

Notes for PX156 Quantum Phenomena

Nicholas d'Ambrumenil

Updated: July 16, 2024

Contents

1	Introduction and Background	2
1.1	Pre-Quantum Theory	3
1.2	Outline of Part I of Module	5
2	Photons	7
2.1	Photoelectric Effect	10
2.2	Compton Effect	12
2.3	Summary	14
3	Matter and Spectra	16
3.1	Bohr's Atom	17
3.2	de Broglie's Hypothesis	19
4	Quantum Mechanics	21
4.1	Schrodinger Equation	23
4.2	Wave packets	26
4.3	Heisenberg's Uncertainty Principle	28
5	Applying Schrodinger's Equation	30
5.1	Time-independent Schrodinger Equation (TISE)	32
5.2	Tunneling	36
5.3	Conclusion	38
A	Wave Packets	40

Chapter 1

Introduction and Background

Any phenomenon that cannot be understood without using quantum theory explicitly is what we call a quantum phenomenon. Examples include most properties of matter (Does it conduct electricity? Is it transparent?) as well as things like 'wave-particle' duality and the uncertainty principle. Classical physics, on the other hand, is physics that makes no reference to quantum theory. Newton's laws and Einstein's theory of general relativity are classical physics. You should avoid thinking that classical physics is old physics. Some problems are classical, some problems need a quantum treatment, some problems are unsolved.

Motivations for studying quantum phenomena include:

- i. To understand and marvel at the phenomena we observe. We can also exploit this understanding. Integrated circuits, which are ubiquitous in IT, only work because they exploit quantum phenomena. Calculations performed by current IT are still called classical computing as the operations performed by the integrated circuits operate on what we call classical bits. These can be 1 or 0. (Quantum computing works with qubits, where information is encoded in linear combinations of classical bits.)
- ii. The development of quantum theory is an intriguing story. It is interesting to see how hard it was to find the correct ideas. Not all the ideas are mathematically complicated, which is good for us. It means that we can crack on with computing the implications of the ideas to explain a range of surprising phenomena.
- iii. The philosophical questions about the nature of the Universe posed by quantum theory are fun to pose. Famously there is Einstein's belief 'dass der [Alter] nicht wuerfelt'—that God does not play dice.

This module concentrates on ii) and then i). Most modules on quantum theory concentrate on i). There is a sort of 'shut up and calculate' feel to them. The theory is so successful, and there are too many interesting numbers that we can compute, that we would be mad not to do this. [Freeman Dyson](#) even said the doing of the sums is all there is:

For me, the important thing about quantum mechanics is the equations, the mathematics. If you want to understand quantum mechanics, just do the math. All the words that are spun around it don't mean very much. It's like playing the violin. If violinists were judged on how they spoke, it wouldn't make much sense.

1.1 Pre-Quantum Theory

Before 1905, when quantum theory was born, physicists knew a lot about

- i. Waves. Light waves were where quantum theory started
- ii. Particles. Newton's laws of motion and the theory of relativity gave an excellent account of their behaviour
- iii. Thermodynamics. The equilibrium properties of simple systems were understood. The theory was developed to help make better steam engines, and it had done this well.

There was even an air of complacency—"We understand almost everything". However, people knew that there were problems at the boundaries between the three sub-areas. When the laws of thermodynamics were applied to wave systems, they predicted a nonsense called the ultra-violet catastrophe. When people studied gas particles interacting with light, they saw emission and absorption lines that could not be explained using Newton's laws.

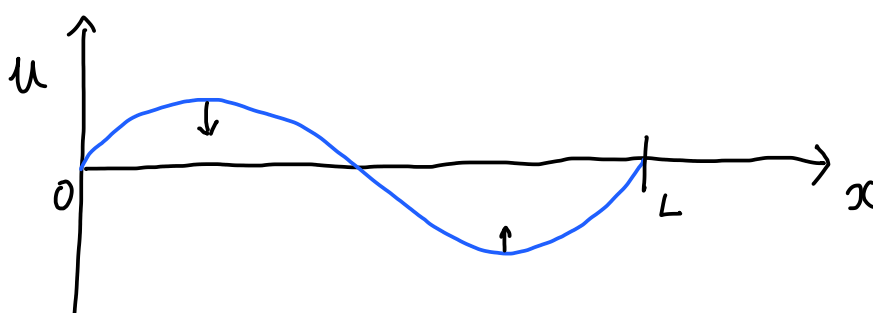
Taking these incompatibilities seriously led to what we now call quantum theory. The story brings out the nature of discovery and should help understand how the boundaries between disciplines, in this case mathematics and physics, change as a result of progress in the understanding of phenomena.

To begin with we should remind ourselves of some terminology.

Waves

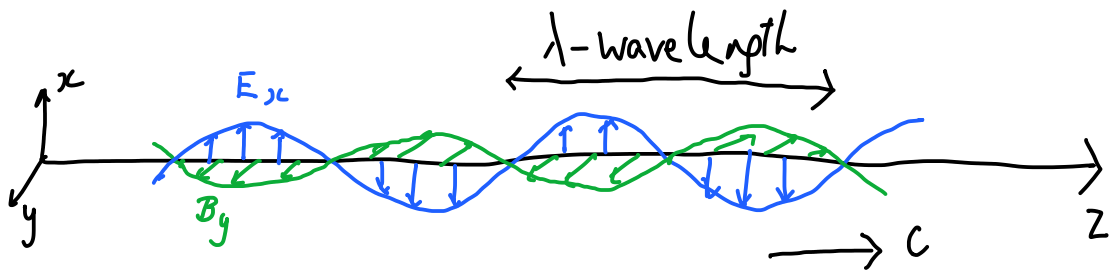
Waves are spatial patterns which fill space and vary as a function of time. For example

- Waves on a tight string which might be fixed at $x = 0$ and $x = L$. The displacement from equilibrium is $u(x, t)$:



Fixing the displacement from equilibrium at the origin and at $x = L$ become boundary conditions $u(0, t) = u(L, t) = 0$. The effect of the boundary condition is to restrict the modes of oscillation to have the form $u(x, t) = A \sin(n\pi x/L)$, here shown for the case $n = 1$. This is an example of a standing wave. The wave pattern is not moving to the right or left.

- Light Waves. These were known to be oscillating patterns of electric and magnetic fields $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$ with $\mathbf{E}(\mathbf{r}, t) \cdot \mathbf{B}(\mathbf{r}, t) = 0$ everywhere in free space:



Here the wave is a travelling wave. It is travelling in the positive x -direction at the speed of light.

The wave form for a sinusoidal travelling wave is ($A = |A|e^{i\phi}$)

$$u(x, t) = A e^{i(kx - \omega t)} = |A| [\cos(kx - \omega t + \phi) + i \sin(kx - \omega t + \phi)].$$

Here the quantity A is the complex-valued amplitude which can be written in terms of its magnitude $|A|$ and a phase ϕ . If u is a real quantity, for example the displacement from equilibrium of a tight string, we should understand that we need to take either $\text{Re}[u] = \cos(kx - \omega t + \phi)$ or $\text{Im}[u] = \sin(kx - \omega t + \phi)$. One thing we will need to be wary of in quantum theory is that the wave forms are complex-valued.

The quantity λ is called the wavelength while $k = 2\pi/\lambda$ is called the wavenumber. The wavenumber has a natural generalisation to a vector for waves in three dimensions which is why we tend to refer to k instead of λ . If the period of the wave (the time taken for the pattern to repeat) is T , the frequency $\nu = 1/T$ and the angular frequency $\omega = 2\pi\nu = 2\pi/T$. Everyone has their shorthands and ω is often referred to as the frequency.

Particles

Particles were thought to be simpler than waves. Ideally they are points with well-defined mass, momentum, position and energy. They can also be charged.



Newton's laws (after including relativity if necessary) explain how particles behaved as a function of time.

Thermodynamics

Laws of thermodynamics had been established. They appeared to govern heat and had a long list of triumphs to their name

- Ideal gas law. This explains things like the pressure of a gas as a function of temperature and why hot air rises
- Thermal energy. It should be distributed ‘fairly’ amongst all the available degrees of freedom of a system. So, for example, each particle in a gas should have an average kinetic energy $3kT/2$ associated with each direction it can move in ($k/2$ for each of the three independent directions). Here k is called Boltzmann’s constant.

This was a major insight into systems in general. Like many insights it should seem obvious with hindsight. Unless you have added information, you must assume that each way of exciting the system is equally likely.

- Probabilities. Boltzmann had established that the probability of thermal excitation of a mode of excitation, sometimes called a degree of freedom, with energy E is

$$p(E) \propto e^{-E/kT}. \quad (1.1)$$

Degrees of Freedom

Degree of freedom is a commonly used expression. Take it to mean how much needs to be specified to define the state of a system. Classically, a point particle’s position and its momentum must be specified to characterise its behaviour. In classical thermodynamics, any degree of freedom, that can change the energy of the system independently of the others, should have an average thermal energy $kT/2$.

The problem with applying thermodynamics to wave systems is that there are always infinitely many degrees of freedom even in finite systems. According to classical thermodynamics, there should therefore be infinite thermal energy in any finite system ($\infty \times kT = \infty$).

1.2 Outline of Part I of Module

The structure of the module will follow loosely the historical development of quantum theory. Following the thinking behind the ideas helps understand the structure of the theory (I hope!). In the case of quantum theory, many experimental results preceded the theory. It was attempting to understand these that helped people to develop the theory. An alternative approach (taken in later modules) is to state some postulates and see what they imply.

Photons—light as particles

We will look first at the idea that light consists of particles, which we call photons. This was introduced to get round the so-called **ultraviolet catastrophe** associated with the infinitely many light wave modes that can fit into any cavity. According to classical thermodynamics, each of these modes should have thermal energy kT associated with them ($kT/2$ for both the kinetic and the potential energy of the mode). There would therefore be an infinite thermal energy in the cavity. As some of this energy would “leak out” and radiate away, any body (not just a cavity) should radiate at an infinite rate. It is not observed and is logically impossible.

Planck proposed in 1900 that light particles have energy $h\nu$ (or equivalently $\hbar\omega$). Here h or $\hbar = h/2\pi$ is a fundamental physical constant, which we call Planck's constant.

This idea was developed by Einstein in 1905 to explain what the **photoelectric effect**. Light incident on a metal surface leads to electrons being emitted. The current released can be measured. Einstein showed that observations were consistent with the idea that light particles, the photons, were absorbed by individual electrons. If the extra energy given to the electron were sufficient, it would escape from the system. This explained the dependence of the collected current on the frequency of the light incident on the system.

The **Compton effect** was discovered in 1923. Here light is scattered by electrons. The wavelength of the light is shifted in a way that cannot be explained classically but is accounted for perfectly by treating the scattering as a collision between a photon and an electron.

Particles as waves

The absorption and emission of light from molecules in a gas was known from experiment to be limited to discrete frequencies. One series of lines for Hydrogen had been known since 1885. (Remember that discrete means detached or non-continuous, while discreet means something like judicious in one's speech or unobtrusive.) This implied that the energies of electrons in an atom, *ie* bound to a nucleus, were restricted to discrete values. If the initial and final energies of the electron were E_i and E_f , the frequency of the absorbed photon given by $h\nu = E_f - E_i$.

Bohr (1913) suggested thinking about atomic levels classically but with angular momentum quantised. This condition automatically ensures that the energy levels allowed for an electron encircling a proton are discrete. Better than that, assuming classical orbits with angular momentum $n\hbar$ with n an integer, gave the observed frequencies for the Balmer series for a hydrogen atom. This is sometimes referred to as the **Bohr atom**.

An important idea came in 1924 with **de Broglie's hypothesis**. If waves can behave like particles, he argued, then particles should also behave like waves. de Broglie postulated that the wavelength of a particle with momentum p should be given by

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

Wave Mechanics

Following de Broglie's hypothesis quantum mechanics followed quickly. Heisenberg (1925) proposed that systems were described by matrix mechanics (observables like momentum were represented infinite-dimensional matrices), while Schrodinger proposed that systems should be described by wave mechanics. The two approaches are equivalent. However, it is usual to work with wave mechanics rather than the more abstract matrix formulation and this is what we will do. The idea is motivated by de Broglie's hypothesis. If particles are to behave like waves, what is the correct wave equation to describe these waves? It is the **Schrodinger equation**.

Looking for solutions to the Schrodinger equation (there are other related equations) is what most quantum mechanics modules do. How to solve the equation, how to find approximate solutions to more involved problems, and how to extract predictions for observations is essentially what we want to do. We will look at some idealised problems where we can solve the equation easily.

Chapter 2

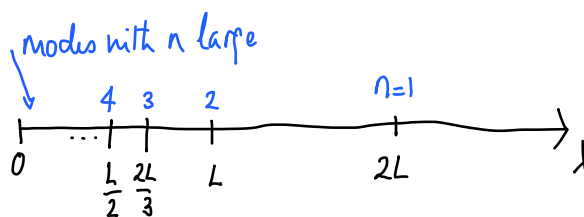
Photons

Planck introduced the notion of quantisation to explain the spectrum of light emitted by bodies as a function of temperature T . All objects emit radiation. Hot stoves emit infra-red radiation, hotter objects emit light as in red hot or white hot. In fact everything not at absolute zero emits radiation. It is usual to concentrate on black-body radiation. A black body is defined to be one that absorbs all incident light independent of wavelength. (Coloured bodies are ones that preferentially absorb and emit some frequencies.)

Light waves will be generated by thermal excitation of light waves. We should assume that all possible excitations of light waves that are possible in a body are equally likely to be excited, and should carry, on average, kT of energy (k is Boltzmann's constant). This is a premise of classical thermodynamics. On this basis, we can predict how the energy radiation rate should vary with wavelength. As we will see, it leads to a nonsense—the so-called ultraviolet catastrophe.

The argument is illustrated by a hypothetical 1D cavity of length L (we will quote but not derive the result for a 3D body later). The modes allowed in the 1D body are

$$u(x, t) = A \sin \frac{n\pi x}{L} e^{i\omega_n t} \quad \text{where} \quad \omega_n = \frac{n\pi c}{L}, \quad n \text{ is a positive integer.} \quad (2.1)$$



These satisfy the conditions that $u(0, t) = u(L, t) = 0$, ie there is no amplitude at the boundaries. Here the quantity u would be either the electric or magnetic field. We are not being precise here and not worrying about different polarisations in 1D. This is a hypothetical 1D system and the result we are looking for is the functional dependence on wavelength.

The modes labelled by n in 2.1 are the degrees of freedom for the light. As there is no bound on the integer n , there are infinitely many of them. According to classical thermodynamics, each of the modes has thermal energy kT on average. This means the cavity should contain an infinite thermal energy.

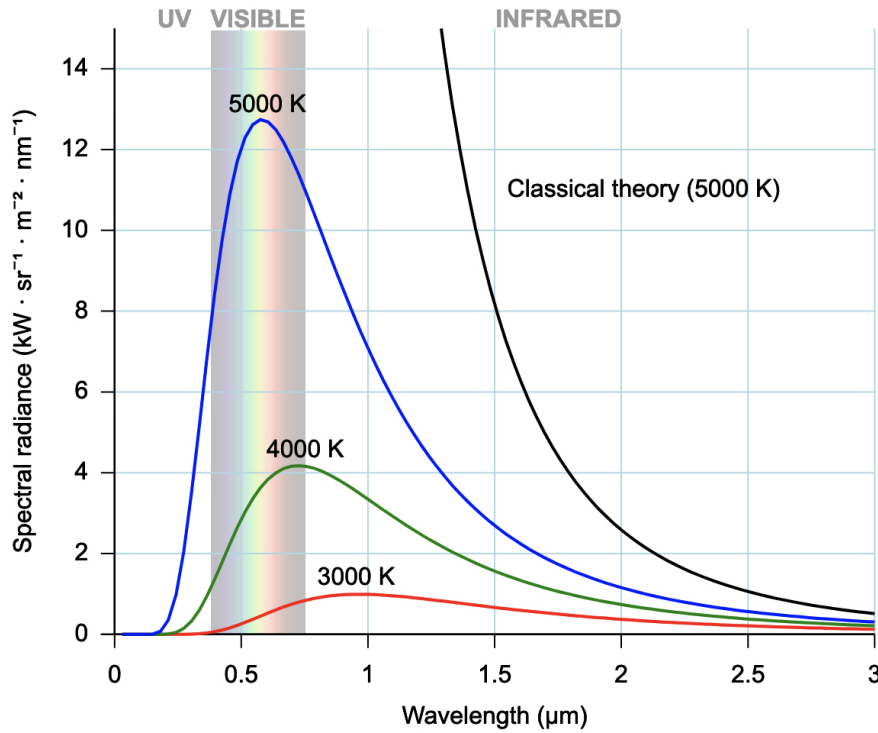


Figure 2.1: The observed spectral radiance, $I(\lambda, T)$, for a black-body at different temperatures as well as the prediction of classical theory.

The wavelengths of the modes in 2.1 are $\lambda_n = (L/2n)$. For large n , or small λ , we can treat λ as a function of a continuous variable n and find the number of different modes with wavelengths between λ and $\lambda - d\lambda$

$$n(\lambda) = \frac{L}{2\lambda} \quad \text{and} \quad \Delta n = \frac{dn}{d\lambda}(-d\lambda) = L \frac{2}{\lambda^2} d\lambda. \quad (2.2)$$

Assuming each of these modes has energy kT , the total thermal energy with wavelengths between λ and $\lambda - d\lambda$ at temperature T , $e(\lambda, T)$, is kT times Δn

$$e_{1D}(\lambda)d\lambda = kT \frac{dn}{d\lambda}(-d\lambda) = L \frac{2kT}{\lambda^2} d\lambda. \quad (2.3)$$

(We use $-d\lambda$ as λ is decreasing with increasing n . We count modes starting from the longest wavelength. The 1D subscript denotes that we are working with an idealised 1D model.)

3D Black Body

A similar calculation for a 3D system gives the result

$$e(\lambda) d\lambda = V \frac{2kT}{\lambda^4} d\lambda. \quad (2.4)$$

Taking account of how frequently the light hits the walls (L/c seconds for a box of side L) and is reradiated, we would expect the energy radiated per unit time per unit area and per steradian¹ with wavelengths between λ and $\lambda - d\lambda$ is

$$B_{\lambda}^{\text{cl}}(T)d\lambda = \frac{c kT d\lambda}{\lambda^4}. \quad (2.5)$$

¹A steradian is the SI unit for solid angle. It is dimensionless.

$B_{\lambda}^{\text{cl}}(T)$ is called the spectral radiance. The superscript cl is to denote classical. The λ^{-4} dependence suggests a rapidly increasing radiated intensity as λ gets smaller. For blue and red light $\lambda_{\text{blue}} \sim 380 \text{ nm}$ and $\lambda_{\text{red}} \sim 760 \text{ nm}$ and

$$\left(\frac{1}{\lambda_{\text{blue}}}\right)^4 \approx 16 \left(\frac{1}{\lambda_{\text{red}}}\right)^4.$$

If correct, it would mean that 16 times as much blue light as red light should be radiated from any body. Everything would appear blue (including the Sun). This problem is called the ultraviolet catastrophe.

The dependence predicted in 2.5 is not observed as can be seen in Figure 2.1. The classical theory predicts the spectrum that diverges in the limit $\lambda \rightarrow 0$. What is needed is an explanation for why the spectrum is cut off at small wavelengths/large frequencies.

Planck's Solution

Planck suggested that energy is only emitted/absorbed from/into a light field in units of $h\nu$, where ν is the frequency of the light:

$$\Delta E = h\nu \quad \text{where } h \text{ is (now) called Planck's constant.} \quad (2.6)$$

Each mode can only have energy $0, h\nu, 2h\nu, \dots$.

Thermodynamics says that the average occupation of one of these levels is given by Eq 1.1 $p(nh\nu) \sim e^{-nh\nu/kT} \equiv e^{-\beta nh\nu}$, where $\beta = 1/kT$. The constant of proportionality is given by the requirement that the probability distribution is normalised

$$p(nh\nu) = \frac{e^{-\beta nh\nu}}{Z} \quad \text{where} \quad Z = 1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + e^{-3\beta h\nu} + \dots = \frac{1}{1 - e^{-\beta h\nu}}.$$

The right-hand side follows as the sum is a geometric progression with ratio $r = e^{-\beta h\nu}$. The final result is

$$p(h\nu) = e^{-\beta h\nu} (1 - e^{-\beta h\nu}). \quad (2.7)$$

The average energy in a mode with frequency is no longer kT as assumed classically, but

$$\begin{aligned} \langle E \rangle &= \sum_{n=0}^{\infty} n h\nu p(nh\nu) = \sum_{n=0}^{\infty} n h\nu e^{-\beta h\nu} (1 - e^{-\beta h\nu}) \\ &= (1 - e^{-\beta h\nu}) \sum_{n=0}^{\infty} \left(-\frac{d}{d\beta} e^{-\beta nh\nu} \right) = (1 - e^{-\beta h\nu}) \left(-\frac{d}{d\beta} \sum_{n=0}^{\infty} e^{-\beta nh\nu} \right) \\ &= -(1 - e^{-\beta h\nu}) \frac{d}{d\beta} \left(\frac{1}{1 - e^{-\beta h\nu}} \right) = (1 - e^{-\beta h\nu}) \frac{h\nu e^{-\beta h\nu}}{(1 - e^{-\beta h\nu})^2}. \end{aligned}$$

Planck's result for the energy in a mode with frequency ν is therefore

$$\langle E \rangle = \frac{h\nu}{e^{\beta h\nu} - 1}, \quad \text{where } \beta = 1/kT. \quad (2.8)$$

This solved the problem and generated a result that explained the experimental observations perfectly.

To see how 2.8 explains things, let's look at two limiting cases

- **High temperatures**

If $\beta h\nu \ll 1$, we can expand the exponential in the denominator to find

$$\frac{h\nu}{e^{\beta h\nu} - 1} = \frac{h\nu}{1 + \beta h\nu + \frac{(\beta h\nu)^2}{2!} + \frac{(\beta h\nu)^3}{3!} + \dots} \approx \frac{h\nu}{\beta h\nu} = \frac{1}{\beta} = kT.$$

This is the classical result. The energy in the mode is kT . (Classical thermodynamics says that both the kinetic energy and the potential energy in the mode should be $kT/2$ on average giving kT in total.) This is going to be a recurring theme. The results of quantum theory must reproduce the classical results where we expect them.

- **Low temperatures**

Low means low with respect to $h\nu$ and so $e^{\beta h\nu} \gg 1$:

$$\frac{h\nu}{e^{\beta h\nu} - 1} \approx h\nu e^{-\beta h\nu}.$$

The expected energy in a high frequency (short wavelength mode) is exponentially small.

The suggestion that energy could only come in quanta of $h\nu$ eliminated the ultraviolet catastrophe. Better than that, it predicted a form for the spectral radiance (replace ν by c/λ and kT by $\langle E \rangle$ in 2.5)

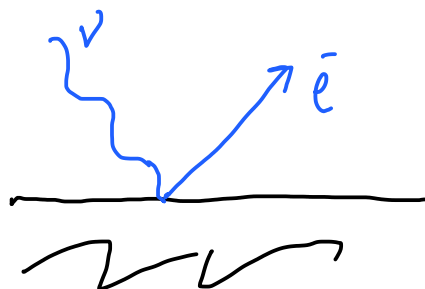
$$B_\lambda(T)d\lambda = c \frac{(\beta hc/\lambda)}{(e^{\beta hc/\lambda} - 1)} \frac{d\lambda}{\lambda^4}. \quad (2.9)$$

This is the form plotted in Figure 2.1 for 3 different temperatures. The theory and observations match exactly.

People worked to understand why Planck's formula worked so well. Some seemed to think that quantisation had something to do with the emission process but not that quantisation was a property of the light itself. Einstein was the first to suggest this. There was already partially understood experimental evidence that guided Einstein.

2.1 Photoelectric Effect

Experimental data on the photoelectric effect had been collected over many years and by 1902 (Lenard) the phenomenon was well characterised experimentally. The experimental setup was simple in principle. Light incident on a metal surface can lead to the emission of electrons.



The electrons are collected at an electrode at a voltage, V , with respect to the metal surface. This voltage allows measurement of the energy of the emitted electrons (it is used to stop the electrons reaching the electrode).

Classical physics says the energy given to electrons depends on intensity—"more light = more energy". It cannot explain the observations shown in 2.2.

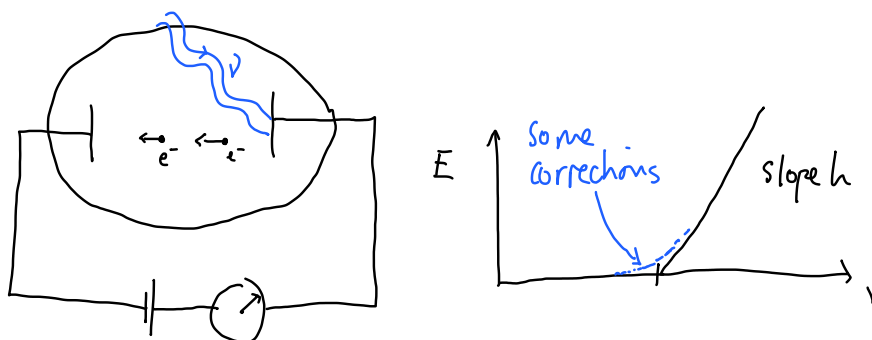


Figure 2.2: The photoelectric effect. Light with frequency ν is incident on a metal plate. This leads to electrons being emitted (image on left), which travel towards another metal plate. A voltage applied to this plate allows the electrons to be stopped (they are gaining potential energy as they approach the negatively charged plate). What is measured is the voltage needed to stop the oncoming electrons and measures their kinetic energy E . This is plotted against the frequency of the incident light (right). The result is not consistent with classical physics which associates energy in light waves with their intensity not their frequency. There may be corrections close to threshold frequency associated with higher order effects.

Einstein's Hypothesis

Einstein (1905) argued that light rays consist of discrete particles, now called photons, with energy

$$E = h\nu.$$

An electron in the metal absorbs a photon's energy. If $h\nu$ is large enough, the electron has the energy to escape. To escape, it has to have enough energy to overcome the attractive potential of the ions. This gives rise to the so-called work function, ϕ_0 . If it does escape the electron has kinetic energy

$$h\nu - \phi_0$$

after leaving the surface. This is the energy measured by the stopping voltage.

Worked Example

Ultraviolet (uv) light with wavelength 350 nm and intensity 1 W m^{-2} is directed at a potassium metal surface with $\phi_0 = 2.2 \text{ eV}$.

- Find the maximum kinetic energy of photoelectrons. Put your answer in eV .
- If 0.5% of incident photons produce photoelectrons, how many are emitted per second if the surface area is 1 cm^2 .

Answer

- i. The photon energy is according to Planck's hypothesis

$$E(\text{eV}) = \frac{h\nu}{e} = 6.6 \times 10^{-24} \times \frac{3 \times 10^8}{350 \times 10^{-9}} \times \frac{1}{1.6 \times 10^{-19}} \approx 3.5 \text{ eV}.$$

The kinetic energy

$$\text{KE} = E - \phi_0 = 3.5 - 2.2 = 1.1 \text{ eV}.$$

- ii. Number of electrons emitted per second, $0.005 \times$ photons per second,

$$\begin{aligned} i_n &= 0.005 \times \frac{\text{Energy per second}}{h\nu} = \frac{0.005 \times \text{intensity} \times \text{area}}{h \times (c/\lambda)} \\ &= \frac{0.005 \times 1 \times 10^{-4}}{6.6 \times 10^{-34} \times (3 \times 10^8 / 350 \times 10^{-9})} \approx 8.8 \times 10^{11} \text{ s}^{-1}. \end{aligned}$$

Remember to think about any answer like this. Is 1.1 eV reasonable? Probably, because the energy is comparable to the work function. One wouldn't want to set up an experiment which needed kilovolts to stop the emitted electrons. The 10^{11} for i_n might seem large but corresponds to a tiny current ($i_e = e \times i_n \sim 1.4 \times 10^{-4}$ A).

2.2 Compton Effect

The Compton effect was reported in 1923, so 18 years after Einstein's hypothesis appeared. It is a beautiful demonstration that light photons are genuinely behaving as particles. They have not just energy but also momentum. As particles, they can collide with other particles. Both momentum and energy are conserved in such collisions. The discovery of the Compton effect showed that we can treat this collision using notions from classical mechanics.

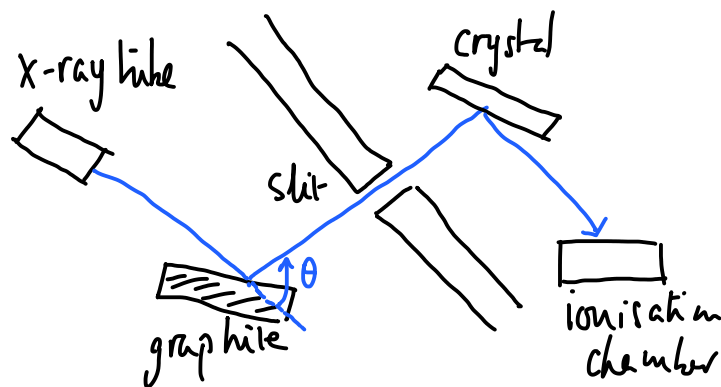


Figure 2.3: Schematic diagram showing Compton's experimental setup. X-rays (high frequency, short wavelength) light scatters off electrons in a graphite target. The slit, crystal and ionisation chamber together allow the photon wavelength of the scattered light to be measured as a function of the scattering angle θ . The slit selects the angle, the crystal selects for wavelength and the ionisation chamber counts photons.

According to the theory of special relativity photons must have zero rest mass. The theory gives

$$E = mc^2 = \gamma m_0 c^2 = \frac{1}{\sqrt{1 - v^2/c^2}} m_0 c^2 \stackrel{(v=c)}{\infty} \neq h\nu.$$

We have used that fact that the photon's velocity $v = c$ (light travels at the speed of light!). The only solution to this is that $m_0 = 0$ and the assumption of a non-zero m_0 is wrong.

Using the formula (also from special relativity, with p the momentum), $E^2 = p^2 c^2 + m_0^2 c^4$, we find that $m_0 = 0$ means

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}. \quad (2.10)$$

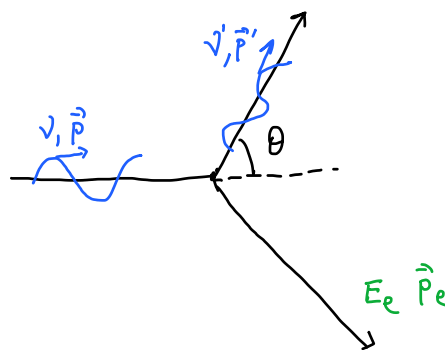
This result relating momentum and wavelength is central to all of quantum theory. Understanding that this was the result which applied to all particles and fields is central to quantum phenomena and not just to photons. Together with de Broglie's hypothesis, which we will study in the next chapter, it led to the rapid development of what we call quantum mechanics and quantum field theory. Quantum mechanics, also called wave mechanics, is what we will discuss in the next chapter.

Compton's Experiment

Compton's experiment shone X-rays on a graphite target and studied the wavelength of the waves emitted, see Fig 2.3.

If an incident photon collides with an electron in the graphite layer the total momentum of the photon and electron pair as well as their energy should be conserved. According to the quantum hypothesis, the frequency of the X-rays would imply that the photon energy $h\nu$ were much larger than the kinetic energy of individual electrons in the graphite target. Compton argued that we can therefore treat the electrons in the graphite as stationary (their initial momentum $p_e \ll h/\lambda$) and can be treated as zero).

The idealised picture of the scattering is as follows. A photon with frequency ν collides with a stationary electron. After the collision the electron has energy E_e and momentum \mathbf{p}_e and a photon has frequency ν' and momentum \mathbf{p}' :



Writing the energy of photons as pc and $p'c$ gives and the rest mass energy of the electron as $m_0 c^2$

$$\begin{aligned} pc + m_0 c^2 - p'c &= E_e \quad \text{conservation of energy} \\ \Rightarrow p + m_0 c - p' &= (E_e/c) \\ \mathbf{p} - \mathbf{p}' &= \mathbf{p}_e \quad \text{conservation of momentum.} \end{aligned}$$

Squaring both sides of the second equation and taking the inner product of both sides of the second equation gives (using Einstein's result that $E_e^2 = p^2 c^2 + (m_0 c^2)^2$)

$$p^2 + p'^2 + (m_0 c)^2 + 2(p m_0 c - p' m_0 c - p p') = p_e^2 + (m_0 c)^2$$

$$p^2 + p'^2 - 2pp' \cos \theta = p_e^2$$

Subtracting the second equation from the first (and dividing by 2) gives

$$m_0 c (p - p') - p p' (1 - \cos \theta) = 0 \quad \Rightarrow \quad \left(\frac{1}{p'} - \frac{1}{p} \right) = \frac{1}{m_0 c} (1 - \cos \theta).$$

This result is usually written in terms of the difference in wavelength of the photons (remember the hypothesis of quantum theory that $p = h/\lambda$ for a particle):

$$\lambda' - \lambda = \lambda_C (1 - \cos \theta) \quad \text{where} \quad \lambda_C = \frac{h}{m_0 c}. \quad (2.11)$$

λ_C is called the Compton wavelength. The variation of wavelength predicted by this calculation matches what is observed.

The difference in wavelength in 2.11 is a quantum phenomenon. The wavelength of light scattering off a stationary particle cannot change according to classical physics (some changes associated with the Doppler effect if the particle is moving or in very intense light but nothing along the lines predicted here). This effect is an excellent example of what is sometimes called wave-particle duality in quantum theory. Light is sometimes well-described as a wave. The experiment here uses wave theory to describe the diffraction by the crystal used to analyse the wavelength of the scattered light. However, it analyses the interaction with the graphite target by treating the light as a stream of particles which collide with electrons.

2.3 Summary

We have looked at three quantum phenomena:

Black-body Radiation This made clear that classical physics was in difficulty. There are infinitely many em-wave modes (degrees of freedom) in any body. According to classical thermodynamics, these should have (on average) kT thermal energy. This infinity of modes would lead to a body radiating at an infinite rate at any non-zero temperature. Planck suggested that energy in light modes is radiated in quanta of $h\nu$. If $h\nu \gg kT$, the probability of these modes radiating is exponentially reduced by the Boltzmann factor $e^{-h\nu/kT}$. This hypothesis correctly describes observations.

Photoelectric Effect The dependence of the energy of electrons emitted from an irradiated surface on the frequency of the incident light is inconsistent with classical theory. Einstein interpreted the results of the experiment in terms of particles of light carrying energy $h\nu$ which interacted with individual electrons.

Compton Effect The scattering of light by a stationary electron can be understood if the light particles carried not just energy $h\nu$ but momentum h/λ . Then the scattering of the light is correctly accounted for as a collision between a photon and an electron, which conserves energy and momentum.

Describing light fully requires quantising what in physics is called a field (not to be confused with what mathematicians call a field²). Classically, the electric and magnetic fields need to be defined everywhere as a function of time. This is why there are infinitely many degrees of freedom (there are infinitely many points in space). Planck's hypothesis may have dealt with the thermal excitation of these degrees of freedom. However, this was not the end of the matter. Fields with many degrees of freedom have been (and remain) difficult for quantum theory.

We will leave photons behind from now on and concentrate on the quantum theory of individual matter particles—electrons and protons principally. The second half of the module will discuss other elementary particles. The classical description of a single particle is simpler than light. If we can treat the particle as a point particle we need only fix its position as a function of time $\mathbf{r}(t)$. In 3D, there are therefore only 3 things to specify as a function of time (the three coordinates of the particle). This is one reason why quantum mechanics came (albeit shortly) before quantum field theory.

²Roughly speaking, a field in maths is a set. The operations of addition and multiplication should be defined on this set and behave as they do for real numbers.

Chapter 3

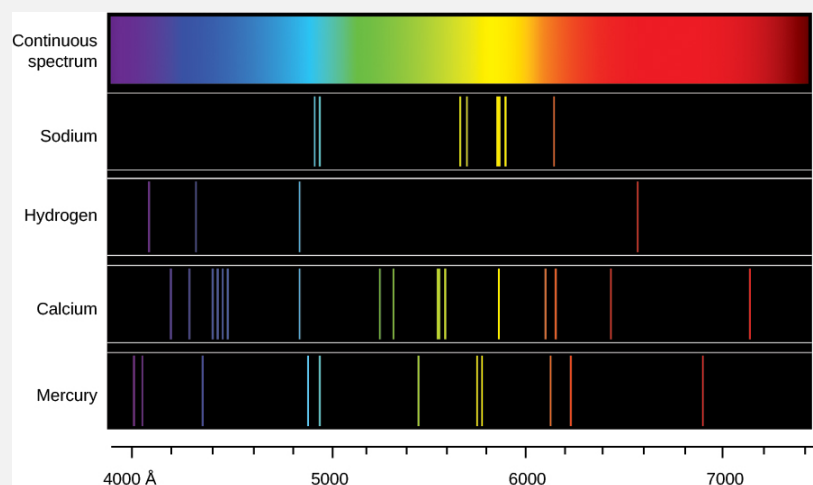
Matter and Spectra

Emission and absorption spectra of atoms show sharp spectral lines. Understanding these was one thing that quantum theory applied to matter was initially concerned with. Rutherford's experiment (1911) had showed that matter consisted of atoms with a heavy positively-charged nucleus and light negatively-charged electrons bound to this nucleus. Describing the nature of these bound states of electrons and nuclei is a major first challenge for quantum theory.

Something on Names

What are spectra and why are they called spectral lines? A spectrum is usually used to describe the amplitude of some signal as a function of frequency. The word spectrum in this context was introduced by [Newton](#) to describe the range of colours seen after white light passes through a prism. His motivation is thought to relate to his observation that light remained visible in his eyes after closing them in a way reminiscent of ghosts. (Spectrum means apparition in Latin.)

Spectrometers used prisms to split light beams according to frequencies. Different frequencies showed up as lines on photographic plates. This graphic ([source](#)) illustrates schematically what the emission spectrum of some atomic species looks like as a function of wavelength in Å.



The lines associated with absorption and emission observed for atomic Hydrogen were fitted by the following formula:

$$\frac{1}{\lambda} = \tilde{R} \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad m < n. \quad (3.1)$$

Here $\tilde{R} = 1.0968 \times 10^7 \text{m}^{-1}$ is called the Rydberg constant. The tilde indicates that the constant is quoted in inverse meters. (More commonly the Rydberg constant is quoted as an energy $R = 13.6 \text{eV}$ as we will see.) The series for hydrogen are named after the people who reported them first

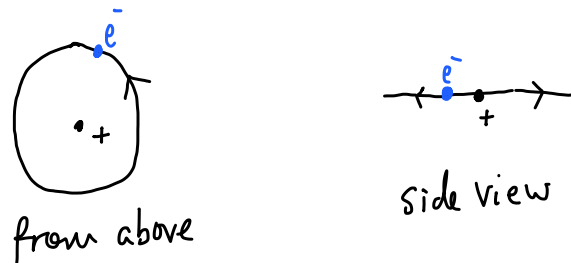
- $m = 1$ Lyman series (1906) which is in the ultraviolet
- $m = 2$ Balmer series (1885), some of these lines are in the visible
- $m = 3$ Paschen series (1908) in the infra-red

For other atoms (ones with more electrons) the spectral lines obey formulas

$$\frac{1}{\lambda} = T_m - T_n, \quad m < n. \quad (3.2)$$

with corresponding 'Term Numbers' T_n .

These discrete lines were a problem for classical physics, which quantum mechanics was able to solve. The problem is that in classical physics electrons orbiting a nucleus in similar way to planets orbiting a star would not be stable and would not explain the discrete spectral lines.



All frequencies would be possible depending on the orbit of the electron. However, charged electrons orbiting a nucleus would be oscillators and would radiate electromagnetic energy (looked on sideways they are a charged particle oscillating backwards and forwards as in a radio antenna).

3.1 Bohr's Atom

If light is absorbed as photons with energy $h\nu$ then a discrete spectral line suggests a transition between orbits with well-defined initial and final energies, E_i and E_f ,

$$h\nu = \frac{hc}{\lambda} = E_f - E_i, \quad \text{with } E_f > E_i \quad \text{for absorption.}$$

Bohr postulated (1913) that only states with a discrete set of energies E_n is possible (here n is an integer). Rydberg's formula would become

$$\frac{1}{\lambda} = \frac{E_f}{hc} - \frac{E_i}{hc}. \quad (3.3)$$

Comparing 3.2 and 3.3 suggests identifying ($m < n$)

$$\frac{E_i}{hc} = -\frac{\tilde{R}}{m^2} \quad \text{or} \quad E_i = \frac{hc\tilde{R}}{m^2} \equiv -\frac{R}{m^2}, \quad \text{and} \quad E_f = -\frac{R}{n^2}. \quad (3.4)$$

Here $R = hc\tilde{R}$ is the definition of the Rydberg constant as an energy (see just after 3.1). The energies need to be identified as negative, otherwise the electron would not be bound to the nucleus.

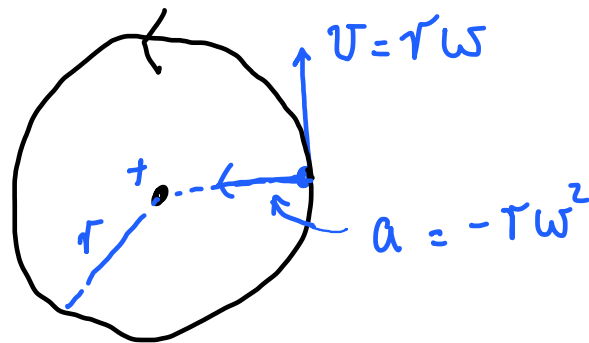
Quantisation of Angular Momentum

Bohr also suggested that electrons describe circular orbits with quantised angular momentum

$$ma^2\omega = n\hbar, \quad \hbar = \frac{h}{2\pi}. \quad (3.5)$$

This empirical suggestion can be seen as the extension of Planck's original idea. If energy can be quantised with the introduction of the constant h , it seems reasonable to argue that angular momentum might also be quantised given that h has the same dimensions as angular momentum. The quantisation in units of \hbar (rather than h) cannot given deduced just by considering dimensions. It is the following calculation that confirms this—it gives correctly the values for the frequencies seen in experiment.

For the H atom



we set the centrifugal force equal to the attractive (Coulomb) force between the electron and the nucleus $mr\omega^2 = e^2/4\pi\epsilon_0r^2$. The angular momentum $mr^2\omega = n\hbar$ (by Bohr's hypothesis). We rewrite these results as

$$r^3\omega^2 = \frac{e^2}{4\pi\epsilon_0m} \quad \text{and} \quad \omega^2 = \frac{n^2\hbar^2}{m^2r^4}. \quad (3.6)$$

Inserting the expression for ω^2 into the first equation gives

$$r = n^2 \frac{\hbar^2 4\pi\epsilon_0}{me^2} \equiv n^2 a_0. \quad (3.7)$$

The allowed radii of the orbits are given in terms of the quantity called the Bohr radius

$$a_0 = \frac{\hbar^2 4\pi\epsilon_0}{me^2} = 0.53 \text{ \AA}. \quad (3.8)$$

Using the result 3.6 (in the form $r^3\omega^2 = e^2/4\pi\epsilon_0 m$) gives the energy in the circular orbit

$$E = \text{KE} + \text{PE} = \frac{1}{2}mr^2\omega^2 - \frac{e^2}{4\pi\epsilon_0 r} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r}.$$

When we set $r = n^2 a_0$ (from 3.7), we obtain

$$E_n = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0} \frac{1}{n^2} \equiv -\frac{R}{n^2}. \quad (3.9)$$

This is a beautiful result. It is exactly the dependence needed to explain experiment, see 3.4, and gives the Rydberg constant in terms of other fundamental constants

$$R = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{me^2}{\hbar^2 4\pi\epsilon_0} = \frac{m}{2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \approx 13.6 \text{ eV}. \quad (3.10)$$

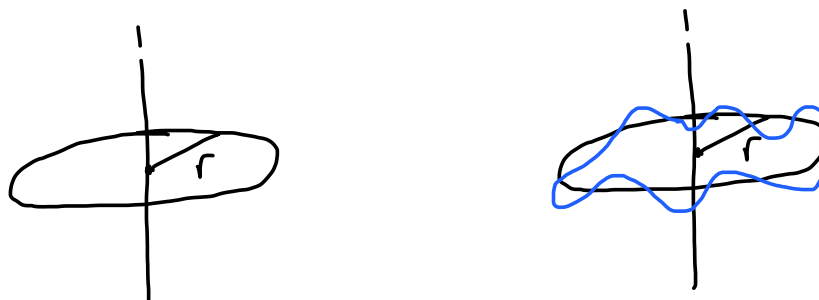
These results 3.9 and 3.10 explained the spectra observed for atomic hydrogen perfectly. It was difficult to explain the more complicated term numbers seen in many-electron atoms 3.2. This is not surprising as solving for the orbits of many electron atoms is not easy classically. It would also not be clear how to incorporate relative angular momentum of the different electrons. What is also not wholly satisfactory is why angular momentum should be quantised—it would be unsatisfactory if we had to assert that each new quantity needed to describe some problem was quantised. The resolution to this problem was provided by de Broglie.

3.2 de Broglie's Hypothesis

de Broglie (1924) suggested that all particles behaved like waves with

$$\lambda = \frac{h}{p} \quad \text{or equivalently} \quad p = \frac{h}{\lambda} = \hbar k. \quad (3.11)$$

Here $k = 2\pi/\lambda$ is the wavenumber. Why do this? Well, it only seems natural that, if light waves can behave like particles, particles should also behave like waves. Note that 3.11 is the same relation that Compton used in his analysis of the scattering of light photons off particles. It also gives a rough and ready justification for Bohr's quantisation of angular momentum:



If the electrons behave like waves then Bohr's suggestion that $l = rp = n\hbar$ implies

$$rp = r\hbar k = n\hbar \quad \Rightarrow \quad r \frac{2\pi}{\lambda} = n \quad \text{or} \quad \frac{2\pi r}{\lambda} = n.$$

This is the statement that the length of the classical orbit of the electron around the nucleus needs an integer number of wavelengths for the electron wave to fit around the ring.

Of course the electron waves would be waves in 3D not just on a ring. The idea that particles behaved like waves was quickly verified in experiment. Thomson (1925) found evidence for diffraction (a wave phenomenon) when scattering electrons off a crystal.

Summary

I have presented the development of quantum theory like a detective story. Experimental evidence suggested something was going on which was not understood. Various detectives (Planck, Einstein, Bohr, de Broglie and others) formulated hypotheses of what might be happening and tried to explain the evidence. Theories or ideas were validated by whether they explained, and predicted new, observations and data. This is how science works. Essentially all sciences, including social sciences, work like this. It is called empiricism. The principal exception to this is pure mathematics which relies on proof to validate conjectures rather than comparison with data taken from observation or experiment.

As we will see, quantum theory developed quickly after this. The main ideas were there, but they needed to be pieced together mathematically. From 1924 until 1932 or so most of what could be done was done. This left us with the tools needed to explain the quantum properties of matter such as atoms, molecules and solids. They are being used all the time nowadays to explain and predict phenomena across physics, chemistry, biology, engineering and computer science.

Quantum theory did run into another huge problem which held things back for another decade and a half. The problem turned out to be the same problem that Planck had first confronted namely that of infinities. While the issue with the thermal excitation of the infinitely many modes had been resolved by suppressing short wavelength excitations using a Boltzmann factor, the theory still had infinitely many degrees of freedom. Once interactions between these degrees of freedom (in particular between light and charges) were switched on, the infinities came back with a vengeance. The theory predicted observable quantities which were infinite. The partial resolution of the problem appeared in the 1940's (Tomonaga, Bethe, Schwinger, Feynman and Dyson made important contributions—look up Quantum Electrodynamics for more on this).

The nature of the module will change now. We will look at the construction of the new mechanics, quantum mechanics, and its assumptions. Most of the work will be in setting up the equations and interpreting their solutions.

Chapter 4

Quantum Mechanics

Quantum mechanics became the new mechanics for particles. The theory developed quickly. Heisenberg (1925) with Born and Jordan developed the theory on the basis of matrices while Schrodinger (1925/6) introduced wave mechanics. We will concentrate on Schrodinger's approach which is equivalent to the original matrix mechanics version.

Felix Bloch in his reminiscences¹ said that Schrodinger had been criticised at a colloquium where he had explained de Broglie's idea (essentially the sketch on page 20 showing an integer number of wavelengths). He was told that he needed a wave equation if he wanted to talk about waves. Bloch writes

Just a few weeks later he [Schrodinger] gave a talk in the colloquium which he started by saying: "My colleague Debye suggested that one should have a wave equation; well, I have found one".

We will see how a correspondence principle attributed to Bohr, which Schrodinger put together with de Broglie's hypothesis & Planck's relation, led to the correct wave equation for matter.

The argument is unusual but only in the sense that it works backwards from the answer. The canonical approach would be to deduce the correct wave equation for something from the tested or postulated laws of motion (Newton's laws in classical mechanics, laws of electromagnetism for light, general relativity for gravitational waves), and then solve it to find wave-like solutions. Here we are in the unusual position of knowing the solutions (particles behave like waves) but don't know their equation of motion.

We should remind ourselves what the solution to a wave equation should look like. We expect the simplest travelling waves to have the form

$$\psi(x, t) \sim e^{i(kx - \omega t)} = e^{ik(x - vt)} \quad \text{and} \quad \psi(x, t) \sim e^{i(-kx - \omega t)} = e^{-ik(x + vt)}. \quad (4.1)$$

These describe right-travelling, $\psi \sim e^{ik(x - vt)}$, and left-travelling $\psi \sim e^{i(-k)(x + vt)}$ waves. The quantity v is called the phase velocity, $v = \omega/k = \lambda\nu$. From here on we will consider k to have a direction and think of it as a vector. Positive k is the wavevector for a wave travelling in the positive x -direction and negative k for a wave travelling in the negative x -direction.

¹Physics Today 29(1976)23

The displacement variable in 4.1 is called ψ . In mechanical systems the displacement might be the displacement of a string from its equilibrium configuration as a function of position along the string and of time. It would be real. One issue, that Schrodinger and others had to resolve for quantum theory, was what ψ described.

The relation between the angular frequency $\omega(k)$ and the wavevector k for a wave is called the dispersion relation. Normally it comes from inserting wave solutions of the type 4.1 into the known equation of motion:

$$\begin{aligned} \frac{\partial^2 \psi}{\partial t^2} - v^2 \frac{\partial^2 \psi}{\partial x^2} = 0 & \stackrel{(wave)}{\Rightarrow} (-\omega^2 + v^2 k^2) \psi = 0 \quad \text{hence } \omega = \pm v k \\ \frac{\partial \psi}{\partial t} + v \frac{\partial \psi}{\partial x} = 0 & \stackrel{(wave)}{\Rightarrow} (-\omega + v k) \psi = 0 \quad \text{hence } \omega = v k. \end{aligned} \quad (4.2)$$

The first of these equations is often called the wave equation. Here $\psi(x, t)$ might be the deviation from equilibrium of points on a tight string. The second equation is called the advection equation and is used to describe traffic flow problems with $\psi(x, t)$ the traffic density as a function of position and time along a road.

We will use the relations between frequency and energy and between momentum and wavevector to deduce the dispersion relation ($\omega = \omega(k)$) in quantum theory and reverse the argument in 4.2 using Bohr's correspondence principle to find the equation describing ψ . We will multiply the dispersion relation by $\psi(x, t)$. Where we see $\omega \times \psi$ we will guess that this comes from taking a time-derivative of ψ and where we see $k \times \psi$ we relate this to a spatial derivative of ψ . In summary, we

$$\text{replace } \omega \psi \text{ by } i \frac{\partial \psi}{\partial t}, \quad \text{and replace } \pm k \psi \text{ by } \frac{1}{i} \frac{\partial \psi}{\partial x} \quad (4.3)$$

to find the equation of motion. (In the second of these relations, remember that k now includes the sign.)

Correspondence Principle

The correspondence principle is not as well-defined as its name suggests. It is essentially the common sense idea that, when a physical theory is overthrown, the new theory and the old theory must agree in those realms where the old theory has been tested and shown to describe reality correctly. In the context of mechanics, the old theory is Newton's laws of motion and the new theory is quantum mechanics. In this case the classical limit is identified with systems far from their ground state ("in the limit of large quantum numbers" is the technical term).

The correspondence we need to take account of is that in classical physics the kinetic energy is $p^2/2m$. Planck tells us that $E = \hbar\omega$ and de Broglie says that $p = \hbar k$. Taken together this means

$$E = \frac{p^2}{2m} \stackrel{(wave)}{\Rightarrow} \hbar\omega - \frac{\hbar^2 k^2}{2m} = 0. \quad (4.4)$$

We imagine the relation between ω and k multiplies a function ψ and write it using the identifications in 4.3:

$$\left(\hbar\omega \psi - \frac{\hbar^2 k^2}{2m} \right) \psi = 0 \quad \xrightarrow{\text{Eq 4.3}} \quad \left(i\hbar \frac{\partial \psi}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \right) = 0. \quad (4.5)$$

This gives us the new equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}. \quad (4.6)$$

Equation 4.6 is called the **Schrodinger equation**, actually the Schrodinger equation for free particles as we have not yet included the effect of a potential energy. It is the correct answer. The reason we know it is correct is because it gives the right answers for what can be observed. You should think of the argument given here, as Schrodinger did, as a plausibility argument. The test that matters is “does it work?”.

In fact this line of argument throws up alternative equations. We could have demanded correspondence with the classical result from special relativity, $E^2 = p^2c^2 + m_0^2c^4$. It is **reported** that Schrodinger did consider this but rejected it because it did not correctly describe the energy levels of a hydrogen atom. The equation is called the Klein-Gordon (KG) equation after the people who first published it. It turns out that a variant of the KG equation describes well the behaviour of the Higgs boson (see second half of the module).

4.1 Schrodinger Equation

The equation 4.6 was constructed to have wave-like solutions with the right dispersion, see Eq 4.4. But what does it mean? Given the presence of the factor i , it is inevitable that solutions will be complex-valued. (This is not the same as using the complex exponential form and taking the real part as you may have seen used elsewhere. The solutions to the Schrodinger equation will only be valid when fully complex.) No measurement device can measure imaginary Amps or imaginary Volts or any other imaginary quantity. We can only measure real-valued quantities, which means ψ itself cannot be a directly measurable quantity.

We need to know what ψ represents and would like to know where the particle is and what its other measurable properties are.

Interpreting ψ

It is natural to assume that, where ψ is large, is where the particle is likely to be. This suggests that ψ is related to the probability of finding the particle.

Born proposed, and we will assume, that

$$|\psi(x, t)|^2 dx = \psi^*(x, t)\psi(x, t) dx \quad (4.7)$$

gives the probability of finding the particle at time t between x and $x + dx$. This makes $|\psi(x, t)|^2$ a probability density. This proposal means that $\psi(x, t)$ should be normalised

$$\int_L dx |\psi(x, t)|^2 dx = 1, \quad (4.8)$$

where L is the space on which ψ is defined. This condition states that, if there is a particle somewhere in the system, the probability of finding it somewhere must be 1.

Superpositions—Standing Waves

Equation 4.6 involves a linear operator acting on ψ . (You should have met the notion of a linear operator in maths modules. The reminder on page 32 recaps the ideas.) This means that linear superpositions of the solutions we already know (those in 4.1) will also be solutions.

We will look at combinations of two waves and, in the next section, at the more general idea of a wave packet.

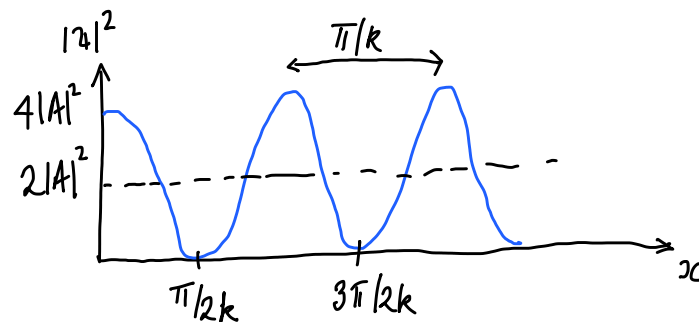
Consider the superposition

$$\psi = Ae^{ikx-i\omega(k)t} + Ae^{-ikx-i\omega(-k)t}.$$

The amplitude A is the same for each component and may be complex. Since $\hbar\omega(-k) = \hbar^2\omega(k)/2m (= \hbar^2k^2/2m)$, this reduces to

$$\psi = 2Ae^{-i\omega(k)t} \cos kx \quad \text{and} \quad |\psi|^2 = 4|A|^2 \cos^2 kx = 2|A|^2 (1 + \cos 2kx). \quad (4.9)$$

This is a standing wave. ψ oscillates at each point in space with angular frequency $\omega(k)$ and amplitude $2A \cos kx$:



The probability density of finding the particle is given by $|\psi|^2$ which is largest when $\cos 2kx = 1$ and a minimum when $\cos 2kx = -1$.

Standing waves oscillating at a constant frequency correspond in quantum theory to what are called stationary states (we will discuss these further in the next chapter). They describe a system with a constant energy and no measurable quantities which depend on time ($|\psi|^2$ is time-independent). Atomic orbitals are probably the best-known examples of such states. They will be the solutions of interest when we include the interaction of the particle with a potential. The boundary conditions will be that the wave function ψ must be single-valued (it must map onto itself when going round any axis through the nucleus) and must vanish as $r \rightarrow \infty$, where r is the distance of the electron from the nucleus. We will not get onto atoms in this module as we will restrict ourselves to systems in 1D.

Superpositions—Group Velocity

Now consider the superposition of two waves with the same amplitude but slightly different wavevectors with $k > 0$:

$$\psi = Ae^{ik_1x-i\omega(k_1)t} + Ae^{ik_2x-i\omega(k_2)t} \quad (4.10)$$

choosing $k_1 = k_0 + \Delta k$ and $k_2 = k_0 - \Delta k$. Taking the case $\Delta k/k_0 \ll 1$, we can expand $\omega(k)$ in a Taylor series about k_0 and keep only the constant and the term linear in Δk :

$$\omega(k_0 \pm \Delta k) \approx \omega(k_0) \pm \Delta k \left. \frac{d\omega}{dk} \right|_{k_0} \equiv \omega_0 \pm \Delta k \omega'_0. \quad (4.11)$$

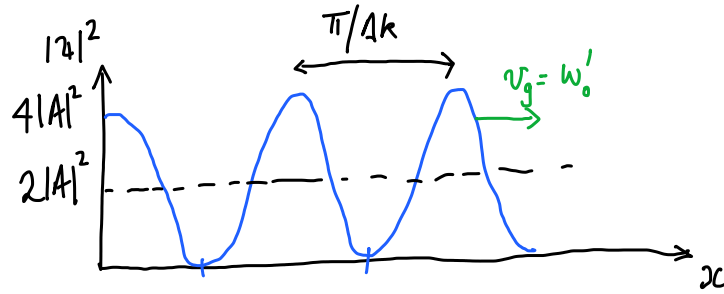
The vertical bar with the subscript k_0 means that $d\omega/dk$ should be evaluated at $k = k_0$. The superposition can be written

$$\begin{aligned} \psi &= Ae^{i(k_0x - \omega_0t + \Delta kx - \Delta k\omega'_0t)} + Ae^{i(k_0x - \omega_0t - \Delta kx + \Delta k\omega'_0t)} \\ &= 2Ae^{i(k_0x - \omega_0t)} \left[\frac{e^{i\Delta k(x - \omega'_0t)} + e^{-i\Delta k(x - \omega'_0t)}}{2} \right] = 2Ae^{i(k_0x - \omega_0t)} \cos \Delta k(x - \omega'_0t). \end{aligned}$$

The probability distribution is

$$|\psi|^2 = 4|A|^2 \cos^2 \Delta k(x - \omega'_0t) = 2|A|^2 [1 + \cos 2\Delta k(x - \omega'_0t)]. \quad (4.12)$$

which looks like



It is common to call the quantity $v_g = \omega'_0$ the group velocity. The pattern in $|\psi|^2$ is a function of $(x - v_g t)$. It describes a right-travelling wave moving at speed v_g . Using $\hbar\omega(k) = \hbar^2 k^2 / 2m$ from 4.4 we find

$$\omega' = \frac{d}{dk} \left(\frac{\hbar k^2}{2m} \right) = \frac{\hbar k}{m} \Rightarrow v_g = \omega'_0 = \frac{\hbar k_0}{m} = \frac{p_0}{m}, \quad (4.13)$$

where p_0 is the average momentum of the particle ($p_0 = \hbar(k_1 + k_2)/2$). This is reassuring. The speed at which the pattern in the probability density moves is what we should expect from classical physics.

Normalisation

There is a slight problem with all three solutions of Schrodinger's equation we have looked at

- i. $\psi = A e^{ikx - i\omega(k)t}$ (plane wave)
- ii. $\psi = 2A e^{-i\omega(k)t} \cos kx$ (standing wave)
- iii. $\psi = 2A e^{i(k_0x - \omega_0t)} \cos \Delta k(x - \omega'_0t)$.

None of these wave functions can be normalised. We argued that wave functions need to be normalised according to 4.8 because of the identification of $|\psi|^2$ as a probability density. For example, for i)

$$\int_{-\infty}^{\infty} dx |\psi|^2 = \int_{-\infty}^{\infty} dx |A|^2 = \infty \quad \text{if } A \neq 0.$$

However if $A = 0$ we have no wave function. Ways of getting round this difficulty are essentially technical tricks rather than anything profound. One of these is to think of working with a large finite length $2L$:

$$\int_{-L}^L dx |\psi|^2 = \int_{-L}^L dx |A|^2 = 2L |A|^2 \Rightarrow |A| = 1/\sqrt{2L}.$$

Another way around this issue is to work with wave packets. These are an essential part of understanding the relation between particles and waves.

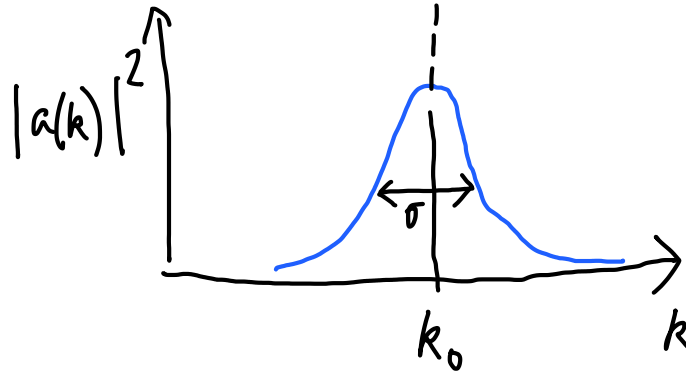
4.2 Wave packets

We call a linear superposition of waves with wavenumbers k grouped around some value, say k_0 , a wave packet or wave group. We looked at the case of two waves with $k_1 = k_0 + \Delta k$ and $k_2 = k_0 - \Delta k$ in the last section. We are going to generalise this to the case where we sum over a continuous distribution of wave amplitudes, $a(k)$, and replace the sum by an integral. We write

$$\psi = \int dk a(k) e^{i(kx - \omega(k)t)}. \quad (4.14)$$

We haven't specified the region of integration. This can be taken as the whole real line, even when the region is finite, so long as we set $a(k) = 0$ for the values of k outside the region in which $a(k) \neq 0$.

We imagine that $|a(k)|^2$ looks like



When we need to be quantitative about the width of the distribution in k we will use the standard or root mean squared (rms) deviation σ where

$$\sigma^2 = \frac{\int dk |a(k)|^2 (k - k_0)^2}{\int dk |a(k)|^2}. \quad (4.15)$$

We show $|a(k)|^2$, and not $a(k)$, because it is real and can be measured.

We expand $\omega(k)$ about k_0 as we did in 4.11

$$\omega(k) \approx \omega(k_0) + \omega'(k_0)(k - k_0) = \omega_0 + \omega'_0 \Delta k.$$

This will be a good approximation if the distribution of k about k_0 , characterised by σ (see sketch), is narrow. Narrow means that the effect of the corrections to the expansion are small compared to that of the terms we keep. These corrections are of order $\sigma^2 |d^2\omega/dk^2|$. We will assume that it is a good approximation in all cases we will look at. With the expansion for $\omega(k)$ we obtain

$$\psi \approx \int dk a(k) e^{ik_0x + i(k-k_0)x - i\omega_0t - i\omega'_0 \Delta k t} = e^{ik_0x - i\omega_0t} \underbrace{\int dk a(k) e^{i\Delta k(x - \omega'_0 t)}}_{\text{a function } f(x - v_g t)}, \quad (4.16)$$

where we have identified the group velocity v_g with ω'_0 . As indicated by the brace under the integral, ψ is a function of $(x - v_g t)$. It therefore describes a right-travelling wave moving at speed v_g . The shape of the waveform described by f will be determined by the function $a(k)$. For some standard cases it can be computed analytically, as we show here and in Appendix A.

Gaussian wave packet

For a first example we will take $a(k)$ to be a Gaussian. We introduce the variable $s = x - v_g t$ and identify the domain of integration as the whole real line $(-\infty$ to $\infty)$. This gives

$$\begin{aligned} a(k) &= A e^{-(k-k_0)^2/2\sigma^2} \quad \text{put } k' = (k - k_0) \\ f(s) &= A \int_{-\infty}^{\infty} dk' e^{-k'^2/2\sigma^2} e^{ik's} \\ &= A \sigma \int_{-\infty}^{\infty} \frac{dk'}{\sigma} \exp \left[\frac{-\left(\frac{k'}{\sigma} - is\sigma\right)^2 - s^2\sigma^2}{2} \right] \quad \text{put } \tilde{k} = k'/\sigma \\ &= A e^{-s^2\sigma^2/2} \underbrace{\sigma \int_{-\infty}^{\infty} d\tilde{k} \exp \left[-\left(\tilde{k} - is\sigma\right)^2/2 \right]}_{\text{a standard integral} = \sqrt{\pi}} = A \sigma \sqrt{\pi} e^{-s^2\sigma^2/2}. \end{aligned}$$

The wave function ψ for the Gaussian wave packet is ($s = x - v_g t$)

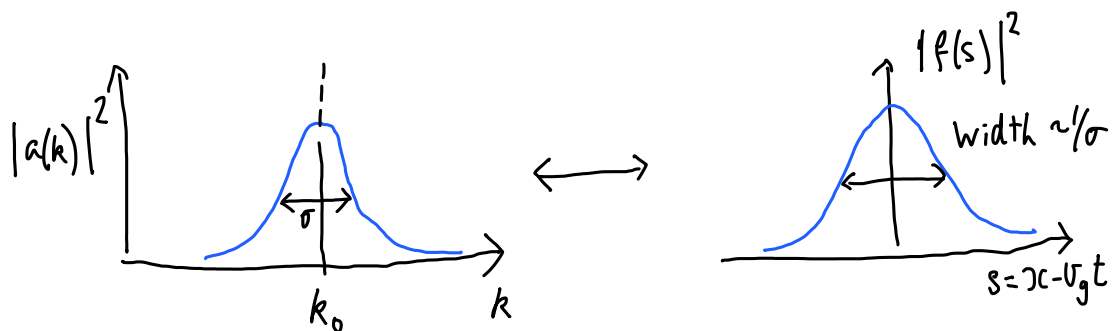
$$\psi = e^{i(k_0 x - \omega_0 t)} A f(s) = A \sigma \sqrt{\pi} e^{-s^2\sigma^2/2},$$

and the corresponding probability distribution

$$|\psi|^2 \approx |A|^2 \sigma^2 \pi e^{-s^2\sigma^2}. \tag{4.17}$$

This is approximate because the dispersion relation $\omega(k)$ has been approximated by a Taylor expansion.

Two features in 4.17 are particularly important as they apply to a whole class of wave packets. The probability distribution $|\psi|^2$ is normalisable. The other important property is the reciprocal relation between the width in wave-numbers, σ , and the width of the propagating waveform in real space which $\sim 1/\sigma$. A narrow width in the space of wavenumbers becomes a large width in real space and *vice versa*:



Summary

The concept of the wave packet and the group velocity are important as is the result 4.17. While it is not true that the functional forms of $f(s)$ and $a(k)$ will be the same (here they

were both Gaussians), the reciprocal relation between the two widths is true for wave packets where the Taylor series for $\omega(k)$ is a good one. In Appendix A we give two more examples of standard wave packets and derive explicitly the reciprocal relation between the width of the distribution in wave numbers and the width of the wave packet.

Wave packets help us resolve some of the conceptual issues:

- i. We can use waves of the form $e^{ikx-i\omega(k)t}$ to form wave functions which are localised in space. A wave packet which is localised in space has a width $1/\sigma$ which is small. The corresponding width in the space of wavenumbers σ is large.
- ii. The quantity $|\psi|^2$ for wave packets is normalisable and the difficulty of the non-normalisability of corresponding quantity for the waves $e^{ikx-i\omega(k)t}$ is no longer present.
- iii. A particle described by a wave packet moves with the group velocity derived in 4.13

$$v_g = \frac{d\omega}{dk}(k_0) = \frac{\hbar k_0}{m} = \frac{p_0}{m}.$$

This is consistent with expectation. Anything else would have contradicted the correspondence principle ($v = p/m$ is what we expect from classical physics).

- iv. As we discuss in the next section, the result helps understand the idea of wave-particle duality.

4.3 Heisenberg's Uncertainty Principle

Writing wave functions as wave packets as in 4.14 shows that we can think of them both as a sum over waves and as a function in real space. A broad distribution in wave numbers (large σ) corresponds to narrow distribution in real space (small $1/\sigma$) and vice versa.

Choosing σ small (see 4.15) corresponds to a small uncertainty in momentum and energy. Remember that quantum theory assumes that $p = \hbar k$ and $E = \hbar\omega(k)$. In this case the particle position will not be well-defined as $1/\sigma$ will be large. The particle will appear more wave-like. Choosing σ large, means the particle has a reasonably well-defined position. The uncertainty in position $\sim 1/\sigma$ is small while the uncertainty in its momentum is large.

At least for the Gaussian wave packet we looked at explicitly, the product of the uncertainty in wavenumber and the uncertainty in position appears to be constant.

Heisenberg stated this as a principle of quantum theory (1927). He stated that

$$\Delta x \times \Delta p \geq \frac{\hbar}{2}$$

where $(\Delta p)^2 = \langle (p - \bar{p})^2 \rangle$, $(\Delta x)^2 = \langle (x - \bar{x})^2 \rangle$. (4.18)

To use this inequality quantitatively, would need being precise about the definitions of Δx and Δp . The principle uses the RMS definition which we introduced in 4.15 in the context of wave packets. The quantities \bar{p} and \bar{x} are the average (sometimes called expected) values of the observable quantities momentum and position. The angle brackets also denote average or expected values (of the square of the deviation from the average values).

Quite often Heisenberg's uncertainty principle (HUP) is used to give only order of magnitude estimates of quantities. We will look at two examples.

Classical Limit

Describing the position and momentum of a cricket ball is not expected to require a quantum theoretic treatment. To see why, we can appeal to the HUP. Suppose we measure the position of the ball to an accuracy of $10\ \mu\text{m} = 10^{-5}\ \text{m}$. We can estimate the quantum limit on the accuracy of a measurement of its speed (take its mass to be 200 g)

$$\Delta p \sim \frac{\hbar}{\Delta x} = \frac{10^{-34}}{10^{-5}} = 10^{-29}\ \text{kg m s}^{-1} \quad \Rightarrow \quad \Delta v = \frac{\Delta p}{m} \approx \frac{e-29}{0.2} = 5 \times 10^{-30}\ \text{m s}^{-1}.$$

We would not measure anything like this accuracy. Quantum uncertainty is irrelevant for the cricket ball—and almost all aspects of the macroscopic world. There are two well-known exceptions to this, namely superconductivity and the quantum Hall effect. In macroscopic samples the measured response to electric and magnetic fields in both cases is given exactly in terms of h and e .

Bohr's Hydrogen Atom

Bohr's empirical suggestion was that angular momentum is quantised in units of \hbar , see 3.5. This led to the requirement that the classical orbits of the electrons were at a distance $r = n^2 a_0$ from the nucleus where $a_0 = 0.53\ \text{\AA}$ is the Bohr radius, see 3.8. If we take the ground state ($n = 1$) we find that the electron's position is localised on a scale of a_0 . HUP gives $\Delta p \geq \hbar/a_0$. On the other hand, the quantised angular momentum means $l = mva_0 = \hbar$. This would mean

$$|p| = mv = \frac{\hbar}{a_0} \quad \text{and from HUP} \quad \frac{\Delta p}{|p|} \geq \frac{\hbar/a_0}{\hbar/a_0} = 1. \quad (4.19)$$

This suggests that the uncertainty in momentum is comparable to (or larger) than its expected value. According to the HUP, the hydrogen atom is clearly in the quantum limit. It is something of a fluke that Bohr's hypothesis yielded the frequencies of the absorption and emission lines correctly.

Some Background

Heisenberg clearly got there first with his formulation of quantum theory. But Schrodinger's approach gained traction quickly. Heisenberg did not like Schrodinger's approach and even called it *Mist* (look up *Misthaufen* in google translate to get a feeling for what he meant). Heisenberg argued that quantum theory should be based only on observable quantities. These are represented by infinite-dimensional matrices. Schrodinger's approach appeared to contain phantom information associated with features in the wave function which are not observable. The approaches were subsequently shown to be equivalent and both approaches can help understanding. If you are interested in the historical background to the uncertainty principle, the Stanford Encyclopedia of Philosophy includes a good [account](#).

Chapter 5

Applying Schrodinger's Equation

Schrodinger's equation is hugely successful. With some modifications the equation is the basis for most of the theory of matter. Dirac wrote in 1929

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

This quotation annoys some chemists and is not strictly true, but the bit about equations being too complex to solve is true. This is why we will concentrate on simplified models for which we can solve Schrodinger's equation. It is also why physics, and science in general, almost always works with approximate methods for making predictions.

In this chapter we will do three things

- i. Include in Schrodinger's equation the effects of a potential
- ii. Look at systems which conserve energy. If energy is conserved, we will see that we can work with what are called stationary states. These are states for which all observable properties are independent of time.
- iii. Study the phenomenon of tunneling. This is where a system can exist in configurations which are classically forbidden. It is how we describe phenomena such as nuclear decay.

Schrodinger's Equation including a Potential

Working from the correspondence principle, we argued that a free particle of mass m should be described by 4.6

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}. \quad (5.1)$$

Using Planck's hypothesis $E = \hbar\omega$ and de Broglie's relation $p = \hbar k$, we used the correspondence principle to put the two quantities into the relation $\hbar\omega = \hbar^2 k^2 / 2m$ and multiplied the

relation by ψ (see 4.5). In the presence of a potential energy, which we will assume depends on position, we expect

$$E = \frac{p^2}{2m} + V.$$

This suggests writing (instead of 5.1)

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x) \psi. \quad (5.2)$$

This is the full Schrodinger equation for a 1D system in the presence of a potential.

As in the case of the Schrodinger equation for a free particle (this means $V(x) = \text{constant}$), its justification is ultimately empirical. When working with an electron in the presence of a proton in 3 D (*i.e.* hydrogen), its solutions correctly gave the energy levels of the orbitals as well as leading to a number of important predictions that were subsequently confirmed. It quickly became accepted as 'the theory'.

Looking for the equivalent of wave packets is possible. We would have to find the equivalent of the waves, $e^{ikx - i\omega(k)t}$, to give us a basis of states with which to form linear superpositions. However, finding these states in the presence of a potential is where most of the interesting results are to be found. Many systems of interest conserve energy and their properties can be found from states with well-defined energy. This is why most studies on quantum theory concentrate on finding these states.

Stationary States

If all components of a wave function oscillate with the same frequency,

$$\psi(x, t) = e^{-i\omega t} \phi(x) = e^{-iEt/\hbar} \phi(x), \quad (5.3)$$

the system is said to be in a **stationary state**. If the wave function for a system can be written as in 5.3, the probability distribution, see 4.7, is time-independent

$$|\psi(x, t)|^2 dx = |\phi(x)|^2 dx.$$

Measurable properties of the system are independent of time—hence the name stationary state.

(Note: We will use $\psi(x, t)$ for the time-dependent wave function. In the case of stationary states, we work with a function of spatial coordinates which we have labelled ϕ . Many authors will refer to both ψ and ϕ as the wave function. It should be clear from the context what is meant. Not everyone uses the same notation so you need to be on your guard.)

The concept of stationary (and non-stationary) states also applies in the case $V = \text{constant}$, which we were considering in the previous chapter. The solutions of Schrodinger's equation in this case were

- i. The wave

$$\psi(x, t) = e^{ikx - i\omega(k)t} = e^{-i\omega(k)t} e^{ikx} = e^{-i\omega(k)t} \phi(x)$$

is a stationary state with $\phi = e^{ikx}$.

- ii. The standing wave, see 4.9,

$$\psi = 2Ae^{-i\omega(k)t} \cos kx = 2Ae^{-i\omega(k)t} \phi(x)$$

is already in the form of a stationary state. Here $\phi(x) = 2A \cos kx$.

iii. The wave-packet 4.14

$$\psi = \int dk a(k) e^{i(kx - \omega(k)t)},$$

is **not** in general a stationary state. Different k can have different frequencies $\omega(k)$.

5.1 Time-independent Schrodinger Equation (TISE)

Understanding stationary states is how we find what quantum theory predicts for many systems. This is because of energy conservation. Essentially all systems not being driven by an external source of energy conserve energy. Their properties can be deduced from their stationary states. In many experiments we deliberately perturb systems with an external source of energy and, provided the driving is small, we can usually understand the response to this driving by considering the stationary states of the system. This is what happens in spectroscopic measurements. We shine light onto the system and record what happens. It is also what happens when we study systems' response to an applied voltage.

Assuming that a system is in a state of the form 5.3 the left-hand side of Schrodinger's equation 5.2 gives

$$i\hbar \frac{\partial \psi}{\partial t} = i\hbar \frac{\partial}{\partial t} e^{-i\omega t} \phi(x) = \underbrace{i\hbar(-i\omega)}_{\hbar\omega = E} e^{-i\omega t} \phi(x) = E e^{-i\omega t} \phi(x),$$

while the right-hand side becomes

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} e^{-i\omega t} \phi(x) + V(x)e^{-i\omega t} \phi(x) = e^{-i\omega t} \left[\frac{d^2 \phi}{dx^2} + V(x)\phi \right].$$

Because $\phi(x)$ depends only on one variable the partial derivative has become an ordinary derivative. Setting the left- and right-hand sides equal and cancelling the common factor of $e^{-i\omega t}$ gives the time-independent Schrodinger equation or **TISE** :

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi}{dx^2} + V(x)\phi = E\phi. \quad (5.4)$$

Note on Terminology

The left-hand side of 5.4 involves an operator acting on a function. An operator in this context takes the function and maps it to another function. For example taking the derivative would map the function $\phi(x)$ to $d\phi/dx$. Here the operator takes the second derivative of ϕ , multiplies it by a constant, and subtracts it from $V(x)$ multiplying $\phi(x)$:

$$\underbrace{\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right)}_{\text{Hamiltonian}} \phi = H\phi$$

For historical reasons, this operator is denoted by H and called the **Hamiltonian**. Hamilton (1833) had introduced a formulation of classical mechanics with a function called H which played an analogous role to the operator in the TISE. The Hamiltonian

operator in quantum mechanics is a linear operator because acting on the sum of two functions gives the sum of the operator acting on the two functions separately.

The TISE is solved by functions $\phi(x)$, which when acted on by the Hamiltonian operator, yield the original function multiplied by a constant. We say that solutions for $\phi(x)$ are eigenfunctions of the operator H with E the corresponding eigenvalue.

You will notice that the language of quantum theory is similar to that of linear algebra with functions playing the role of vectors and operators that of matrices. This is not a coincidence. Hilbert and others had shown in the early twentieth century that, in many cases, functions should be thought of as elements in an infinite-dimensional vector space. There are natural generalisations from finite-dimensional vector spaces of the inner product (sometimes called dot product), basis vectors and sizes (or norms) of the functions.

The study of stationary states normally follows the procedure

- i. Set up the TISE with appropriate potential and establish the boundary conditions
- ii. Solve the resulting boundary value problem (TISE + boundary conditions) for states with fixed energy, E . Often only certain values of E will lead to solutions
- iii. Think about the answer

We will look at two examples: the infinite potential well and a potential barrier. The first of these will illustrate how bound states arise in quantum theory. Examples of bound states are the orbitals occupied by electrons in atoms and molecules. The electrons are bound to the nucleus. While the calculations for atoms involve the TISE in 3D and are hard work, our 1D calculation will show how the spectrum of allowed energies becomes discrete. The second of these examples (the potential barrier) will illustrate the final quantum phenomenon of the module, namely quantum tunneling. In quantum theory systems explore configurations which are classically forbidden. This is how we understand decay of a nucleus.

Particle in an Infinite Potential Well

We take the potential to be

$$\begin{aligned} V(x) &= \infty & x < 0, x > L \\ V(x) &= 0 & 0 \leq x \leq L. \end{aligned}$$

We want to solve the TISE with this potential

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + V(x)\phi = E\phi.$$



What happens at $x = 0$ and $x = L$? For $x < 0$ and $x \geq L$, we have

$$E\phi = -\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + \infty \times \phi \Rightarrow \phi = 0, \quad \text{otherwise } E = \infty.$$

This leads to the boundary conditions $\phi(0) = \phi(L) = 0$.

Introducing $k^2 = 2mE/\hbar^2$, we need to solve

$$\frac{d^2\phi}{dx^2} = -k^2\phi, \quad 0 \leq x \leq L, \quad \text{subject to } \phi(0) = \phi(L) = 0.$$

The solutions are

$$\phi = A \sin kx + B \cos kx \quad \text{or} \quad \phi = \alpha e^{ikx} + \beta e^{-ikx}.$$

(We can use either form.) Using the first, the boundary conditions give

$$\begin{aligned} \phi(0) = 0 &\Rightarrow B = 0 \\ \phi(L) = 0 \quad A \sin kL = 0 &\Rightarrow k = \frac{n\pi}{L}, \quad n \text{ integer} \\ \phi_n(x) = A \sin \frac{n\pi x}{L}, \quad \text{with} \quad E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2m L^2}, \end{aligned}$$

where we have labeled the states and energies by the integer n . Normalisation requires

$$1 = \int_0^L dx A^2 \sin^2 \frac{n\pi x}{L} = \int_0^L dx \frac{A^2}{2} \left[1 - \cos \frac{2n\pi x}{L} \right] = \frac{A^2}{2} \left[x - \frac{\sin 2n\pi x/L}{2n\pi/L} \right]_0^L = \frac{A^2 L}{2}.$$

This is satisfied if $A = \sqrt{2/L}$.

What have learnt? The energy quantisation is the result of the boundary condition, which restricts the wavenumber k to be:

$$k = \frac{n\pi}{L}.$$

Only an integer number of half-wavelengths fit in the potential well.

If we were to make a spectroscopic measurement (absorption or emission of light as a function of frequency), we could only expect to see absorption or emission lines at frequencies

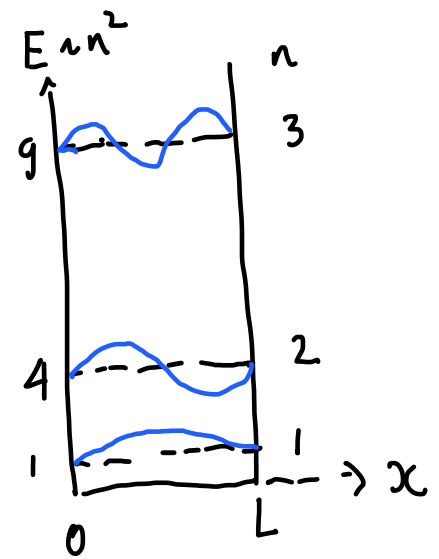
$$h\nu = \frac{\hbar^2 \pi^2}{2m L^2} (n^2 - n'^2),$$

where n and n' label the two states involved in the transition. Actually, there may also be restrictions on which transitions would be possible as the form of the coupling between the light and the levels in the well may mean some transitions are not allowed by symmetry. These are called selection rules.

The quantities n and n' are examples of what are called quantum numbers. These are the numbers or labels that specify quantum states. If you are lucky enough to have studied some chemistry, you may have studied the quantum numbers which identify the allowed quantum levels of a hydrogen (or hydrogen-like) atom. These are (n, l, m, σ) where n is the principal quantum number, l and m relate to angular momentum and σ is the spin quantum number.

Boundaries

The boundary condition in the previous example was particularly simple. Choosing $V = \infty$ for



$x < 0$ meant that $\phi(x)$ had to be zero to avoid infinite energies. In the more general case of boundaries between regions in which $V(x)$ changes between finite values, we need that

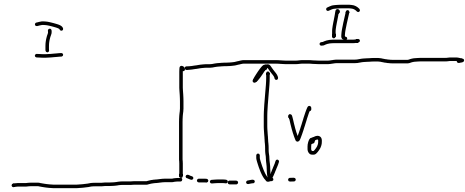
$$\phi(x) \text{ and } \frac{d\phi}{dx} \text{ are continuous.} \quad (5.5)$$

Why? The TISE involves $d^2\phi/dx^2$. Both of ϕ or $d\phi/dx$ need to be continuous for $d^2\phi/dx^2$ and Schrodinger's equation to be defined.

Particle incident on a potential step

We take the potential to be

$$\begin{aligned} V(x) &= 0 & x < 0 \\ V(x) &= V_0 & x > 0. \end{aligned}$$



As before, we want to solve the TISE with this potential

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + V(x)\phi = E\phi.$$

We rewrite the equation as

$$\begin{aligned} \text{Region I } x < 0 : & \quad \frac{d^2\phi}{dx^2} = -k^2\phi, \quad k^2 = \frac{2mE}{\hbar^2} \\ \text{Region II } x > 0 : & \quad \frac{d^2\phi}{dx^2} = -k'^2\phi, \quad k'^2 = \frac{2m(E - V_0)}{\hbar^2}. \end{aligned} \quad (5.6)$$

We will assume $E > V_0$ which makes k' real. The solutions to the equations are of the form

$$\begin{aligned} \phi_I(x) &= e^{ikx} + re^{-ikx}, \\ \phi_{II}(x) &= te^{ik'x} + se^{-ik'x}. \end{aligned}$$

We have taken the amplitude of the term varying as e^{ikx} in Region I to be one.

If we add back in the factors of $e^{-i\omega(k)t}$ from the original (time-dependent) Schrodinger equation, we see that these solutions correspond to a right-travelling wave, $e^{ikx-i\omega(k)t}$, and a left-travelling wave $e^{-ikx-i\omega(k)t}$ in region I, with the same on the right with k' instead of k .

We will consider the case of a left-travelling wave incident on the barrier from the left. There will be a reflected wave re^{-ikx} in region I and a transmitted wave $te^{ik'x}$ in region II. We will therefore set $s = 0$ (no wave incident on the barrier from the right).

Now apply the boundary conditions 5.5

$$\begin{aligned} \phi_I(0) = \phi_{II}(0) & \Rightarrow 1 + r = t \\ \frac{d\phi_I(0)}{dx} = \frac{d\phi_{II}(0)}{dx} & \Rightarrow ik(1 - r) = ik't. \end{aligned}$$

Inserting t from the first relation into the second and simplifying gives

$$r = \frac{k - k'}{k + k'} \quad \text{and} \quad t = \frac{2k}{k + k'}. \quad (5.7)$$

The variables r and t are reflection and transmission amplitudes. In general they can be complex, although here they are real. The probabilities of reflection and transmission are given by $|r|^2$ and $(k'/k)|t|^2$ if k' real. Then

$$|r|^2 + \frac{k'}{k}|t|^2 = \frac{1}{(k+k')^2} ((k-k')^2 + 4kk') = 1, \quad (5.8)$$

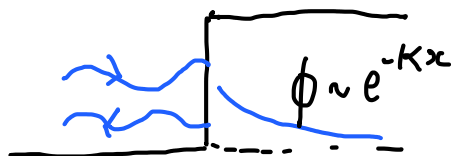
which we need. We expect that flux should be conserved. We have not derived this formally here, but we would interpret 5.8 in terms of a flux incident from the left. The flux moving away from the barrier, in the reflected and transmitted waves, should equal the incident flux. We should expect the flux to be proportional to both the velocity and the density. (The factor k'/k multiplying $|t|^2$ in 5.8 is the ratio of the two velocities.) Talking about the flux rather than the number of particles gets round the problem with normalisation of the waves $e^{ikx-i\omega t}$, see page 25, and is why we were able to choose the amplitude of the incident wave to be one.

5.2 Tunneling

What happens when $E < V_0$ for the potential step? In Eq 5.6 the wave number in Region II becomes imaginary with $k' = \pm i\kappa$, where κ is real. This gives

$$\phi_I(x) = e^{ikx} + re^{-ikx} \quad \text{and} \quad \phi_{II}(x) = te^{-\kappa x} + se^{+\kappa x}. \quad (5.9)$$

We must set $s = 0$ as this would be an unbounded wave function. (This component can be important but only if the system does not continue to $x = \infty$ as we will see later in this section.) We have an incident and reflected wave in Region I, but the wave in Region II is exponentially decaying (it is sometimes called an evanescent wave).



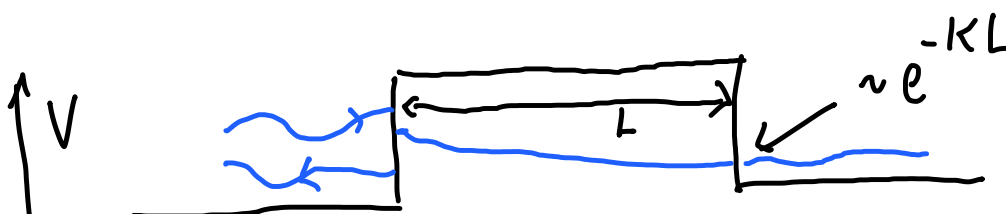
Applying the boundary conditions as before, see 5.7, gives:

$$r = \frac{k - i\kappa}{k + i\kappa} \quad \text{and} \quad t = \frac{2k}{k + i\kappa}. \quad (5.10)$$

Now the incident wave is totally reflected $|r|^2 = 1$. The non-zero value of t means that the wavefunction is non-zero for $x > 0$ but there is no flux for $x > 0$.

Multiplying by $e^{-i\omega t}$ does not give a travelling wave as before. We will take this as the signature of no flux.

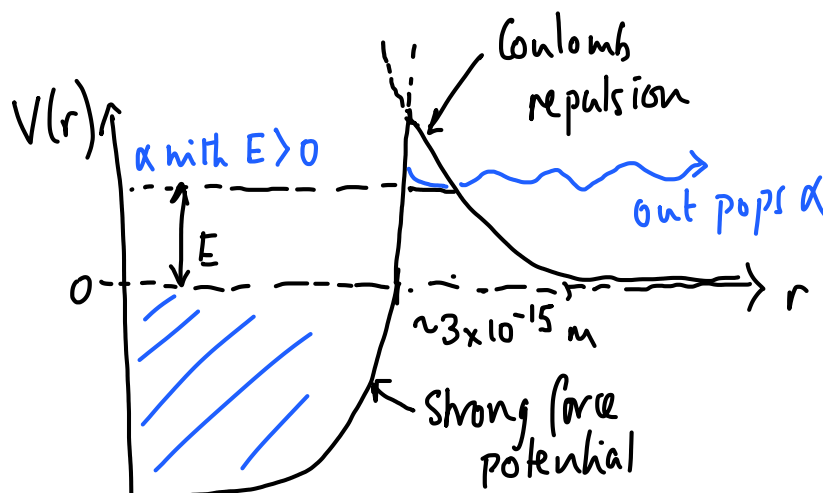
The phenomenon of finding particles where classically they cannot be found is a quantum phenomenon. One consequence is quantum tunneling. A particle can come out on the other side of a finite potential barrier.



An incident left-travelling wave impinges on a barrier. The energy of the wave is less than the height of the barrier and the wave has a decaying amplitude inside the barrier. Satisfying the boundary conditions 5.5 at both boundaries leads to a non-zero amplitude for the transmitted wave beyond the barrier ($x > L$). We say that a particle has tunneled through the barrier. The exponentially decaying solution from 5.9 suggests that the amplitude at $x = L$ will be $\sim e^{-\kappa L}$ and that the probability of particles tunneling through the barrier $|t|^2 \sim e^{-2\kappa L}$. The calculation given after the discussion of α -decay confirms that this is what happens.

α -decay

A process which illustrates tunneling is the α -decay of a nucleus. This is a radioactive decay process in which an α -particle is emitted from a nucleus. For example, uranium-238 decays to thorium-234 via this process. The α -particle is a helium nucleus and is a bound state of two protons and two neutrons. Inside a large nucleus it can form as an excitation which can then be treated approximately as a single particle in a potential. Classically it is trapped inside the nucleus by the strong force but the potential barrier holding it inside the nucleus is finite. There is a small probability that it tunnels through this barrier. When it does, we say that the original nucleus decays into a daughter nucleus + α .



Full solution for the 1D barrier with length L

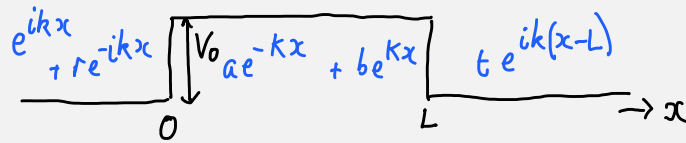
Solving the Schrodinger equation for the finite-width barrier needs to account for the boundary conditions at two boundaries. We are assuming $V_0 > E$

$$\begin{aligned}
 \text{Region I } x < 0 : & \quad \frac{d^2\phi}{dx^2} = -k^2\phi, \quad k^2 = \frac{2mE}{\hbar^2} \\
 \text{Region II } 0 < x < L : & \quad \frac{d^2\phi}{dx^2} = -\kappa^2\phi, \quad \kappa^2 = -k^2 = -\frac{2m(V_0 - E)}{\hbar^2} \\
 \text{Region III } x > L : & \quad \frac{d^2\phi}{dx^2} = -k^2\phi, \quad k^2 = \frac{2mE}{\hbar^2}.
 \end{aligned} \tag{5.11}$$

This gives

$$\phi_I(x) = e^{ikx} + re^{-ikx}, \quad \phi_{II}(x) = ae^{-\kappa x} + be^{+\kappa x}, \quad \text{and} \quad \phi_{III}(x) = te^{ik(x-L)}.$$

We will consider the case with no incident flux from the right (no term of the form $e^{\kappa x}$ in region III) . Writing $te^{ik(x-L)}$ for region III is equivalent to writing $t'e^{ikx}$ with $t' = te^{-ikL}$.



Requiring ϕ and its derivative to be continuous at $x = L$, see 5.5, gives

$$ae^{-\kappa L} + be^{+\kappa L} = t$$

$$-ae^{-\kappa L} + be^{+\kappa L} = \frac{ik}{\kappa}t \Rightarrow a = \frac{t}{2}e^{\kappa L} \left(1 + \frac{k}{i\kappa}\right), \quad b = \frac{t}{2}e^{-\kappa L} \left(1 - \frac{k}{i\kappa}\right).$$

Matching at the boundary at $x = 0$ gives, using the results for a and b in terms of t , gives

$$1 + r = a + b = t \left[\frac{e^{\kappa L} + e^{-\kappa L}}{2} + \frac{k}{i\kappa} \frac{e^{\kappa L} - e^{-\kappa L}}{2} \right] = t \left[\cosh \kappa L + \frac{k}{i\kappa} \sinh \kappa L \right]$$

$$1 - r = \frac{\kappa}{ik}(-a + b) = \frac{i\kappa}{k}(a - b)$$

$$= \frac{i\kappa}{k}t \left[\frac{e^{\kappa L} - e^{-\kappa L}}{2} + \frac{k}{i\kappa} \frac{e^{\kappa L} + e^{-\kappa L}}{2} \right] = t \left[\cosh \kappa L + \frac{i\kappa}{k} \sinh \kappa L \right].$$

Adding the equations for $1 + r$ and $1 - r$ gives

$$t = \frac{1}{\left[\cosh \kappa L + \sinh \kappa L \left(\frac{k}{2i\kappa} + \frac{i\kappa}{2k} \right) \right]}.$$

The result for the transmission amplitude t is less fearsome than it might look. We have used the definition of the hyperbolic functions

$$\cosh y = \frac{e^y + e^{-y}}{2} \underset{y \gg 1}{\approx} \frac{e^y}{2} \quad \text{and} \quad \sinh y = \frac{e^y - e^{-y}}{2} \underset{y \gg 1}{\approx} \frac{e^y}{2}.$$

When the barrier is thick, $\kappa L \gg 1$, $|t|^2 \sim e^{-2\kappa L}$ which is what we expected.

5.3 Conclusion

The properties of systems which conserve energy are determined by their stationary states. These are the solutions of the time-independent Schrodinger equation or TISE. We have looked at the states in a potential well. We also looked at waves incident on a potential barrier. Even though the solutions in the latter case describe a particle flux, the states are still stationary states.

An important prediction of quantum theory is that particles can have a non-zero probability of being found where classically they cannot be—inside a potential barrier for example. Particles can tunnel through these forbidden regions. Tunneling is how the phenomenon of nuclear

decay by α -particle emission is understood.

The Schrodinger equation accounts for most phenomena in matter. The methodology is clear. Solve the equation subject to the relevant boundary conditions and interpret the results. Many of the triumphs of quantum theory follow from this approach. The stationary states of a hydrogen atom, usually called energy-levels in this context, can even be found analytically.

There are things that need adding. Once there is more than one identical particle in the system, we need to worry about the symmetry of the wave function under interchange of the coordinates of different particles. Quantum mechanics can be made consistent for two cases: if the wave function is invariant, or if the wave function changes sign. Both cases occur. When the wave function maps to itself, the particles are called bosons. Examples include the photon and Higgs boson. When the wave function changes sign under interchange of particle coordinates, the particles are called fermions. Elementary matter particles like electrons are fermions. The existence of these two separate types of particles appears naturally in the theory once the theory has taken account of special relativity.

Appendix A

Wave Packets

Provided the dispersion relation $\omega = \omega(k)$ for solutions to the Schrodinger equation can be approximated by a Taylor expansion (see 4.11) we can talk of a group velocity $v_g = d\omega/dk$ and work with the idea of a wavepacket.

An important feature relevant to the idea of so-called wave-particle duality is that the uncertainty in momentum (the width of the distribution of wave-vectors of the wavefunction) is inversely proportional to the uncertainty in position (the corresponding width in real space). It is also an illustrative example of the Heisenberg uncertainty principle. We derived this relation explicitly for the Gaussian wave packet in 4.17.

Here we introduce two other standard examples where we can compute the waveform (see 4.14) analytically given the distribution $a(k)$:

$$\psi = \int dk a(k) e^{i(kx - \omega(k)t)}. \quad (\text{A.1})$$

Top Hat distribution

If we take

$$\begin{cases} a(k) = A & k_0 - \sigma \leq k \leq k_0 + \sigma \\ a(k) = 0 & \text{otherwise,} \end{cases}$$

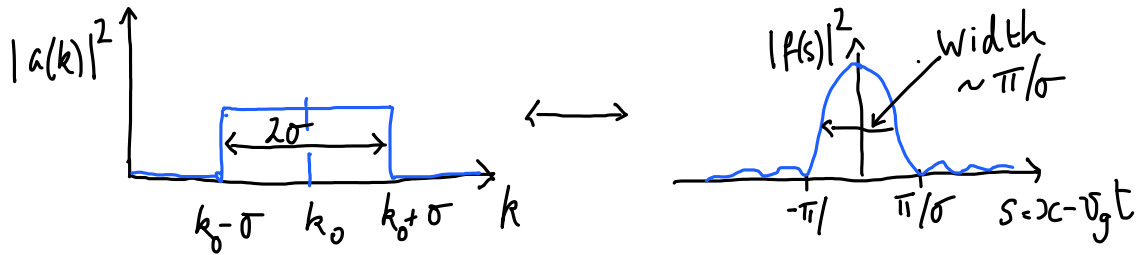
we can compute the integral in A.1. We write $k = k_0 + \Delta k$ and use the expansion $\omega(k) \approx \omega(k_0) + v_g \Delta k$. Using this in 4.16 gives ($s = x - v_g t$, $k' = k - k_0$)

$$f(s) = A \int_{-\sigma}^{\sigma} dk' e^{ik's} = 2A \left[\frac{e^{ik's}}{2is} \right]_{-\sigma}^{\sigma} = 2A \frac{\sin \sigma s}{s}$$

and

$$|f(s)|^2 = 4|A|^2 \sigma^2 \left| \frac{\sin \sigma s}{\sigma s} \right|^2$$

for the probability distribution.



(By using the variable s we are in the frame in which the wave packet is moving to the right at speed v_g .) The width of the distribution in real-space can be taken as the distance to the first zero at $\sigma s = \pi$ so $s = \pi/\sigma$. As expected the width of the distribution in wavenumbers $\sim \sigma$ and the width of the distribution in real space $\sim 1/\sigma$ are inversely related.

Lorentzian

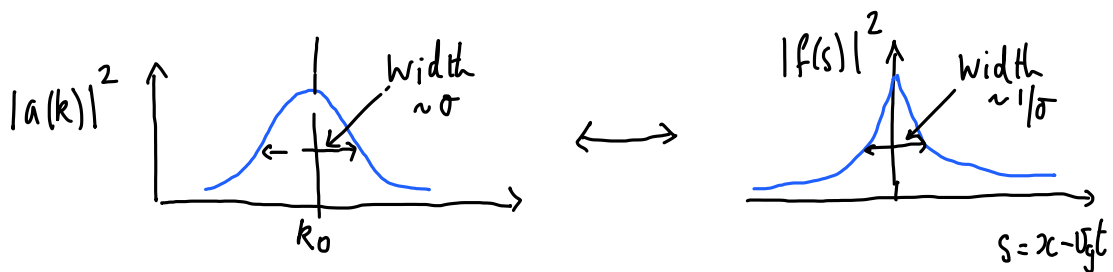
Another commonly used distribution is called the Lorentzian

$$a(k) = \frac{A}{\sigma^2 + k'^2} \quad \text{where } k' = k - k_0$$

$$f(s) = A \int_{-\infty}^{\infty} dk' \frac{e^{ik's}}{k'^2 + s^2} = \frac{\pi A}{\sigma} e^{-\sigma|s|}.$$

(We have used a theorem from complex analysis to compute the integral.) This gives

$$|f(s)|^2 = \pi^2 A^2 \frac{e^{-2\sigma|s|}}{\sigma^2}.$$



Again the width of the distribution in k , characterised by σ , is inversely proportional to the width in real space $1/\sigma$.