

(1) INTRODUCTION: Arguments leading to Schrödinger’s equation.

I will begin this course with a quick review of the basic ideas of quantum mechanics. Many of these you should have learned from Quantum Physics and Quantum Mechanics A, but I will present them in my own way, adding some additional concepts as we proceed. Students often feel that Quantum Mechanics comes from thin air, but this is far from true: the theory was arrived at through an enormous intellectual struggle, driven by a truly remarkable range of experiments. Your first two years of formal study and your own reading (?) of the history of 20th century physics should by now have given you a full appreciation of how the ideas developed through physicists’ attempts to understand the experimental facts. Today there is no more successful theory in all of science, providing explanations for many long-standing as well as new mysteries of nature. One of the aims of this course is to show you some further examples of these explanations; a second aim is to provide you with the concepts, language and techniques to enable you to proceed further in the subject on your own.

I will begin my simplified version of the story with Planck’s idea that electromagnetic radiation is emitted and absorbed as quanta of energy,

$$E = h\nu = \hbar\omega. \tag{1}$$

He was reluctantly forced to this in his successful attempt to fit the new experiments (1900) of Lummer & Pringsheim and Rubens & Kurlbaum on black body radiation. It was Einstein (1905) who grasped the significance of the idea when he applied it to the photoelectric effect. His predictions were beautifully confirmed in Millikan’s experiments (1916). Compton’s experiments (1923) on the scattering of X-rays by electrons provided an important step forward when he successfully explained his results by treating the X-rays as relativistic zero mass particles - Einstein’s photons - colliding with electrons. Of course in this period of history Rutherford’s nuclear atom and Bohr’s model had added further puzzles which could not be solved by classical physics (Newton’s laws and the laws of electromagnetism summarised in Maxwell’s equations).

At this stage in the story electromagnetic radiation seems to be playing a dual role: in some experiments, such as interference and diffraction, it undoubtedly behaves like waves; in others it behaves like particles. These particles must be massless to travel at the velocity of light, with the momentum given by Einstein’s relativistic formula:

$$E = \sqrt{(pc)^2 + (mc^2)^2} \tag{2}$$

$$= pc \quad \text{for } m = 0 \text{ for photons only.} \tag{3}$$

If we combine this with Planck’s formula $E = h\nu = \hbar\omega$ and use the expression $v = c/\lambda$ for the wavelength we discover an expression for the momentum in terms of wavelength,

$$p = \frac{h}{\lambda} \tag{4}$$

$$\equiv \hbar k \tag{5}$$

where $k = 2\pi/\lambda$ is the usual definition of wave number. In his doctoral thesis de Broglie (1923) made a very simple but profound conjecture: if waves can behave like particles, perhaps particles such as electrons, protons and even atoms can behave like waves. If so, what wavelength would they have? In his reasoning de Broglie understood clearly that some of the expressions above apply only to zero mass particles, so he took as his starting point the expression

$$\boxed{p = \frac{h}{\lambda} \equiv \hbar k} \quad \text{for all particles.}$$

This gives a relation between the momentum p , a particle-like property, and a wave-like property, the wavelength λ (or equivalently the wave number, k). Once we accept this we can find the energy (or equivalently the angular frequency, ω , defined by $E \equiv \hbar\omega$) from Einstein's relativistic formula for massive particles,

$$\boxed{E = \sqrt{(pc)^2 + (mc^2)^2} \equiv \hbar\omega} \quad \text{for all particles.}$$

Note that ω is *defined* by this expression by analogy with a photon. A plane monochromatic de Broglie wave, with wave number and frequency $\{k, \omega\}$ would therefore describe a beam of monoenergetic electrons with momentum and energy $\{p, E\}$ given by the boxed expressions. With this simple, even naive, idea de Broglie had made a definite prediction that diffraction and interference effects would be seen with beams of electrons, protons or even atoms; moreover the prediction was quantitative and could be experimentally tested in full detail. Indeed this was first done with electron beams by Davisson & Germer (1927) and completely independently by G.P. Thomson (1928); subsequent years have seen many confirmations using proton, neutron and atomic beams, leading to many practical uses in science and technology.

If matter can behave like waves, then one assumes that a monochromatic de Broglie wave's amplitude $\Psi(x, t)$ can be represented by an expression just like that of classical running waves:

$$\Psi(x, t) = \cos(kx - \omega t) = \cos(px - Et)/\hbar$$

or, in complex notation (see your 'Vibrations & Waves' course),

$$\Psi(x, t) = e^{i(kx - \omega t)} = e^{i(px - Et)/\hbar}$$

In both cases we have used de Broglie's relations to translate the wave-like pair (k, ω) to the particle-like pair (p, E) . At this juncture two questions immediately come to mind:

Question (1): What is the wave equation for de Broglie waves? Is it our old friend the classical wave equation?

$$\frac{\partial^2 \Psi}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} = 0 \quad (6)$$

Question (2): What physical quantity does the wave function $\Psi(x, t)$ represent? In the case of sound waves it would represent the longitudinal displacement of the molecules from their equilibrium positions; for surface water waves or waves on a string it would be the transverse displacement of the water's surface or of the string; for electromagnetic waves it would stand for the components of the electric and magnetic fields constituting the wave.

Answer to Question (1): Assume the classical wave equation and ask for any of the above plane waves to be a solution. Substitution into the equation then gives the condition for Ψ to be a solution:

$$\left(-\frac{p^2}{\hbar^2} + \frac{1}{v^2} \frac{E^2}{\hbar^2} \right) \Psi(x, t) = 0 \quad (7)$$

Notice that this follows whichever of the above forms for Ψ , real or complex, we use. Since this equation must hold for all (x, t) , the only possibility is that the bracketed factor vanish, leading to

$$\left(-\frac{p^2}{\hbar^2} + \frac{1}{v^2} \frac{E^2}{\hbar^2} \right) = 0 \quad (8)$$

$$\text{ie.} \quad p^2 + \frac{1}{v^2} E^2 = 0 \quad (9)$$

$$\text{or, taking the positive square root,} \quad E = pv \quad (10)$$

This is only correct for a zero mass particle with $v = c$, but for a massive relativistic one we require $E^2 = (pc)^2 + (mc^2)^2$. It's easy to see what modification is needed to get this relativistic formula: just add an extra term to generate $(mc^2)^2$ and replace v^2 by c^2 ,

$$\frac{\partial^2 \Psi}{\partial x^2} - \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2} - \left(\frac{mc}{\hbar}\right)^2 \Psi = 0 \quad (11)$$

Substitution of our plane monochromatic Ψ then gives, as before,

$$\left(-\frac{p^2}{\hbar^2} + \frac{1}{c^2} \frac{E^2}{\hbar^2} - \left(\frac{mc}{\hbar}\right)^2\right) = 0 \quad (12)$$

$$\text{ie.} \quad -p^2 + \frac{1}{c^2} E^2 - (mc)^2 = 0 \quad (13)$$

$$\text{or, taking the positive square root,} \quad E = \sqrt{(pc)^2 + (mc^2)^2} \quad (14)$$

which is indeed correct for a massive relativistic particle. This equation is known as the Klein-Gordon equation (1926) and is used in *relativistic* quantum mechanics. The Klein-Gordon equation has its problems, however. It has negative energy solutions (the \pm sign in taking the square root) which only get a proper interpretation in quantum field theory with creation and annihilation of particles and antiparticles.

But we are seeking a non-relativistic equation, where the rest mass energy is fixed and plays no role, so that the interesting part of a free particle's energy is just its kinetic energy,

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad (15)$$

It's clear that the wave equation which generates such an equation by the substitution procedure we performed above must have a double derivative in x to generate the p^2 factor, *but only a single derivative in time* to generate only one power of E . A minimally modified version of the wave equation is then:

$$\frac{\partial^2 \Psi}{\partial x^2} + A \frac{\partial \Psi}{\partial t} = 0 \quad (16)$$

where A is a constant to be chosen. Now we demand that our plane monochromatic free particle Ψ be a solution. We immediately see that the cos doesn't work as a solution because, although the spatial second derivative generates the cos again, the first time derivative generates a sin from the cos. However the complex exponential form is perfectly designed for the job because no matter how many derivatives we take we still generate only the exponential. Thus for $\Psi = \exp i(px - Et)/\hbar$ to be a solution we require:

$$\left(-\frac{p^2}{\hbar^2} - iA \frac{E}{\hbar}\right) \Psi(x, t) = \left(-\frac{p^2}{\hbar^2} - iA \frac{E}{\hbar}\right) e^{i(px - Et)/\hbar} = 0 \quad (17)$$

Notice the appearance of the imaginary i . Thus for *this* Ψ to be a solution we require the factor in brackets to vanish,

$$-\frac{p^2}{\hbar^2} - iA \frac{E}{\hbar} = 0 \quad \text{giving} \quad E = -\frac{p^2}{iA\hbar} \quad (18)$$

To get the correct non-relativistic kinetic energy requires $iA\hbar = -2m$, or $A = 2mi/\hbar$, which gives the equation

$$\frac{\partial^2 \Psi}{\partial x^2} + i \frac{2m}{\hbar} \frac{\partial \Psi}{\partial t} = 0 \quad (19)$$

or, multiplying by $\hbar^2/2m$ to make all terms have the dimensions of [energy] \times [Ψ], we obtain the Schrödinger equation (1925) for a *free non-relativistic particle* of mass m :

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t} \quad (20)$$

The final step is to guess the generalisation for the same particle moving in a potential field $V(x, t)$. Since the energy is now kinetic plus potential energy, $E=KE+PE$, we need to obtain

$$E = \frac{1}{2}mv^2 + V(x, t) = \frac{p^2}{2m} + V(x, t). \quad (21)$$

We immediately see that the above manipulations would give this expression with our complex Ψ if we simply added a term $V\Psi$:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (22)$$

This is the **Time Dependent Schrödinger equation** (hereafter **TDSE**)¹) and plays the same fundamental role in quantum mechanics as Newton's Second law plays in classical mechanics: it determines the time evolution of the system and has the status of a *postulate*. It is *assumed* to be true but can never be *proved* to be true; because of its immensely successful application in understanding many experimental results, both qualitatively and quantitatively, we have every reason to accept it as an excellent approximation to the true law of Nature. The arguments I have given are only meant to provide some idea how one might have arrived at this equation through some reasoning process, to convince you that it does not simply come out of thin air. The actual historical process was in fact rather more complicated and indirect!

(2) The Superposition Principle.

In general there are many, often infinitely many, independent solutions, $\Psi_i(x, t)$, to the time-dependent Schrödinger equation. Because the TDSE is linear and homogeneous, any linear combination of these solutions is also a solution:

$$\Psi(x, t) = \sum_i c_i \Psi_i(x, t); \quad (23)$$

indeed, this is the most general solution, a fact familiar to you from your study of classical waves. This property is the source of the most unexpected (non-classical) aspects of quantum mechanics where particles behave like waves, can tunnel through forbidden barriers, where 'cats' may be both 'alive' and 'dead', and where so-called 'ghostly' instantaneous interactions appear to take place over large distances. The interpretation (and misinterpretation?) of these phenomena arises from the physical interpretation of the wave function.

(3) The Born (or probability) Interpretation of the Wave Function.

Answer to Question (2): The question of the physical significance of the wave function $\Psi(x, t)$ caused some considerable difficulties and even today is not completely settled. It was Max Born (1926) who was finally led to the currently accepted and hugely successful probability interpretation. It is the misuse of this this Born, or probability, interpretation which is at the heart of many of the conceptual difficulties students (and others) have in understanding quantum mechanics.

¹In 3-dimensions the TDSE is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial x^2} + \frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial y^2} + \frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial z^2} \right) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$

or, equivalently, $-\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$

The Born Postulate:

$$|\Psi(x,t)|^2 dx$$

is the **probability** that a **measurement** at time t of the particle's position will yield a value lying between x and $x + dx$ - Fig.1a.

or, in 3-dimensions:

$$|\Psi(\mathbf{r},t)|^2 d^3x, \quad \text{where } d^3x \equiv dx dy dz \equiv dV$$

is the **probability** that a **measurement** at time t of the particle's position will yield a value lying in the volume element $dV = d^3x$ at position \mathbf{r} - Fig.1b.

This is the **Born interpretation** or the **probability interpretation** of the wave function.

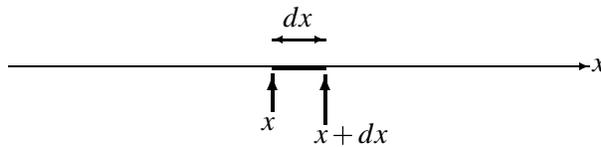


Figure 1a: Illustrates the Born interpretation in 1-dimension: the probability of finding the particle in the infinitesimal region between x and $x + dx$ at time t is $|\Psi(x,t)|^2 dx$.

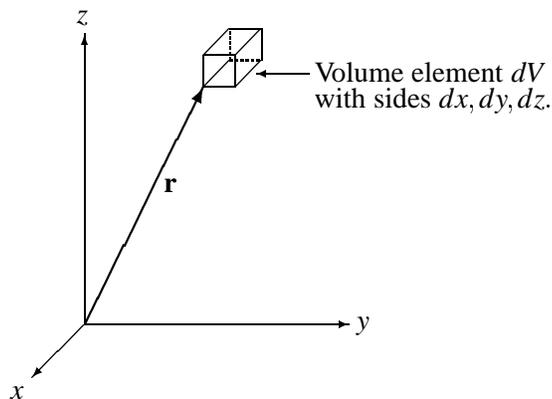


Figure 1b: Illustrates the Born interpretation in 3-dimensions: the probability of finding the particle in the infinitesimal volume dV at position \mathbf{r} at time t is $|\Psi(\mathbf{r},t)|^2 dV$.

(4) The Time Independent Schrödinger Equation (TISE).

An important special case often encountered in elementary as well as advanced applications of quantum mechanics is that of the *time independent potential*,

$$V(x, t) = V(x) \quad (24)$$

In this special case we can solve for the time dependence of the wave function $\Psi(x, t)$ by a mathematical technique known as *separation of variables*. The way to proceed is to notice that the time dependence and space dependence in the Time Dependent Schrödinger Equation (TDSE) can be put on different sides of the equation by searching for solutions of the form,

$$\Psi(x, t) = \psi(x)f(t) \quad (25)$$

where the factors $\psi(x)$ and $f(t)$ are to be found by demanding that this form be a solution to the TDSE. After dividing both sides of the equation by $\Psi(x, t) = \psi(x)f(t)$, then moving all functions of x to the left side and all functions of t to the right, we obtain

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x) = i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} \quad (26)$$

Now this equation must be true for *all values of the independent variables x and t* ; this means that for any chosen t , we may choose x to have any value whatever, and the equation must still be satisfied. But the left side of the equation is a function of x alone; the right a function of t alone. For them to be equal for any pair (x, t) whatever, they clearly cannot vary, ie. they are constant.² Since both sides have the dimensions of $V(x)$, ie. of energy, we call this constant E :

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x) = i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} \quad (27)$$

$$= E \quad (28)$$

Thus, we obtain an easily solved equation for $f(t)$:

$$\frac{df}{dt} = -\frac{i}{\hbar} E f(t) \quad (29)$$

which can be integrated to give

$$f(t) = A e^{-iEt/\hbar} \quad (30)$$

where A is the integration constant.

We have now discovered the full time-dependence of the wave function:

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}, \quad (31)$$

where we have absorbed the constant A into $\psi(x)$. Going back to the separated equation above we also see that $\psi(x)$ must obey the **Time Independent Schrödinger Equation (TISE)**:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (32)$$

This equation has the form of an *eigenvalue equation*:

$$\hat{H}\psi(x) = E\psi(x) \quad (33)$$

²Choose a pair of values x, t for which the right side equals the left. Now, keeping t fixed at this value, change x to *any other* value you like. Clearly if the left side varies with x it will change its value and no longer be equal to the right side; so it must be a constant, and therefore so too must the right side since they are equal.

where \hat{H} is a (differential) *operator*; the Hamiltonian operator,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (34)$$

The action of this operator on $\psi(x)$ is to leave unchanged the *form* of the function, but merely to multiply it by a constant E , the energy eigenvalue. Of course since only particular functions can be solutions to the TISE, depending on the value of E , we should really label these solutions with E ,

$$\hat{H}\psi(x) = E\psi(x) \quad (35)$$

$\psi_E(x)$ is known as the *eigenfunction* of the operator \hat{H} belonging to the eigenvalue E . More commonly in Quantum mechanics we call $\psi_E(x)$ an *energy eigenstate* of the operator \hat{H} belonging to the energy eigenvalue E . Since E is real and so are all terms in the TISE, one always finds real solutions $\psi_E(x)$; but of course the full wave function, $\Psi_E(x,t)$, a solution of the TDSE, *is* complex.

We will shortly discover that the Hamiltonian operator \hat{H} is the operator representing the energy in quantum mechanics, and that its eigenvalues E are the only possible results of an energy measurement.

(5) Consequences of the Born interpretation of the Wave Function.

The Born interpretation of the wave function is expressed above in terms of an *infinitesimal* portion dx of the x -axis; the probability of finding the particle at time t somewhere between two points a and b separated by a finite distance is simply the ‘sum’ of the probabilities,

$$P_{ab}(t) = \int_a^b |\Psi(x,t)|^2 dx \quad (36)$$

If a wave function $\Psi(x,t)$ describes the state of a *single* particle, then we are certain to find the particle *somewhere*, i.e. the probability for finding it anywhere on the x -axis is 1:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \quad (37)$$

In three dimensions this becomes,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(\mathbf{r},t)|^2 d^3x = 1 \quad (38)$$

This is known as the **normalisation** of the wave function: any proper single-particle wave function must be normalised (to 1).

The Born interpretation implies a profound change in our concept of measurement. The wave function is meant to encode all that we can possibly know about the system in quantum mechanics; the Born interpretation tells us that a measurement of position does not lead to a unique or definite result, but only to one of an infinite set of possible results. What is definite is the *probability* of obtaining a *particular* result; it’s just like throwing a dice: each throw of a dice yields a definite result, although we only know *after* the throw what that result is. A particular result (say a 6) has a probability of 1/6, and this is all we can say before the throw is made. Similarly, if we **prepare** the system in the quantum state $\Psi(x,t)$ then we can only predict the probability of a given result for a position measurement ($|\Psi(x,t)|^2 dx$ for the result to lie between x and $x + dx$); but once the measurement has been made then we know where the particle is at time t of the measurement. Suppose we had computed the wave function and wished to check our calculation against experiment. The Born interpretation tells us that we can only use our wave function to predict probabilities. These probabilities can only be determined experimentally by doing very many (in principle infinitely many) repetitions of the measurement, each time **preparing** the system anew in the same state $\Psi(x,t)$ before repeating the measurement. This corresponds to the process of

checking whether a dice is biased, i.e. what the probabilities are for the various outcomes and whether they are equal: we would have to throw the dice infinitely many times and compare the relative *frequencies* of the different outcomes; these are proportional to the probabilities of the different outcomes and if they are equal, the dice is unbiased. Preparation of the system is like throwing the dice; measuring position is like looking at the dice when it's landed and noting the outcome. Just as with any repeated measurement, we can compute the **average** of the individual measurements: the weight of each value of x is its probability, $|\Psi(x,t)|^2 dx$, and the average is obtained by summing over all the possibilities,

$$\langle x \rangle \equiv \int_{-\infty}^{\infty} x |\Psi(x,t)|^2 dx \quad (39)$$

Note that we did not divide by the integral of $|\Psi|^2$ because the wave function is normalised. $\langle x \rangle$ is often called the **expectation value** for x in quantum mechanics; it is usually written in an equivalent form resembling that for other quantum mechanical variables which are represented by operators where the order of factors is important:

$$\langle x \rangle \equiv \int_{-\infty}^{\infty} \Psi^*(x,t) x \Psi(x,t) dx \quad (40)$$

The measurement process can either be performed as described above or by preparing an infinite number of identical replicas of the system, each in the same state Ψ , and measuring the position of every one; this collection of systems is known as an **ensemble**, and the interpretation of the wave function I have described is known as the **ensemble interpretation of quantum mechanics**. (A practical example of an ensemble is a beam of identical particles, all in the same state.) This is usually called the Copenhagen interpretation because it was the one developed by Niels Bohr and his many collaborators, especially Heisenberg, in Copenhagen during the 1920's. You should particularly notice that this interpretation is rather careful not to identify Ψ with the state of a single system, but with an ensemble; Ψ is the outcome of a preparation process and is our tool for computing the probabilities of various results for individual measurements, and the expectation values obtained in ensemble measurements.

In an ensemble measurement of the particle's position we measure many *different* values of x and compute their average $\langle x \rangle$. $|\Psi(x,t)|^2 dx$ gives the probability for the result of a single one of these measurements lying between x and $x + dx$; the expectation value $\langle x \rangle$ is then obtained by averaging all the individual results. Since individual results differ from each other, we would like to find a measure of the spread of these values about the mean. This is given by the variance or **uncertainty** Δx :³

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \quad (41)$$

where

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} \Psi^* x^2 \Psi dx \quad (42)$$

We can interpret this as saying that 'the position of the particle is' $\langle x \rangle \pm \Delta x$. I put this statement in quotation marks because it is not really the position of a *single* particle, but the average position of an *ensemble* of particles, each prepared in the state Ψ . We can usefully think of our particle in state Ψ as 'smeared out' over this region $\langle x \rangle \pm \Delta x$, but you should be careful not to take this interpretation

³From laboratory measurements you may be familiar with the definition of the squared 'error' as the result of taking the difference between each measurement and the mean, squaring, and then averaging:

$$\begin{aligned} (\Delta x)^2 &= \langle (\langle x \rangle - x)^2 \rangle \\ &= \langle (\langle x \rangle^2 - 2x \langle x \rangle + x^2) \rangle \\ &= \langle x \rangle^2 - 2 \langle x \rangle \langle x \rangle + \langle x^2 \rangle \\ &= \langle x^2 \rangle - \langle x \rangle^2 \end{aligned}$$

This is therefore equivalent to the definition given in the text.

too literally. Physicists usually loosely identify Ψ as the state of an individual system; this works well enough in most situations, but is also a source of misconceptions in others.

Let me illustrate the trouble caused by saying the particle ‘is’ literally in the state Ψ . Take the example of Young’s two-slit experiment using an electron beam. Let Ψ_1 be the wave function for the electron arriving at position x on the screen after going through slit 1; Ψ_2 for going through slit 2. To explain why an electron *beam* produces interference at the screen we need to write the wave function as $\Psi = (\Psi_1 + \Psi_2)/\sqrt{2}$: it is equally likely to go through either slit. At the screen we measure the number of electrons arriving at each point, which is proportional to the probability of an electron arriving there; ⁴ this probability is

$$|\Psi|^2 = \frac{1}{2} \{ |\Psi_1|^2 + |\Psi_2|^2 + 2\Re(\Psi_1^* \Psi_2) \}. \quad (43)$$

It is the cross-term - the real part, \Re - which gives the constructive and destructive interference observed in the experiment; without the linear combination of both Ψ_1 and Ψ_2 there would be no interference. We are tempted to conclude that the state of a particle just before it arrives at the screen ‘is’ in some sense *both* Ψ_1 and Ψ_2 ; has the particle gone through *both* slits, half through slit 1; the other half through slit 2? Surely not! The electron is not a particle which can be broken up in that way: we have never seen such a division in any experiment and have good reasons to believe that this is impossible: lepton number conservation, quantisation of electric charge, no known particles with mass anywhere near one-half the electron mass. ⁵ What then should we say? In the Copenhagen version of quantum mechanics we refuse to identify Ψ as the actual state of a *particular* particle and so we avoid saying that it went through both slits or either slit; instead we take Ψ to represent the result of a preparation process (sending the particle into the apparatus) which tells us the possible outcomes and probabilities of a measurement process (detection at the screen); we cannot say which slit the particle went through because we did not carry out an appropriate measurement to investigate this - indeed we avoided doing so in order to measure an interference pattern on the screen. To experimentally determine detailed information about the wave function we must carry out an ensemble measurement, and so Ψ represents the entire ensemble rather than a single member of the ensemble. In practice we all loosely think of Ψ as representing the state of a single particle - its actuality - although we have to be careful when doing so. You should be aware that this is a controversial aspect of quantum mechanics: there is so far no experiment contradicting the Copenhagen interpretation - and I believe it derives its power from the fact that it is a rather conservative interpretation - but it makes many people uneasy. Both experimental and theoretical research continues to explore this crucial area of quantum mechanics. ⁶

(6) Physical Constraints on the behaviour of the Wave Function: Boundary Conditions.

(1) All physical systems we study are localized in some finite region of space, so that the probability of finding the system at spatial infinity, $x \rightarrow \pm\infty$, is zero:

$$\lim_{x \rightarrow \pm\infty} \psi(x) = 0 \quad (44)$$

(2) Since the probability interpretation requires that $\int |\psi(x)|^2 dx = 1$, which is finite, $\psi(x)$ must be *square integrable*. This says that not only must the wave function vanish at infinity (see (1) above) but it must

⁴Notice that the use of a beam amounts to an ensemble measurement of position on the screen; if we had sent just *one* electron through the apparatus it would have arrived *somewhere* on the screen, but on its own that would have told us virtually nothing about the probability distribution $|\Psi|^2$, and we would not have noticed the interference. Only by passing many electrons through the apparatus, either in an intense beam or one at a time, can we get to see the interference pattern.

⁵Also, if we tried to check whether the electron went through one or both slits by putting counters at the slits to detect the electron as it passed through on its way to the screen, quantum mechanics - in the form of Heisenberg’s uncertainty relation - would show that the pattern on the screen is so smeared out as to remove any trace of interference.

⁶At this point you should read as much as you can about the interpretation of the wave function. One excellent example attached to these notes is from Chapter 1 of the book by D.J. Griffiths, ‘Introduction to Quantum Mechanics’. The attached article by David Mermin from Physics Today, January 1993 provides a amusing satirical account of the interpretation problem.

vanish sufficiently rapidly. (e.g. $\psi \sim 1/\sqrt{x}$ would fail this test.)

(3) Since $|\psi(x)|^2$ represents a physical probability density, it must have a unique value, ie. be single-valued. This is usually taken to imply that $\psi(x)$ be *single-valued*, although there are cases, such as spin-half particles – electrons, protons, quarks, etc. – where the wave function is double-valued.

(4) $\psi(x)$ must be *continuous everywhere*, otherwise $|\psi(x)|^2$ would not have a unique value and could not represent a physical probability density.

(5) The derivative, $d\psi/dx$, must be *continuous everywhere*. This implies that there are no kinks in $\psi(x)$. If this were not the case then $d^2\psi/dx^2$ would be infinite, thereby contributing an infinite term to the Schrödinger equation where all other terms are finite.

An exception to this rule occurs at points where the potential is infinite, such as the boundaries of the escape-proof box. But note that at such points the wave function itself must still be continuous because of its probability interpretation – see (4) – and so it only acquires a kink. At points where the potential is finite, but discontinuous, the second derivative of $\psi(x)$ will be discontinuous, although the first derivative will still remain continuous. At points where the wave function enters a classically forbidden region the second derivative changes sign – this is a point of inflexion – because the sign of $E - V(x)$ changes there. These requirements are best illustrated graphically with a few examples given in the Figures on the following two pages.

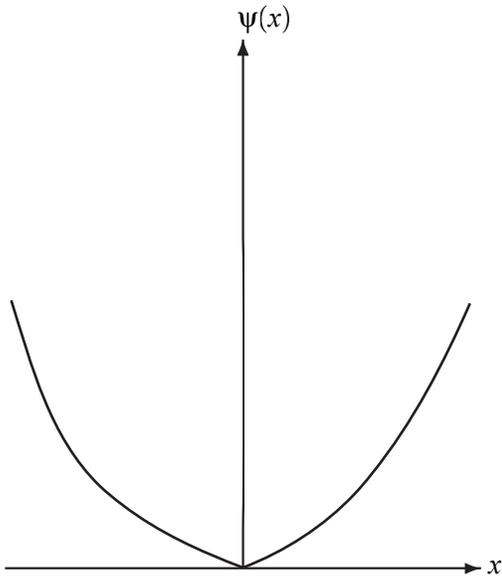


Figure 3a. $\psi(x) = Nx^2$ violates both conditions (1) and (2).

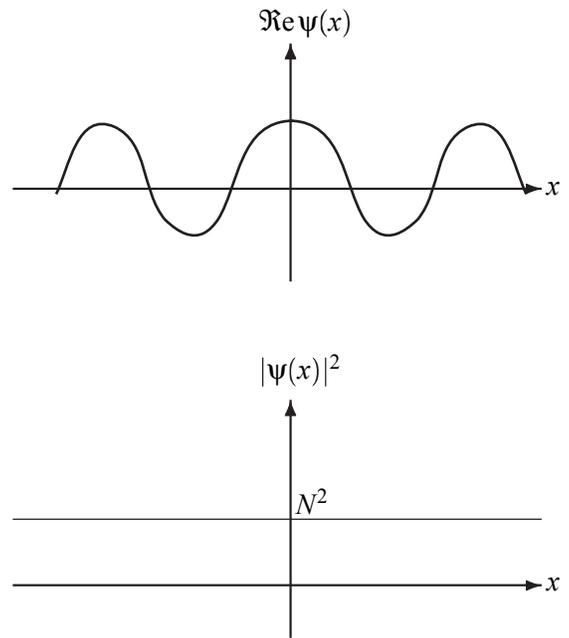


Figure 3b. Momentum eigenstate $\psi = Ne^{+ikx}$, violates both conditions (1) and (2). $\Re\psi(x) = N \cos kx$, $\Im\psi(x) = N \sin kx$, and $|\psi|^2 = N^2 = \text{const}$. Nevertheless we use this as representative of one component of a wave packet which *does* satisfy the requirements.

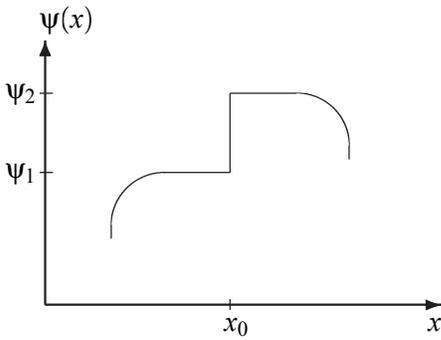


Figure 3c. This violates (3) and (4) at $x = x_0$: $|\psi(x_0)|^2$ is double-valued and is also discontinuous; but not (5): $d\psi/dx$ is still continuous there – no kink!

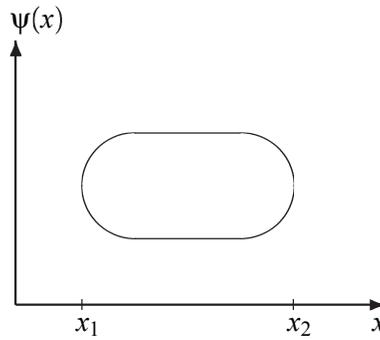


Figure 3d. This violates (3) everywhere in region $x_1 < x < x_2$. But ψ and $d\psi/dx$ are still continuous even with $d\psi/dt$ infinite at x_1 & x_2 .

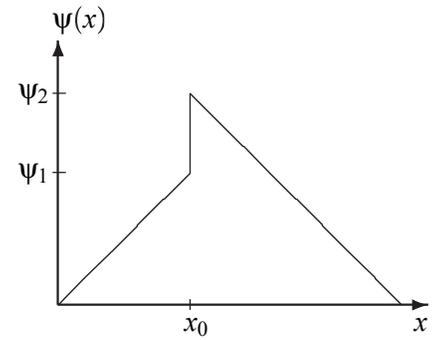


Figure 3e. This violates (3), (4) and (5) at x_0 because now the slope is also discontinuous there.

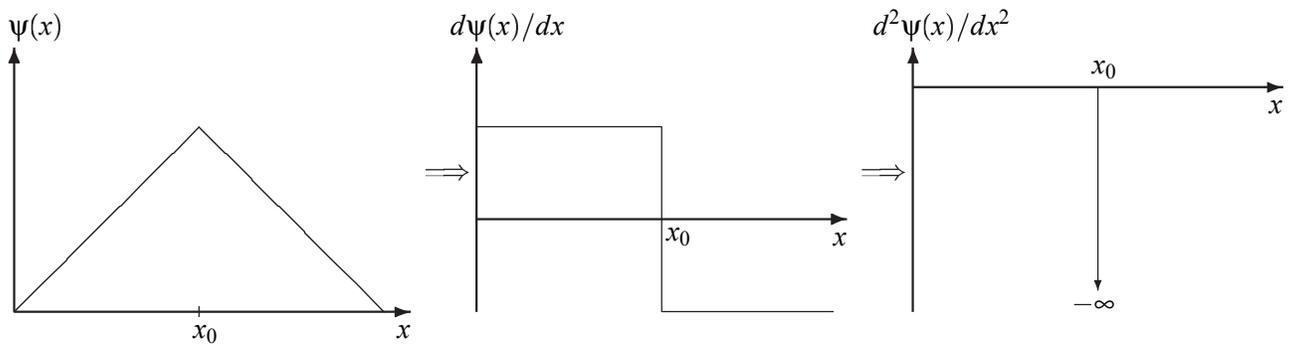


Figure 3f. Consequences of a kink in $\psi(x)$: with $d^2\psi/dx^2$ infinite the TISE cannot be solved if $V(x)$ is finite at x_0 .

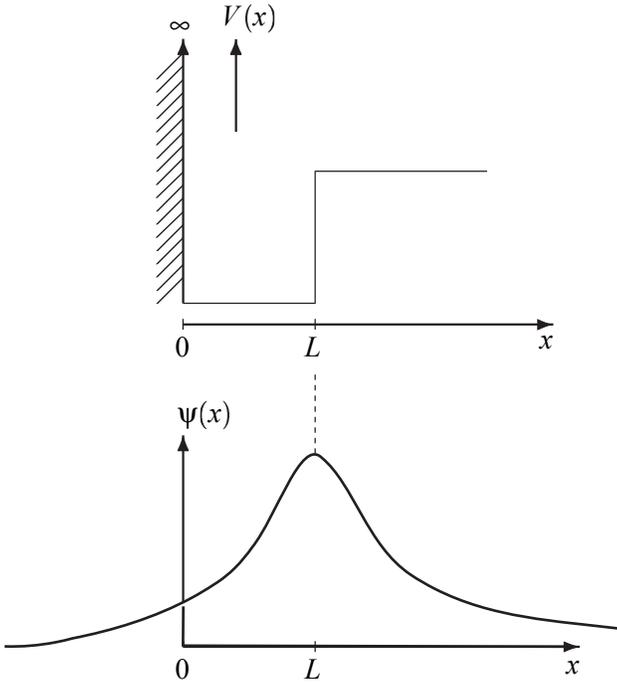


Figure 3g. With $V(0)$ infinite, $\psi(0) = 0$, producing a kink in ψ . However $V(L)$ is discontinuous but finite, so both ψ and $d\psi/dx$ are continuous at $x = L$.

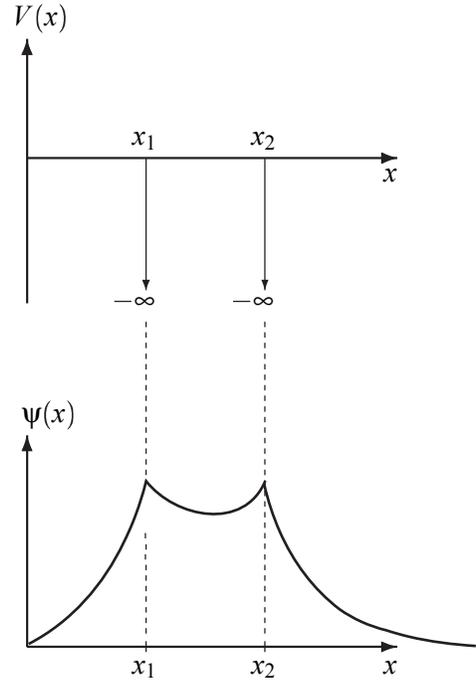


Figure 3h. Here $V(x)$ is infinite at two isolated points. These two delta function wells give a very simple model for H_2^+ .

(7) The Infinite Square Well (or the Escape-proof Box) in 1-dimension.

To remind you of the role played by the above conditions on the wave function, let us solve the familiar infinite square well problem. The potential $V(x)$ is time-independent, so the wave function for a given energy (energy eigenfunctions) have the form obtained in Section 4:

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \quad (45)$$

Our aim is to find the energy eigenvalues E and the corresponding eigenfunctions $\psi(x)$ by solving the **Time Independent Schrödinger Equation (TISE)**:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (46)$$

For the infinite square well the particle of mass m is confined to the region $-L/2 < x < +L/2$; it cannot escape from that region because it cannot surmount the infinitely high potential barriers at the ends: $V(\pm L/2) = \infty$. Physically, this means there is zero probability of finding the particle outside the box; mathematically this is expressed as

$$\psi(x) = 0 \quad \text{for } x \leq -L/2 \text{ \& for } x \geq +L/2 \quad (47)$$

Since the potential is constant inside the box we take $V(x) = 0$ there. The wave function inside the box is therefore given by solving the TISE:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (48)$$

A simple rearrangement gives

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x), \quad (49)$$

where

$$k \equiv \sqrt{\frac{2m}{\hbar^2}E}, \quad (50)$$

and is real because $E > 0$ (it cannot be less than the bottom of the well). Mathematically this differential equation is of the classical simple harmonic oscillator form and therefore the general solution is a linear combination of sin and cos,⁷

$$\psi(x) = A \cos(kx) + B \sin(kx) \quad (51)$$

The boundary conditions at $x = \pm L/2$ determine the constants A, B and the energy eigenvalue. From Section 6 we know that *the wave function must be continuous* everywhere: in particular, at $x = \pm L/2$ the wave function must vanish to match its value just outside the well:⁸

$$\psi(x = -\frac{kL}{2}) = A \cos(\frac{kL}{2}) - B \sin(\frac{kL}{2}) = 0 \quad (52)$$

$$\psi(x = +\frac{L}{2}) = A \cos(\frac{kL}{2}) + B \sin(\frac{kL}{2}) = 0 \quad (53)$$

⁷We could equally well use complex exponentials:

$$\psi(x) = ae^{ikx} + be^{-ikx}$$

This is equivalent to our choice because it's just a linear combination of the sin and cos. Our choice is more convenient for imposing the boundary conditions.

⁸We do not match the derivatives because the potential is infinite at $x = \pm L/2$: there is a kink in the wave function at these points. See Section 6 for a discussion.

Adding and subtracting these equations gives two simple conditions:

$$A \cos\left(\frac{kL}{2}\right) = 0 \quad (54)$$

$$B \sin\left(\frac{kL}{2}\right) = 0 \quad (55)$$

To find all possible solutions we must explore all the possibilities; since the sine and cosine cannot both vanish, there are just two cases:

(A) $A \neq 0, B = 0$: the second equation is then satisfied, while the first equation demands that $\cos(kL/2) = 0$, i.e. $kL/2 = n\pi/2$ for n odd; this gives energy quantisation:

$$E = E_n \equiv n^2 \frac{\pi^2 \hbar^2}{2mL^2} \quad \text{for } n = 1, 3, 5, \dots, \quad (56)$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \cos\left(n\pi \frac{x}{L}\right) \quad (57)$$

The constant $A = \sqrt{2/L}$ was determined by normalising the wave function.

(B) $B \neq 0, A = 0$: the first equation is then satisfied, while the second equation demands that $\sin(kL/2) = 0$, i.e. $kL/2 = n\pi/2$ for n even; this gives energy quantisation:

$$E = E_n \equiv n^2 \frac{\pi^2 \hbar^2}{2mL^2} \quad \text{for } n = 2, 4, 6, \dots, \quad (58)$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(n\pi \frac{x}{L}\right) \quad (59)$$

The constant $B = \sqrt{2/L}$ was determined by normalising the wave function. The solutions are summarised in the following two pages.

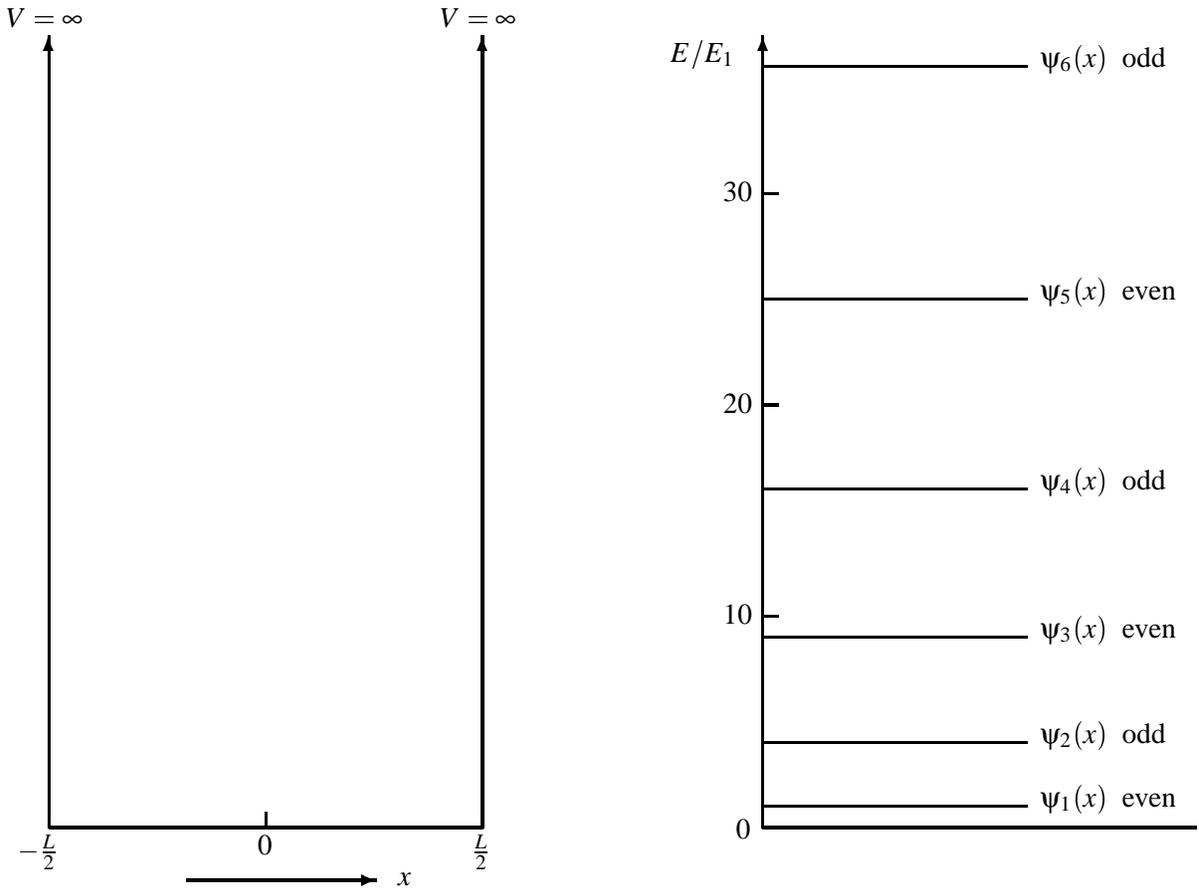


Figure 4. Potential (left) and energy-level diagram (right, drawn to scale in units of the ground state energy E_1) for a particle in an escape-proof box.

The eigenfunctions, $\Psi_n(x, t)$, specified by the quantum number n correspond to the energy eigenvalues

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3, \dots$$

Note that the even functions of x (parity $+1$) have n odd; the odd functions (parity -1) have n even.

$$\Psi_1(x, t) = \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) e^{-iE_1 t/\hbar} \quad E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \quad (60)$$

$$\Psi_2(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) e^{-iE_2 t/\hbar} \quad E_2 = \frac{4\pi^2 \hbar^2}{2mL^2} \quad (61)$$

$$\Psi_3(x, t) = \sqrt{\frac{2}{L}} \cos\left(\frac{3\pi x}{L}\right) e^{-iE_3 t/\hbar} \quad E_3 = \frac{9\pi^2 \hbar^2}{2mL^2} \quad (62)$$

$$\Psi_4(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{4\pi x}{L}\right) e^{-iE_4 t/\hbar} \quad E_4 = \frac{16\pi^2 \hbar^2}{2mL^2} \quad (63)$$

There are several noteworthy general features of these eigenstates; we will encounter these throughout the course:

(1) The **ground state** (i.e. the lowest energy state, $n = 1$) has non-zero energy. This is a uniquely quantum mechanical effect - a consequence of Heisenberg's uncertainty principle for a localized particle. Can you show this?

(2) The eigenstates are either odd or even functions of x ; i.e. $\psi(-x) = \pm\psi(x)$. Thus the **ground state** ($n=1$) is even; the **first excited state** ($n=2$) is odd; the **second excited state** ($n=3$) is even; etc. We will discover later that this is a consequence of a *symmetry* of the potential, $V(-x) = V(x)$.

(3) Eigenstates corresponding to different energies are **orthogonal**:

$$\int_{-\infty}^{+\infty} \psi_n^*(x)\psi_m(x)dx = 0 \quad \text{for } n \neq m \quad (64)$$

Can you show this explicitly for a few of the infinite square well eigenstates? ⁹ We can combine this with the normalisation condition into the **orthonormality** condition:

$$\int_{-\infty}^{+\infty} \psi_n^*(x)\psi_m(x)dx = \delta_{nm}, \quad (65)$$

where δ_{nm} is the Kronecker delta symbol ($= 1$ for $n = m$, $= 0$ for $n \neq m$).

(4) The most general solution, $\Psi(x, t)$, to the **Time Dependent Schrödinger Equation (TDSE)** for the infinite square well is a linear superposition of these eigenstates:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \Psi_n(x, t), \quad (66)$$

where c_n are constants and the time-dependent energy eigenstates are

$$\Psi_n(x, t) = \psi_n(x)e^{-iE_n t/\hbar} \quad (67)$$

You may wonder about the physical significance of a state Ψ which does not have a definite energy: what does it mean? This question is at the heart of quantum mechanics and will be addressed at various stages in the course.

(8) Momentum in Quantum Mechanics.

Our next task is to find a definition for the momentum variable in quantum mechanics. This may seem obvious because according to de Broglie, by analogy with a classical monochromatic plane wave, a free particle of momentum $p = \hbar k$ and energy $E = \hbar\omega$ has a wave function:

$$\Psi(x, t) = Ne^{i(kx - \omega t)} \quad (68)$$

$$= Ne^{i(px - Et)/\hbar} \quad (69)$$

where N is a normalisation constant. So far so good; but we now face two difficulties:

(a) There is apparently no sign of the momentum p in the energy eigenstates for the infinite square well:

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin(n\pi \frac{x}{L}) e^{-iE_n t/\hbar} \quad (70)$$

⁹To perform the integrals use the trigonometric identities

$$\cos A \cos B = \frac{1}{2}(\cos(A - B) + \cos(A + B))$$

$$\sin A \sin B = \frac{1}{2}(\cos(A - B) - \cos(A + B))$$

¹⁰In this simple case it is there, but in the form of both a p and a $-p$. Can you see how?

(b) The de Broglie wave has a constant probability density, $|\Psi(x,t)|^2 = N^2$, presumably representing a particle (or particles) which are equally likely to be found anywhere in space, but is therefore not normalisable. This is actually an idealization, just as a plane monochromatic light wave is. To represent a more realistic situation, which is a particle localized in some finite region of space, we need to construct a **wave packet** by superposing infinitely many different wavelengths (or momenta). This provides our first way of discovering quantum mechanical momentum.

Momentum discovered by Method (1).

Let each de Broglie wave of momentum p have amplitude $\phi(p)$; then a wave packet is made by ‘summing’ all of these:

$$\begin{aligned}\Psi(x,t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \phi(p) e^{i(px-Et)/\hbar} dp \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Phi(p,t) e^{ipx/\hbar} dp\end{aligned}\quad (71)$$

where we have introduced the **momentum wave function** $\Phi(p,t)$ which seems to be rather like the momentum space version of the configuration space wave function $\Psi(x,t)$. We can solve for $\Phi(p,t)$ by doing an inverse Fourier transform:

$$\Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x,t) e^{-ipx/\hbar} dx \quad (72)$$

which also explains the choice of the square root factor. Now it is not difficult to show that the two wave functions have the same normalisation; this is Parseval’s Theorem:

$$\int_{-\infty}^{+\infty} |\Phi(p,t)|^2 dp = \int_{-\infty}^{+\infty} |\Psi(x,t)|^2 dx = 1 \quad (73)$$

which suggests that

$$|\Phi(p,t)|^2 dp = \text{Probability that a measurement of momentum at time } t \quad (74)$$

gives a value lying in the range $p \rightarrow p + dp$.

If we accept this very reasonable interpretation of $\Phi(p,t)$, then the Expectation value for momentum is given by:

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Phi^*(p,t) p \Phi(p,t) dp \quad (75)$$

We can now translate this expression into one involving only the configuration space wave function $\Psi(x,t)$ by judicious use of the formulae (??) and (??) to eliminate the momentum space wave function – for details see the Appendix. The result is:

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x,t) dx \quad (76)$$

We are finally led to *postulate* that momentum in quantum mechanics is represented by the *operator*:

$$\hat{p} \equiv -i\hbar \frac{\partial}{\partial x} \quad (77)$$

The hat (or circumflex) in \hat{p} is there to emphasize that the quantity is an operator – in this case a differential operator.

Momentum discovered by Method (2).

The above may seem to be rather complicated; here we give a rather simpler and perhaps more intuitive argument using the analogy of momentum defined classically as

$$p = m \frac{dx}{dt} \quad \text{classical momentum.}$$

Now the quantum measurements don't determine the variables themselves but their expectation values, so we might try to postulate that it is these which have the same relationship as the classical ones (this is an example of Bohr's correspondence principle):

$$\langle p \rangle := m \frac{d \langle x \rangle}{dt} \quad \text{quantum momentum.} \quad (78)$$

We can then carry out the following steps:

$$\begin{aligned} \langle p \rangle &= m \frac{d \langle x \rangle}{dt} \\ &= m \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} (\Psi^* x \Psi) dx \\ &= m \int_{-\infty}^{+\infty} \left\{ \frac{\partial \Psi^*}{\partial t} x \Psi + \Psi^* x \frac{\partial \Psi}{\partial t} \right\} dx \end{aligned}$$

For the time derivatives we now we use the TDSE and its complex conjugate, remembering that the potential is real:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} \quad (79)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*(x,t)}{\partial x^2} + V(x,t) \Psi^*(x,t) = -i\hbar \frac{\partial \Psi^*(x,t)}{\partial t} \quad (80)$$

The terms involving the potential cancel out and we obtain:

$$\langle p \rangle = -\frac{i\hbar}{2} \int_{-\infty}^{+\infty} \left\{ \frac{\partial^2 \Psi^*}{\partial x^2} x \Psi - \Psi^* x \frac{\partial^2 \Psi}{\partial x^2} \right\} dx \quad (81)$$

We now carry out an integration by parts on each term, thereby moving one of the derivatives over to the other factor in the integrand:

$$\langle p \rangle = -\frac{i\hbar}{2} \int_{-\infty}^{+\infty} \left\{ -\frac{\partial \Psi^*}{\partial x} \frac{\partial (x\Psi)}{\partial x} - \frac{\partial (x\Psi^*)}{\partial x} \frac{\partial \Psi}{\partial x} \right\} dx \quad (82)$$

$$= -\frac{i\hbar}{2} \int_{-\infty}^{+\infty} \left\{ -\frac{\partial \Psi^*}{\partial x} \Psi - \frac{\partial \Psi^*}{\partial x} x \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi^*}{\partial x} x \frac{\partial \Psi}{\partial x} \right\} dx \quad (83)$$

$$= -\frac{i\hbar}{2} \int_{-\infty}^{+\infty} \left\{ -\frac{\partial \Psi^*}{\partial x} \Psi + \Psi^* \frac{\partial \Psi}{\partial x} \right\} dx \quad (84)$$

Notice the cancellation of the term with x . In doing this integration by parts we have also discarded the so-called surface terms

$$\left[\frac{\partial \Psi^*}{\partial x} x \Psi - \Psi^* x \frac{\partial \Psi}{\partial x} \right]_{-\infty}^{+\infty}$$

using the condition that the wave function vanish at spatial infinity – see equation (??). This process of integrating by parts and discarding the surface terms is a frequently used procedure in quantum mechanics; you should familiarise yourself with it, thereby avoiding writing down all the rather messy steps in long calculations like the above. We are not yet finished: there is one more integration by parts to do –

on the first term only – which shows it is identical to the second term – once again after discarding the surface term. The two identical terms therefore add to give:

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x,t) dx, \quad (85)$$

which we recognize as the result (??) we obtained by Method (1) above. This wonderful consistency should provide strong evidence that we are on the right track.

A few comments about 3-dimensions: when working in 1-dimension we usually use x as our coordinate but \hat{p} as shorthand for the x -component of the operator representing the momentum vector $\hat{\mathbf{p}}$. When we tackle 3-dimensional problems we have to use this fully explicit notation:

$$\hat{p}_x \equiv -i\hbar \frac{\partial}{\partial x} \quad (86)$$

with

$$\langle p_x \rangle \equiv \int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t) \hat{p}_x \Psi(\mathbf{r},t) d^3x \quad (87)$$

$$\equiv \int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(\mathbf{r},t) d^3x \quad (88)$$

$$\equiv -i\hbar \int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t) \left\{ \frac{\partial}{\partial x} \Psi(\mathbf{r},t) \right\} d^3x \quad (89)$$

The generalisation to 3-dimensions follows the same pattern:

$$\hat{\mathbf{p}} = -i\hbar \nabla, \quad (90)$$

or, in cartesian coordinates,

$$\hat{p}_i = -i\hbar \frac{\partial}{\partial x_i}, \quad i = 1, 2, 3 \quad \text{where } (x_1, x_2, x_3) = (x, y, z) \quad (91)$$

(9) Dynamical variables and the Operator Postulate

In classical mechanics we are familiar with the fact that all dynamical variables - angular momentum and energy, for example - can be expressed in terms of position and momentum. In quantum mechanics we therefore expect the same. The discovery that quantum mechanics requires momentum to be represented by an operator means that other dynamical variables must also be represented by operators. This may seem a rather abstract mathematical concept, but its physical and philosophical implications are profound. Thus, the classical kinetic energy of a particle, $T = mv^2/2 = p^2/2m$, becomes an operator in quantum mechanics: $\hat{T} = \hat{p}^2$. We now also see the significance of the operator \hat{H} in the Schrödinger equation,

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

and the reason why it is called the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \quad (92)$$

$$= \frac{\hat{p}^2}{2m} + V(x,t) \quad (93)$$

This is just the classical Hamiltonian, (Kinetic Energy + Potential Energy) expressed in terms of momentum and coordinate x , with the classical momentum replaced by the quantum mechanical momentum operator \hat{p} . This identification carries over to 3-dimensions also. This should provide the decisive evidence that momentum is indeed the operator we have discovered in the previous discussion.

We can now apply our postulate to all dynamical variables; thus the classical angular momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (94)$$

leads us to the quantum mechanical angular momentum:

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} = -i\hbar \mathbf{r} \times \nabla, \quad (95)$$

or, in cartesian components,

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad (96)$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad (97)$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (98)$$

The properties of angular momentum and the physical consequences of its representation as an operator will be a central topic in this course.

The Operator Postulate: Dynamical variables in quantum mechanics can be obtained from their classical counterparts by replacing the classical momentum variables by the corresponding quantum mechanical *operators*. For any classical variable $A(x, p)$ the corresponding quantum mechanical operator is $\hat{A} = A(x, \hat{p})$.

(10) Heisenberg's Uncertainty Principle & Non-commuting Operators.

It is well known that matrices are operators, operating on each other and on vectors. Most often they do not commute: for example, define the two matrices,

$$A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad B = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}; \quad (99)$$

they do not commute, i.e. $AB \neq BA$. In fact, $BA = -AB$:

$$AB = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad BA = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad (100)$$

We can express this property by saying that the **commutator** of A and B ,

$$[A, B] \equiv AB - BA \quad (101)$$

does not vanish,

$$[A, B] = 2C \neq 0 \quad (102)$$

where C is the matrix:

$$C = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (103)$$

Less familiar might be that the differentiation operation has similar non-commuting properties when operating on functions. This is therefore the case for the momentum operator:

$$[x, \hat{p}_x] = i\hbar \quad (104)$$

Proof: We apply the commutator to an *arbitrary* wave function $\psi(x)$:

$$[x, \hat{p}_x]\psi(x) = (x\hat{p}_x - \hat{p}_x x)\psi(x) \quad (105)$$

$$= -i\hbar \left\{ x \left(\frac{\partial}{\partial x} \psi(x) \right) - \frac{\partial}{\partial x} (x\psi(x)) \right\} \quad (106)$$

$$= -i\hbar \left\{ x \frac{\partial \psi(x)}{\partial x} - x \frac{\partial \psi(x)}{\partial x} - \psi(x) \frac{\partial x}{\partial x} \right\} \quad (107)$$

$$= -i\hbar \left\{ x \frac{\partial \psi(x)}{\partial x} - x \frac{\partial \psi(x)}{\partial x} - \psi(x) \right\} \quad (108)$$

$$= i\hbar \psi(x) \quad (109)$$

where we used the product rule of differentiation to operate on the product $x\psi$. Now comes the subtle part of the argument: since this result is true for any function whatever (i.e. for arbitrary $\psi(x)$) we can immediately assert that the two *operators* $[x, \hat{p}_x]$ and $i\hbar$ *always* act the same way, i.e. they are identical operators, $[x, \hat{p}_x] = i\hbar$. Q.E.D.

I leave it as an exercise to show that, for any function $f(x)$,

$$[f(x), \hat{p}_x] = i\hbar \frac{\partial f(x)}{\partial x} \quad (110)$$

Introducing operators into quantum physics has a profound effect on our understanding of Nature. This was first noticed by Heisenberg in his justly renowned uncertainty principle. An elementary - and very general - argument shows that for any two operators \hat{A} and \hat{B} ,

$$\Delta A \Delta B \geq \frac{1}{2} | \langle [\hat{A}, \hat{B}] \rangle | \quad (111)$$

where ΔA and ΔB are the respective uncertainties in an ensemble measurement of the two observables on a system in a given quantum state. This is **Heisenberg's generalised uncertainty principle**. For a proof see Bransden & Joachain, pp.213–215.

For the special case $\hat{A} = x$, $\hat{B} = \hat{p}_x$ we obtain the well-known position-momentum uncertainty relation:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad (112)$$

In words this states that,

(a) we cannot determine experimentally *both* the position and momentum of a particle with 100% precision;

(b) a particle cannot be said to 'have' both a position and a momentum; these are **complementary** properties;

(c) Planck's constant \hbar sets the limit to the combined magnitudes of these uncertainties.

It should be emphasised that the uncertainty principle does not imply that we cannot observe the position of a particle with 100% precision; in principle we can, but the uncertainty principle says the consequence is that we then know nothing about the momentum: $\Delta x = 0$ implies $\Delta p_x = \infty$.

(11) Energy Eigenstates are Stationary States.

Energy eigenstates are particularly important in applications of quantum mechanics. Here we discuss some of their properties, which we will see later in the course in a more general form. This section and the following ones also provide practice at some of the mathematical manipulations common to many calculations in quantum mechanics. First we note that energy eigenstates are solutions of the TISE and have the form

$$\Psi_E(x, t) = \psi_E(x) e^{-iEt/\hbar}$$

We have seen an example of such eigenstates for the escape-proof box in §7, where the quantum number n labels the energy eigenvalue E_n and the energy eigenstate $\Psi_n(x, t)$. Since this is common to many other examples, we adopt the more convenient notation:

$$\Psi_n(x, t) = \psi_n(x)e^{-iE_n t/\hbar} \quad (113)$$

Since the complex conjugate wave function has the opposite sign on the time-dependent exponential,

$$\Psi_n^*(x, t) = \psi_n^*(x)e^{+iE_n t/\hbar} \quad (114)$$

the time-dependence drops out of the probability density because these exponentials cancel,

$$P(x, t) := |\Psi_n(x, t)|^2 \quad (115)$$

$$= \psi_n^*(x)\psi_n(x)e^{+iE_n t/\hbar}e^{-iE_n t/\hbar} \quad (116)$$

$$= |\psi_n(x)|^2 \quad (117)$$

$$= P(x), \text{ independent of } t \quad (118)$$

It also follows that both $\Psi_n(x, t)$ and $\psi_n(x)$ are normalized to 1:

$$1 = \int_{-\infty}^{+\infty} \Psi_n^*(x, t)\Psi_n(x, t) dx \quad (119)$$

$$= \int_{-\infty}^{+\infty} \psi_n^*(x)\psi_n(x)e^{+iE_n t/\hbar}e^{-iE_n t/\hbar} dx \quad (120)$$

$$= \int_{-\infty}^{+\infty} \psi_n^*(x)\psi_n(x) dx \quad (121)$$

States whose probability density $|\Psi_n(x, t)|^2$ is time-independent are known as **stationary states**. Furthermore, the time-dependence drops out of all expectation values for time-independent physical observables, \hat{O} , again, because the time-dependent exponentials cancel for energy eigenstates:

$$\langle \hat{O} \rangle_t := \int_{-\infty}^{+\infty} \Psi_n^*(x, t)\hat{O}\Psi_n(x, t) dx \quad (122)$$

$$= \int_{-\infty}^{+\infty} \psi_n^*(x)\hat{O}\psi_n(x)e^{+iE_n t/\hbar}e^{-iE_n t/\hbar} dx \quad (123)$$

$$= \int_{-\infty}^{+\infty} \psi_n^*(x)\hat{O}\psi_n(x) dx \quad (124)$$

$$= \langle \hat{O} \rangle, \text{ independent of } t \quad (125)$$

In the above I have continued to use the notation $\psi_n^*(x)$ for the space-dependent part of the eigenstate even though it is real. The reason for calling these states stationary is that their momentum expectation value is zero: they do not move, at least on the average. The proof depends on the fact that the x -dependent part of the wave function is real, $\psi_n^*(x) = \psi_n(x)$. Using the representation of the momentum operator,

$$\hat{p} = -i\hbar \frac{\partial}{\partial x},$$

the complex conjugate of the momentum expectation value is

$$(\langle \hat{p} \rangle)^* = \left[-i\hbar \int_{-\infty}^{+\infty} \psi_n(x) \frac{\partial}{\partial x} \psi_n(x) dx \right]^* \quad (126)$$

$$= +i\hbar \int_{-\infty}^{+\infty} \psi_n(x) \frac{\partial}{\partial x} \psi_n(x) dx, \text{ since } \psi_n(x) \text{ \& } x \text{ are real} \quad (127)$$

$$= -\langle \hat{p} \rangle, \quad (128)$$

i.e. the expectation value is imaginary. But, being an observable quantity, it must be real: the only possibility is therefore that

$$\langle \hat{p} \rangle = 0, \text{ for energy eigenstates.} \quad (129)$$

What is the expectation value of the energy? For an energy eigenstate we expect it to be the energy eigenvalue itself; let us see if this is so. The operator representing energy in quantum mechanics is the hamiltonian, so the expectation value is¹¹

$$\langle \hat{H} \rangle := \int_{-\infty}^{+\infty} \Psi_n^*(x,t) \hat{H} \Psi_n(x,t) dx \quad (130)$$

$$= \int_{-\infty}^{+\infty} \Psi_n^*(x) \hat{H} \Psi_n(x) dx \quad (131)$$

$$= E_n \int_{-\infty}^{+\infty} \Psi_n^*(x,t) \Psi_n(x,t) dx, \quad (132)$$

$$= E_n \quad (133)$$

where we first used the fact that $\Psi_n(x)$ is an eigenstate,

$$\hat{H} \Psi_n(x) = E_n \Psi_n(x), \quad (134)$$

and finally that it is normalized,

$$\int_{-\infty}^{+\infty} \Psi_n^*(x) \Psi_n(x) dx = 1. \quad (135)$$

Since the expectation value is the energy eigenvalue itself, the eigenstate state seems to 'have' a definite energy; therefore we expect it's energy uncertainty to be zero. First we calculate

$$\langle \hat{H}^2 \rangle := \int_{-\infty}^{+\infty} \Psi_n^*(x,t) \hat{H}^2 \Psi_n(x,t) dx \quad (136)$$

$$= \int_{-\infty}^{+\infty} \Psi_n^*(x) \hat{H}^2 \Psi_n(x) dx \quad (137)$$

$$= E_n^2 \int_{-\infty}^{+\infty} \Psi_n^*(x,t) \Psi_n(x,t) dx, \quad (138)$$

$$= E_n^2. \quad (139)$$

Here we simply acted with the hamiltonian on the eigenstate twice in succession:

$$\hat{H}^2 \Psi_n(x) = \hat{H} [\hat{H} \Psi_n(x)] \quad (140)$$

$$= E_n [\hat{H} \Psi_n(x)] \quad (141)$$

$$= E_n^2 \Psi_n(x). \quad (142)$$

Hence the energy uncertainty is,

$$\Delta E := \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2} \quad (143)$$

$$= \sqrt{E_n^2 - (E_n)^2} \quad (144)$$

$$= 0 \quad (145)$$

¹¹In quantum mechanics one often uses the shorthand notation $\langle E \rangle$ for the expectation value $\langle \hat{H} \rangle$ even for states which are not energy eigenstates. I shall give a simple example of such a state at the end of this section.

(13) Orthogonality and Orthonormality of Energy Eigenstates.

Perhaps the most important mathematical property of energy eigenstates is the orthogonality of eigenstates corresponding to different energies. In this section we suppress the arguments (x, t) of the wave functions. To prove both orthogonality and the reality of the energy eigenvalues we consider the integral:

$$H_{ij} := \int_{-\infty}^{+\infty} \Psi_i^* \hat{H} \Psi_j dx \quad (146)$$

$$= E_j \int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx, \quad (147)$$

where we used the fact that the states are eigenstates of the hamiltonian,

$$\hat{H} \Psi_j = E_j \Psi_j \quad (148)$$

The trick now is to somehow move the hamiltonian so that it acts on the other eigenstate. We will show below that this is possible, with the amazingly simple result:

$$H_{ij} := \int_{-\infty}^{+\infty} \Psi_i^* \hat{H} \Psi_j dx = \int_{-\infty}^{+\infty} \left\{ \hat{H} \Psi_i \right\}^* \Psi_j dx \quad (149)$$

This shows that the Hamiltonian is a **Hermitian operator**; later in the course we will show that this is a property of all operators representing physical observables in quantum mechanics. On a first reading I suggest you skip or merely skim through the following proof of equation (??).

The proof:

To proceed we need to use the explicit form for the hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (150)$$

and perform two successive integrations by parts. First let us deal with the first term in the hamiltonian:

$$\int_{-\infty}^{+\infty} \Psi_i^* \frac{\partial^2}{\partial x^2} \Psi_j dx = \left[\Psi_i^* \frac{\partial}{\partial x} \Psi_j \right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \left\{ \frac{\partial}{\partial x} \Psi_i^* \right\} \left\{ \frac{\partial}{\partial x} \Psi_j \right\} dx. \quad (151)$$

The first term in this expression evaluates the wave functions and their first derivative at $\pm\infty$ where all wave functions vanish: the probability of finding our particle at infinity is zero – see equation (??). As discussed in §8 in ‘Momentum discovered by Method (2)’, these so-called ‘surface terms’ occur frequently. From now on we shall always omit them because wave functions must vanish at spatial infinity. We now carry out the second integration by parts, omitting any surface terms generated:

$$\int_{-\infty}^{+\infty} \Psi_i^* \frac{\partial^2}{\partial x^2} \Psi_j dx = - \int_{-\infty}^{+\infty} \left\{ \frac{\partial}{\partial x} \Psi_i^* \right\} \left\{ \frac{\partial}{\partial x} \Psi_j \right\} dx \text{ by parts, as above} \quad (152)$$

$$= + \int_{-\infty}^{+\infty} \left\{ \frac{\partial^2}{\partial x^2} \Psi_i^* \right\} \Psi_j dx \text{ by parts again} \quad (153)$$

$$= + \int_{-\infty}^{+\infty} \left\{ \frac{\partial^2}{\partial x^2} \Psi_i \right\}^* \Psi_j dx. \quad (154)$$

In the last line we used the fact that x is real to place the derivative inside the complex conjugation; similarly the potential $V(x)$, being a real function, can be placed anywhere. The result is that the entire hamiltonian has been moved over to act on the i -th eigenfunction. Thus we have proved equation (??) showing that the Hamiltonian is a Hermitian operator.

End of the proof.

This enables us to obtain another expression for our integral:

$$\begin{aligned} H_{ij} &= \int_{-\infty}^{+\infty} \Psi_i^* \hat{H} \Psi_j dx, \text{ our first expression} \\ &= E_j \int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx, \text{ our first result} \end{aligned} \quad (155)$$

$$\begin{aligned} &= \int_{-\infty}^{+\infty} \{ \hat{H} \Psi_i \}^* \Psi_j dx, \text{ our second expression} \\ &= E_i^* \int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx, \text{ our second result} \end{aligned} \quad (156)$$

where we have used the fact that Ψ_i is an energy eigenfunction. Notice that the same integral occurs in each result; since they are equal, their difference is zero:

$$(E_j - E_i^*) \int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx = 0 \quad (157)$$

There are two cases to consider:

Case 1: For $i = j$ the expression gives

$$(E_j - E_j^*) \int_{-\infty}^{+\infty} |\Psi_j|^2 dx = 0 \quad (158)$$

Since the integrand is positive the integral cannot vanish; indeed it must be equal to 1 since the eigenstate is normalised. Hence the other factor must vanish, i.e. the energy is real,

$$E_j^* = E_j \quad (159)$$

Case 2: For $i \neq j$, and using the fact that the energies are real, the expression gives

$$(E_j - E_i) \int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx = 0, \text{ for } i \neq j \quad (160)$$

The energy factor is not zero if we assume that there is no degeneracy, i.e. that the energies corresponding to different eigenfunctions are different.¹² Hence the integral, involving different eigenstates, must vanish:

$$\int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx = 0, \text{ for } i \neq j \quad (161)$$

This is the statement that eigenstates corresponding to different eigenvalues are **orthogonal**. We can combine this statement with the normalization condition in one elegant statement of **orthonormality**:

$$\int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx = \delta_{ij} \quad (162)$$

where the kronecker delta is defined as

$$\delta_{ij} = 1, \text{ for } i = j \quad (163)$$

$$= 0, \text{ for } i \neq j \quad (164)$$

Notice that the orthonormality conditions also apply to the spatial part of the eigenstates alone because the time-dependent exponential factors are independent of the integration variable x and cancel out when $i = j$:

$$\int_{-\infty}^{+\infty} \Psi_i^* \Psi_j dx = \delta_{ij} \quad (165)$$

¹²The case of degeneracy does occur in situations where there are symmetries. They can be easily handled by making particular linear combinations of the eigenstates in question, leading to the same results.

I suggest you check one or two cases of this orthogonality for the infinite square well wave functions - for eigenstates of opposite symmetry (odd and even functions of x) this is trivial! Do you know why?

(13) A Simple Example: a state which is not an energy eigenstate.

Suppose we illuminate an ensemble of systems (such as a gas of H-atoms at low temperature) in their ground state with a short laser pulse. Let the laser have a low enough frequency that it can only excite the system into its first excited state. Also suppose that there is a 50:50 chance of this excitation happening. The resulting wave function describing the ensemble prepared in this way is the particular linear combination of eigenstates,

$$\Psi(x, t) = \frac{1}{\sqrt{2}} [\Psi_1(x, t) + \Psi_2(x, t)] \quad (166)$$

$$= \frac{1}{\sqrt{2}} [\psi_1(x)e^{-iE_1t/\hbar} + \psi_2(x)e^{-iE_2t/\hbar}] \quad (167)$$

With a linear combination of two eigenstates the exponentials do not cancel in expectation values but generate time dependence; for example, the probability density,

$$\Psi^*(x, t)\Psi(x, t) = \frac{1}{2} [|\Psi_1(x, t)|^2 + |\Psi_2(x, t)|^2 + \Psi_1^*(x, t)\Psi_2(x, t) + \Psi_2^*(x, t)\Psi_1(x, t)] \quad (168)$$

$$= \frac{1}{2} [|\Psi_1(x, t)|^2 + |\Psi_2(x, t)|^2 + 2\Re(\Psi_1^*(x, t)\Psi_2(x, t))] \quad (169)$$

$$= \frac{1}{2} \left[|\psi_1(x)|^2 + |\psi_2(x)|^2 + 2\psi_1(x)\psi_2(x) \cos\left(\frac{(E_2 - E_1)t}{\hbar}\right) \right],$$

is oscillatory with angular frequency proportional to the energy difference,

$$\omega_{12} = \frac{(E_2 - E_1)}{\hbar} \quad (170)$$

However, not *all* expectation values are time-dependent. For example, the normalization of this wave function remains fixed for all time.

Proof:

Using the expression (??) for the probability density:

$$\int_{-\infty}^{+\infty} \Psi^*(x, t)\Psi(x, t) dx = \frac{1}{2} \left[\int_{-\infty}^{+\infty} |\psi_1(x)|^2 dx + \int_{-\infty}^{+\infty} |\psi_2(x)|^2 dx + 2\cos\omega t \int_{-\infty}^{+\infty} \psi_1(x)\psi_2(x) dx \right],$$

$$= \frac{1}{2} [1 + 1 + 0]$$

$$= 1 \quad (171)$$

where we have used unit normalization of the two eigenstates in the first two integrals and their orthogonality in the third.

A more illuminating proof shows the generality of our result by using the full wave functions $\Psi_1(x, t)$, $\Psi_2(x, t)$ and the expression (??) for the probability density:

$$\int_{-\infty}^{+\infty} \Psi^*(x, t)\Psi(x, t) dx = \frac{1}{2} \left[\int_{-\infty}^{+\infty} |\Psi_1(x, t)|^2 dx + \int_{-\infty}^{+\infty} |\Psi_2(x, t)|^2 dx \right. \\ \left. + \int_{-\infty}^{+\infty} \Psi_1^*(x, t)\Psi_2(x, t) dx + \int_{-\infty}^{+\infty} \Psi_2^*(x, t)\Psi_1(x, t) dx \right]$$

$$= \frac{1}{2} [1 + 1 + 0 + 0]$$

$$= 1 \quad (172)$$

where we have again used unit normalization of the two wave functions in the first two integrals and their orthogonality in the third and fourth.

The expectation values for the energy and its powers are also time-independent.

Proof:

$$\begin{aligned}
\langle \hat{H} \rangle &:= \int_{-\infty}^{+\infty} \Psi^*(x,t) \hat{H} \Psi(x,t) dx \\
&= \frac{1}{2} \left[\int_{-\infty}^{+\infty} \Psi_1^* \hat{H} \Psi_1 dx + \int_{-\infty}^{+\infty} \Psi_2^* \hat{H} \Psi_2 dx \right. \\
&\quad \left. + \int_{-\infty}^{+\infty} \Psi_1^*(x,t) \hat{H} \Psi_2(x,t) dx + \int_{-\infty}^{+\infty} \Psi_2^*(x,t) \hat{H} \Psi_1(x,t) dx \right] \\
&= \frac{1}{2} \left[E_1 \int_{-\infty}^{+\infty} \Psi_1^* \Psi_1 dx + E_2 \int_{-\infty}^{+\infty} \Psi_2^* \Psi_2 dx \right. \\
&\quad \left. + E_2 \int_{-\infty}^{+\infty} \Psi_1^*(x,t) \Psi_2(x,t) dx + E_1 \int_{-\infty}^{+\infty} \Psi_2^*(x,t) \Psi_1(x,t) dx \right] \\
\text{i.e. } \langle \hat{H} \rangle &= \frac{1}{2} [E_1 + E_2] \tag{173}
\end{aligned}$$

where we have used the fact that the two states are energy eigenstates,

$$\hat{H} \Psi_n = E_n \Psi_n,$$

and the normalization and orthogonality of the two states, as before. Note that the expectation value is just the average energy, $\langle E \rangle = \langle \hat{H} \rangle$, with equal weighting for the two possibilities, E_1 and E_2 . We shall see the explanation for this in more general form shortly under the heading ‘The Measurement Postulate’. You should check for yourself that if instead we used a wave function,

$$\Psi(x,t) = c_1 \Psi_1(x,t) + c_2 \Psi_2(x,t), \tag{174}$$

then its normalization requires that

$$|c_1|^2 + |c_2|^2 = 1, \tag{175}$$

and furthermore, that for this wave function,

$$\langle E \rangle = |c_1|^2 E_1 + |c_2|^2 E_2 \tag{176}$$

The weighting now is in the ratio $|c_1/c_2|^2$, as one might have guessed.

What about the uncertainty in energy, ΔE ? Here we encounter the essentially quantum mechanical feature: a system with this wave function does not have a definite energy – indeed, we might say that it does not ‘have’ an energy at all until we measure it. First we must calculate $\langle \hat{H}^2 \rangle$. This is easy, especially with a word-processor such as the one I am using for writing these notes: all I do is replace \hat{H} everywhere in the calculation of $\langle \hat{H} \rangle$ with \hat{H}^2 by inserting an extra \hat{H} next to each \hat{H} :

$$\hat{H} \Psi_n = E_n \Psi_n \rightarrow \hat{H} \hat{H} \Psi_n = E_n^2 \Psi_n \tag{177}$$

Therefore every E_n is replaced by an E_n^2 , but otherwise the calculation proceeds as before, with the result:

$$\langle \hat{H}^2 \rangle = \frac{1}{2} [E_1^2 + E_2^2] \tag{178}$$

Hence the energy uncertainty for this state is:

$$\Delta E := \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2}$$

$$\begin{aligned}
&= \sqrt{\frac{1}{2}[E_1^2 + E_2^2] - \frac{1}{4}[E_1 + E_2]^2} \\
&= \sqrt{\frac{1}{4}[E_1^2 + E_2^2] - \frac{1}{2}E_1E_2} \\
&= \sqrt{\frac{1}{4}[E_2 - E_1]^2} \\
\text{i.e. } \Delta E &= \frac{1}{2}[E_2 - E_1] \tag{179}
\end{aligned}$$

This is not perhaps surprising: since the system has equal probability of being in either state, the average spread in energy is determined by the energy difference ($E_2 - E_1$).

(14) Quantum Mechanical Fundamentals and the Measurement Postulate.

We end these introductory lectures with a discussion some of the most fundamental aspects of quantum mechanics. We have already noted the superposition principle: mathematically this is a consequence of the Schrödinger equation's linearity in Ψ . For all potentials of physical interest it can be proved that the most general solution of the TDSE can be written as a linear combination of energy eigenstates. This is the **Expansion Theorem**:

$$\Psi(x, t) = \sum_n c_n \Psi_n(x, t) \tag{180}$$

$$= \sum_n c_n \Psi_n(x) e^{-iE_n t / \hbar} \tag{181}$$

where the sum extends over all eigenstates and the c_n are constants. The expansion theorem encodes an important implication of the Time-dependent Schrödinger: even though quantum mechanics is **indeterministic**, the time-evolution of the wave function itself is **deterministic**. By **indeterministic** we mean that quantum mechanics can only predict the *probability* of a given outcome for a measurement; but the wave function is **deterministic** because, given $\Psi(x, 0)$, its value at $t = 0$, the TDSE precisely determines its evolution to later times $t > 0$, $\Psi(x, t)$. The proof follows from the expansion theorem and orthonormality: put $t = 0$ in eq. (??), multiply the equation by $\Psi_m^*(x)$, integrate over all x , and use the fact that all integrals in the series vanish except the m-th one – multiplication by $\Psi_m^*(x)$ and integration projects out all except the m-th term.

$$\begin{aligned}
\int_{-\infty}^{+\infty} \Psi(x, 0) \Psi_m^*(x) dx &= \sum_n c_n \int_{-\infty}^{+\infty} \Psi_m^*(x) \Psi_n(x) dx \\
&= \sum_n c_n \delta_{mn} \\
&= c_m \tag{182}
\end{aligned}$$

Hence we have an expression for the expansion coefficients, c_m , in terms of known quantities: the initial wave function, $\Psi(x, 0)$, and the eigenstates $\Psi_m(x)$,

$$c_m = \int_{-\infty}^{+\infty} \Psi(x, 0) \Psi_m^*(x) dx \tag{183}$$

Having found these expansion coefficients from this integral, we can then insert them into the expansion theorem, eq. (??), to find the wave function $\Psi(x, t)$ at all later times $t > 0$, given that we already know the energy eigenvalues E_n belonging to each known eigenstate $\Psi_n(x)$. There is a proviso, however: the wave function evolves according to this prescription *provided the system is left undisturbed after the initial time $t = 0$.*

The complex expansion coefficients c_n clearly play an important role in determining the wave function and its evolution. But what is their physical significance? Here we have to introduce an additional

postulate into our development of quantum mechanics; just as we did with the momentum operator, we shall justify this new postulate by showing that it is a reasonable one. We begin by calculating the energy expectation value,

$$\langle \hat{H} \rangle \equiv \langle E \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) \hat{H} \Psi(x,t) dx$$

for the wave function given by the expansion theorem. Inserting the series eq. (??) for each of the wave functions, we obtain a double sum,

$$\begin{aligned} \langle E \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x,t) \hat{H} \Psi(x,t) dx \\ &= \sum_m \sum_n c_m^* c_n e^{i(E_m - E_n)t/\hbar} \int_{-\infty}^{+\infty} \Psi_m^*(x) \hat{H} \Psi_n(x) dx \\ &= \sum_m \sum_n c_m^* c_n E_n e^{i(E_m - E_n)t/\hbar} \int_{-\infty}^{+\infty} \Psi_m^*(x) \Psi_n(x) dx \quad \text{using } \hat{H} \Psi_n = E_n \Psi_n, \\ &= \sum_m \sum_n c_m^* c_n E_n e^{i(E_m - E_n)t/\hbar} \delta_{mn} \quad \text{using orthonormality,} \\ &= \sum_n |c_n|^2 E_n \\ \text{i.e. } \langle E \rangle &= \sum_n |c_n|^2 E_n \end{aligned} \tag{184}$$

Using orthonormality to evaluate the integral, only the term with $m = n$ survives in the sum over m which also makes the time-dependence drop out. Thus the average energy is a weighted sum over all the energies with the weighting $|c_n|^2$ for energy E_n . This suggests that $|c_n|^2$ is the probability that the energy E_n be the result of a measurement of energy for a particle in the state specified by the wave function $\Psi(x,t)$. To check that the $|c_n|^2$ are indeed probabilities, we use the fact that the wave function is normalised; this calculation is identical to the preceding one, but without the Hamiltonian and therefore without the factor E_n :

$$\begin{aligned} 1 &= \int_{-\infty}^{+\infty} \Psi^*(x,t) \Psi(x,t) dx \\ &= \sum_m \sum_n c_m^* c_n e^{i(E_m - E_n)t/\hbar} \int_{-\infty}^{+\infty} \Psi_m^*(x) \Psi_n(x) dx \\ &= \sum_m \sum_n c_m^* c_n e^{i(E_m - E_n)t/\hbar} \delta_{mn} \\ &= \sum_n |c_n|^2, \end{aligned} \tag{185}$$

confirming that the $|c_n|^2$ indeed have the normalisation necessary to be probabilities:

$$\sum_n |c_n|^2 = 1 \tag{186}$$

Finally we are led to the key **Measurement Postulate** of quantum mechanics: For a particle in the quantum state,

$$\Psi(x,t) = \sum_n c_n \Psi_n(x,t) \tag{187}$$

the only possible result of a single energy measurement is one of the eigenvalues E_n with probability $|c_n|^2$.

There is more to the Measurement Postulate – the ‘**Collapse of the Wave Function**’ or the ‘**Reduction of the Wave Packet**’: If the energy measurement yields a result E_n at time t , then immediately after the measurement the wave function ‘collapses’ to the corresponding eigenstate,

$$\Psi_{\text{after}}(x,t) = \Psi_n(x,t) \tag{188}$$

Note the absence of the c_n : the state after the measurement must of course be a normalised state. Furthermore, if the energy is subsequently measured, with the particle now in the state $\Psi_{\text{after}}(x, t) = \Psi_n(x, t)$, there is only *one* possible outcome: the energy will be E_n – with probability 1. Of course the particle should not be disturbed between the first measurement and this subsequent one. It is the process of state reduction on measurement which is still controversial, although it is consistent with all experiments so far performed. Some claim that the process can in principle be described by the TDSE, the so-called unitary evolution; but others say this is not possible and that quantum mechanics is incomplete. We shall see all the components of the expansion and measurement postulates illustrated and confirmed in experiments on spin one half particles. The oscillations of neutral K-mesons and also of neutrinos also provide experimentally clear evidence for these postulates.

Appendix A: Momentum space expectation value.

Here we show how the expression for the momentum operator, eq. (??) follows from our postulate that $|\Phi(p, t)|^2$ is the momentum space probability density:

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Phi^*(p, t) p \Phi(p, t) dp \quad (189)$$

Inserting the inverse Fourier transform for the Φ factor,

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x, t) e^{-ipx/\hbar} dx \quad (190)$$

we obtain:

$$\langle p \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Phi^*(p, t) p e^{-ipx/\hbar} \Psi(x, t) dx dp \quad (191)$$

Now comes a neat trick: we recognize that the factor p can be obtained by writing

$$p = i\hbar \frac{\partial}{\partial x} (e^{-ipx/\hbar})$$

We follow that with an integration by parts with respect to x , thereby moving the differentiation over to $\Psi(x, t)$ (and dropping the surface term as usual):

$$\begin{aligned} \langle p \rangle &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Phi^*(p, t) p e^{-ipx/\hbar} \Psi(x, t) dx dp \\ &= (i\hbar) \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Phi^*(p, t) \Psi(x, t) \frac{\partial}{\partial x} (e^{-ipx/\hbar}) dx dp \\ &= (-i\hbar) \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Phi^*(p, t) e^{-ipx/\hbar} \frac{\partial \Psi(x, t)}{\partial x} dx dp \quad \text{by parts on } x \\ &= (-i\hbar) \int_{-\infty}^{+\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} dx dp \end{aligned}$$

which is the result for the momentum operator quoted in eq. (??). In the last step we used the complex conjugate of the wave packet $\Psi(x, t)$, eq. (??),

$$\Psi^*(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Phi^*(p, t) e^{-ipx/\hbar} dp \quad (192)$$

to do the p -integration and finally eliminate all reference to the momentum space wave function.