Measurement of energy

In section 2.2 we found separable solutions to the time-dependent Schrödinger equation (2.5). The corresponding stationary states (2.9) have definite frequency, and hence definite energy E. For example, the complete set of stationary state wave functions for a particle in a box is given by (3.7). Since the time-dependent Schrödinger equation is *linear*, any linear combination of such stationary state wave functions also solves the Schrödinger equation. Thus we may in general write

$$\Psi(\mathbf{r}, t) = \sum_n \alpha_n \, \psi_n(\mathbf{r}) \, e^{-iE_n t/\hbar} \, , \tag{3.23}$$

where n labels some set of stationary states $\psi_n(\mathbf{r})$ of energy E_n, and $\alpha_n \in \mathbb{C}$ are constants.

For the particle in a box, (3.23) is simply a *Fourier sine series*. From Prelims you know that any sufficiently well-behaved[3] function $f : [0, a] \to \mathbb{C}$ with $f(0) = f(a) = 0$ can be expanded as a Fourier sine series

$$f(x) \;=\; \sum_{n=1}^{\infty} \alpha_n \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \;=\; \sum_{n=1}^{\infty} \alpha_n \, \psi_n(x) \, , \tag{3.24}$$

for appropriate α_n. Then given *any* such function $f(x)$, we obtain a corresponding solution to the time-dependent Schrödinger equation using (3.23):

$$\Psi(x, t) \;=\; \sum_{n=1}^{\infty} \alpha_n \, \psi_n(x) \, e^{-iE_n t/\hbar} \, , \tag{3.25}$$

where the coefficients α_n are determined via (3.24), and for the particle in a box the energies E_n are given by (2.19). We have thus solved the initial value problem for the Schrödinger equation, with $\Psi(x, t = 0) = f(x)$. Note that the normalized stationary state wave functions $\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ are also orthonormal

$$\int_0^a \psi_m(x) \, \psi_n(x) \, dx \;=\; \delta_{mn} \, . \tag{3.26}$$

Definition / interpretation Suppose that the *normalized* wave function for a particle in a box is given by (3.25). Then the *probability* of measuring the energy of the particle to be E_n is $|\alpha_n|^2$.

This definition makes sense, since

$$1 \;=\; \int_0^a |\Psi(x, t)|^2 \, dx \;=\; \sum_{m,n=1}^{\infty} \overline{\alpha}_m \, \alpha_n \, e^{-i(E_n - E_m)t/\hbar} \int_0^a \overline{\psi}_m(x) \, \psi_n(x) \, dx \;=\; \sum_{n=1}^{\infty} |\alpha_n|^2 \, . \tag{3.27}$$

Notice that if the particle's wave function is a stationary state of energy E_n, then the probability of measuring the particle's energy to be E_n is 1. It thus makes sense to say that a stationary state (2.9) describes a particle of *definite energy E*.

---

[3]* For the application to wave functions below, we require the wave function to be *normalizable* as in (3.3). For the particle in a box example, this implies that $\int_0^a |f(x)|^2 \, dx < \infty$. In fact this is then sufficient for the Fourier series (3.24) to converge almost everywhere to $f(x)$.

In fact the expansion (3.23) of any wave function $\Psi(\mathbf{r},t)$ exists under very general conditions, *i.e.* for general choices of potential $V(\mathbf{r})$, and generalizes to cases with degenerate energy levels or even a continuous energy spectrum.

4   The harmonic oscillator

The quantum harmonic oscillator is probably the most important solution to the Schrödinger equation.

4.1   The one-dimensional harmonic oscillator

By this we mean simple harmonic motion which is ubiquitous in classical mechanics as the following discussion shows:

Consider a particle of mass m moving in one dimension under the influence of a potential $V(x)$. Near to a critical point x_0 of V, where $V'(x_0) = 0$, we have the Taylor expansion

$$V(x) = V(x_0) + \tfrac{1}{2}V''(x_0)(x - x_0)^2 + O\left((x - x_0)^3\right) \ .$$

If $V''(x_0) > 0$ then x_0 is a *local minimum* of the potential. Without loss of generality let us choose coordinates where the critical point x_0 is at the origin. Then to lowest order the potential near to $x_0 = 0$ is

$$V(x) = V(0) + \frac{1}{2}m\omega^2 x^2 \ ,$$

where we have defined $\omega^2 = V''(0)/m$. The dynamics is not affected by the value of $V(0)$, since an additive constant drops out of the force $F = -V'$. The *harmonic oscillator potential* is

$$V(x) \;=\; \frac{1}{2}m\omega^2 x^2 \ . \tag{4.1}$$

The above analysis shows that *any* system near to a point of stable equilibrium is described by this potential. Classically, we have the force $F = -V' = -m\omega^2 x$ so that Newton's equation can be taken to be

$$m\ddot{x} = -m\omega^2 x.$$

We now turn to the corresponding quantum mechanical problem. The stationary state Schrödinger equation (2.12) of energy E is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi \;=\; E\psi \ . \tag{4.2}$$

The first thing to do is to redefine variables so as to remove the various physical constants:

$$\epsilon \;\equiv\; \frac{2E}{\hbar\omega} \ , \qquad \xi \;\equiv\; \sqrt{\frac{m\omega}{\hbar}}x \ , \tag{4.3}$$

so that (4.2) becomes

$$-\frac{d^2\chi}{d\xi^2} + \xi^2\chi \;=\; \epsilon\chi \ , \tag{4.4}$$
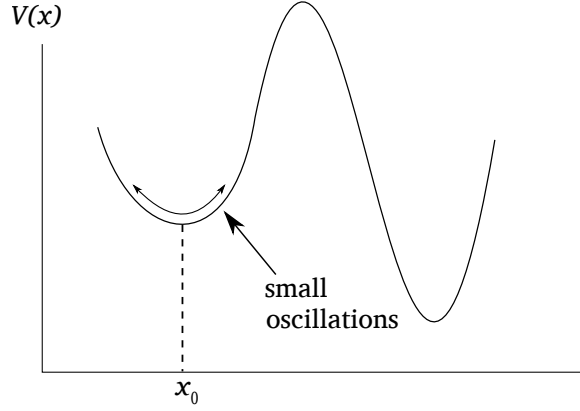
Figure 7: A particle performing small oscillations around a point of stable equilibrium of any potential $V(x)$ is described to lowest order by a harmonic oscillator.

where we have defined

$$\psi(x) \;\equiv\; \chi(\xi) \;=\; \chi\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \;. \tag{4.5}$$

Although at first sight (4.4) looks like a fairly simple ODE, depending on a single constant ϵ, in fact it is not so simple to solve. However, it is not difficult to spot that $\chi(\xi) = e^{\mp \xi^2/2}$ solve (4.4) with $\epsilon = \pm 1$. To see this, we compute

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left(e^{\mp\xi^2/2}\right) \;=\; \mp\xi\, e^{\mp\xi^2/2} \;, \qquad \frac{\mathrm{d}^2}{\mathrm{d}\xi^2}\left(e^{\mp\xi^2/2}\right) \;=\; (\xi^2 \mp 1)\, e^{\mp\xi^2/2} \;. \tag{4.6}$$

As discussed in section 3, we are only interested in *normalizable* solutions to the Schrödinger equation. For a stationary state, this means that

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, \mathrm{d}x < \infty \;. \tag{4.7}$$

Via the change of variable (4.3), (4.5), for $\chi(\xi) = e^{\mp \xi^2/2}$ the left hand side of (4.7) is

$$\sqrt{\frac{\hbar}{m\omega}} \int_{-\infty}^{\infty} e^{\mp\xi^2} \, \mathrm{d}\xi \;, \tag{4.8}$$

which is finite only for the minus sign, giving a Gaussian integral. Thus the solution $\chi(\xi) = e^{+\xi^2/2}$, with $\epsilon = -1$, is *not* normalizable, and we thus discard it.

We now again change variables by defining

$$\chi(\xi) \;\equiv\; f(\xi)\, e^{-\xi^2/2} \;, \tag{4.9}$$

so that

$$\begin{aligned}
\frac{\mathrm{d}\chi}{\mathrm{d}\xi} &= \left(\frac{\mathrm{d}f}{\mathrm{d}\xi} - \xi f\right) e^{-\xi^2/2} \;, \\
\frac{\mathrm{d}^2\chi}{\mathrm{d}\xi^2} &= \left[\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} - \xi\frac{\mathrm{d}f}{\mathrm{d}\xi} - f - \xi\left(\frac{\mathrm{d}f}{\mathrm{d}\xi} - \xi f\right)\right] e^{-\xi^2/2} \;,
\end{aligned} \tag{4.10}$$

and hence (4.4) becomes

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}f}{\mathrm{d}\xi} + (\epsilon - 1)\, f \;=\; 0 \;. \tag{4.11}$$

If anything, this looks worse than (4.4), so you might wonder why we bothered with (4.9)! The reasoning here is that for large values of $|\xi|$ the $\xi^2 \chi$ term in (4.4) will dominate over the $\epsilon \chi$ term; thus for large $|\xi|$ one expects solutions for different ϵ to have the same behaviour to leading order. This is why we have written $\chi(\xi)$ in (4.9) as the above normalizable $\epsilon = +1$ solution times some other function $f(\xi)$.

It is still not clear how to solve (4.11) exactly, so as usual for this type of equation we try a power series solution.[4] Thus we write

$$f(\xi) \;=\; \sum_{k=0}^{\infty} a_k\, \xi^k \;, \tag{4.12}$$

and compute

$$\xi \frac{\mathrm{d}f}{\mathrm{d}\xi} \;=\; \sum_{k=0}^{\infty} k\, a_k\, \xi^k \;, \tag{4.13}$$

and

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} \;=\; \sum_{k=0}^{\infty} (k+1)(k+2)\, a_{k+2}\, \xi^k \;. \tag{4.14}$$

Notice that the last expression involves a relabelling of the original sum. By substituting (4.12), (4.13) and (4.14) into (4.11) we obtain

$$\sum_{k=0}^{\infty} \left[(k+1)(k+2)\, a_{k+2} - 2k\, a_k + (\epsilon - 1)\, a_k \right] \xi^k \;=\; 0 \;. \tag{4.15}$$

The coefficient of every power of ξ must be separately zero, so we obtain the recurrence relation

$$a_{k+2} \;=\; \frac{2k + 1 - \epsilon}{(k+1)(k+2)}\, a_k \;. \tag{4.16}$$

The even and odd powers are then decoupled, giving rise to the two linearly independent series solutions

$$
\begin{aligned}
f_{\text{even}}(\xi) \;&=\; a_0 \left[1 + \frac{(1-\epsilon)}{2!}\xi^2 + \frac{(5-\epsilon)(1-\epsilon)}{4!}\xi^4 + \cdots \right] \;, \\
f_{\text{odd}}(\xi) \;&=\; a_1 \left[\xi + \frac{(3-\epsilon)}{3!}\xi^3 + \frac{(7-\epsilon)(3-\epsilon)}{5!}\xi^5 + \cdots \right] \;.
\end{aligned}
\tag{4.17}
$$

Definition In one dimension a stationary state wave function satisfying $\psi(-x) = \pm \psi(x)$ is said to describe an $\begin{Bmatrix} \text{even} \\ \text{odd} \end{Bmatrix}$ parity state.

Recalling equations (4.3), (4.5) and (4.9), the total stationary state wave functions are $f_{\text{even/odd}}(\xi)\, \mathrm{e}^{-\xi^2/2}$, which then describe even and odd parity states, respectively.

We must now determine when these solutions are normalizable. It turns out that this is the case if and only if the series in (4.17) *terminate*. We shall not provide a full, rigorous proof

---

[4] * This is a topic that could have been included in the 'core' Part A Differential Equations course, but has been left to the DE2 option. The point $\xi = 0$ is an *ordinary point* of (4.11), and then *Fuchs' theorem* guarantees that any solution may be expressed as a convergent Taylor series (4.12). The interested reader is referred to appendix A. Having said this, most quantum mechanics textbooks suppress these details.

of this here, but instead sketch the proof. This is purely for reasons of time. A more detailed treatment may be found in the book by Hannabuss.

Notice first that either of the series in (4.17) terminating is equivalent to the statement that $f(\xi)$ is a *polynomial*, which in turn is equivalent to the statement that $a_{n+2} = 0$ for some integer $n \geq 0$, since then the recurrence relation (4.16) implies that $a_k = 0$ for all $k \geq n + 2$. Note that a_0 and a_1 are necessarily non-zero, otherwise $f_{\text{even/odd}}(\xi) \equiv 0$, respectively.

Suppose that either series in (4.17) does *not* terminate. Then all the coefficients are non-zero, and the ratio

$$\frac{a_{k+2}}{a_k} \longrightarrow \frac{2}{k} , \qquad \text{as } k \to \infty . \tag{4.18}$$

Compare this asymptotic behaviour of the power series coefficients with that of the function e^{ξ^2}:

$$e^{\xi^2} = \sum_{q=0}^{\infty} \frac{1}{q!} \xi^{2q} = \sum_{k=0}^{\infty} b_k \xi^k , \tag{4.19}$$

where we have defined the coefficients

$$b_k = \begin{cases} \frac{1}{q!} , & k = 2q , \\ 0 , & k = 2q + 1 . \end{cases} \tag{4.20}$$

For $k = 2q$ even we then have

$$\frac{b_{k+2}}{b_k} = \frac{\left(\frac{k}{2}\right)!}{\left(\frac{k+2}{2}\right)!} = \frac{2}{k+2} \longrightarrow \frac{2}{k} , \qquad \text{as } k \to \infty . \tag{4.21}$$

Comparing to (4.18), we thus see that $f_{\text{even}}(\xi)$ and e^{ξ^2} have the same asymptotic expansion. Hence the total stationary state wave function is

$$\chi(\xi) = f(\xi) e^{-\xi^2/2} \sim e^{\xi^2/2} , \tag{4.22}$$

and thus $\psi(x) = \chi(\xi)$ is not normalizable.[5] A similar argument applies to $f_{\text{odd}}(\xi)$ and the function $\xi\, e^{\xi^2}$. Thus for a normalizable solution the series in (4.17) must terminate. If $n \geq 0$ is the least integer for which $a_{n+2} = 0$ then the recurrence relation (4.16) implies

$$2n + 1 - \epsilon = 0 . \tag{4.23}$$

Recalling the definition $\epsilon = 2E/\hbar\omega$ in terms of the energy E in (4.3) then gives

$$E = E_n = \left(n + \tfrac{1}{2}\right) \hbar\omega . \tag{4.24}$$

The quantum harmonic oscillator energies are hence labelled by the quantum number $n \in \mathbb{Z}_{\geq 0}$; compare to (2.19) for the particle in a box (and notice there that we instead defined n so that $n \in \mathbb{Z}_{>0}$). Also note that our initial solution with $f \equiv 1$ and $\epsilon = +1$ is in fact the *ground state*, with $n = 0$. Reverting back to the original spatial coordinate x via (4.3) and (4.5), the ground state wave function is hence

$$\psi_0(x) = a_0\, e^{-m\omega x^2/2\hbar} , \tag{4.25}$$

---

[5]It is the last step in (4.22) that needs a little more work to make rigorous.

where a_0 is a normalization constant, with corresponding *ground state energy* $E_0 = \frac{1}{2}\hbar\omega$. The normalized ground state wave function may be obtained by imposing

$$1 = |a_0|^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar}\, dx \ . \tag{4.26}$$

The Gaussian integral is that for a normal distribution of variance $\sigma^2 = \hbar/2m\omega$, and thus via the standard result for this integral we have

$$|a_0|^2 = \sqrt{\frac{m\omega}{\pi\hbar}} \ , \tag{4.27}$$

leading to the full, normalized time-dependent ground state wave function

$$\Psi_0(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-(m\omega x^2 + i\,\hbar\omega t)/2\hbar} \ . \tag{4.28}$$

More generally the stationary state wave functions are $\chi_n(\xi) = f_n(\xi)\, e^{-\xi^2/2}$, where $f_n(\xi)$ is an even/odd polynomial in $\xi = \sqrt{\frac{m\omega}{\hbar}}x$ of degree n, for n even/odd, respectively. The polynomials f_n may be determined explicitly by setting $\epsilon - 1 = 2n$ in the recurrence relation (4.16).

* Appropriately normalized, $f_n(\xi) \equiv H_n(\xi)$ is called the *nth Hermite polynomial*. The first few polynomials are given in Table 1, with the corresponding wave functions shown in Figure 8.

n	$H_n(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$

Table 1: The first four Hermite polynomials.

4.2 Higher dimensional oscillators

Having discussed the one-dimensional oscillator, it is now straightforward to extend this to oscillators in higher dimensions.

Let us begin by considering a quantum harmonic oscillator in two dimensions, with potential

$$V(x,y) = \frac{1}{2}m\left(\omega_1^2 x^2 + \omega_2^2 y^2\right) \ . \tag{4.29}$$

The corresponding stationary state Schrödinger equation (2.10) is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) + V(x,y)\psi = E\psi \ . \tag{4.30}$$

As for the particle in a box, this may be solved by separation of variables. One writes $\psi(x,y) = X(x)Y(y)$, so that (4.30) separates into

$$-\frac{\hbar^2}{2m}\frac{d^2 X}{dx^2} + \frac{1}{2}m\omega_1^2 x^2 X = E_1\, X \ ,$$
$$-\frac{\hbar^2}{2m}\frac{d^2 Y}{dy^2} + \frac{1}{2}m\omega_2^2 y^2 Y = E_2\, Y \ , \tag{4.31}$$
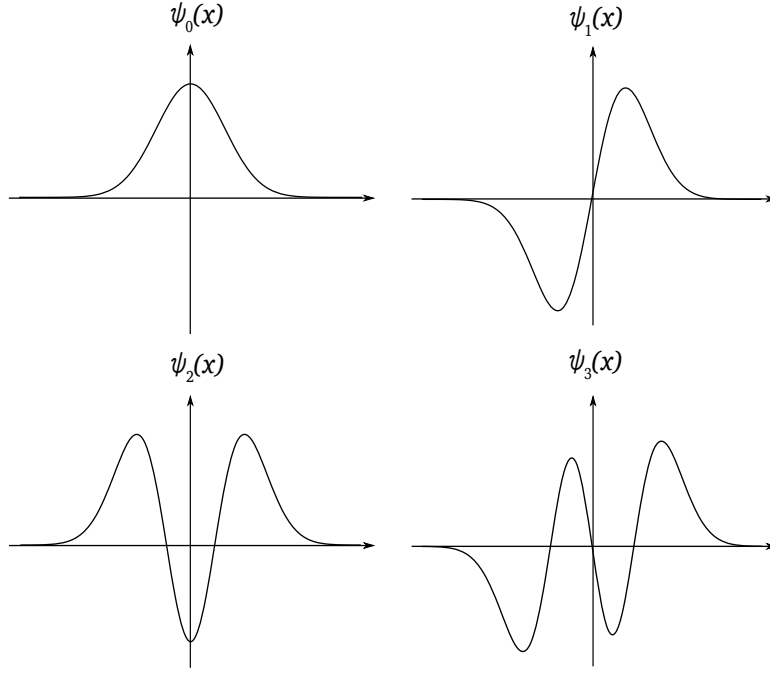
Figure 8: The ground state and first three excited state wave functions of the harmonic oscillator.

where $E_1 + E_2 = E$. We thus have two decoupled one-dimensional oscillators, and it follows from the previous section that

$$E \;=\; E_{n_1, n_2} \;=\; \left(n_1 + \tfrac{1}{2}\right)\hbar\omega_1 + \left(n_2 + \tfrac{1}{2}\right)\hbar\omega_2 \,, \tag{4.32}$$

where the quantum numbers $n_1, n_2 \in \mathbb{Z}_{\geq 0}$. The wave-functions will be products

$$\psi_{n_1 n_2}(x, y) = \psi_{n_1}(x)\psi_{n_2}(y).$$

Of course the quadratic form appearing in (4.29) is rather special, in that it is diagonal. One can treat more general quadratic forms by first changing to *normal coordinates*, *i.e.* one first diagonalizes V by an *orthogonal transformation*. Let us illustrate with an example:

Example Consider the oscillator potential

$$V(x, y) \;=\; m\omega^2(x^2 + xy + y^2) \;=\; \frac{1}{2}m\omega^2 \left(\begin{array}{cc} x & y \end{array}\right)\left(\begin{array}{cc} 2 & 1 \\ 1 & 2 \end{array}\right)\left(\begin{array}{c} x \\ y \end{array}\right). \tag{4.33}$$

The matrix here has eigenvalues 3 and 1, so there exists an orthogonal transformation to coordinates u, v with corresponding new potential

$$\begin{aligned}
\widetilde{V}(u, v) \;&=\; \frac{1}{2}m\omega^2 \left(\begin{array}{cc} u & v \end{array}\right)\left(\begin{array}{cc} 3 & 0 \\ 0 & 1 \end{array}\right)\left(\begin{array}{c} u \\ v \end{array}\right), \\
&=\; \frac{1}{2}m\left(3\omega^2 u^2 + \omega^2 v^2\right),
\end{aligned} \tag{4.34}$$

which is now of the form (4.29).[6] The orthogonality of the transformation ensures that the Laplacian/kinetic term in the Schrödinger equation is invariant, so

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \;=\; \frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial v^2}\,. \tag{4.35}$$

---

[6]Explicitly, $u = \frac{1}{\sqrt{2}}(x + y)$, $v = \frac{1}{\sqrt{2}}(x - y)$.

Of course, since any quadratic form for V is described by a *symmetric matrix*, we may always diagonalize the potential by an orthogonal transformation, thus reducing the problem to a diagonal form for V, as in (4.29). These remarks apply in any dimension: first change to normal coordinates, then separate variables one at a time. The Schrödinger equation for *any* quadratic potential then reduces to a decoupled set of one-dimensional oscillators, so that the total energy = sum of one-dimensional energies, and the total wave functions = product of one-dimensional wave functions.

We conclude this section with another example of degenerate energy levels:

Example (Degeneracy) Consider the original two-dimensional oscillator potential (4.29) with $\omega_1 = \omega_2 = \omega$. Then

$$E \;=\; E_n \;=\; (n+1)\hbar\omega \;, \tag{4.36}$$

where $n = n_1 + n_2$. The ground state is $n_1 = n_2 = 0$, which is the unique state of energy $\hbar\omega$. However, more generally at level n there are $n + 1$ linearly independent wave functions with energy E_n, given by taking (n_1, n_2) to be $(n, 0)$, $(n - 1, 1)$, ..., $(1, n - 1)$, $(0, n)$. Thus E_n has degeneracy $n + 1$. Again, notice this degeneracy is related to the symmetry of the potential.

5 The Mathematical Structure of Quantum Theory

Now that we have made some progress with quantum theory, we take some time to look at what we have and give a more formal mathematical account.

5.1 States and Observables

Making precise where we've been led to, we introduce some formal definitions:

- the *states* of a quantum system are elements of a complex vector space $\mathcal{H}$, finite or infinite dimensional, equipped with a Hermitian inner product that we'll write $< u|v >$ for $u, v \in \mathcal{H}$;

- proportional vectors represent the same state;

- a state ψ is *normalised* if
$$||\psi||^2 :=< \psi|\psi >= 1,$$
(which allows the freedom $\psi \to \psi e^{i\theta}$) and *normalisable* if $||\psi||^2$ is finite.

- the *observables* of the quantum system are self-adjoint linear transformations A of $\mathcal{H}$ (so $A = A^*$ where A^* is defined by
$$< A^*\phi|\psi >=< \phi|A\psi > \quad \text{for } \phi, \psi \in \mathcal{H}).$$

The important example is for $\mathcal{H}$ to be complex-valued functions $\psi(\mathbf{x})$ on $\mathbb{R}^3$ with

$$< \phi|\psi >:= \int_{\mathbb{R}^3} \bar{\phi}\psi.$$

Then there are some special observables:

- the *position operator* $\mathbf{X} = (X_1, X_2, X_3)$ defined by

$$X_j \psi(\mathbf{x}) = x_j \psi(\mathbf{x}) \text{ for } j = 1, 2, 3;$$

- the *momentum operator* $\mathbf{P} = (P_1, P_2, P_3)$ defined by

$$P_j \psi(\mathbf{x}) = -i\hbar \frac{\partial}{\partial x_j} \psi(\mathbf{x}) \text{ for } j = 1, 2, 3.$$

- Once we have those we can introduce a name for one we've seen before:

$$H :== \frac{1}{2m}(P_1^2 + P_2^2 + P_3^2) + V(X_1, X_2, X_3),$$

which is the *Hamiltonian* for a particle of mass m nmoving in a potential V.

If we are concerned with the one-dimensional case we have instead

$$X\psi = x\psi, \quad P\psi = -i\hbar\psi'.$$

Self-adjointness for $\mathbf{X}$ and X are obvious. We'll check self-adjointness for the one-dimensional P:

$$< P^*\phi | \psi > = < \phi | P\psi > = \int_{-\infty}^{\infty} \bar{\phi}(-i\hbar)\psi' dx$$

$$= [-i\hbar\phi\psi]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} i\hbar\bar{\phi}'\psi dx = < P\phi | \psi >,$$

so $P^* = P$. (This assumes that ϕ, ψ are both differentiable and fall off to zero at large distances. This raises some technical issues which we'll note but not deal with: X and P are in fact only defined on a subspace of $\mathcal{H}$.)

5.2   More mathematical refinements (not for examination)

More restrictions are actually necessary on $\mathcal{H}$ to be prevent it being 'too infinite'. I'll mention these but not dwell on them.

- $\mathcal{H}$ must be *complete*, in the sense that every Cauchy sequence converges i.e. if $\{\psi_n\}$ is a sequence such that, for any ϵ there is an integer N with $||\psi_m - \psi_n|| < \epsilon$ for $m, n > N$ then there is a limit $\psi_\infty \in \mathcal{H}$ with $||\psi_n - \psi_\infty|| \to 0$.

- call a subset S of $\mathcal{H}$ *dense* if for any $\psi \in \mathcal{H}$ and any positive real ϵ there is a $\phi \in S$ with $||\psi - \phi|| < \epsilon$. Then we insist that $\mathcal{H}$ contains a *countable, dense subset*.

With these two conditions, $\mathcal{H}$ is a *Hilbert space*. We've seen that there will also be technical issues surrounding self-adjoint operators.

5.3   Statistical Aspects of Quantum Theory

One of the assumptions of quantum theory is that the only possible result of the measurement of an observable is one of the eigenvalues of the corresponding operator. This motivates the definition: *the expectation of an observable A in a normalisable state ψ is*

$$\mathbb{E}_\psi(A) = \frac{<\psi|A\psi>}{<\psi|\psi>}. \tag{5.1}$$

Evidently this simplifies for a normalised state to $\mathbb{E}_\psi(A) =< \psi|A\psi >$. With $\mathcal{H}$ being functions on the line, this would give, for e.g. an operator $V(x)$

$$\mathbb{E}_\psi(V) =< \psi|V\psi >= \int \bar{\psi}V\psi dx = \int \rho V dx,$$

which is natural, and in line with (3.14) and (3.27).

5.3.1   Some Properties of Expectation

1. For the identity operator I, $\mathbb{E}_\psi(I) = 1$;

2. For self-adjoint A, $\mathbb{E}_\psi(A)$ is real;

3. For positive A, $\mathbb{E}_\psi(A) \geq 0$ (here positive just means $< \psi|A\psi >\geq 0$);

4. Linearity in A:
$$\mathbb{E}_\psi(\alpha A + \beta B) = \alpha\mathbb{E}_\psi(A) + \beta\mathbb{E}_\psi(B).$$

Only the second is not obvious. For that

$$< \psi|A\psi >=< A\psi|\psi >= \overline{< \psi|A\psi >}.$$

Expectation is like mean in probability. Then for standard deviation we define: the *dispersion* of A in a state ψ is

$$\Delta_\psi(A) = (\mathbb{E}_\psi(A^2) - (\mathbb{E}_\psi(A))^2)^{1/2}. \tag{5.2}$$

Proposition

$\Delta_\psi(A) = 0$ iff ψ is an eigenstate of A.

Proof

Suppose ψ is normalised and consider, for real μ

$$\mathbb{E}_\psi((A - \mu I)^2) =< \psi|(A - \mu I)^2\psi >=< (A - \mu I)\psi|(a - \mu I)\psi >= ||(A - \mu I)\psi||^2,$$

but also

$$= \mathbb{E}_\psi(A^2) - 2\mu\mathbb{E}_\psi(A) + \mu^2.$$

Now set $\mu = \mathbb{E}_\psi(A)$ then this is

$$= (\Delta_\psi(A))^2.$$

So $\Delta_\psi(A) = 0$ iff $||(A - \mu I)\psi|| = 0$ iff $(A - \mu I)\psi = 0$, i.e. iff $A\psi = \mu\psi$, which proves it.

To make a connection with the Born interpretation, section 3, suppose that $\mathcal{H}$ has an orthonormal basis of eigen-vectors of A, say $\{\psi_\lambda\}$ such that $\langle \psi_\lambda | \psi_{\lambda'} \rangle = \delta_{\lambda,\lambda'}$ and with

$$A\psi_\lambda = \alpha_\lambda \psi_\lambda,$$

then for any other normalised $\psi \in \mathcal{H}$ we have

$$\psi = \sum_\lambda c_\lambda \psi_\lambda$$

so that $< \psi_\lambda | \psi >= c_\lambda$ and

$$\mathbb{E}_\psi(A) =< \psi | A\psi >= \sum c_\lambda < \psi | A\psi_\lambda >$$

$$= \sum c_\lambda \alpha_\lambda < \psi | \psi_\lambda >= \sum \alpha_\lambda |c_\lambda|^2.$$

We make the identification:

$$|c_\lambda|^2 = \text{Prob(measurement of } A \text{ gives } \alpha_\lambda)$$

then this is the expectation in the usual sense from probability theory.

An Important Point

We can't assume for any observable that there exists a basis of normalisable eigenvectors. For example with $P = -i\hbar\partial/\partial x$ the eigenvectors are $\psi = e^{ikx}$ which is never normalisable, while with $X = x$ the situation is worse: the eigenvalue equation would be

$$X\psi(x) = x\psi(x) = a\psi(x) \text{ or } (x-a)\psi(x) = 0$$

so that $\psi(x) = 0$ whenever $x \neq a$; now continuity would force $\psi = 0$ always and there don't even exist continuous eigenfunctions.

5.3.2 Example

Recall the square well with Hamiltonian $H = \frac{1}{2m}P^2$ and $0 \leq x \leq a$. This has stationary state eigenfunctions $\psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$ with corresponding energy eigenvalue $E_n = \frac{n^2\pi^2\hbar^2}{a^2}$ for any positive integer n. For any stationary state we calculate

$$\mathbb{E}_{\psi_n}(P) = \int_0^a \bar{\psi}_n(-i\hbar)\psi_n' dx$$

$$= -i\hbar.\frac{2}{a}.\frac{n\pi}{a}\int_0^a \sin\frac{n\pi x}{a}\cos\frac{n\pi x}{a}dx = 0.$$

Thus the expectation of P in a stationary state is zero: on the average the particle moves neither left nor right. Next

$$\mathbb{E}_{\psi_n}(P^2) = 2m\mathbb{E}_{\psi_n}(H) = 2mE_n = 2m\frac{n^2\pi^2\hbar^2}{a^2},$$

and this is then $(\Delta_{\psi_n}(P))^2$: the momentum has zero mean but nonzero dispersion.

5.4   Measurements and Collapse of the Wave Function

An assumption of quantum mechanics that we noted in subsection 5.3 is that a measurement of an observable A in a state ψ must yield an eigenvalue of A, with different probabilities which depend on ψ. However it is an assumption of physical reasonableness on the theory that a second measurement immediately following the first must give the same answer with probability one. This entails that, after the first measurement, the wave-function is in an eigenstate with the measured eigenvalue. One says that the wave-function has *collapsed into the eigenspace*, or just simply *collapsed*. The norm will no longer be one: the Schrödinger equation preserves the norm with time but measurements do not.

* There may be *degeneracy*, i.e. the eigenspace for a particular eigenvector may have dimension greater than one. In this case one is led to make *Luder's Postulate*:
if Q is the projection to the subspace of $\mathcal{H}$ spanned by eigenvectors of A consistent with the measurement on ψ then after the measurement the wave-function is $Q\psi$.

6 The Commutation Relations and the Uncertainty Principle

6.1 The Commutation Relations

Recall from section 5.1 the definitions

$$X\psi = x\psi, \quad P\psi = -i\hbar\psi'.$$

Then

$$PX\psi = -i\hbar(x\psi)' = -i\hbar(x\psi' + \psi),$$

while

$$XP\psi = x(-i\hbar\psi'),$$

so that

$$(PX - XP)\psi = -i\hbar\psi,$$

and this will hold for all ψ.

Define *the commutator* of observables A, B as

$$[A, B] = AB - BA \tag{6.1}$$

then we have found that

$$[P, X] = -i\hbar I, \tag{6.2}$$

where I is the identity operator. Repeating in 3 dimensions we see that

$$[P_i, X_j] = -i\hbar\delta_{ij}I, \tag{6.3}$$

in terms of the *Kronecker delta*:

$$\delta_{ij} = 1 \text{ if } i = j \text{ and is otherwise zero,}$$

and that

$$[P_i, P_j] = 0 = [X_i, X_j]. \tag{6.4}$$

6.1.1 Properties of Commutators

1. antisymmetry: $[A, B] = -[B, A]$;

2. if $[A, B] = iC$ with A, B self-adjoint, then C is also self-adjoint;

3. the Leibniz rule: $[A, BC] = B[A, C] + [A, B]C$;

4. linearity in A (and therefore in B too);

5. the Jacobi identity: $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

These can all be proved by expanding the commutator (remembering to preserve the order of terms).

6.2 Heisenberg's Uncertainty Principle

We'll prove a proposition first:

Proposition

Given self-adjoint A, B, C with $[A, B] = iC$:

1. for real t, $(A - itB)^*(A - itB) = A^2 + tC + t^2B^2$;

2. for any normalised ψ

$$||(A - itB)\psi||^2 = \mathbb{E}_\psi(A^2) + t\mathbb{E}_\psi(C) + t^2\mathbb{E}_\psi(B^2);$$

3. for any normalised ψ

$$\mathbb{E}_\psi(A^2)\mathbb{E}_\psi(B^2) \geq \frac{1}{4}(\mathbb{E}_\psi(C))^2, \tag{6.5}$$

with equality iff for some ψ and some real t, $(A - itB)\psi = 0$.

Proof

For 1:

$$(A - itB)^*(A - itB) = (A + itB)(A - itB) = A^2 - it(AB - BA) + t^2B^2 = A^2 + tC + t^2B^2.$$

For 2:

$$||(A - itB)\psi||^2 = < (A - itB)\psi|(A - itB)\psi > = < \psi|(A - itB)^*(A - itB)\psi >$$

$$= < \psi|(A^2 + tC + t^2B^2)\psi > = \mathbb{E}_\psi(A^2) + t\mathbb{E}_\psi(C) + t^2\mathbb{E}_\psi(B^2).$$

Finally for 3, the LHS in 2 is greater than or equal to zero and vanishes only if $(A - itB)\psi = 0$, so the RHS is a quadratic with nonpositive discriminant and this is (6.5).

Corollary: Heisenberg's Uncertainty Principle

For normalised ψ we have

$$\Delta_\psi(P)\Delta_\psi(X) \geq \frac{1}{2}\hbar, \tag{6.6}$$

with equality iff

$$\psi = \text{constant} \times \exp\left(-\frac{t}{2\hbar}(x - \mu)^2\right), \tag{6.7}$$

with positive real t and complex μ. (It is traditional to use t here but **N.B. t is not time here**).

Proof

Set

$$A = P - \mathbb{E}_\psi(P), \quad B = X - \mathbb{E}_\psi(X),$$

Then

$$A, B] = [P, X] = -i\hbar I \text{ so } C = -\hbar I.$$

Next
$$\mathbb{E}_\psi(A^2) = (\Delta_\psi(P))^2, \ \ \mathbb{E}_\psi(B^2) = (\Delta_\psi(X))^2, \ \ \mathbb{E}_\psi(C) = -\hbar,$$

and now (6.5) gives (6.6).

For (6.7), equality means there are t, ψ with $(A - itB)\psi = 0$. Set $\lambda = \mathbb{E}_\psi(P) - it\mathbb{E}_\psi(X)$ then

$$0 = (A - itB)\psi = (-i\hbar\frac{d}{dx} - itx - \lambda)\psi,$$

which can be rearranged as

$$\frac{\psi'}{\psi} = -\frac{1}{\hbar}(tx - i\lambda)$$

and integrated

$$\log \psi = -\frac{1}{2\hbar}(tx^2 - 2i\lambda x + C) = -\frac{t}{2\hbar}(x - \mu)^2 + C',$$

introducing $\mu = it/\lambda$. This is (6.7)

We call a state which attains the minimum in (6.6) a *minimum uncertainty* state. We've seen an example: the ground state of the harmonic oscillator is

$$\Psi_0(x) = \text{constant} \ \times \ \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

which is (6.7) with $\mu = 0, t = m\omega$.

6.3 Simultaneous Measurability

Why was this called Heisenberg's Uncertainty Principle? From (6.6) a reduction in the dispersion in momentum leads to an increase in the dispersion in position, and vice versa. Thus X and P cannot simultaneously be measured to arbitrary accuracy – this is the uncertainty. They are referred to as *complementary observables* and the same conclusion will hold for any pair of observables A, B with $[A, B] \neq 0$.

For finite-dimensional $\mathcal{H}$, if A, B commute then there will be a basis of common eigenvectors and evidently if ψ is a common vector then $\Delta_\psi(A) = 0 = \Delta_\psi(B)$. Now A and B can be simultaneously measured to arbitrary accuracy. For infinite-dimensional $\mathcal{H}$ and commuting A, B the most we can say is that on the subspace spanned by common eigenvectors this precision is possible, but this may be sufficient for many purposes.

6.4 The Harmonic Oscillator Revisited

This is the big payoff with the method of abstraction. Recall the harmonic oscillator Hamiltonian:

$$H = \frac{1}{2m}P^2 + \frac{1}{2}m\omega^2 X^2,$$

and introduce the operator

$$a_- = P - im\omega X. \tag{6.8}$$

This is not self-adjoint and in fact

$$a_+ := (a_-)^* = P + im\omega X.$$

We explore these operators:

6.4.1 Properties of $a_\pm$

1.

$$
\begin{aligned}
a_+ a_- &= 2m(H - \frac{1}{2}\hbar\omega), \\
a_- a_+ &= 2m(H + \frac{1}{2}\hbar\omega), \\
[a_-, a_+] &= 2m\hbar\omega;
\end{aligned}
$$

2. For normalised ψ:

$$
\begin{aligned}
||a_-\psi||^2 &= 2m(\mathbb{E}_\psi(H) - \frac{1}{2}\hbar\omega), \\
||a_+\psi||^2 &= 2m(\mathbb{E}_\psi(H) + \frac{1}{2}\hbar\omega);
\end{aligned}
$$

3.

$$
\begin{aligned}
[H, a_-] &= -\hbar\omega a_-, \\
[H, a_+] &= \hbar\omega a_+;
\end{aligned}
$$

Proofs

For the first, calculate

$$
a_+ a_- = (P + im\omega X)(P - im\omega X) = P^2 - im\omega(PX - XP) + m^2\omega^2 X^2 = 2m\omega H - m\hbar\omega,
$$

and the others are similar.

For the second,

$$
||a_-\psi||^2 = < a_-\psi | a_-\psi > = < \psi | a_+ a_-\psi >
$$

and use the first, etc.

For the third,

$$
[H, a_-] = \frac{1}{2m}[a_+ a_-, a_-] = -\hbar\omega a_-,
$$

etc.

Given these we can solve the harmonic oscillator algebraically:

6.4.2 The Harmonic Oscillator by Algebra

Suppose H has one normalisable eigenvector $\psi \in \mathcal{H}$, then

1. H has a normalisable ground state $\psi_0 \in \mathcal{H}$ with energy $E_0 = \frac{1}{2}\hbar\omega$;

2. H has normalisable excited states $\psi_n = (a_+)^n \psi_0 \in \mathcal{H}$ with energy $E_n = (n + \frac{1}{2})\hbar\omega$;

3. if $P = -i\hbar\frac{d}{dx}$ and $X = x$ then these are all the eigenstates and $\psi_0 \sim \exp(-\frac{m\omega x^2}{2\hbar})$.

Proofs

Suppose the assumed ψ has $H\psi = E\psi$ and consider $a_-\psi$, then

$$Ha_-\psi = (a_-H + Ha_- - a_-H)\psi = (E - \hbar\omega)a_-\psi,$$

using part 3 of 8.4.1. Thus $a_-\psi$ is also an eigenvector now with eigenvalue $E - \hbar\omega$, and it's normalisable since

$$||a_-\psi||^2 = 2m(E - \frac{1}{2}\hbar\omega)||\psi||^2$$

by part 2 of 8.4.1.

Call this process *lowering*, then we may repeat it to obtain normalisable eigenvectors $(a_-)^k\psi$ with eigenvalue $E - k\hbar\omega$ and $||(a_-)^k\psi||^2 \sim (\mathbb{E}_\psi(H) - (k - \frac{1}{2})\hbar\omega)$. Since the norm must be positive, this process must terminate and it can only terminate on a (nonzero) state ψ_0 with energy $E = E_0 = \frac{1}{2}\hbar\omega$ for then $||a_-\psi_0||^2 = 0$ and so $a_-\psi_0 = 0$.

We've found the (or strictly *a*) ground state. Now we raise: introduce $\psi_1 = a_+\psi_0$ and calculate:

$$H\psi_1 = (Ha_+ - a_+H + a_+H)\psi_0 = \hbar\omega(1 + \frac{1}{2})\psi_1.$$

This is an eigenvector with the eigenvalue raised and it's easy to check it's normalisable. Inductively set $\psi_n = a_+\psi_{n-1} = (a_+)^n\psi_0$ then this is a normalisable eigenvector with eigenvalue $E_n = (n + \frac{1}{2})\hbar\omega$. We've proved the second part.

For an abstract $\mathcal{H}$ there could be more than one linearly independent ground state but in the case considered in the third part we have

$$0 = a_-\psi_0 = (P - im\omega X)\psi_0 = (-i\hbar\psi_0' - im\omega x\psi_0),$$

so that $\psi_0'/\psi_0 = -m\omega x/\hbar$ which integrates to give

$$\psi_0 \sim \exp(-\frac{m\omega x^2}{2\hbar}),$$

as expected. It's important to notice that this is normalisable, and then one has a unique ground state (up to scale), from which uniqueness of all the excited states follows.

6.4.3 Uniqueness of the Commutation Relations (not for examination)

In the last proof, we only used the explicit forms of $\mathcal{H}$, P and X at the very end. In the earlier parts, the important thing was just the commutator $[P, X]$. If we had assumed instead an abstract Hilbert space say $\mathcal{H}^\Omega$ containing a unique one-dimensional kernel for a_-, spanned say by Ω, then the eigenvectors would have been $\psi_n^\Omega := (a_+)^n\Omega$. Now we could set up an isomorphism of the two Hilbert spaces $\mathcal{H}$ and $\mathcal{H}^\Omega$ by mapping $\psi_n(x)$ to ψ_n^Ω and this would map x to X and $-i\hbar d/dx$ to P. We can conclude that this identification of X, P and $\mathcal{H}$, while not unique, is unique up to isomorphism.

7 Angular Momentum in Quantum Mechanics

7.1 Angular Momentum Operators

From classical mechanics we have the definition of angular momentum as $\mathbf{L} = \mathbf{x} \wedge (m\mathbf{v}) = \mathbf{x} \wedge \mathbf{p}$, so here we define the observables:

$$
\begin{aligned}
L_1 &= X_2 P_3 - X_3 P_2, \\
L_2 &= X_3 P_1 - X_1 P_3, \\
L_3 &= X_1 P_2 - X_2 P_1.
\end{aligned}
\tag{7.1}
$$

An elegant why to write these uses the *alternating symbol* ϵ_{ijk} defined by

$$
\begin{aligned}
\epsilon_{ijk} &= +1 \text{ if } ijk \text{ is an even permutation of 123} \\
&= -1 \text{ if } ijk \text{ is an odd permutation of 123} \\
&= 0 \text{ otherwise}
\end{aligned}
\tag{7.2}
$$

for then $(\mathbf{A} \wedge \mathbf{B})_i = \sum_{j,k} \epsilon_{ijk} A_j B_k$ and so

$$
L_i = \sum_{j,k} \epsilon_{ijk} X_j P_k.
\tag{7.3}
$$

We calculate some commutators:

Proposition

1. $[L_i, P_j] = i\hbar \sum_k \epsilon_{ijk} P_k$,

2. $[L_i, X_j] = i\hbar \sum_k \epsilon_{ijk} X_k$,

3. $[L_i, L_j] = i\hbar \sum_k \epsilon_{ijk} L_k$.

Proof

These are just exercises. As an example let's do

$$
[L_1, L_2] = [X_2 P_3 - X_3 P_2, X_3 P_1 - X_1 P_3]
$$

$$
= X_2 [P_3, X_3] P_1 + X_1 [X_3, P_3] P_2 = -i\hbar X_2 P_1 + i\hbar X_1 P_2 = i\hbar L_3.
$$

Others follow by symmetry.

We'll call any set of operators J_i with

$$
[J_i, J_j] = i\hbar \sum_k \epsilon_{ijk} J_k
\tag{7.4}
$$

an *angular momentum operator*. We can deduce:

Lemma

If $\mathbf{A}$ and $\mathbf{B}$ satisfy $[J_i, A_j] = i\hbar \sum_k \epsilon_{ijk} A_k$ and the same with B_j then

$$
[J_i, \mathbf{A} \cdot \mathbf{B}] = 0.
\tag{7.5}
$$

This is just checking:

$$[J_i, \mathbf{A} \cdot \mathbf{B}] = \sum_j [J_i, A_j B_j] = \sum_j (A_j [J_i, B_j] + [J_i, A_j] B_j)$$

$$= -i\hbar \sum_{j,k} \epsilon_{ijk} (A_j B_k + A_k B_j),$$

which vanishes (because $\epsilon_{ijk} = -\epsilon_{ikj}$).

From (7.5) we see at once that $\mathbf{P} \cdot \mathbf{P}, \mathbf{X} \cdot \mathbf{P}, \mathbf{X} \cdot \mathbf{X}, \mathbf{L} \cdot \mathbf{L}$ and many similar expressions commute with L_i.

7.2 Ladder Operators

We want to work our way through to finding eigenvalues and eigenvectors for angular momentum and we'll do that following the algebraic treatment of the harmonic oscillator. We assume (7.4) and then from (7.5), with $J^2 = \mathbf{J} \cdot \mathbf{J} = J_1^2 + J_2^2 + J_3^2$,

$$[J^2, J_i] = 0.$$

We single out one direction, usually J_3, and look for common eigenvectors of J^2 and J_3 (since they commute). Introduce the *ladder operators*

$$J_\pm = J_1 \pm i J_2. \tag{7.6}$$

Note that $(J_+)^* = J_-$ if the J_i are self-adjoint (which we assume).

7.2.1 Properties of Ladder Operators

1.
$$[J^2, J_\pm] = 0;$$

2.
$$\begin{aligned} J_+ J_- &= J^2 - J_3^2 + \hbar J_3, \\ J_- J_+ &= J^2 - J_3^2 - \hbar J_3, \\ [J_+, J_-] &= 2\hbar J_3; \end{aligned} \tag{7.7}$$
$$\tag{7.8}$$

3.
$$[J_3, J_\pm] = \pm\hbar J_\pm. \tag{7.9}$$

The first follows from (7.5). For the second calculate

$$J_+ J_- = (J_1 + i J_2)(J_1 - i J_2) = J_1^2 + J_2^2 - i(J_1 J_2 - J_2 J_1) = J^2 - J_3^2 + \hbar J_3,$$

and the other two are similar. For the third

$$[J_3, J_\pm] = [J_3, J_1 \pm i J_2] = i\hbar J_2 \pm \hbar J_1 = \pm\hbar J_\pm.$$

7.2.2 Using the Ladder Operators

Now suppose we have a common eigenvector, ψ say, of J^2 and J_3, so that

$$J^2\psi = \lambda\hbar^2\psi, \quad J_3\psi = m\hbar\psi,$$

for some real λ, m.

Consider $\psi_+ = J_+\psi$ and $\psi_- = J_-\psi$. Calculate

$$J^2\psi_+ = J^2 J_+\psi = J_+ J^2\psi = \lambda\hbar^2 J_+\psi$$

so that ψ_+ is also an eigenvector of J^2 with the same eigenvalue (and ditto for ψ_-).

Next

$$J_3\psi_- = J_3 J_-\psi = (J_3 J_- - J_- J_3 + J_- J_3)\psi = (m-1)\hbar\psi_-,$$

so the J_3-eigenvalue has been lowered by $\hbar$ (and raised by $\hbar$ for ψ_+). For the norm we find

$$||J_-\psi||^2 =< J_-\psi|J_-\psi >=< \psi|J_+ J_-\psi >$$

so from section 7.2.1

$$||J_-\psi||^2 = (\lambda - m^2 + m)\hbar^2||\psi||^2. \tag{7.10}$$

Similarly

$$||J_+\psi||^2 = (\lambda - m^2 - m)\hbar^2||\psi||^2. \tag{7.11}$$

We argue as with the harmonic oscillator: we can raise and lower m in integer steps but these processes cannot be performed indefinitely as the norms in (7.10) and (7.11) cannot be negative. We deduce

$$\lambda \geq m(m-1) \text{ and equality implies } J_-\psi = 0, \tag{7.12}$$

$$\lambda \geq m(m+1) \text{ and equality implies } J_+\psi = 0. \tag{7.13}$$

We have enough results to deduce conditions on λ and m.

7.3 Representations of the Angular momentum Operators

Here 'representations' means as operators acting on some explicit vector space, so we suppose we have a finite-dimensional, complex vector space $\mathcal{H}$ of eigenvectors of J^2:

$$J^2\psi = \lambda\hbar^2\psi \text{ for all } \psi \ \epsilon \ \mathcal{H}.$$

J_3 will have an eigenvector in $\mathcal{H}$ say ψ with

$$J_3\psi = m\hbar\psi$$

We can obtain more eigenvectors of J_3 by raising and lowering with $J_\pm$, when m will go up and down in integer steps. This can't be repeated indefinitely, since (7.12,7.13) imply

$$\lambda + \frac{1}{4} \geq m^2 \pm m + \frac{1}{4} = (m \pm \frac{1}{2})^2$$

so that $|m|$ can't be arbitrarily large. Thus there will be a maximum m, call it j with corresponding ψ_j, and further raising must give zero:

$$J_+ \psi_j = 0$$

By (7.11), if the LHS vanishes, we find

$$\lambda = j(j+1)$$

We lower ψ_j in integer steps and this will stop at a value of m at which further lowering gives zero. By (7.10) this will happen when

$$0 = \lambda - m^2 + m = j(j+1) - m^2 + m = (j+m)(j-m+1)$$

i.e. at $m = -j$ since $m = j+1$ is not allowed (m must be less than its maximum value which was j)

Thus we lower in integer steps from $m = j$ to $m = -j$, which requires $2j$ to be a non-negative integer.

Summarizing:

- the eigenvalues of J^2 are $j(j+1)\hbar^2$ where $j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, ...$;

- for each fixed j, the eigenvalues of J_3 are $m\hbar$ with $m = -j, -j+1, ..., j-1, j$;

- assuming no degeneracies, the eigenspace on which $J^2 = j(j+1)\hbar$ has dimension $2j+1$.

- we can choose an orthonormal basis $\{\psi_m\}$ whith

$$J_3 \psi_m = m\hbar\psi_m$$
$$J_\pm \psi_m = c_m^\pm \psi_{m\pm 1}$$
$$c_m^\pm = [(j \mp m)(j \pm m + 1)]^{1/2}$$

We have proved all of this except the last part which comes from (7.10) and (7.11).

Important example: $j = \frac{1}{2}$ (also called the spin representation)

Now $2j + 1 = 2$ so $\mathcal{H}$ is 2-dimensional. The allowed values of m are $m = \pm\frac{1}{2}$ so write $\psi_\pm$ for $\psi_{\pm 1/2}$, then

$$J_3 \psi_\pm = \pm\frac{1}{2}\hbar\psi_\pm \tag{7.14}$$

and

$$J_+ \psi_+ = J_- \psi_- = 0, \quad J_+ \psi_- = \hbar\psi_+, \quad J_- \psi_+ = \hbar\psi_- \tag{7.15}$$

We can introduce a matrix formalism by taking as basis

$$\psi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \psi_+ = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Then (7.14) and (7.15) fix the form of the operators to be

$$J_3 = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad J_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad J_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

so also

$$J_1 = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad J_2 = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

and one may check all the commutation relations. These formulae bring to our attention the *Pauli spin matrices*:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{7.16}$$

which are Hermitian, trace zero and define the J_i for $j = 1/2$ via

$$J_i = \frac{1}{2}\hbar\sigma_i \tag{7.17}$$

from which many algebraic relations follow.

7.4   Orbital Angular Momentum and Spherical Harmonics

Let us focus in the particular case of orbital angular momentum $\mathbf{J} = \mathbf{L} = \mathbf{X} \wedge \mathbf{P}$. We seek a space of functions for $\mathbf{L}$ to act on. As we will shortly see, we need j to be an integer, and it is usually denoted by ℓ. To justify this claim recall

$$L_3 = X_1 P_2 - X_2 P_1 = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right),$$

which in spherical polars becomes

$$L_3 = -i\hbar \frac{\partial}{\partial \phi}.$$

The eigenvector equation becomes

$$L_3 \psi_m = -i\hbar \frac{\partial \psi_m}{\partial \phi} = m\hbar \psi_m,$$

so that

$$\psi_m(r, \theta, \phi) = F(r, \theta)e^{im\phi}.$$

Now the important point: if this is genuinely a function, *i.e.* single-valued, then we need periodicity 2π in ϕ, so that as claimed m must be integral and therefore so must j. (This also gives a hint about the strangeness of spin – if $j = 1/2$ then the wave-function changes sign under 2π-rotation.)

To pursue this line further, let's calculate the other operators in spherical polar coordinates

$$L_+ = L_1 + iL_2 = \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$

and

$$L_- = L_1 - iL_2 = -\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right).$$

Knowing L_3 we then obtain

$$L^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

so the eigenvalue equation for L^2 becomes

$$\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi = -\ell(\ell+1)\psi.$$

This is recognisable as the separated angular part of the Laplacian in spherical polar coordinates (8.6) and so is the missing link in the study of the hydrogen atom. We don't need to solve this eigenvalue problem – we already know that the solutions will take the form

$$\psi = P_{\ell m}(\theta)e^{im\phi}, \tag{7.18}$$

where $P_{\ell m}(\theta)$ satisfies

$$L^2 P_{\ell m}(\theta)e^{im\phi} = \ell(\ell+1)\hbar^2 P_{\ell m}(\theta)e^{im\phi}.$$

From problem 4 on sheet 4 we know that

$$P_{\ell\ell}(\theta)e^{i\ell\phi} \sim (\sin\theta)^\ell e^{i\ell\phi}$$

so we can if desired find $P_{\ell m}(\theta)e^{im\phi}$ by lowering $\ell - m$ times on this. Conventionally, and with an appropriate normalisation, one defines

$$Y_{\ell m}(\theta,\phi) = P_{\ell m}(\theta)e^{im\phi},$$

and calls this *the spherical harmonic of order ℓ, m.*

8 The hydrogen atom: a first look

8.1 Atoms

We begin with a discussion of *Coulomb's law.*[7] In general, a point charge e_2 at the origin induces an *electrostatic force* on another point charge e_1 at position $\mathbf{r}$ given by the inverse square law

$$\mathbf{F} = \frac{1}{4\pi\epsilon_0}\frac{e_1 e_2}{r^2}\frac{\mathbf{r}}{r}, \tag{8.1}$$

where as usual $r = |\mathbf{r}|$. Notice that the Coulomb force (8.1) is proportional to the product of the charges, so that opposite (different sign) charges attract, while like (same sign) charges repel.

---

[7] * Coulomb discovered his law in 1783. From a modern point of view, this law is subsumed into Maxwell's classical theory of electromagnetism (*i.e.* Coulomb's law can be derived from Maxwell's equations).

Electric charge is measured in *Coulombs*, C, and the proportionality constant $\epsilon_0 \simeq 8.85 \times 10^{-12}$ $\text{C}^2\,\text{N}^{-1}\,\text{m}^{-2}$ in (8.1) is called the *permittivity of free space*. The Coulomb force is conservative, of the form $\mathbf{F} = -\nabla V$ where

$$V(\mathbf{r}) \;=\; V(r) \;=\; \frac{1}{4\pi\epsilon_0}\,\frac{e_1 e_2}{r}\;, \tag{8.2}$$

is the *Coulomb potential*.

An atom consists of negatively charged electrons e^- orbiting a positively charged nucleus, where the force of attraction is (predominantly) electrostatic. An electron carries electric charge $-e$, where $e \simeq 1.60 \times 10^{-19}$ C. In general, the nucleus of an atom consists of Z positively charged protons, each of charge $+e$, and A neutrons, of charge 0, and these are tightly bound together (by the *strong force*). In the following we consider an atom of *atomic number* Z, with a *single* orbiting electron. In particular, the hydrogen atom has $Z = 1$. Since the nucleus is vastly heavier than the electron ($m_{\text{proton}} \simeq 1836\,m_{e^-}$), this implies that the centre of mass of the atomic system will always be very close to the nucleus. We thus make the simplifying assumption that the nucleus is *fixed*, at the origin. The potential for the force acting on the electron is then given by (8.2) with $e_1 = -e$, $e_2 = Ze$ (see Figure 9):

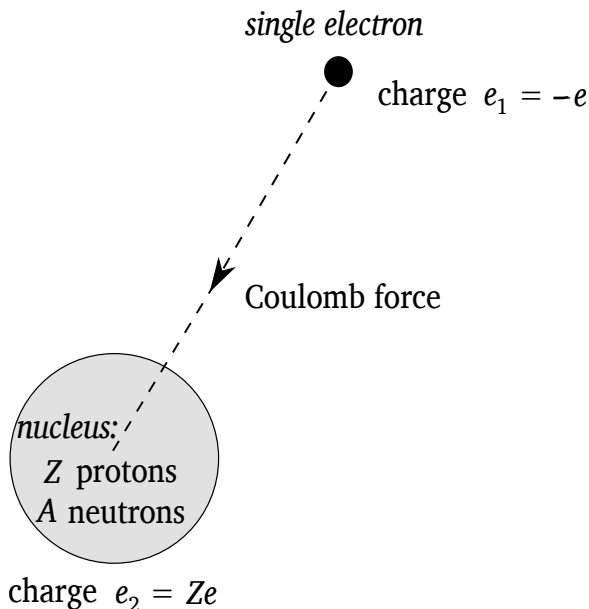$$V(r) \;=\; -\frac{Z\,e^2}{4\pi\epsilon_0\,r}\;. \tag{8.3}$$

Figure 9: An atom consisting of a nucleus of atomic number Z and a single orbiting electron.

Recall that in section 1.2 we discussed the empirical formula (1.3) for the energy levels of the hydrogen atom. Our task in the remainder of this course is to derive this formula theoretically, using the Schrödinger equation. However, before moving on to this, as usual we pause to make some comments on the corresponding *classical* problem. The $1/r$ Coulomb potential is formally the same as Newton's gravitational potential that you encountered in Prelims, the only difference being that gravity is *always* attractive. Thus classically the atomic system in Figure 9 is similar

to a planet orbiting the sun under gravity.[8] In particular, the energy levels are continuous, not discrete as in (1.3).

* There is an even more serious problem with the classical picture above. Maxwell's classical theory of electromagnetism predicts that an *accelerating* charge, such as an electron in orbit around a nucleus, emits electromagnetic radiation, and thus continuously loses energy. The electron would quickly spiral in towards the nucleus, and all atoms would hence be unstable! We shall see how quantum theory gets around this problem.

8.2 The spectrum of the hydrogen atom

For hydrogen-like atoms then we must solve the three-dimensional stationary state Schrödinger equation (2.10) with potential (8.3):

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Z\,e^2}{4\pi\epsilon_0\,r}\,\psi \;=\; E\psi\;, \tag{8.4}$$

where $m = m_{e^-} \sim 9.12 \times 10^{-31}$ kg is the mass of an electron.

We'll get a little way with this now and then return to it when we have more technology available. It is no more complicated at the outset to consider any *central force* in other words any potential which depends only on r, so

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi. \tag{8.5}$$

Separate in spherical polars so that

$$\psi = R(r)P(\theta,\phi).$$

Then we need the Laplacian in spherical polars from Prelims, which is

$$\nabla^2\psi = P\frac{1}{r}(rR)'' + R\frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)P. \tag{8.6}$$

Substituting into (8.5) we see that we can separate all r-dependent terms to one side, leaving

$$\frac{1}{P}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)P = \frac{2mr^2}{\hbar^2}(V(r) - E) - \frac{r(rR)''}{R}.$$

Both sides must be constant, say λ. Then separate again: $P(\theta,\phi) = Y(\theta)\Phi(\phi))$ to find

$$\frac{1}{Y}\left(\frac{\partial^2 Y}{\partial\theta^2} + \cot\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} = \lambda.$$

Now we can separate again to find

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = \mu = \lambda\sin^2\theta - \frac{\sin^2\theta}{Y}\left(\frac{\partial^2 Y}{\partial\theta^2} + \cot\theta\frac{\partial Y}{\partial\theta}\right),$$

for some constant μ. The ϕ-equation can be solved in terms of exponentials but we require periodicity:$\Phi(\phi + 2\pi) = \Phi(\phi)$; since otherwise the wave-function is not single-valued. This

---

[8]Of course there is *also* a gravitational attraction between the electron and nucleus, but this is many orders of magnitude smaller.

forces $\mu = -m^2$ for some integer m which we may assume is non-negative, and then $\Phi = e^{\pm mi\phi}$. The equation for Y becomes

$$\frac{\partial^2 Y}{\partial \theta^2} + \cot\theta \frac{\partial Y}{\partial \theta} + \left(\frac{\mu}{\sin^2\theta} - \lambda\right)Y = 0,$$

and we still have the equation for R:

$$-\frac{r(rR)''}{R} + \frac{2mr^2}{\hbar^2}(V(r) - E) = \lambda.$$

It is possible to solve these equations by series solutions but instead we will use some of the ingredients we have developed in previous sections.

9 The Hydrogen Atom Revisited

9.1 Central Potentials

We saw in section 8 how to separate the time-independent Schrödinger equation with any central potential, so that $V = V(r)$ in spherical polars. The equation is

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

and we separate in spherical polars so that

$$\psi = R(r)Y(\theta, \phi).$$

Then

$$\nabla^2\psi = Y\frac{1}{r}(rR)'' + R\frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y,$$

but now, by the previous section we see at once we can take $Y = Y_{\ell m}(\theta, \phi)$ and this is simplified to

$$= Y_{\ell m}\left(\frac{1}{r}(rR)'' - \frac{\ell(\ell+1)}{r^2}R\right).$$

The Schrödinger equation, after multiplication by $-2m/\hbar^2$ and cancellation of $Y_{\ell m}$, becomes

$$\frac{1}{r}(rR)'' - \frac{\ell(\ell+1)}{r^2}R - \frac{2m}{\hbar^2}V(r)R = -\frac{2mE}{\hbar^2}R. \tag{9.1}$$

(There is an inevitable clash of notation here between m the mass of the electron and m the eigenvalue in $Y_{\ell m}$: there is no way of avoiding this as both usages are firmly embedded in custom.)

At this point we see that, for any central potential, the stationary states are simultaneously eigenstates of the Hamiltonian H (of course!) and J^2 and J_3. This could have been foreseen: with

$$H = \frac{1}{2m}P^2 + V(r),$$

one can calculate

$$[H, J^2] = 0 = [H, J_3],$$

and commuting operators can have simultaneous eigenvectors.

9.1.1   The Hydrogen Atom

We model the hydrogen atom by writing down the Schrödinger equation for the electron, assuming the nucleus is fixed and the force is inverse-square electrostatic. It is no more difficult to treat 'hydrogen-like' atoms so suppose the nucleus has charge Ze for positive integer Z and the electron has charge $-e$ and mass m. Then the potential is

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}.$$

We can substitute this into (9.1) but it is easier first to redefine some constants as

$$-\frac{2mE}{\hbar^2} = \kappa^2, \quad \beta = \frac{2Z}{a}, \quad a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}. \tag{9.2}$$

Here a has dimensions of length and is known as the *Bohr radius* – it gives a measure of the size of an atom and comes out to be 5.29×10^{-11} m.

Now set $R = f(r)e^{-\kappa r}$, then (9.1) becomes

$$f'' + \left(\frac{2}{r} - 2\kappa\right)f' - \left(\frac{2\kappa - \beta}{r} + \frac{\ell(\ell+1)}{r^2}\right)f = 0. \tag{9.3}$$

As before we seek a series solution:

$$f = \sum_0^\infty a_n r^{n+c} \text{ with } a_0 \neq 0,$$

and substitute into (9.3):

$$\sum (a_n(n+c)(n+c-1)r^{n+c-2} + (\frac{2}{r} - 2\kappa)a_n(n+c)r^{n+c-1}$$

$$-(2\kappa - \beta + \frac{\ell(\ell+1)}{r})a_n r^{n+c-1}) = 0.$$

The coefficient of r^{c-2} gives the indicial equation:

$$a_0(c - \ell)(c + \ell + 1) = 0.$$

Here $c = -\ell - 1$ is forbidden as then ψ would not be continuous at $r = 0$, so $c = \ell$. Then the coefficient of r^{n+c-1} gives the recurrence relation:

$$((n+c+1)(n+c) + 2(n+c+1) - \ell(\ell+1))a_{n+1} = (2\kappa(n+c) + 2\kappa - \beta)a_n.$$

Suppose the series does not terminate, then for large n this implies

$$\frac{a_n}{a_{n-1}} \sim 2\kappa/n,$$

at least to highest order, and this is unacceptable: compare with the power series

$$e^{2\kappa r} = \sum_0^\infty b_k r^k,$$

then $b_k = (2\kappa)^k/k!$ so that

$$\frac{b_n}{b_{n-1}} = 2\kappa/n.$$

The two series look the same for large n and with a little more care one can deduce that $f(r) \sim e^{2\kappa r}$ so that

$$R = fe^{-\kappa r} \sim e^{\kappa r}$$

and ψ would not be normalisable.

Thus the series must terminate, which means there is an n for which

$$2\kappa(n + c + 1) = \beta.$$

Then $a_k = 0$ for $k > n$ and the series is a polynomial of degree n. This makes f a polynomial of degree $N = n + c = n + \ell$, call it $f_{N,\ell}$ since both N and ℓ enter it's definition, and $\kappa = \kappa_N = \frac{\beta}{2(N+1)}$. In particular, (9.2) now gives the energy levels as

$$E_N = -\frac{\hbar^2 \kappa_N^2}{2m} = -\frac{\hbar^2 \beta^2}{8m(N+1)^2}, \tag{9.4}$$

for non-negative integer N. This is precisely of the form of (1.3) and was a great triumph for quantum theory.

To summarise:

- the energy eigenvalue is

$$E = E_N = -\frac{\hbar^2 \kappa_N^2}{2m} = -\frac{\hbar^2 \beta^2}{8m(N+1)^2};$$

- the wave-function is a simultaneous eigenfunction of the Hamiltonian, J^2 and J_3 and can be written

$$\psi_{N\ell m} \sim f_{N,\ell}(r)e^{-\kappa_N r}Y_{\ell m}(\theta, \phi);$$

- the J^2 eigenvalue is $\ell(\ell+1)\hbar^2$ and the J_3 eigenvalue is $m\hbar$;

- one can count the degeneracy of the energy eigenstates as follows: E_N depends on $N = n + \ell$, so $0 \le \ell \le N$ and for each ℓ there are $2\ell + 1$ allowed values of m; thus

$$\text{degeneracy} = \sum_{\ell=0}^{N} (2\ell + 1) = (N+1)^2;$$

- the ground state has $N = 0$ and is nondegenerate;

There is some traditional terminology associated with the numbers N, ℓ, m: conventionally $N + 1, \ell, m$ are called the *principal* quantum number, the *azimuthal* quantum number and the *magnetic* quantum number respectively. Thus the energy level is inversely proportional to the square of the principal quantum number.

9.2 Rotationally symmetric solutions

We'll start with the ground state for which $N = \ell = m = 0$: so the wave-function is independent of θ and ϕ and can be written

$$\psi_{000} = a_0 e^{-\kappa_0 r}, \qquad (9.5)$$

with $\kappa_0 = \beta/2 = Z/a$. One might worry that this function is not differentiable at the origin, but since the origin is the location of the nucleus and is a singular point for the potential that need not be a surprise.

Normalising the wave-function to fix a_0 we find

$$1 = \int \int \int |\psi_{000}|^2 dV = 4\pi |a_0|^2 \frac{a^3}{4Z^3},$$

so that we may take $a_0 = (Z^3/\pi a^3)^{1/2}$.

If we calculate $\mathbb{E}[r]$ for the ground state we obtain

$$\mathbb{E}[r] = \frac{3a}{2Z},$$

so that, for the hydrogen atom ground state the expected value of $r = |\mathbf{r}|$ is $3a/2$ which justifies regarding a as a rough 'size' for the atom.

This is the first in an infinite series of rotationally symmetric or spherically symmetric solutions, one at each energy level: just put $\ell = 0 = m$. The wave-functions are of the form

$$\psi_{N00} = f_{N,0}(r)e^{-\kappa_N r}$$

where $f_{N,0}$ is a polynomial of degree N satisfying (9.3) with $\ell = 0$, which is

$$f'' + \left(\frac{2}{r} - 2\kappa\right) f' - \left(\frac{2\kappa - \beta}{r}\right) f = 0. \qquad (9.6)$$

with $\kappa = \kappa_N == \frac{\beta}{2(N+1)}$ just as before. We know that $f_{N,0}$ will be a polynomial of degree N so that the first few can be easily obtained:

- evidently $f_{0,0} = a_0 =$ constant with $\kappa_0 = \beta/2$;

- then $f_{1,0} = a_a + a_1 r$ and substituting with $\kappa_1 = \beta/4$ rapidly gives $f_{1,0} = a_1(r - 4/\beta)$;

- pressing on, $f_{2,0} = a_2(r^2 - 18r/\beta + 54/\beta^2)$ with $\kappa_2 = \beta/6$.

Various patterns emerge, for example that $f_{N,0}$ has N zeroes, but another substitution is suggested: set $f_{N,0} = F_N(s)$ where $s = r\beta/(N+1)$. Then (9.6) becomes

$$\frac{d^2 F_N}{ds^2} + \left(\frac{2}{s} - 1\right) \frac{dF_N}{ds} - \frac{N}{s} F_N = 0. \qquad (9.7)$$

This is an ODE studied in the 19th century and its polynomial solutions are known for historical reasons as *generalized Laguerre polynomials*, in fact specifically $F_N = L_N^1$. Now

$$\psi_{N00} = L_N^1(r\beta/(N+1)))e^{-\kappa_N r}.$$
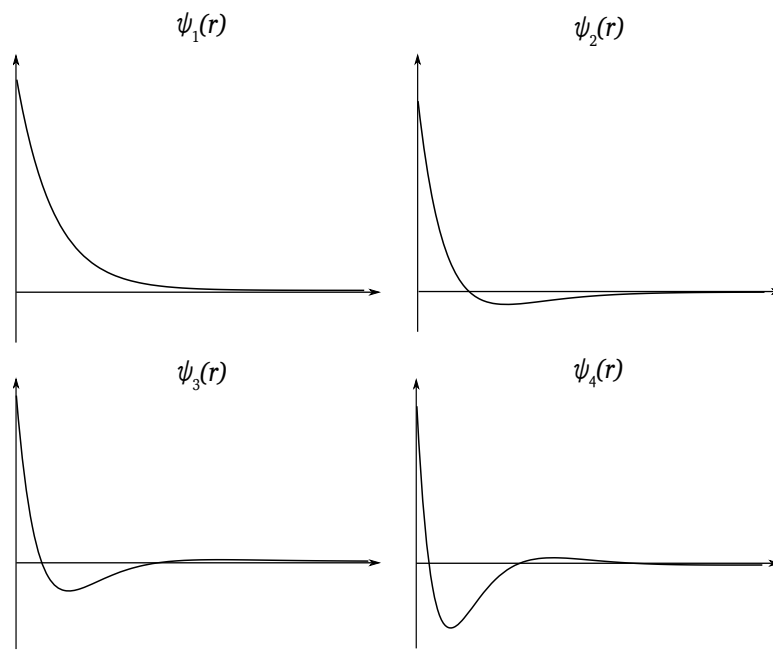
The first few L_N^1 are shown in figure 10.

Figure 10: The ground state and first three (spherically symmetric) excited state wave functions of the hydrogen atom.

10 Schrödinger's Cat etc

Under this heading we'll group a number of the puzzles that quantum mechanics leaves us with.

10.1 Schrödinger's Cat

The idea of this thought experiment is to generate a 'macroscopic superposition', that is to use a wave-function which is an evolving sum of two eigenstates to produce a state of affairs in the classical (nonquantum) world which is also neither one thing nor another.

In its original form, one imagines a cat in a sealed box containing a vial of poison gas and an apparatus for releasing the gas at the moment a radioactive atom decays. The radioactive decay is a quantum process so that the radioactive atom is in a superposition of decayed and nondecayed states which changes with time. What is the state of the cat? Is it also in a superposition of alive and dead?

The state of the atom will collapse into an eigenstate when observed. Suppose this requires opening the box. Does this mean that the cat will only be in an eigenstate when we open the box and observe it?

In another form, one imagines the decay simply turning on a light and one replaces the cat by a person, 'Wigner's friend'. Does the wave-function collapse when Wigner's friend sees the light go on, or only when we open the box?

Evidently this kind of example leads to other questions about the interpretation of the wave-function: who or what is allowed to be an observer? If I make an observation and don't tell you the answer does the wave-function collapse for me but not for you? Can there be macroscopic superpositions or (for example) does the wave-function collapse spontaneously?

10.2   EPR Experiments

EPR stands for Einstein-Podolsky-Rosen who devised a class of thought experiments intended to test the view of the world that quantum mechanics leaves us with, but which eventually led to actual experiments confirming quantum mechanics. A simplified version is as follows: consider a pair of particles, p_1, p_2, each with $j = 1/2$ so with $m = \pm 1/2$, and suppose them produced in such a way that their m-values sum to zero; so either $m_1 = 1/2, m_2 = -1/2$ or vice versa and we can write their wave function as a linear combination of the two possibilities: with an obvious notation

$$\psi = c_1 \psi_{+-} + c_2 \psi_{-+}.$$

Imagine they are fired off in opposite directions and, after some time, arrive respectively at two detectors D_1, D_2 which measure m_1, m_2 respectively. We know that if D_1 measures $m_1 = 1/2$ then D_2 measures $m_2 = -1/2$ and vice versa, even if the detectors are far apart and the measurements are simultaneous. This is already a bit strange ('spooky action at a distance' in a famous phrase) but the interesting case is when D_1 measures J_3 (which is m) but D_2 measures something else, like J_1 or $J_1 \cos \alpha + J_3 \sin \alpha$. Now the predictions of quantum mechanics are at odds with one's classical expectations, but experiments based on these ideas lead to a confirmation of quantum mechanics (one place to look for more is under 'Bell's theorem' on Wikipedia).

A * Fuchs' theorem and Frobenius series

This appendix is included only for interest and completeness. It is certainly not intended to be part of the course.

In the main text we solved both the harmonic oscillator (4.11) and the radial part of the hydrogen atom (9.3) using a (generalized) power series expansion. Here we discuss this problem more generally. Consider the second order ODE

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} + p(x)\frac{\mathrm{d}f}{\mathrm{d}x} + q(x)\,f \;=\; 0\;, \tag{A.1}$$

for the function $f(x)$. A point x_0 is called an *ordinary point* of (A.1) if $p(x)$, $q(x)$ have Taylor expansions about x_0, valid in some positive radius of convergence; otherwise x_0 is called a *singular point*. If x_0 is a singular point, but $(x - x_0)p(x)$, $(x - x_0)^2 q(x)$ both have Taylor expansions around x_0, then x_0 is called a *regular singular point*.

By a *generalized power series*, or *Frobenius series*, about x_0 we mean

$$f(x) \;=\; \sum_{k=0}^{\infty} a_k\,(x - x_0)^{k+c}\;, \tag{A.2}$$

for some real number $c \in \mathbb{R}$. Without loss of generality, $a_0 \neq 0$. Notice that for c a non-negative integer this reduces to a normal power series. Without loss of generality, we now set $x_0 = 0$. The equation obtained from the ODE (A.1) by setting the *lowest power* of x to zero in the expansion (A.2) is called the *indicial equation*. Since (A.1) is second order, this is a quadratic equation for c. Fuchs and Frobenius proved the following result:

Theorem A.1

- *If $x = 0$ is an ordinary point, then (A.1) possesses two distinct power series solutions, so that one can effectively set $c = 0$ in (A.2). These series converge for $|x| < r$, where r is the minimum radius of convergence of $p(x)$ and $q(x)$.*

- *If $x = 0$ is a regular singular point, then there is at least one solution of (A.1) of the form (A.2). Again, this series solution converges for $|x| < r$, where r is the minimum radius of convergence of $xp(x)$ and $x^2 q(x)$.*

The precise behaviour for regular singular points is a little involved. If the indicial equation for c has *distinct* roots that differ by a *non-integer*, then there are *two* series solutions of the form (A.2), with the corresponding values of c solving the indicial equation. Otherwise there is not *necessarily* a second series solution; if there is not one can nevertheless say more about the second solution, but we refer the interested reader to the literature for details.

Reading

- R. P. Feynman, R. B. Leighton and M. Sands, *The Feynman Lectures on Physics, Volume 3* (Addison-Wesley, 1998). Chapters 1, 2 (for physical background).

- K. C. Hannabuss, *An Introduction to Quantum Theory* (Oxford University Press, 1997). Chapters 1–8.

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- P. C. W. Davies and D. S. Betts, *Quantum Mechanics (Physics and Its Applications)* (2nd edition, Taylor & Francis Ltd, 1994). Chapters 1, 2, 4, 6-8.