Quantum Mechanics

MP363

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Preface

>*The steady progress of physics requires for its theoretical formulation a mathematics that gets continually more advanced. This is only natural and to be expected. What, however, was not expected by the scientific workers of the last century was the particular form that the line of advancement of the mathematics would take, namely, it was expected that the mathematics would get more and more complicated, but would rest on a permanent basis of axioms and definitions, while actually the modem physical developments have required a mathematics that continually shifts its foundations and gets more abstract. Non-euclidean geometry and non-commutative algebra, which were at one time considered to be purely fictions of the mind and pastimes for logical thinkers, have now been found to be very necessary for the description of general facts of the physical world. It seems likely that this process of increasing abstraction will continue in the future and that advance in physics is to be associated with a continual modification and generalisation of the axioms at the base of the mathematics rather than with a logical development of any one mathematical scheme on a fixed foundation.*

<div align="right">Paul Dirac [1]</div>

This is a set of notes which supplement my lectures on quantum mechanics. They are reasonably self contained but should not be read *at the expense of* other library material.

There exist a huge number of books on quantum mechanics so that I shall only recommend a few, leaving the reader to consult a library to sample some of the many, many others. The titles I have chosen are

1. Rae A. I. M., *Quantum Mechanics*, Taylor and Francis, (2008).

2. Hannabuss K., *An introduction to quantum theory*, Oxford University Press, (1999).

3. Dirac P. A. M., *The principles of quantum mechanics*, Oxford University Press, (1930,2007)).

4. Feynman R. P., Leighton R. B. and Sands M. L., *The Feynman lectures on physics: volume III*, Addison–Wesley, (1965).

The first book of these four would do as a book for the whole course, the second is a little more mathematical but is clear and well written, the third is a famous classic by

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[1] Paul Dirac, Quantised singularities in the electromagnetic field, *Proc. Roy. Soc. Lond.*, **A133**, 60–72, (1931).

This seminal paper of Dirac, of which this quotation is the entire first paragraph, is the one that introduces the magnetic monopole and shows that its existence would quantise electric charge. The argument used had a topological content though this was not fully appreciated, or followed up on, until 1975, when Yang–Mills theories had begun to be taken seriously, and used for constructing what later became the Standard model of strong, weak and electromagnetic interactions.

Dirac one of the creators of quantum mechanics and the fourth is the volume on quantum mechanics from the celebrated Feynman lectures: it is stimulating but more easily read *after* the course is over than beforehand.

Charles Nash

CHAPTER I

The creation of quantum mechanics: 1900–1928

§ 1. The problems faced by classical physics in 1900

I n 1900, at the turn of the nineteenth century, classical physics faced a number of serious problems. These problems were gradually tackled and solved over the period 1900–1928. This work was highly revolutionary for physics and gave birth to two amazingly successful new theories which are

The special and general theories of relativity

and

Quantum mechanics

§ 2. Relativity

Two important problems whose resolution led to relativity theory were
 (i) The Michelson–Morley experiment
(ii) The advance of the perihelion of Mercury
        However, since these lectures are devoted solely to quantum mechanics, the reader is referred to my lecture notes on relativity for all further information on relativity.

§ 3. Quantum mechanics

We now turn our attention to quantum mechanics. Three problems—which were to be resolved with the new physics of quantum mechanics—stood out as needing explanation in 1900 and these were
  (i) The ultraviolet catastrophe
 (ii) The photoelectric effect
(iii) The instability of an atom
        We shall now have a look at each of these.

The ultraviolet catastrophe

  The ultraviolet catastrophe was the name given to the unsuccessful *Rayleigh–Jeans formula*—cf. 1.1 below—provided by classical physics for the radiation emitted by a black body. [1]

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[1] A *black body* is an idealisation. It is used to refer to a perfectly efficient emitter and absorber of radiation at all frequencies. One should picture a hot oven with an open door emitting radiation into its cooler surroundings or, if the surroundings are hotter, one pictures a cool oven with an open door taking in radiation from its surroundings. It is the open oven door, which is meant to look black—and hence absorbs all colours or frequencies—that gives rise to the term *black body*.

First of all, in *experiments*, the radiation emitted from a black body at temperature T varies with the frequency ν of the radiation and is a smooth curve rising to a single maximum at a particular frequency cf. figure 1 where the vertical axis shows the quantity $I(\nu, T)$ which is radiation emitted per unit frequency, per unit time at temperature T; this quantity $I(\nu, T)$ is called the *spectral radiance*. [2]
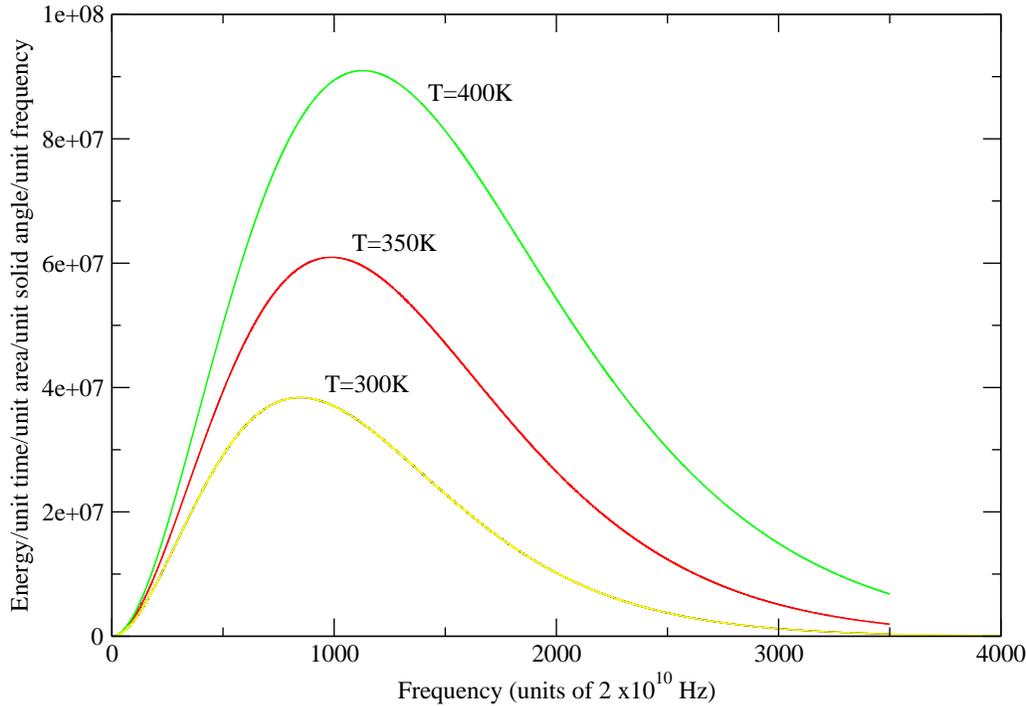
Fig. 1:   Experimental measurements of black body radiation

However the theoretical calculation [3] for this emitted radiation $I(\nu, T)$ gave the formula (known as the Rayleigh–Jeans formula)
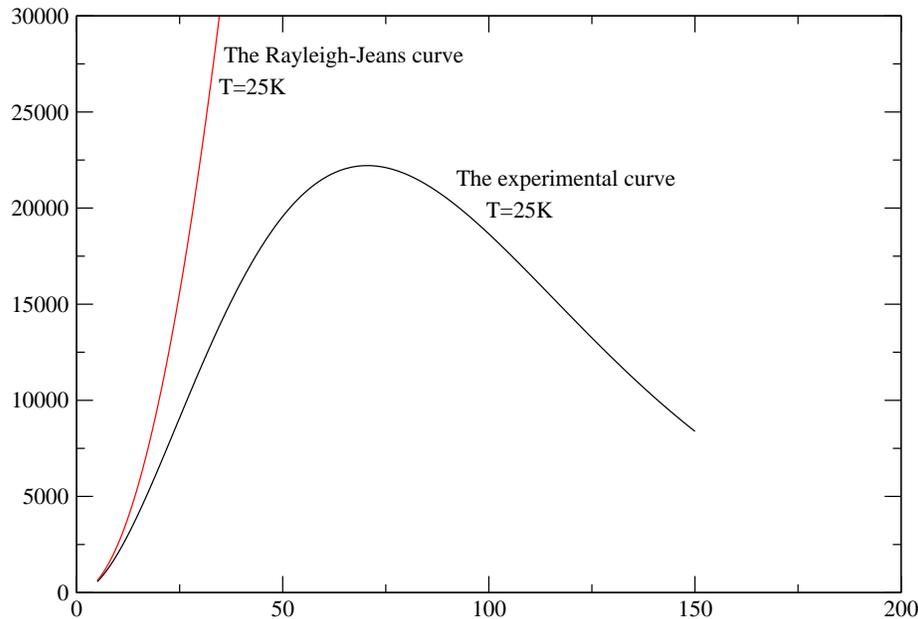
$$I(\nu, T) = \frac{2\nu^2}{c^2} kT \qquad (1.1)$$

The Rayleigh–Jeans formula

and this *totally disagreed* with experiment. We display this disagreement in figure 2 below.

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[2] The definition of the spectral radiance $I(\nu, T)$ is rather cumbersome to state: it is the energy emitted by the body per unit time, per unit surface area, per unit solid angle, per unit frequency. Don't worry, none of this sort of detail need concern us here.

[3] We cannot devote space to giving this calculation here but it is not difficult. It is essentially a counting argument for the number of electromagnetic standing waves in a cavity, together with an application of Maxwell-Boltzmann statistical mechanics to assert that their average energy is kT. For more information consult a textbook, for example Eisberg R. and Resnick R, *Quantum Physics*, Wiley, (1985).

Fig. 2:   The Rayleigh–Jeans curve compared to experiment

In figure 2 one sees the Rayleigh–Jeans curve diverging away, more and more, from the experimental curve as the frequency ν increases: since large frequency ν corresponds to *ultraviolet wavelengths* while low frequency ν corresponds to *infrared wavelengths* this failure of the Rayleigh–Jeans formula for large ν was often called *the ultraviolet catastrophe.*

Planck's famous solution to the ultraviolet catastrophe came from two clever steps:

(i) He postulated that electromagnetic radiation of energy E and frequency ν was *quantised*: that is the values of E were restricted to integer multiples of $h\nu$ where h is a

constant (the famous constant now called *Planck's constant*[4]) whose value is given by $h = 6.6260638 \times 10^{-34} Js$. Note that the notation $\hbar = h/2\pi$ is also very frequently used.

We write this as

$$E = nh\nu, \quad n = 1, 2, 3, \ldots \tag{1.2}$$

(ii) He guessed[5] the correct form of the function $I(\nu, T)$ giving it as

$$I(\nu, T) = \frac{2\nu^2}{c^2} \frac{h\nu}{\exp(\frac{h\nu}{kT}) - 1} \tag{1.3}$$

This choice gives *perfect agreement* with experiment for all frequencies, thus *solving the ultraviolet catastrophe.*

It also agrees with the Rayleigh–Jeans formula for low frequencies since, if we expand the Planck formula 1.3 for $I(\nu, T)$ in powers of the frequency ν, we find that

$$\frac{2\nu^2}{c^2} \frac{h\nu}{\exp(\frac{h\nu}{kT}) - 1} = \frac{2\nu^2}{c^2} kT - \frac{h}{c^2} \nu^3 + \frac{h^2}{6c^2 kT} \nu^4 + \cdots \tag{1.4}$$

Rayleigh–Jeans only works for small ν

And we see that the first term on the RHS of 1.4 is simply the Rayleigh–Jeans expression 1.1 for $I(\nu, T)$: hence the Rayleigh–Jeans expression dominates *only when ν is small.*

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[4] Planck's constant h, and the Boltzmann constant k introduced in the 1870's, are the first new fundamental constants to be introduced into physics since Newton introduced his gravitational constant G in 1687; when special relativity was formulated by Einstein in 1905 the velocity of light c was also raised to the position of being a fundamental constant. The three fundamental constants G, h and c can be combined to give a quantity which has the dimensions of length. This quantity is called the *Planck length* and is denoted by l_P; its definition and value are given by ($G = 6.674 \times 10^{-11} \, m^3 \, kg^{-1} \, s^{-2}$, $c = 2.997 \times 10^8 \, m \, s^{-1}$, $\hbar = \frac{h}{2\pi}$)

$$l_P = \sqrt{\frac{\hbar G}{c^3}} = 1.616 \times 10^{-35} \, m$$

We note that the Planck length is very small: it is at lengths which are of the order of the Planck length, or smaller, that quantum gravity becomes important.

In black hole physics, a black hole is meant to emit black body radiation, and all four fundamental constants G, k, h and c combine with the mass M of the black hole to give a temperature T_H known as the *Hawking temperature* where

$$T_H = \frac{\hbar c^3}{8\pi GMk}$$

T_H is then the temperature of the black body radiation emitted by the black hole.

[5] Planck's guess was motivated by thinking about the problem in a statistical mechanical manner and his formula was later *derived* from first principles by Einstein in 1917—cf. Einstein A., Zur Quantentheorie der Strahlung (On the quantum theory of radiation), Zeit. für physik, **18**, 121–128, (1917).

We cannot go into the details here but this paper gives birth to what are called Bose–Einstein statistics and also describes the phenomenon of *stimulated emission* which is the vital mechanism for producing laser light.

Bose–Einstein statistics replaced the Maxwell–Boltzmann statistics used so successfully to found the kinetic theory gases on a statistical basis; a key difference between the two kinds of statistics is that in Bose–Einstein statistics identical particles (in the Planck example these are photons) are not regarded as distinguishable but in the Maxwell–Boltzmann case identical particles are all distinguishable.

A small digression on black body radiation

Finally it is useful, as a piece of general knowledge, to know at what frequency the *maximum* of the black body curve occurs. Simple calculus applied to

$$I(\nu, T) = \frac{2\nu^2}{c^2} \frac{h\nu}{\exp(\frac{h\nu}{kT}) - 1} \tag{1.5}$$

tells us that the maximum occurs at the value of ν where

$$\frac{h\nu}{kT} \exp(\frac{h\nu}{kT}) - 3\exp(\frac{h\nu}{kT}) + 3 = 0 \tag{1.6}$$

and by actually plotting the graph of this function we find that the maximum occurs at $\nu = \nu_*$ where [6]

$$\nu_* = 2.82 \frac{kT}{h} \tag{1.9}$$

and the temperature of such a body is therefore given by [7]

$$T = \nu_* \frac{h}{2.82k} \tag{1.10}$$

We can apply this formula 1.9 for ν_* to a heated body which is beginning to glow *red hot*: actual experimental measurement will tell us that a red hot body has temperature

A red hot black body

$$T \simeq 1000^0\, K \tag{1.11}$$

So we then compute that

$$\nu_* = 2.82 \frac{1.38 \times 10^{-23} \times 1000}{6.626 \times 10^{-34}} = 5.87 \times 10^{13}\, Hz \tag{1.12}$$

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[6] This result 1.9, when stated in terms of wavelength rather than frequency, becomes the well known *Wien's displacement law* which is

$$\lambda_{max} = \frac{C}{T} \tag{1.7}$$

where λ_{max} is the wavelength for peak emission for the spectral radiance function $I_\lambda(\lambda, T)$; a technical point here is that $I_\lambda(\lambda, T)$ is not quite obtained by substituting $\lambda = c/\nu$ in the function $I(\nu, T)$. The units of the two functions are different: $I_\lambda(\lambda, T)$ has units of energy per unit time, per unit surface area, per unit solid angle, per unit wavelength. This, in turn means that the relation between $I(\nu, T)$ and $I_\lambda(\lambda, T)$ is that $I(\nu, T) = \frac{\lambda^2}{c} I_\lambda(\lambda, T)$. Again don't worry about this, the present section is, as said above, a small digression.

Finally if we integrate the $I(\nu, T)$ over all frequencies ν we obtain the famous *Stefan–Boltzmann law* which states that the total energy J of a black body radiated per unit surface area, per unit time is proportional to T^4 that is

$$J = \sigma T^4, \quad \sigma \text{ a constant} \tag{1.8}$$

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[7] The values of the various physical constants (in SI units) are $c = 2.9979 \times 10^8\, m\, s^{-1}$, $h = 6.6260638 \times 10^{-34}\, J\, s$ and $k = 1.38 \times 10^{-23}\, J\, K^{-1}$.

and this corresponds to a wavelength $\lambda_* = c/\nu_*$ having the value

$$\lambda_* = \frac{2.99 \times 10^8}{5.87 \times 10^{13}} = 5.1 \times 10^{-6} \, m = 5,100 \, nm \tag{1.13}$$

and this value is outside the visible spectrum[8] and lies in the far infrared region. Hence we see that a red hot body is emitting most of its energy at infrared wavelengths and that the red light emitted just corresponds to the tail of the black body curve where $I(\nu, T)$ is beginning to die away: this is shown in figure 3. If one increases the temperature to $5000^0 K$ or so then one can check that the all visible spectrum lies near the middle of the black body curve; such a body is then white hot.
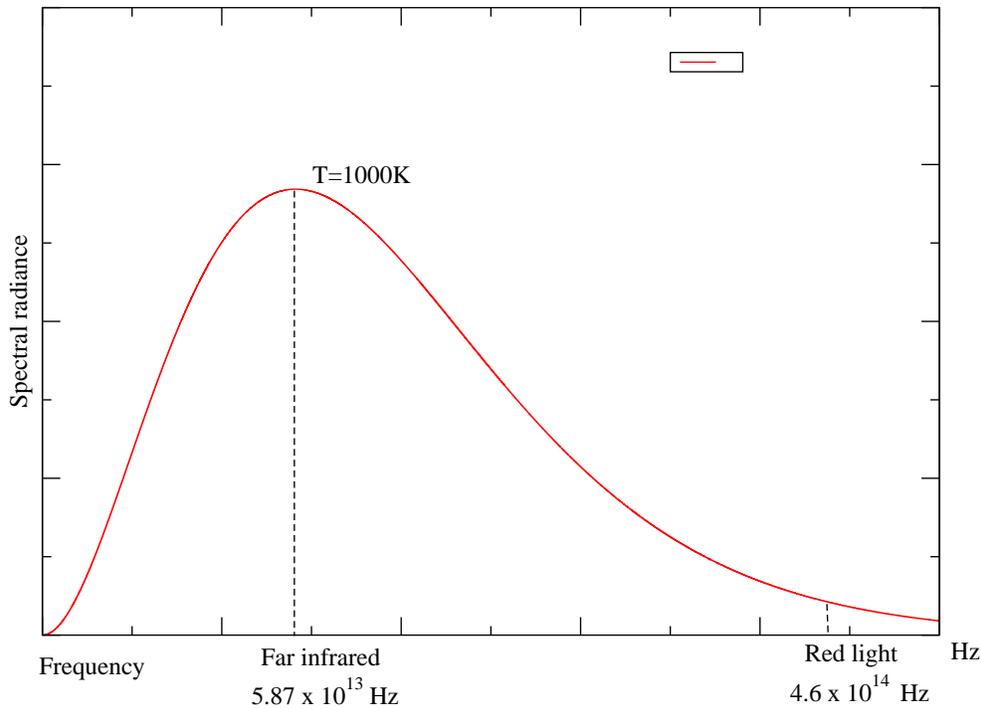
Fig. 3:   A red hot black body

The celebrated cosmic microwave black body radiation (or CMB) left over from the *Big Bang* has a temperature of

$$2.7^0 \, K \tag{1.14}$$

and so one can repeat the above argument for this temperature to deduce that its dominant wavelength is about

$$1.89 \, mm \tag{1.15}$$

The microwave black body radiation left over after the Big Bang

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[8] The range of visible light is about 400–700 nm; $1 \, nm = 10^{-9} m$.

which is in the microwave [9] region.

The photoelectric effect

We have now come to the famous photoelectric effect: this effect is the ejection of electrons by certain metals—e.g. the metal sodium—when light is shined on them.

It was thought, at first, that if the intensity of incident light on the, metal was large enough electrons would always be emitted. This turned out to be *false*, and in some cases, *no electrons were emitted* no matter how intense the incident light. This state of affairs was regarded as a puzzle and it was resolved by Einstein.

In fact, as Einstein showed, the key property of the light which determines whether electrons are emitted is *not its intensity* but its *frequency ν*; in addition Einstein's explanation of the photoelectric effect only works if one accepts Planck's hypothesis that light of frequency ν is made up of individual *photons* each with energy E where

$$E = h\nu \tag{1.16}$$

In other words light has to be *quantised,* and thought of as *a particle* rather than a wave, to produce the experimentally observed photoelectric effect.

Here are the mathematical details which are extremely elementary despite their far reaching consequences. A metal exhibiting the photoelectric effect has a minimum amount of energy

$$W \tag{1.17}$$

that is needed to eject an electron from its surface, W (which we remind the reader is a positive number) is usually called the *work function* of the metal. [10] If a photon of energy E ejects an electron thereby giving it a kinetic energy [11]

$$\frac{1}{2}mv^2 \tag{1.18}$$

then one has

$$E = W + \frac{1}{2}mv^2 \tag{1.19}$$

but $E = h\nu$ so we can write

$$h\nu = W + \frac{1}{2}mv^2 \tag{1.20}$$

So

$$\frac{1}{2}mv^2 = h\nu - W \tag{1.21}$$

and since the LHS of 1.21 is $mv^2/2$ and an emitted electron has a speed $v > 0$ then

$$\frac{1}{2}mv^2 > 0 \tag{1.22}$$

[9] Microwaves are taken to have wavelengths lying in the range of roughly $1\,mm$ to $1\,m$.

[10] For sodium one has $W = 2.75\,eV$.

[11] As should be clear m is the electron mass and v its speed.

then we see that, for electrons to be emitted, one must have

$$h\nu - W > 0$$
$$\Rightarrow \nu > \frac{W}{h} \tag{1.23}$$

So clearly a light beam of frequency ν where

$$\nu < \frac{W}{h} \tag{1.24}$$

will *never* cause photoemission no matter how intense the beam—that is no matter how many photons the beam contains. This is how the theory works and quantisation was *essential* for it to succeed. Einstein received the Nobel prize in 1921, the original citation saying

> *for his services to theoretical physics, and especially for his discovery of the law of the photoelectric effect*

Finally 1.21 suggests a very simple and effective experiment to determine Planck's constant: one simply measures ν and v for a range of values and uses 1.21 to plot the kinetic energy $mv^2/2$ versus the frequency ν. The result is a straight line graph whose slope Planck's constant h—cf. figure 4.
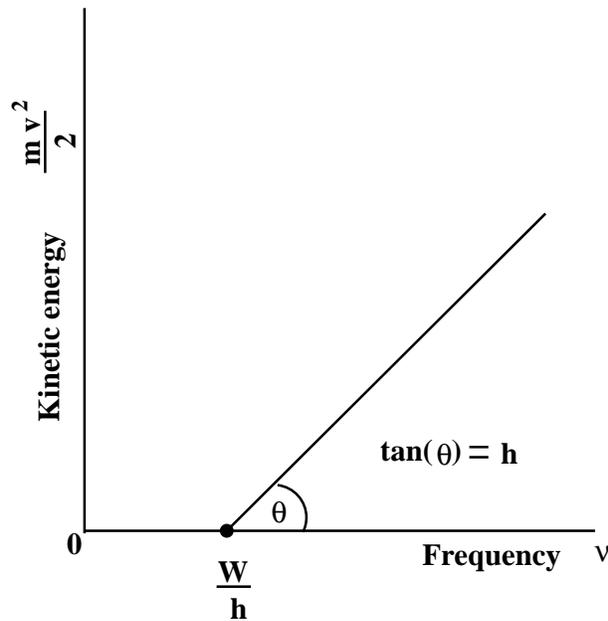

Fig. 4: The photoelectric effect graph with slope h

We move on to consider atoms.

The instability of an atom

Since the force between electric charges, like that for lumps of matter, is an inverse square law in the separation between pairs of objects then one might hope that atoms would imitate planetary systems.

For example, the hydrogen atom, which consists of a positively charged proton and a negatively charged electron, might consist of a proton with an electron orbiting it in an ellipse.

However electric charges absorb or emit radiation when they accelerate and decelerate respectively. This would mean that an electron, on the decelerating portions of its elliptic orbit, would emit radiation and eventually spiral inwards into the proton and cease to orbit. Hence this planetary type model for hydrogen fails, this is what we mean above by the phrase atomic instability: if one started an electron off in elliptical orbit round a proton it would not remain in the orbit—like the Earth does around the Sun—but would shed energy and try to coalesce with the proton. Similar objections apply to atoms with larger numbers of protons and electrons.

Quantum mechanics solves this problem of instability and also gives us the means to calculate lots of detailed quantities about an atom such as its energy levels, transitions between energy levels and other properties too numerous to mention in one sentence.

We now turn our attention to hydrogen since it is the simplest of all atoms.

§ 4. The challenge of hydrogen

In the early nineteenth century Fraunhöfer and others had used diffraction gratings to measure the frequencies of light emitted from the Sun [12] and found it to be a series of *discrete* values: not all frequencies were present. Many other hot gases were studied in the laboratory—for example sodium vapour—and also found to emit radiation only at a discrete series of frequencies. For hydrogen, Balmer found, empirically in 1885, that the frequencies ν_n emitted could be fitted to the formula

The Balmer series

$$\nu_n = B \left\{ \frac{1}{2^2} - \frac{1}{n^2} \right\}, \quad n = 3, 4, \ldots \tag{1.25}$$

where B is a constant known as Balmer's constant whose value is given by

$$B = 3.28 \times 10^{15} \ s^{-1} \tag{1.26}$$

This series of frequencies ν_n $n = 3, 4, \ldots$ is called the *Balmer series*.

It then became a job for physics to explain why radiating atoms in general emit radiation only at certain discrete frequencies. Clearly the first challenge is to explain the spectrum of the simplest atom—i.e. hydrogen.

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[12] The frequencies matched those emitted by hydrogen in laboratory experiments and so provided evidence for hydrogen on the Sun.

The Bohr atom

The first step in response to this challenge was taken by Bohr in 1913. Bohr proposed that the electron of hydrogen went round the proton in a circular orbit but with quantised angular momentum L. The quantisation he proposed for L was that

$$L = n\frac{h}{2\pi}, \quad n = 1, 2, \ldots \tag{1.27}$$

where h is Planck's constant.

The great success of Bohr's quantisation rule 1.27 is that one obtains a discrete spectrum of energies E_n for the electron as we now show.

Let m be the electron mass, v its speed, r the radius of its circular orbit and e the charge on the electron. Now, for a circular orbit the centrifugal force is equal to the Coulomb attraction so that [13]

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r^2}$$
$$\Rightarrow v = \sqrt{\frac{e^2}{4\pi\epsilon_0 mr}} \tag{1.28}$$

We know that the Coulomb potential energy of the electron proton pair is $-e^2/(4\pi\epsilon_0 r)$ so the total energy E of the electron is given by

$$E = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \tag{1.29}$$

and so, using our expression for v, we find that

$$\begin{aligned} E &= \frac{m}{2}\frac{e^2}{4\pi\epsilon_0 mr} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \\ &= -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \end{aligned} \tag{1.30}$$

But the angular momentum $L = mvr$ and this is quantised so we have

$$mvr = n\frac{h}{2\pi}, \quad \text{using 1.27}$$
$$\Rightarrow mr\sqrt{\frac{e^2}{4\pi\epsilon_0 mr}} = n\frac{h}{2\pi}, \quad \text{using 1.28} \tag{1.31}$$
$$\Rightarrow r = \frac{n^2 h^2 \epsilon_0}{\pi e^2 m}$$

so that the orbital radius r is quantised. The allowed values of r we denote by r_n where

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi e^2 m}, \quad n = 1, 2, 3, \ldots \tag{1.32}$$

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[13] This equation is a slight oversimplification because it assumes, incorrectly, that the proton does not move. This is a small effect but we shall actually take account of it in the end: cf. 1.41 below.

The *smallest* value of r_n occurs when $n = 1$ and this value is called the *Bohr radius* and is a good estimate of the size of an atom; setting $n = 1$ we find that

$$r_1 = \frac{h^2\epsilon_0}{\pi e^2 m} = 0.529 \times 10^{-10}\, m, \quad \text{(The Bohr radius of hydrogen)}$$
$$= 0.529\,\text{Å}, \qquad \text{(in Angstroms)}$$

$$(1.33)$$

Next if we substitute these values from 1.32 into the expression 1.29 for the energy we get the result that hydrogen has a *quantised* spectrum of energies E_n given by

$$E_n = -\frac{C}{n^2}, \quad \text{where } C = \frac{e^4 m}{8\epsilon_0^2 h^2}$$
$$n = 1, 2, 3, \ldots$$

$$(1.34)$$

The obtaining of this expression 1.34 for E_n was a great success for the Bohr atom: the energy levels are now discrete, as found in experiments. Now we can compute the emission and absorption of energy by hydrogen and derive the famous Balmer formula 1.25 above which we now do.

To deal with the emission or absorption of energy we suppose that the electron is in the energy level E_m and a photon of frequency ν is emitted by hydrogen. Then the electron moves down to a lower energy level E_n and, since the photon has energy $h\nu$, energy conservation says that

$$h\nu = E_m - E_n \qquad (1.35)$$

i.e. that [14]

$$h\nu = -\frac{C}{m^2} - \left(-\frac{C}{n^2}\right)$$
$$\Rightarrow \nu = -\frac{C}{h}\left\{\frac{1}{m^2} - \frac{1}{n^2}\right\}$$
$$= \nu_{mn}, \quad \text{say}$$

$$(1.36)$$

so that the emitted frequencies ν_{mn} given by 1.36 are indeed quantised, as found in experiments [15].

Lastly, if we set $n = 2$ and $m = 3, 4, \ldots$, we get the set of frequencies ν_{n2} where

$$\nu_{n2} = \frac{C}{h}\left\{\frac{1}{2^2} - \frac{1}{n^2}\right\}, \quad n = 3, 4, \ldots \qquad (1.38)$$

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[14] Note that this equation 1.36 describes both emission *and* absorption because we can take it to mean either that an electron of energy E_m *emits* a photon of frequency ν and *drops down* to the energy level E_n, or, that an electron of energy E_n *absorbs* a photon of frequency ν and *moves up* to the energy level E_m.

[15] On a point of nomenclature, which we only mention in case the reader has come across it, the quantity

$$\frac{C}{hc} = \frac{e^4 m}{8\epsilon_0^2 h^3 c} \qquad (1.37)$$

is often denoted by R, and R is then referred to as the *Rydberg constant*.

which we recognise as the Balmer series 1.25 above *provided*, of course, that C/h is equal to the Balmer constant B so we end by checking this: From 1.26 above we have the experimental fact that

$$B = 3.28 \times 10^{15} \; s^{-1} \qquad (1.39)$$

and since $C = e^4 m / 8\epsilon_0^2 h^2$ we use the values [16] of e, m, ϵ_0 and h to compute that

$$\frac{C}{h} = \frac{e^4 m}{8\epsilon_0^2 h^3} = \frac{(1.602 \times 10^{-19})^4 \cdot 9.109 \times 10^{-31}}{8 \cdot (8.85 \times 10^{-12})^2 \cdot (6.62 \times 10^{-34})^3} \qquad (1.40)$$
$$= 3.288 \times 10^{15} \; s^{-1}$$

We do get Balmer's constant

So we have a good agreement with the Balmer constant B.

Now we comment, as we promised that we would in an earlier footnote, on the fact that we have neglected any motion of the proton in our calculations. Inclusion of the proton in the argument—which is always necessary in high precision theory and experiment—has the effect of replacing the electron mass m in the formula for C by the quantity μ (μ is called the *reduced mass*) where

$$\mu = \frac{mM}{m + M} \qquad (1.41)$$

where M is the proton mass. [17] For the proton mass M we have

We can't completely ignore (kinematically) the presence of the proton

$$M = 1.672 \times 10^{-27} \; kg \qquad (1.42)$$

and if we replace m by μ in C then one calculates not $C/h = e^4 m / 8\epsilon_0^2 h^3$ but $e^4 \mu / 8\epsilon_0^2 h^3$ and we then discover that

$$\frac{e^4 \mu}{8\epsilon_0^2 h^3} = 3.286 \times 10^{15} \; s^{-1} \qquad (1.43)$$

Notice the third decimal place has now changed

which still agrees with B to two decimal places; however we notice that the third decimal places of 1.40 and 1.43 do differ, hence this correction is numerically significant.

A final remark on this matter of numerical accuracy is in order: the Bohr atom is inadequate as an atomic model and so should not be taken too seriously numerically; however the proper description of atoms given by the quantum mechanics created by Schrödinger and Heisenberg does also have to take into account the replacement of the electron mass m by the reduced mass μ as described above. Very high precision is demanded in present day physics from both theory and experiment and is present in the relativistic generalisations of quantum mechanics known as *quantum field theory* with agreement between theory and experiment, for some quantities, reaching *parts per million and better.*

High precision the rule nowadays

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[16] We have not yet given the values of e, m and ϵ_0, so here they are: $e = 1.602 \times 10^{-19} \, coulomb$, $m = 9.109 \times 10^{-31} \, kg$ and $\epsilon_0 = 8.85 \times 10^{-12} \, volt - metre/coulomb$.

[17] The reason that this replacing of m by μ is needed is that we have presumed, falsely, that the proton does not move. If we include the proton's kinetic energy then the m in the electron's kinetic energy term gets replaced by μ. The reader may recall that a similar change from m to $mM/(m + M)$ occurs in classical mechanics when solving the gravitational two body problem for masses m and M. This point is also discussed in chapter 10 of the recommended text *Quantum mechanics* by Rae.

Returning to our frequency formula 1.36 we have obtained a much *larger* set of possible frequencies namely: ν_{mn} where $m = 1, 2, 3, \ldots$ and $n = 1, 2, 3, \ldots$ the point is that most of these frequencies are not in the visible region but the Balmer series frequencies ν_{n2} *are* in the visible region.

The circular orbits of the Bohr atom were inadequate to explain everything and, in 1916, Sommerfeld introduced elliptical orbits and an associated quantisation condition. This resulted in the *Bohr-Sommerfeld atomic theory* which, however, still had many shortcomings.

Some of the more important of these shortcomings were that the spectra of atoms heavier than hydrogen was not explained, nor was the splitting of spectral lines in magnetic fields known as the *Zeeman effect*, nor was what is called the fine and hyperfine structure in spectral lines, due to relativity and electron spin.

The next breakthrough was not to come until 1923 with the work of de Broglie which we consider next.

§ 5. The de Broglie breakthrough: wave particle duality

Einstein's successful explanation of the photoelectric effect had given light a particle nature: a photon of frequency ν was both a particle and a wave. This raised the following question: could particles such as electrons, say, have a wave nature and so also be both a particle and a wave? The answer according to de Broglie was, yes, as we now explain.

The far reaching idea of de Broglie was very simple: he wanted to associate a *wave* ψ to each particle of non-zero mass m. The wavelength λ of this wave ψ was determined by combining special relativity for a photon and Planck's relation $E = h\nu$ in the following way. Special relativity says that the energy E , momentum $\mathbf{p}$ of a zero mass object, such as the photon, are related by

$$E^2 - \mathbf{p}^2 c^2 = 0 \tag{1.44}$$

and if we add in Planck's relation $E = h\nu$ we find that, *for a photon* one has

$$E = h\nu$$
$$\Rightarrow |\mathbf{p}| = \frac{h\nu}{c} \tag{1.45}$$
$$\text{i.e. } |\mathbf{p}| = \frac{h}{\lambda}$$

For a *particle of positive mass m* de Broglie, in 1923, boldly proposed that its energy E and momentum $\mathbf{p}$ be associated with a wave travelling in the direction $\mathbf{n}$, where $\mathbf{n}$ is a unit vector, and one has

$$E = h\nu$$
$$\mathbf{p} = \frac{h}{\lambda}\mathbf{n}, \quad \mathbf{n}^2 = 1 \tag{1.46}$$

This immediately associates a *wavelength λ* with a particle of mass m and raises the question: can massive particles exhibit wave like phenomena such as diffraction?

This question was answered in the affirmative, for electrons, by electron diffraction measurements of Davisson and Germer in 1927. The wavelength measured in the diffraction experiment also agreed with the value given by the de Broglie formula

$$|\mathbf{p}| = \frac{h}{\lambda} \tag{1.47}$$

Wave–particle duality

In summary we can say that we have now learned that radiation—i.e. photons or zero mass particles—has both a wave and a particle nature, and that matter—i.e. positive mass particles—also has both a wave and a particle nature. This is called *wave–particle duality.*

§ 6. The hydrogen spectrum explained: Heisenberg and Schrödinger

Heisenberg and Schrödinger both cracked the problem

The spectrum of hydrogen was finally properly explained by both Heisenberg, in 1925, and Schrödinger [18] in 1926.

These two pieces of work were very different from each other and, at first, were not believed to be equivalent thus suggesting that one of them might be incorrect in some way. However, despite their apparent differences, we now know that they are completely equivalent to one another.

Heisenberg replaces classical physical quantities by operators in quantum mechanics

Heisenberg, like many, had come to the conclusion that classical mechanics needed to be modified at the atomic level. He thought carefully about measurement and wanted, in his new theory, to only include *observable* quantities; classical quantities would also have to be replaced by new quantum quantities. He says, in [8], (cf. the English translation in [24])

> It seems sensible to discard all hope of observing the position and period of electrons... [We here] try to establish a theoretical quantum mechanics, analogous to classical mechanics, but in which only relations between observable quantities occur. ... We may pose the question in its simplest form: If instead of a classical quantity $x(t)$ we have a quantum theoretic quantity, what quantum theoretic quantity will appear in place of $x(t)$?

In studying hydrogen Heisenberg developed a kind of calculus of transition amplitudes in which observable physical quantities become operators–which he later realised could be expressed as matrices. So two physical quantities such as position and momentum, in Heisenberg's quantum mechanics, are represented by *matrices x and p* say. Moreover Heisenberg found that

$$xp \neq px \tag{1.48}$$

something which worried him at first. However, one knows, that two matrices A and B often do not commute: i.e. one often has $AB \neq BA$.

In fact one knows that x and p obey the famous commutation relation

$$xp - px = i\hbar I \tag{1.49}$$

---

[18] Schrödinger spent the years 1940–1956 working in the School of Theoretical Physics of the Dublin Institute for Advanced Studies.

where I denotes the identity matrix. We usually write this commutation relation 1.49 as

$$[x, p] = i\hbar I \qquad (1.50)$$

and we have used the standard notation $[x, p] = xp - px$.

Heisenberg's formulation of these physical quantities enabled him to successfully calculate the hydrogen spectrum; still more: the theory was also applicable to other atoms and the spectrum of helium was soon being calculated.

The work of Schrödinger took the form of a differential equation for the new matter wave ψ introduced by de Broglie. Note, that, from now on we shall give ψ its modern name which is the *wave function.*

Schrödinger was thinking of de Broglie's suggestion of associating a wave function ψ with a particle such as an electron. This led Schrödinger to propose, in 1926, that every particle should have its own wave function ψ, and that this ψ should satisfy the following equation (known ever afterwards as *the Schrödinger equation*)

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + V(x, y, z)\psi = i\hbar\frac{\partial \psi}{\partial t} \qquad (1.51)$$

which we abbreviate to

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial \psi}{\partial t} \qquad (1.52)$$

where m is the mass, V is the potential energy of the particle, and, as usual, $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. Schrödinger also suggested that the energy E of the particle could be obtained from the wave function ψ by solving the simpler equation

$$i\hbar\frac{\partial \psi}{\partial t} = E\psi \qquad (1.53)$$

and if we substitute 1.53 for the RHS of the Schrödinger equation 1.52 above we obtain the important equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \qquad (1.54)$$

This equation 1.54 is known as the *time independent Schrödinger equation*, or just the *Schrödinger equation* if the context makes it clear whether one means the full Schrödinger equation 1.52 or the time independent one 1.54.

Let us now deal with an example. Take the electron of the hydrogen atom, then this has potential energy

$$V = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, \quad r = \sqrt{x^2 + y^2 + z^2} \qquad (1.55)$$

where r is the electron–proton separation, so the (time independent) Schrödinger equation for the electron of hydrogen is

$$\left(\frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)\psi = E\psi \tag{1.56}$$

It turns out there are only solutions to this equation 1.56 for *discrete* values of the energy E and these values are precisely the correct energies E_n given above in 1.34; and there is more: the solution to 1.56 for each E_n gives one a wave function $\psi_n(x, y, z)$ which describes the behaviour of the electron while it occupies that particular energy level E_n.

Note, that the computation of E_n and ψ_n for hydrogen will *not* be done in this introductory course—for reasons of lack of time rather than of difficulty—but *will be done* in its sequel.

§ 7. The equivalence of the Heisenberg and Schrödinger approaches

The two approaches of Heisenberg and Schrödinger seemed at first to be different but work by Dirac in 1925, was important in showing that, despite first appearances, they are in fact completely equivalent and contain the same information.

Dirac was also the first person to explain the spin of the electron and to predict the first antiparticle, that of the electron: the *positron*. This was done in his paper of 1928 in which a relativistic generalisation of the Schrödinger equation for the electron is given. This generalisation is called the *Dirac equation*; unfortunately we will not be able to say any more about it in these lectures.

§ 8. The meaning of the wave function: probability

At first the meaning to be given to the wave function ψ was not clear. But Born in 1926 developed the right approach which is that the quantity $|\psi(x, y, z, t)|^2$ is a *probability density*.

More precisely the physical property that ψ has is as follows: the probability of finding the particle, whose wave function is ψ, in the small interval

$$dx\,\mathbf{i} + dy\,\mathbf{j} + dz\,\mathbf{k} \tag{1.57}$$

about the location

$$x\,\mathbf{i} + y\,\mathbf{j} + z\,\mathbf{k} \tag{1.58}$$

at time t, is

$$|\psi(x, y, z, t)|^2 dx dy dz \tag{1.59}$$

Probability enters at the foundation of physics

Thus, through the wave function ψ, probability enters physics in a fundamental and permanent way, much to the displeasure of some scientists, in particular Einstein who famously said, in a letter [19] to Max Born,

4. Dezember 1926

Lieber Born

---

[19] The English translation given here—cf. [**25**]—is by Born's daughter: Irene Born.

> ....*Die Quantenmechanik ist sehr achtung-gebietend. Aber eine innere Stimme sagt mir, daß das noch nicht der wahre Jakob ist. Die Theorie liefert viel, aber dem Geheimnis des Alten bringt sie uns kaum näher. Jedenfalls bin ich überzeugt, daß der nicht würfelt...*
>
> *Von Eurem Albert Einstein*

which translates to

> *4 December, 1926*
>
> *Dear Born*
>
> ...*Quantum mechanics is certainly imposing. But an inner voice tells me that it is not yet the real thing. The theory says a lot but it does not bring us any closer to the secret of the 'old one'. I, at any rate, am convinced that He is not playing at dice....*
>
> *Your Albert Einstein*

§ 9. The Heisenberg uncertainty principle

Heisenberg's uncertainty principle

In 1927 Heisenberg took another very important step in the construction of quantum mechanics: he formulated what is called the *Heisenberg uncertainty principle* or simply the *uncertainty principle*. The uncertainty principle shows that there are precise limits on the accuracy with which one can simultaneously measure physical quantities. For example position and momentum of a particle cannot be *simultaneously* measured with arbitrary accuracy. We shall see later that this is a very important fact about the physical world.

§ 10. Some motivation for the Schrödinger equation

Let us now return to Schrödinger's equation 1.54 which we recall is

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{1.60}$$

There is no *derivation* that one can give for the Schrödinger equation but one can provide some motivation for what Schrödinger did.

Consider first simply the total energy E of a particle of mass m. It is given by

$$\frac{m\mathbf{v}^2}{2} + V = E \tag{1.61}$$

where V is the potential energy. But

$$\mathbf{p} = m\mathbf{v}$$
$$\Rightarrow \frac{\mathbf{p}^2}{2m} = \frac{m\mathbf{v}^2}{2} \tag{1.62}$$

so we can also write the energy E as being given by

$$E = \frac{\mathbf{p}^2}{2m} + V \tag{1.63}$$

Now we specialise to the case of a particle with potential energy $V = 0$. This is what we call a *free particle*. When $V = 0$ then the Schrödinger equation and the energy are given by

$$\left. \begin{array}{c} \dfrac{-\hbar^2}{2m}\nabla^2\psi = E\psi \\[2mm] E = \dfrac{\mathbf{p}^2}{2m} \end{array} \right\} \quad \text{for a } \textit{free} \text{ particle} \tag{1.64}$$

We shall now see that we can easily solve the Schrödinger equation in this particular case: the solution ψ is just a *plane wave*. We remind the reader that a plane wave ψ, of wavelength λ and frequency ν, travelling in the direction $\mathbf{n}$, where $\mathbf{n}$ is a unit vector, is obtained by writing

A plane wave

$$\psi(x, y, z, t) = \exp\left[2\pi i\left(\frac{\mathbf{n}\cdot\mathbf{r}}{\lambda} - \nu t\right)\right], \quad \begin{cases} \mathbf{r} = x\,\mathbf{i} + y\,\mathbf{j} + z\,\mathbf{k} \\ \mathbf{n} = n_x\,\mathbf{i} + n_y\,\mathbf{j} + n_z\,\mathbf{k} \end{cases} \tag{1.65}$$

Now de Broglie associates the momentum $\mathbf{p} = p_x\,\mathbf{i} + p_y\,\mathbf{j} + p_z\,\mathbf{k}$ and energy E of an electron to ψ by writing

$$\mathbf{p} = \frac{h}{\lambda}\mathbf{n}, \qquad E = h\nu \tag{1.66}$$

and, on substituting this data into our expression for ψ, we find that

$$\begin{aligned} \psi(x, y, z, t) &= \exp\left(\frac{2\pi i}{h}\left(\mathbf{p}\cdot\mathbf{r} - Et\right)\right) \\[2mm] &= \exp\left(\frac{i\mathbf{p}\cdot\mathbf{r}}{\hbar} - \frac{iEt}{\hbar}\right), \qquad \text{using } \hbar = \frac{h}{2\pi} \end{aligned} \tag{1.67}$$

Now notice that one can extract the momentum and energy of the wave by applying the appropriate derivatives. More precisely note that

$$\frac{\partial\psi}{\partial x} = i\frac{p_x}{\hbar}\psi, \quad \frac{\partial\psi}{\partial y} = i\frac{p_y}{\hbar}\psi, \quad \frac{\partial\psi}{\partial z} = i\frac{p_z}{\hbar}\psi \tag{1.68}$$

so that, if we now calculate $-i\hbar\nabla\psi$ we find that

$$\begin{aligned} -i\hbar\nabla\psi &= -i\hbar\left(\frac{\partial\psi}{\partial x}\,\mathbf{i} + +\frac{\partial\psi}{\partial y}\,\mathbf{j} + \frac{\partial\psi}{\partial z}\,\mathbf{k}\right) \\[2mm] &= (p_x\,\mathbf{i} + p_y\,\mathbf{j} + p_z\,\mathbf{k})\,\psi, \quad \text{using 1.68} \end{aligned} \tag{1.69}$$

and also that

$$i\hbar\frac{\partial}{\partial t}\psi = E\psi \tag{1.70}$$

That is we have found that the momentum and energy of the wave are obtained by applying the appropriate derivatives to ψ. Summarising we have

$$-i\hbar\nabla\psi = \mathbf{p}\psi$$
$$i\hbar\frac{\partial\psi}{\partial t} = E\psi \tag{1.71}$$

Hence applying $-i\hbar\nabla$ *twice* to ψ and dividing by $2m$ tells us that, when ψ is a plane wave, i.e. $\psi = \exp(i\mathbf{p}\cdot\mathbf{r}/\hbar + iEt/\hbar)$, we have

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \frac{\mathbf{p}^2}{2m}\psi \tag{1.72}$$

But for a *free particle*

$$E = \frac{\mathbf{p}^2}{2m} \tag{1.73}$$

So 1.72 simply states that, when $E = \mathbf{p}^2/2m$ and $\psi = \exp\left(i\mathbf{p}\cdot\mathbf{r}/\hbar - iEt/\hbar\right)$, then

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \tag{1.74}$$

which is indeed the Schrödinger equation for a free particle given above in 1.64.

Summarising we have found that the wave function for a free particle of energy E is the plane wave

$$\psi = \exp\left(\frac{i\mathbf{p}\cdot\mathbf{r}}{\hbar} - \frac{iEt}{\hbar}\right) \tag{1.75}$$

The wave function for a free particle is a plane wave

since this is a solution to the Schrödinger equation for a free particle quoted in 1.64.

Now take a *non-free particle* of energy E, that is a particle which has some non zero potential energy, as well as non zero kinetic energy, so that

$$E = \frac{\mathbf{p}^2}{2m} + V, \qquad \text{and } V \neq 0 \tag{1.76}$$

The bold step of Schrödinger was to *propose* that the possible energies E are obtained by solving the equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{1.77}$$

which we recognise as the *time independent Schrödinger equation* 1.54 above. Schrödinger also proposed that, in general, as time t varies the wave function ψ satisfies the equation

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi \tag{1.78}$$

and, combining the last two equations, we get the equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{1.79}$$

which we recognise as the full Schrödinger equation 1.52 above.

§ 11. Operators are introduced

Finally since, according to 1.54, the differential operator

$$\frac{-\hbar^2}{2m}\nabla^2 + V \tag{1.80}$$

applied to the wave function ψ gives the energies E of the physical system then this operator is called the *Hamiltonian* of the physical system—in analogy with the terminology of classical mechanics—and is denoted by H.

Summarising the Hamiltonian operator H—or simply the Hamiltonian—is given by

$$H = \frac{-\hbar^2}{2m}\nabla^2 + V \tag{1.81}$$

The Hamiltonian is introduced

Recall, too, that in 1.71 we saw that the operator

$$-i\hbar\nabla \tag{1.82}$$

when applied to a plane wave gave the momentum $\mathbf{p}$. This fact is now promoted to a general statement and the operator $-i\hbar\nabla$ is called the *momentum operator* and is usually denoted (somewhat unfortunately [20] perhaps) by p so that one writes

$$p = -i\hbar\nabla \tag{1.83}$$

The momentum operator defined

So $-i\hbar\nabla$ gives $\mathbf{p}\psi$ when applied to *any wave function ψ*, not just the wave function for a plane wave.

More precisely we say that the momentum $\mathbf{p}$ of a physical system with wave function ψ is given by the equation

$$-i\hbar\nabla\psi = \mathbf{p}\psi \tag{1.84}$$

It is also useful to note that in a one dimensional system $-i\hbar\nabla$ reduces to just

$$-i\hbar\frac{d}{dx} \tag{1.85}$$

which is the momentum operator in this case.

§ 12. People, papers and dates

For those readers interested in who did what, and when, I have provided a short list below followed by references to the main papers. Please note carefully that *you are not required to read this list or these papers at all*; they are just included for general cultural, historical and scientific interest.

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[20] It is unfortunate because p may be confused with the value of the momentum itself rather than the operator $-i\hbar\nabla$—this is particularly true in one dimensional problems where there is no need to use a vector notation such as $\mathbf{p}$ to denote the momentum. However it is hard to make any notation perfect and we must let the context be a guide when there is a chance of some ambiguity in what a particular notation means.

People and dates

1900 Planck: *His constant* [**1**]

1905 Einstein: *Photoelectric effect explained* [**2**]

1913 Bohr: *The Bohr Atom* [**3-5**]

1916 Sommerfeld: *Extension of the Bohr Atom* [**6**]

1923 de Broglie: *Matter as a quantum wave* [**7**]

1925 Heisenberg: *Quantum observables and non-commutativity* [**8**]

1925 Born, Jordan and Born, Heisenberg and Jordan: *Improvements on Heisenberg's first paper including the notion of observables as matrices* [**9–10**]

1925 Dirac: *Proper formulation of Heisenberg's observables* [**11-12**]

1926 Schrödinger: *Wave equation* [**13-19**]

1926 Born: *Probabilistic interpretation of the wave function* [**20–21**]

1927 Heisenberg: *His uncertainty principle* [**22**]

1928 Dirac: *His equation for the electron which is both relativistic and describes an electron with a spin* [**23**]

1964 Bell: *His inequalities which distinguish quantum mechanics from classical theories* [**26**]

1982 Aspect, Dalibard and Roger: *An experiment confirming Bell's ideas and the fundamentally quantum nature of the world* [**27**]

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CHAPTER II
Some linear algebra revisited

§ 1. Vectors

Linear algebra plays an important part in quantum mechanics and so we now take some time to remind the reader of the main results from linear algebra that we need.

Consider a typical vector in 3-dimensions, denote it by v, then we usually display the components v_1, v_2, v_3 of v by writing

$$v = v_1 \, \mathbf{i} + v_2 \, \mathbf{j} + v_3 \, \mathbf{k} \qquad (2.1)$$

where $\mathbf{i}, \mathbf{j}$ and $\mathbf{k}$ are called the basis vectors, or equivalently

$$v = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} \qquad (2.2)$$

These are just alternative notations and are equal, so, one has

$$v = v_1 \, \mathbf{i} + v_2 \, \mathbf{j} + v_3 \, \mathbf{k} = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} \qquad (2.3)$$

The collection of all possible such vectors v form a vector space

$$V \qquad (2.4)$$

whose dimension is 3, and one records this fact by writing

$$\dim V = 3 \qquad (2.5)$$

Three dimensions are rarely enough and one can consider vector spaces of dimension 4, 5 and higher. To this end let V have dimension

$$n \qquad (2.6)$$

where n can be as large as one likes: then the notation we use is that the basis vectors are denoted by

$$\{\mathbf{e_1}, \mathbf{e_2}, \dots, \mathbf{e_n}\} \tag{2.7}$$

and the formula for v is

Vectors in n dimensions

$$v = v_1\, \mathbf{e_1} + v_2\, \mathbf{e_2} + \cdots + v_n\, \mathbf{e_n} \tag{2.8}$$

or, if the basis vectors are to be understood,

$$v = \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix} \tag{2.9}$$

Vectors can have complex components

The basis coefficients $v_1, v_2, \dots v_n$ can be *complex numbers* not just real numbers and, while mentioning complex numbers, we state that our notation for the complex conjugate of a complex number z is $\bar{z}$—i.e. if $z = x + iy$ then $\bar{z} = x - iy$ where x and y are real—some books use the notation z^* instead of $\bar{z}$.

Now we have described an n-dimensional vector space V so that

The dimension of a vector space

$$\dim V = n \tag{2.10}$$

where now, n can be *any* positive integer.

Now given two vectors v and w one can define an *inner product*, or *scalar product*, [1] between them which is denoted by [2]

$$\langle v | w \rangle \tag{2.12}$$

The inner product or scalar product defined

and is defined by

$$\langle v | w \rangle = \bar{v}_1 w_1 + \bar{v}_2 w_2 + \cdots + \bar{v}_n w_n \tag{2.13}$$

If u, v and w are vectors and λ is a complex number—i.e. a scalar—then the following properties of the inner product can be verified instantly and are often used

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[1] The term *dot product* is also used as well as inner product and scalar product; however a dot product, which is denoted by $v \cdot w$, is usually only used for vectors in 2 or 3 dimensions whose components, or basis coefficients, are all *real*. Clearly if all quantities are real then the complex conjugate sign can be omitted: for example, the dot product definition in 3 dimensions is the familiar formula

$$v \cdot w = v_1 w_1 + v_2 w_2 + v_3 w_3, \quad \text{where} \begin{cases} v = v_1\, \mathbf{e_1} + v_2\, \mathbf{e_2} + v_3\, \mathbf{e_3} \\ w = w_1\, \mathbf{e_1} + w_2\, \mathbf{e_2} + w_3\, \mathbf{e_3} \end{cases} \tag{2.11}$$

and all of v_1, v_2, v_3 and w_1, w_2, w_3 are real.

[2] In mathematics books the inner product is often denoted by $\langle v, w \rangle$ instead of $\langle v | w \rangle$. Also the inner product in mathematics books is commonly defined so as to be the complex conjugate of ours. All these matters are only differences of convention rather than of content and need not concern us here.

$$\langle u + v | w \rangle = \langle u | w \rangle + \langle v | w \rangle$$
$$\langle u | v + w \rangle = \langle u | v \rangle + \langle u | w \rangle$$
$$\langle u | \lambda v \rangle = \lambda \langle u | v \rangle \qquad (2.14)$$
$$\langle \lambda u | v \rangle = \bar{\lambda} \langle u | v \rangle$$
$$\langle v | u \rangle = \overline{\langle u | v \rangle}$$

The inner product can be used to compute the *length or norm* of a vector v: to do this one computes

$$\langle v | v \rangle \qquad (2.15)$$

which has the interpretation of being a length squared (as it does in three dimensions). The length of v, or the norm of v, is denoted by $\|v\|$ and defined by

$$\|v\| = \sqrt{\langle v | v \rangle} \qquad (2.16)$$

so we see also that

$$\langle v | v \rangle = \|v\|^2 \qquad (2.17)$$

§ 2. Matrices, or linear maps

Next we come to matrices (also called linear maps). A matrix M acts on a vector v to give a new vector which we denote by Mv. We can show this, in a concise way, by writing

$$M : V \longrightarrow V$$
$$v \longmapsto Mv \qquad (2.18)$$

but, more concretely, one writes

$$M = \begin{pmatrix} m_{11} & m_{12} & \cdots & m_{1n} \\ m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & & & \vdots \\ m_{n1} & m_{n2} & \cdots & m_{nn} \end{pmatrix}, \qquad v = \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix} \qquad (2.19)$$

and then

$$Mv = \begin{pmatrix} m_{11} & m_{12} & \cdots & m_{1n} \\ m_{21} & m_{22} & \cdots & m_{2n} \\ \vdots & & & \vdots \\ m_{n1} & m_{n2} & \cdots & m_{nn} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix} = \begin{pmatrix} m_{11}v_1 + m_{12}v_2 + \cdots + m_{1n}v_n \\ m_{21}v_1 + m_{22}v_2 + \cdots + m_{2n}v_n \\ \vdots \\ m_{n1}v_1 + m_{n2} + \cdots + m_{nn}v_n \end{pmatrix}$$
$$= \begin{pmatrix} \sum_{j=1}^{n} m_{1j}v_j \\ \sum_{j=1}^{n} m_{2j}v_j \\ \vdots \\ \sum_{j=1}^{n} m_{nj}v_j \end{pmatrix} \qquad (2.20)$$

The *trace* of a matrix M is the sum of its diagonal elements [3] and is denoted by

$$\text{tr}\,(M) \qquad\qquad (2.21)$$

Thus

$$\text{tr}\,(M) = m_{11} + m_{22} + \cdots + m_{nn} \qquad\qquad (2.22)$$

Two important properties of the trace, which are easily checked by direct calculation, are that if M and N are two matrices then

$$
\begin{aligned}
(i) && tr(M+N) &= tr(M) + tr(N) \\
(ii) && tr(MN) &= tr(NM)
\end{aligned}
\qquad (2.23)
$$

Using these two properties 2.23 we immediately deduce the following result

$$
\begin{aligned}
\text{tr}\,(MN - NM) &= \text{tr}\,(MN) - \text{tr}\,(NM), && \text{using 2.23 (i)} \\
&= 0, && \text{using 2.23 (ii)}
\end{aligned}
\qquad (2.24)
$$

The difference $MN - NM$ is called the *commutator* of M and N; and the commutator of pairs of matrices turns out to be of central importance in quantum mechanics and it is denoted by $[M, N]$. So one has that, by definition,

$$[M, N] = MN - NM \qquad\qquad (2.25)$$

and by 2.24 above

$$\text{tr}\,([M, N]) = 0 \qquad\qquad (2.26)$$

which, we repeat, is important for quantum mechanics, as we shall make clear at the appropriate time later.

If a matrix M has a vector v ($v \neq 0$) which satisfies the equation

$$Mv = \lambda v \qquad\qquad (2.27)$$

where λ is some real or complex number then v is called an *eigenvector* of M and λ is called the *eigenvalue* of the eigenvector v.

Note it is allowed that the eigenvalue λ can be sometimes zero but *not* the eigenvector: in other words $\lambda = 0$ is a possible eigenvalue but $v = 0$ *is not* a possible eigenvector.

Now if M is any matrix then, purely for purposes of abbreviation, let us write

$$
M = (m_{ij})_{n \times n} =
\begin{pmatrix}
m_{11} & m_{12} & \cdots & m_{1n} \\
m_{21} & m_{22} & \cdots & m_{2n} \\
\vdots & & & \vdots \\
m_{n1} & m_{n2} & \cdots & m_{nn}
\end{pmatrix}
\qquad (2.28)
$$

---

[3] It is frequently useful to know that $\text{tr}\,(M)$ is also equal to the sum of the eigenvalues of M, though a little calculation is needed to verify this.

Then any matrix M has what is called an *adjoint matrix* which is denoted by $M^\dagger$ and defined by

$$M^\dagger = \left(\overline{m}_{ji}\right)_{n \times n} \qquad (2.29)$$

What this definition means is that the adjoint matrix $M^\dagger$ is obtained from the matrix M by the following procedure: *reflect M along its diagonal and then take the complex conjugate of all the entries.* As the adjoint $M^\dagger$ is important in quantum mechanics we illustrate the matter with an example. Let

$$M = \begin{pmatrix} 5 & -1 & 6+7i \\ 3i & 0 & e^{3\pi i} \\ 22 & 4-i & 3+2i \end{pmatrix} \qquad (2.30)$$

then we calculate straightaway that

$$M^\dagger = \begin{pmatrix} 5 & -3i & 22 \\ -1 & 0 & 4+i \\ 6-7i & e^{-3\pi i} & 3-2i \end{pmatrix} \qquad (2.31)$$

which the reader should verify.

A more general basis independent definition of the adjoint $M^\dagger$ can be given using the inner product: this definition is simply that the adjoint $M^\dagger$, of a matrix M, is defined by requiring that $M^\dagger$ is that matrix which satisfies the equation

$$\langle M^\dagger v | w \rangle = \langle v | Mw \rangle \quad \text{for all vectors } v \text{ and } w \qquad (2.32)$$

A matrix M may sometimes be equal to its own adjoint, if that is the case then M is called *self-adjoint* or *Hermitian*. Since we shall meet many self-adjoint matrices in quantum mechanics we emphasise this by repeating that

$$\text{If } M^\dagger = M \text{ then } M \text{ is called self-adjoint or Hermitian} \qquad (2.33)$$

and we see that a self-adjoint matrix therefore satisfies the equation

$$\langle Mv | w \rangle = \langle v | Mw \rangle, \qquad (\text{for all } v \text{ and } w) \qquad (2.34)$$

and indeed this may be used as the *definition* of a self adjoint matrix.

Another important point for quantum mechanics is that the eigenvalues of a self-adjoint matrix are always *real* rather than complex. Here is the proof: let M be a self-adjoint matrix and let v be an eigenvector of M with eigenvalue λ then

$$Mv = \lambda v \qquad (2.35)$$

Taking the inner product of both sides with v gives

$$\begin{aligned} \langle v | Mv \rangle &= \langle v | \lambda v \rangle \\ &= \lambda \langle v | v \rangle, \quad \text{using 2.14} \end{aligned} \qquad (2.36)$$

But since

$$M = M^\dagger \tag{2.37}$$

then definition 2.32 says that

$$\begin{aligned}
\langle v|Mv\rangle &= \langle Mv|v\rangle \\
&= \langle \lambda v|v\rangle \\
&= \bar{\lambda}\,\langle v|v\rangle, \quad \text{using 2.14}
\end{aligned} \tag{2.38}$$

But the RHS's of 2.36 and 2.38 are equal so we have

$$\begin{aligned}
\lambda\,\langle v|v\rangle &= \bar{\lambda}\,\langle v|v\rangle \\
\Rightarrow \lambda &= \bar{\lambda}
\end{aligned} \tag{2.39}$$

$$\text{i.e. } \lambda \text{ is real}$$

Finally let us prove the following frequently used result: if v and w are eigenvectors of any *self-adjoint* matrix M corresponding to *different* eigenvalues then v and w are orthogonal—by which we mean, of course, that $\langle w|v\rangle = 0$. Proceeding to the proof we begin with the fact that

$$\begin{aligned}
Mv &= \lambda v \\
Mw &= \mu w, \quad \mu \neq \lambda
\end{aligned} \tag{2.40}$$

Next note that

$$\begin{aligned}
\lambda\,\langle w|v\rangle &= \langle w|\lambda v\rangle \\
&= \langle w|Mv\rangle \\
&= \langle Mw|v\rangle, \qquad \text{since } M = M^\dagger \\
&= \langle \mu w|v\rangle \\
&= \mu\,\langle w|v\rangle, \qquad \text{since } \mu \text{ is real}
\end{aligned} \tag{2.41}$$

Hence we have deduced that

$$\begin{aligned}
\lambda\,\langle w|v\rangle &= \mu\,\langle w|v\rangle \\
\Rightarrow \langle w|v\rangle &= 0, \qquad \text{since } \lambda \neq \mu
\end{aligned} \tag{2.42}$$

The eigenvectors of a self-adjoint matrix corresponding to distinct eigenvalues are always orthogonal

which is the result we wanted to prove.

§ 3. Some quantum mechanical notation

Some simple notational points need to be made now to avoid any confusion later.

In quantum mechanics a vector can be denoted by

$$v \tag{2.43}$$

or

$$|v\rangle \tag{2.44}$$

and both these notations, v and $|v\rangle$ mean the same thing. This leads on to an equation like

$$Mv = \lambda v \tag{2.45}$$

having the alternate form

$$M \left|v\right\rangle = \lambda \left|v\right\rangle \tag{2.46}$$

Again both the equations 2.45 and 2.46 above have exactly the same content: they differ only in the notation used.

Another common practice is to write down the quantity

$$\left\langle u\right| M \left|v\right\rangle \tag{2.47}$$

This is simply an alternative notation for $\langle u|Mv\rangle$. To spell this out: by definition

$$\left\langle u\right| M \left|v\right\rangle = \langle u|Mv\rangle \tag{2.48}$$

To end this section on a purely historical note: Dirac introduced the notation

Dirac notation

$$\langle u|v\rangle \tag{2.49}$$

which he called a *bracket*. Then, to fit in with this nomenclature, he called the vector

This object $\langle u|$ is called a bra.

$$\langle u| \tag{2.50}$$

a bra and the vector

This object $|u\rangle$ is called a ket.

$$|v\rangle \tag{2.51}$$

a ket. This ends our recapitulation of results in linear algebra but we shall finish by explaining the use of linear algebra applied to wave functions.

§ 4. Functions as vectors and differential operators as matrices

Functions as vectors

It is a very fruitful practice to apply the ideas of linear algebra to functions and differential equations. The reader may have already learned this fact from a previous course in mathematical methods. In any case we set out here some of the more important results that we shall be using in our account of quantum mechanics.

First we show how functions can be thought of as vectors.

Suppose that ψ and ϕ are two separate solutions of the Schrödinger equation, for some given potential V, so that we have

$$\begin{aligned}
\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi &= i\hbar\frac{\partial\psi}{\partial t} \\
\frac{-\hbar^2}{2m}\nabla^2\phi + V\phi &= i\hbar\frac{\partial\phi}{\partial t}
\end{aligned} \tag{2.52}$$

then, if we add these two last equations we see that

$$\frac{-\hbar^2}{2m}\nabla^2(\psi + \phi) + V(\psi + \phi) = i\hbar\frac{\partial(\psi + \phi)}{\partial t} \tag{2.53}$$

so that

$$\psi + \phi \tag{2.54}$$

is *also a solution* to the Schrödinger equation; it also clear that if ψ is a solution then so is

$$\alpha\psi \tag{2.55}$$

where α is any constant.

In other words any linear combination

$$\alpha\psi + \beta\phi \tag{2.56}$$

of solutions ψ and ϕ to the Schrödinger equation, is *also* a solution.

This means that such ψ and ϕ form a *vector space*: namely the space of *all solutions to the Schrödinger equation*. We shall denote this space by $S(\psi)$ so that we have

$$\begin{aligned}
S(\psi) &= \left\{ \psi : \frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \right\} \\
&= \left\{ \psi : H\psi = i\hbar\frac{\partial\psi}{\partial t} \right\}, \quad \text{where } H = \frac{-\hbar^2}{2m}\nabla^2 + V
\end{aligned} \tag{2.57}$$

H being, of course, the Hamiltonian for the system with potential V. Viewing H as an operator from $S(\psi)$ to $S(\psi)$ itself can be displayed symbolically by writing

$$\begin{aligned}
H : S(\psi) &\longrightarrow S(\psi) \\
\psi &\longmapsto H\psi
\end{aligned} \tag{2.58}$$

For carrying out calculations we should like to have a *basis* for the space $S(\psi)$: this can be obtained by considering the eigenfunctions or eigenvectors for the Hamiltonian[4] H.

To this end suppose that all the eigenvectors of H are given by

$$\{\psi_1, \psi_2, \ldots\} \tag{2.59}$$

and the corresponding eigenvalues of H by

$$\{E_1, E_2, \ldots\} \tag{2.60}$$

so that we have

$$\begin{aligned}
H\psi_1 &= E_1\psi_1 \\
H\psi_2 &= E_2\psi_2 \\
\vdots \quad & \quad \vdots
\end{aligned} \tag{2.61}$$

---

[4] Note that the eigenvectors of any other (self-adjoint) operator L, say, $L : S(\psi) \longrightarrow S(\psi)$ can be used to provide an alternative basis. The significance of L being self-adjoint is elaborated on in the next chapter but, for the moment, we just point out that physically measurable quantities, or *observables*, are represented by self-adjoint operators.

then the basis of $S(\psi)$ is given by the set $\{\psi_1, \psi_2, \ldots\}$. In other words

$$\{\psi_1, \psi_2, \ldots\} = \text{ The basis of } S(\psi) \tag{2.62}$$

The fact that $\{\psi_1, \psi_2, \ldots\}$ is the basis of $S(\psi)$ means that any wave function ψ—i.e. any element of $S(\psi)$—is given by some linear combination of the ψ: more precisely one can say that

$$\psi \in S(\psi), \qquad \left(\text{i.e. } H\psi = i\hbar \frac{\partial \psi}{\partial t}\right)$$

$$\Rightarrow \psi = \alpha_1 \psi_1 + \alpha_2 \psi_2 + \cdots \tag{2.63}$$

$$= \sum_{i=1}^{\infty} \alpha_i \psi_i$$

Note that the number of eigenvectors of H will be in general *infinite*: this means that the space $S(\psi)$ is an *infinite dimensional vector space*;[5] we need this infinite dimensionality in order to be able to express *any* function ψ in terms of the basis elements ψ_i.

To finish our description of $S(\psi)$ we must give it an inner product. This we now do by defining the inner product of two elements of $S(\psi)$ to be $\langle \psi | \phi \rangle$ where

$$\langle \psi | \phi \rangle = \int_{-\infty}^{\infty} \overline{\psi} \phi \, dx \, dy \, dz \tag{2.67}$$

Note, in passing, that we must require ϕ and ψ to go to zero at infinity for the integrations in this definition to converge.

It is perfectly straightforward to express this inner product in terms of components: suppose the basis $\{\psi_1, \psi_2, \ldots\}$ for $S(\psi)$ is an *orthonormal* one, so that

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{2.68}$$

---

[5] This encounter with infinite dimensional spaces of functions is not new to any reader who has met Fourier series. Recall that a Fourier series expresses any function $f(x)$ of period 2π on the interval $[-\pi, \pi]$ in terms of an infinite series of the form

$$f(x) = a_0 + a_1 \cos(x) + a_2 \cos(2x) + \cdots + a_n \cos(nx) + \cdots$$
$$+ b_1 \sin(x) + b_2 \sin(2x) + \cdots + b_n \sin(nx) + \cdots$$
$$= \cdots + d_{-2} e^{-2ix} + d_{-1} e^{-ix} + d_0 + d_1 e^{ix} + d_2 e^{2ix} + \cdots \tag{2.64}$$
$$= \sum_{-\infty}^{\infty} d_n e^{inx}, \qquad \text{where } \begin{cases} d_n = (a_n - ib_n)/2 \\ d_0 = a_0 \\ d_{-n} = (a_n + ib_n)/2 \end{cases} \quad n = 1, 2, \ldots$$

Hence the periodic functions on $[-\pi, \pi]$ are an infinite dimensional vector space of functions whose basis is given *either* by the pair of semi infinite sets of trigonometric functions

$$\{\cos(nx), n = 0, 1, 2, \ldots\} \text{ and } \{\sin(nx), n = 1, 2, \ldots\} \tag{2.65}$$

or equivalently, and more symmetrically, by the single infinite set

$$\{e^{inx}, n \in \mathbf{Z}\} \tag{2.66}$$

where, as usual, δ_{ij} is the Kronecker delta defined by

$$\delta_{ij} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \end{cases} \tag{2.69}$$

then we can write

$$\psi = \sum_{i=1}^{\infty} \alpha_i \psi_i, \qquad \phi = \sum_{j=1}^{\infty} \beta_i \psi_j \quad \text{for } \psi, \phi \in S(\psi) \tag{2.70}$$

and we see that

$$\langle \psi | \phi \rangle = \int_{-\infty}^{\infty} \overline{\left(\sum_{i=1}^{\infty} \alpha_i \psi_i \right)} \left(\sum_{j=1}^{\infty} \beta_j \psi_j \right) dx \, dy \, dz$$

$$= \sum_{i,j=1}^{\infty} \bar{\alpha}_i \beta_j \int_{-\infty}^{\infty} \overline{\psi_i} \psi_j = \sum_{i,j=1}^{\infty} \bar{\alpha}_i \beta_j \langle \psi_i | \psi_j \rangle \tag{2.71}$$

$$= \sum_{i,j=1}^{\infty} \bar{\alpha}_i \beta_j \, \delta_{ij} = \sum_{i=1}^{\infty} \bar{\alpha}_i \beta_i$$

and so

$$\langle \psi | \phi \rangle = \sum_{i=1}^{\infty} \bar{\alpha}_i \beta_i = \bar{\alpha}_1 \beta_1 + \bar{\alpha}_2 \beta_2 + \cdots \tag{2.72}$$

which we see is just an infinite dimensional version of the formula 2.13 for the finite dimensional case.

One can, and should, verify that this definition satisfies the properties 2.14 required for an inner product.

We move on to the matter of showing how differential operators can be thought of as matrices.

Differential operators as matrices

For simplicity we just consider functions of one variable x. This said, take the momentum operator in one dimension that we introduced in 1.85, namely,

$$p = -i\hbar \frac{d}{dx} \tag{2.73}$$

and apply it to the wave function $\psi(x)$ thereby obtaining the new function ϕ where

$$\phi = -i\hbar \frac{d\psi}{dx} \tag{2.74}$$

The point is that ϕ is just a new function so that

$$p = -i\hbar \frac{d}{dx} \tag{2.75}$$

just maps old functions to new ones in the same way as a matrix M maps a vector v to a new vector w where

$$w = Mv \tag{2.76}$$

As a another example take the Hamiltonian H for a particular potential V so that

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \\ &= \frac{p^2}{2m} + V(x), \qquad \text{using } p = -i\hbar\frac{d}{dx} \end{aligned} \tag{2.77}$$

Then H applied to ψ simply gives another new function ϕ where, this time,

$$\begin{aligned} \phi(x) &= H\psi(x) \\ &= -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) \end{aligned} \tag{2.78}$$

Summarising we see that differential operators applied to functions produce new functions, just as matrices applied to vectors give new vectors. [6]

§ 5. The momentum p and the Hamiltonian H are self-adjoint

It is now time to verify that the momentum operator p is self-adjoint. We shall again simplify matters by temporarily working in one dimension so that the inner product is given by $\langle\psi|\phi\rangle = \int_{-\infty}^{\infty} \overline{\psi}\phi\, dx$.

The definition 2.34 of self-adjointness just requires us to show that

$$\langle\phi|p\psi\rangle = \langle p\phi|\psi\rangle \tag{2.81}$$

Proceeding with the calculation we have

$$\begin{aligned} \langle\phi|p\psi\rangle &= \int_{-\infty}^{\infty} \overline{\phi}\left(-i\hbar\frac{d\psi}{dx}\right) dx = -i\hbar \int_{-\infty}^{\infty} \overline{\phi}\frac{d\psi}{dx}\, dx \\ &= -i\hbar\left[\overline{\phi}\psi\right]_{-\infty}^{\infty} + i\hbar \int_{-\infty}^{\infty} \overline{\frac{d\phi}{dx}}\psi\, dx, \qquad \text{using integration by parts} \\ &= i\hbar \int_{-\infty}^{\infty} \overline{\frac{d\phi}{dx}}\psi\, dx, \qquad \text{since } \phi \text{ and } \psi \text{ go to zero at infinity} \\ &= \int_{-\infty}^{\infty} \overline{\left(-i\hbar\frac{d\phi}{dx}\right)}\psi\, dx = \int_{-\infty}^{\infty} \overline{(p\phi)}\psi\, dx, \qquad \text{since } p = -i\hbar\frac{d}{dx} \\ &= \langle p\phi|\psi\rangle \end{aligned} \tag{2.82}$$

---

[6] More formally we could have said that just a matrix M is a map from a vector space V of the form

$$\begin{aligned} M : V &\longrightarrow V \\ v &\longmapsto Mv \end{aligned} \tag{2.79}$$

then a differential operator, such as the Hamiltonian H, is a map from $S(\psi)$ to $S(\psi)$ of the form

$$\begin{aligned} H : S(\psi) &\longrightarrow S(\psi) \\ \psi &\longmapsto H\psi \end{aligned} \tag{2.80}$$

as we already said in eq. 2.58 above.

So p is indeed self-adjoint as claimed.

It is now easy to check that the Hamiltonian is self-adjoint—we leave the reader to verify this—but all one needs to do is to observe that multiplication by a real valued function $V(x)$, such as the potential, is a self-adjoint operator. Further p being self-adjoint means that *any power* of p is self-adjoint, so that, in particular, p^2 is self-adjoint. Hence the linear combination

$$H = \frac{p^2}{2m} + V(x) \tag{2.83}$$

is also self-adjoint so that one has

$$\langle \phi | H\psi \rangle = \langle H\phi | \psi \rangle \tag{2.84}$$

§ 6. Final details including Hilbert spaces

Let us return to the space $S(\psi)$ of all solutions to the Schrödinger equation and the expansion 2.63. Recall that we had

$$\psi \in S(\psi), \qquad \left(\text{i.e. } H\psi = i\hbar \frac{\partial \psi}{\partial t} \right)$$

$$\Rightarrow \psi = \alpha_1 \psi_1 + \alpha_2 \psi_2 + \cdots \tag{2.85}$$

$$= \sum_{i=1}^{\infty} \alpha_i \psi_i$$

We now calculate the all important constants α_i. Note that the fact that H is self-adjoint means that its eigenvectors ψ_i are mutually orthogonal—i.e. that

$$\langle \psi_i | \psi_j \rangle = 0, \quad \text{for } i \neq j \tag{2.86}$$

Also if we normalise each eigenvector ψ_i to unity then we obtain the familiar orthonormality statement

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{2.87}$$

where δ_{ij} is the Kronecker delta. Hence taking the inner product of ψ with the eigenvector ψ_i we find that

$$\langle \psi_i | \psi \rangle = \sum_{j=1}^{\infty} \alpha_j \langle \psi_i | \psi_j \rangle$$

$$= \sum_{j=1}^{\infty} \alpha_j \, \delta_{ji} = \alpha_i \tag{2.88}$$

In other words α_i is given by the formula [7]

$$\alpha_i = \langle \psi_i | \psi \rangle \tag{2.89}$$

---

[7] Of course the same formula holds in finite dimensions with orthonormal bases

and this formula should be noted as it is frequently very useful.

The infinite dimensional vector spaces $S(\psi)$ used in quantum mechanics, when equipped with their inner product $\langle \phi | \psi \rangle$, are called *Hilbert spaces* [8] and we shall denote them by

$$\mathcal{H} \tag{2.90}$$

as well as $S(\psi)$. Strictly speaking $\mathcal{H}$ is not quite *all* of $S(\psi)$ but is only a certain *subspace* of $S(\psi)$, that is

$$\mathcal{H} \subset S(\psi) \tag{2.91}$$

cf. the explanation of this point in the next paragraph.

The main example of a vector ψ belonging to $S(\psi)$ but *not* to $\mathcal{H}$ is when $\psi \in S(\psi)$ is the wave function for a free particle which we recall from 1.75 is given by

$$\psi(x, y, z, t) = \exp\left(\frac{i\mathbf{p} \cdot \mathbf{r}}{\hbar} - \frac{iEt}{\hbar}\right) \tag{2.92}$$

and we can straightaway calculate that

$$\begin{aligned}
\langle \psi | \psi \rangle &= \int_{-\infty}^{\infty} \overline{\psi(x,y,z,t)}\, \psi(x,y,z,t)\, dx\, dy\, dz \\
&= \int_{-\infty}^{\infty} \exp\left(-\frac{i\mathbf{p} \cdot \mathbf{r}}{\hbar} + \frac{iEt}{\hbar}\right) \exp\left(\frac{i\mathbf{p} \cdot \mathbf{r}}{\hbar} - \frac{iEt}{\hbar}\right) dx\, dy\, dz \\
&= \int_{-\infty}^{\infty} dx\, dy\, dz = \infty
\end{aligned} \tag{2.93}$$

So

$$\langle \psi | \psi \rangle = \infty \tag{2.94}$$

because the x, y and z integrations diverge—such a behaviour is *not allowed* in Hilbert space $\mathcal{H}$ where, if $\phi, \psi \in \mathcal{H}$, it is required that all inner products $\langle \psi | \psi \rangle$, or $\langle \phi | \psi \rangle$, be *finite*.

The fact that the wave function ψ for a free particle belongs to $S(\psi)$ but not to the Hilbert space $\mathcal{H}$, since $\langle \psi | \psi \rangle = \infty$ is not a pathology: in fact it makes perfect physical sense as we now explain.

First of all any wave function $\psi \in \mathcal{H}$ has, by definition,

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} \overline{\psi}\phi \, dx\, dy\, dz < \infty \tag{2.95}$$

and this—as we already observed above when giving the definition 2.67 of $\langle \psi | \psi \rangle$—requires that ψ dies away to zero at infinity to make the integrations converge. Now a free particle

---

[8] The full definition of the Hilbert space $\mathcal{H}$, as well as requiring an inner product, has some technical requirements about the convergence of what are called *Cauchy sequences* of vectors and a completeness condition that requires all such sequences to converge to a vector in $\mathcal{H}$ rather than just outside it. We shall not need any of these refinements but the interested reader can find more information in the book by Hannabuss mentioned in the preface.

must be allowed to move unimpeded off to infinity if nothing physical intervenes; this means that its wave function must not die away to zero at infinity otherwise it would have zero probability for ever getting there.

For a particle that is in what is called a *bound state*—such as the electron of a Hydrogen atom—one does require $\langle\psi|\psi\rangle$ to be finite and this corresponds to the physical fact that the electron does not escape to infinity (without outside intervention). However, in any *scattering experiment*—where particles may come in from and go out to infinity—one must allow the wave functions to be non zero at infinity and, in particular, to have $\langle\psi|\psi\rangle = \infty$. Remember though, ψ will still be a solution to the Schrödinger equation—i.e. a member of $S(\psi)$—so one has

$$\psi \in S(\psi)$$
$$\text{but} \qquad \psi \notin \mathcal{H} \tag{2.96}$$

Lastly a purely notational point: the reader should be careful *not to confuse* the Hilbert space $\mathcal{H}$ with the Hamiltonian operator H, the context should usually prevent any such confusion.

CHAPTER III
The formalism of quantum mechanics

§ 1. The mathematical setting and rules of calculation in quantum mechanics

We can now begin to explain how to calculate physical quantities in quantum mechanics. First of all have in mind some particular physical system: e.g. a free particle, the hydrogen atom, the helium atom, all the atoms in a gram of some lump of matter etc.

Such a physical system can be in many states and quantum mechanics says that *each state* has its own wave function

$$\psi \tag{3.1}$$

which specifies it completely. Further the energy E of the state ψ is obtained by solving the time independent Schrödinger equation 1.54 which is

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{3.2}$$

If we write

$$H = \frac{-\hbar^2}{2m}\nabla^2 + V \tag{3.3}$$

then the Schrödinger equation abbreviates to

$$H\psi = E\psi \tag{3.4}$$

As we have seen already, in the material preceding this chapter, this operator H is called the *Hamiltonian*.

The Hamiltonian operator makes a more formal entry.

Also, we can take the point of view where the wave function ψ is considered as a vector

$$|\psi\rangle \tag{3.5}$$

in a vector space of all possible states. In this vector space point of view the Schrödinger equation becomes

The Schrödinger equation using vector notation.

$$H|\psi\rangle = E|\psi\rangle \tag{3.6}$$

so that solving the Schrödinger equation for the possible energies of the system becomes simply finding the *eigenvalues E* of the Hamiltonian H.

In quantum mechanics, each physically measurable quantity such as position, momentum, energy, angular momentum, velocity, electric charge and so on is associated to its own operator which the acts on the wave function ψ.

When the physical quantity is the energy E we have already seen that E is associated to the Hamiltonian H.

Physical quantities as observables or self-adjoint operators

We call any physical quantity A, say, that we can measure an *observable* and require that it be represented by a *self-adjoint operator* which we also denote by A.

Any observable A acts on the Hilbert space $\mathcal{H}$, a fact which we display by writing

$$A : \mathcal{H} \longrightarrow \mathcal{H} \tag{3.7}$$

§ 2. The probability density and its meaning

As we have said already in § 8 on p. 16, a physical system specified by the wave function ψ has a probability density given by

$$\overline{\psi(x,y,z,t)}\psi(x,y,z,t) = |\psi(x,y,z,t)|^2 \tag{3.8}$$

and

$$\langle \psi | \psi \rangle = \int |\psi(x,y,z,t)|^2 \, dx \, dy \, dz \tag{3.9}$$

Suppose this system has Hamiltonian

$$H \tag{3.10}$$

and corresponding set of eigenstates $\{\psi_1, \psi_2, \ldots\}$ so that

$$H\psi_i = E_i \psi_i, \qquad i = 1, 2, \ldots \tag{3.11}$$

These eigenstates form a basis—cf. 2.63—for the Hilbert space of possible states $\mathcal{H}$ and so we can expand our wave function ψ in this basis yielding

$$\psi = \alpha_1 \psi_1 + \alpha_2 \psi_2 + \cdots \tag{3.12}$$

Now, as we saw in 2.86, these eigenstates ψ_i are automatically mutually orthogonal and can also be adjusted to be of unit length which means that the basis $\{\psi_1, \psi_2, \ldots\}$ becomes an *orthonormal basis* for $\mathcal{H}$. We then have

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{3.13}$$

which is simply 2.87 repeated. Recall, too, that from 2.89 we know that the α_i are given by the simple inner product formula

$$\alpha_i = \langle \psi_i | \psi \rangle \tag{3.14}$$

Using this orthonormal basis we now calculate that

$$\psi = \alpha_1\psi_1 + \alpha_2\psi_2 + \cdots$$

$$\Rightarrow \langle\psi|\psi\rangle = \sum_{i,j} \langle\alpha_i\psi_i|\alpha_j\psi_j\rangle = \sum_{i,j} \overline{\alpha_i}\,\alpha_j \,\langle\psi_i|\psi_j\rangle$$

$$= \sum_{i,j} \overline{\alpha_i}\,\alpha_j\delta_{ij}, \quad \text{since } \langle\psi_i|\psi_j\rangle = \delta_{ij} \tag{3.15}$$

$$= \sum_{i} \overline{\alpha_i}\,\alpha_i = |\alpha_1|^2 + |\alpha_2|^2 + \cdots$$

So we now know that

$$\langle\psi|\psi\rangle = \sum_{i} |\alpha_i|^2 \tag{3.16}$$

$$\text{with } \alpha_i = \langle\psi_i|\psi\rangle$$

Now we normalise the state ψ itself to unity—i.e. we adjust ψ so that

$$\langle\psi|\psi\rangle = 1 \tag{3.17}$$

and thereby obtain the statement that

$$\sum_{i} |\alpha_i|^2 = 1 \tag{3.18}$$

The probabilistic interpretation of the above statement 3.18 can now be given. It is this: let a system be in the state

$$\psi \tag{3.19}$$

and let the energy be measured, then

$$|\alpha_i|^2 = \begin{cases} \text{The probability that the physical system} \\ \text{is now found in the state } \psi_i \end{cases} \tag{3.20}$$

Probability system is now in state ψ_i

In other words

$$|\alpha_i|^2 \tag{3.21}$$

is the probability that, on measurement, the system makes a transition from the state ψ to the state ψ_i.

Since the system must be in one of the states then we must have $\sum_i |\alpha_i|^2 = 1$ as indeed is asserted in 3.18. Also note that, since $\alpha_i = \langle\psi_i|\psi\rangle$ then the probability of such a transition from ψ to ψ_i is equal to

$$|\langle\psi_i|\psi\rangle|^2 \tag{3.22}$$

Probability of a transition from a state ψ to a state ψ_i

and if the system happens to be *already in the state* ψ_i then the transition probability is just

$$|\langle\psi_i|\psi_i\rangle|^2 = 1 \tag{3.23}$$

$$\text{by orthonormality}$$

What this means physically is the following: if the system is *already in some energy eigen-state* ψ_i then, on measurement of the energy, it *stays* in the eigenstate ψ_i and the energy will be found to have the value E_i.

§ 3. Measurement and probability

The calculation of physical quantities in quantum mechanics rests on just two simple laws. We are now ready to be introduced to these laws, so here they are

(i) **The measurement law**

Let a system be in an eigenstate ψ of the observable A with eigenvalue λ. Hence we have

$$A\psi = \lambda\psi \tag{3.24}$$

Then if the observable A is measured the result will be the value

$$\lambda \tag{3.25}$$

(ii) **The probability law**

The probability of a system making a transition from a state ψ to another state ϕ is

$$|\langle\phi|\psi\rangle|^2 \tag{3.26}$$

So we see that given an initial state of the system there is no fixed outcome to an experiment in quantum mechanics: instead probability has come into play.

To make sure that no probability can ever exceed unity all physical states ψ of systems must be normalised so that

$$\langle\psi|\psi\rangle = 1 \tag{3.27}$$

Since, for any two ψ and ϕ, linear algebra tells us that [1]

$$|\langle\phi|\psi\rangle|^2 \leq \langle\phi|\phi\rangle\langle\psi|\psi\rangle \tag{3.28}$$

then it follows that, for *normalised* ϕ and ψ, one has that

$$0 \leq |\langle\phi|\psi\rangle|^2 \leq 1 \tag{3.29}$$

so all probabilities do lie between 0 and 1 as we require.

§ 4. Probability conservation

Since the use of probabilistic interpretation of the wave function $\psi(x, y, z, t)$ requires that

$$\langle\psi|\psi\rangle = 1 \tag{3.30}$$

---

[1] This is called the Cauchy-Schwarz inequality in linear algebra textbooks and in finite dimensional vector spaces just asserts that $0 \leq |\cos(\theta)|^2 \leq 1$ where θ is the angle between the two vectors ϕ and ψ. This is not so easy to prove in infinite dimensions—which are needed in quantum mechanics—but we need not concern ourselves with this point.

then this statement 3.30 should remain true for all time. In other words it should be true
that

$$\frac{\partial}{\partial t} \langle \psi | \psi \rangle = 0 \qquad (3.31)$$

We can prove this rather easily as we shall now see. First of all consider the special
case of an *energy eigenfunction* $\psi_i(x, y, z, t)$. Since, by definition, $\psi_i(x, y, z, t)$ is a solution
to the Schrödinger equation with energy E_i we can write

$$H\psi_i = i\hbar \frac{\partial \psi_i}{\partial t}$$

$$\text{and } H\psi_i = E_i \psi_i, \qquad \text{with } H = \frac{-\hbar^2}{2m} \nabla^2 + V \qquad (3.32)$$

Hence we have

$$i\hbar \frac{\partial \psi_i(x, y, z, t)}{\partial t} = E_i \psi_i(x, y, z, t)$$

$$\Rightarrow \psi_i(x, y, z, t) = e^{-iE_i t/\hbar} \psi_i(x, y, z, 0), \quad \text{(check that both sides agree for } t = 0)$$

$$(3.33)$$

Notice that all the time dependence of the energy eigenfunction $\psi_i(x, y, z, t)$ is concen-
trated in the exponential factor

$$e^{-iE_i t/\hbar} \qquad (3.34)$$

Now take any wave function ψ and expand it, in the usual way, using the basis $\{\psi_1, \psi_2, \ldots\}$
of energy eigenstates giving

$$\psi = \alpha_1 \psi_1 + \alpha_2 \psi_2 + \cdots \qquad (3.35)$$

Remember too that the ψ_i satisfy the orthonormality property

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

$$\Rightarrow \int \overline{\psi_i(x, y, z, t)} \psi_j(x, y, z, t) \, dx \, dy \, dz = \delta_{ij} \qquad (3.36)$$

But if we use the explicit formula 3.33 for $\psi_i(x, y, z, t)$ this becomes the statement

$$\int e^{+iE_i t/\hbar} \overline{\psi_i(x, y, z, 0)} e^{-iE_j t/\hbar} \psi_j(x, y, z, 0) \, dx \, dy \, dz$$

$$= e^{i(E_i - E_j)t/\hbar} \int \overline{\psi_i(x, y, z, 0)} \psi_j(x, y, z, 0) \, dx \, dy \, dz \qquad (3.37)$$

$$= \delta_{ij}$$

Hence, after division by $e^{i(E_i - E_j)t/\hbar}$, we find that

$$\int \overline{\psi_i(x, y, z, 0)} \psi_j(x, y, z, 0) \, dx \, dy \, dz = \delta_{ij} \qquad (3.38)$$

Note: no need for $e^{i(E_i - E_j)t/\hbar}$ in RHS denominator of 3.38

a result which we shall need shortly.

Next we return to 3.35 and, if we spell out the (x, y, z, t) dependence of ψ, we obtain

$$
\begin{aligned}
\psi(x, y, z, t) &= \alpha_1 \psi_1(x, y, z, t) + \alpha_2 \psi_2(x, y, z, t) + \cdots \\
&= \alpha_1 e^{-iE_1 t/\hbar} \psi_1(x, y, z, 0) + \alpha_2 e^{-iE_2 t/\hbar} \psi_2(x, y, z, 0) + \cdots, \qquad \text{using 3.33} \\
&= \sum_{i=1}^{\infty} e^{-iE_i t/\hbar} \alpha_i \psi_i(x, y, z, 0)
\end{aligned}
$$

$$(3.39)$$

Now since

$$
\langle \psi | \psi \rangle = \int \overline{\psi(x, y, z, t)}\, \psi(x, y, z, t)\, dx\, dy\, dz \tag{3.40}
$$

then, on substituting for $\psi(x, y, z, t)$ from 3.39 and paying attention to complex conjugation, we find that

$$
\begin{aligned}
\langle \psi | \psi \rangle &= \int \left\{ \sum_{i=1}^{\infty} e^{+iE_i t/\hbar}\, \overline{\alpha_i}\, \overline{\psi_i(x, y, z, 0)} \sum_{j=1}^{\infty} \alpha_j e^{-iE_j t/\hbar} \psi_j(x, y, z, 0) \right\} dx\, dy\, dz \\
&= \sum_{i,j=1}^{\infty} e^{i(E_i - E_j)t/\hbar} \overline{\alpha_i} \alpha_j \int \overline{\psi_i(x, y, z, 0)}\, \psi_j(x, y, z, 0)\, dx\, dy\, dz \\
&= \sum_{i,j=1}^{\infty} e^{i(E_i - E_j)t/\hbar} \overline{\alpha_i} \alpha_j \delta_{ij}, \qquad \text{using 3.38} \\
&= \sum_{i=1}^{\infty} \overline{\alpha_i} \alpha_i = \sum_{i=1}^{\infty} |\alpha_i|^2 = 1, \qquad \text{by 3.18}
\end{aligned}
$$

$$(3.41)$$

Summarising, we can say that

$$
\langle \psi | \psi \rangle = 1, \quad \textit{for all time } t \tag{3.42}
$$

and so

Probability is conserved

$$
\frac{\partial}{\partial t} \langle \psi | \psi \rangle = 0 \tag{3.43}
$$

meaning that probability is indeed conserved. [2]

§ 5. The expectation value of an observable A

---

[2] Another proof of probability conservation, which we just provide as an extended footnote since we don't want to have too much material, goes as follows. Denote the probability density by ρ where $\rho(x, y, z, t) = \overline{\psi(x, y, z, t)}\psi(x, y, z, t)$, then, taking the time derivative under the integral sign, we have,

$$
\frac{\partial}{\partial t} \langle \psi | \psi \rangle = \int \frac{\partial \rho(x, y, z, t)}{\partial t}\, dx\, dy\, dz = \int \overline{\frac{\partial \psi}{\partial t}}\, \psi\, dx\, dy\, dz + \int \overline{\psi}\, \frac{\partial \psi}{\partial t}\, dx\, dy\, dz \tag{3.44}
$$

In quantum mechanics the nearest thing to the average of an an observable A is the quantity

$$\langle\psi|A\psi\rangle \tag{3.50}$$

which is called the *expectation value* of A in the state ψ and is also denoted by $\langle A\rangle_\psi$ or even just $\langle A\rangle$ when the state ψ is understood.

Since, as we quoted in 2.48, another notation for the quantity $\langle u|Mv\rangle$ is $\langle u|\,M\,|v\rangle$, then

and the Schrödinger equation says that

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \Rightarrow \begin{cases} \dfrac{\partial\psi}{\partial t} = \left(\dfrac{1}{i\hbar}\right)\left(\dfrac{-\hbar^2}{2m}\nabla^2\psi + V\psi\right) \\[3mm] \dfrac{\partial\overline\psi}{\partial t} = -\left(\dfrac{1}{i\hbar}\right)\left(\dfrac{-\hbar^2}{2m}\nabla^2\overline\psi + V\overline\psi\right) \end{cases} \tag{3.45}$$

remembering that $\overline V = V$ since V is real. Now if we substitute for $\partial\psi/\partial t$ and $\partial\overline\psi/\partial t$ from 3.45 into 3.44 we find that

$$\int \frac{\partial\rho(x,y,z,t)}{\partial t}\,dx\,dy\,dz = \left(\frac{1}{i\hbar}\right)\int\left\{-\left(\frac{-\hbar^2}{2m}\nabla^2\overline\psi + V\overline\psi\right)\psi + \overline\psi\left(\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi\right)\right\}dx\,dy\,dz$$

$$= -\int\frac{i\hbar}{2m}\left(\psi\nabla^2\overline\psi - \overline\psi\nabla^2\psi\right)dx\,dy\,dz \tag{3.46}$$

$$= -\int\nabla\cdot\mathbf{j}\,dx\,dy\,dz, \qquad \text{where } \mathbf{j} = \frac{i\hbar}{2m}\left(\psi\nabla\overline\psi - \overline\psi\nabla\psi\right)$$

and we have used the fact that $\nabla\cdot(f\nabla g) = \nabla f\cdot\nabla g + f\nabla^2 g$ twice in the last line. Now by thinking of three dimensional space $\mathbf{R}^3$ as being the interior of a sphere S_R in the limit as the radius $R\longrightarrow\infty$, Gauss's divergence theorem tells us that

$$\int\nabla\cdot\mathbf{j}\,dx\,dy\,dz = \lim_{R\to\infty}\int_{S_R}\mathbf{j}\cdot d\mathbf{S}$$

$$= 0, \qquad \text{if } \psi\to 0 \text{ fast enough at infinity (which is the case to maintain } \langle\psi|\psi\rangle < \infty) \tag{3.47}$$

and so we have our sought after result that

$$\frac{\partial}{\partial t}\langle\psi|\psi\rangle = \int\frac{\partial\rho(x,y,z,t)}{\partial t}\,dx\,dy\,dz = 0 \tag{3.48}$$

Note that, during this proof, we have deduced that the probability density $\rho = \overline\psi\psi$ and the probability current $\mathbf{j} = i\hbar/2m(\psi\nabla\overline\psi - \overline\psi\nabla\psi)$ satisfy the (conservation) equation

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0 \tag{3.49}$$

an equation which is familiar in both electromagnetic theory—where ρ is the charge density and $\mathbf{j}$ the electric current density—and in fluid dynamics—where ρ is the density of the fluid and $\mathbf{j} = \rho\mathbf{v}$, $\mathbf{v}$ being the fluid velocity.

the expectation value of A in the state ψ can also be written as

$$\langle \psi | A | \psi \rangle \tag{3.51}$$

Summarising all four notations below means the same thing: the expectation of A in the state ψ

Four nota-
tions for the
same thing

$$\langle A \rangle_\psi = \langle \psi | A \psi \rangle = \langle \psi | A | \psi \rangle = \langle A \rangle \tag{3.52}$$

Expectations
as averages

The expectation value $\langle \psi | A \psi \rangle$ should be regarded loosely as the *average* of the operator A in the state ψ in the sense that it is the average value of A after a large number of measurements all described by the same wave function. For example, the expectation value of position of the electron in the ground state of the hydrogen atom is the average value you would expect to obtain from making position measurements of the ground state for a large number of hydrogen atoms.

Note that, because all observables A are self-adjoint operators, the expectation $\langle \psi | A \psi \rangle$ is always a real number: one has

Expectations
are always
real

$$\overline{\langle \psi | A \psi \rangle} = \langle A\psi | \psi \rangle, \quad \text{since } \langle v | u \rangle = \overline{\langle u | v \rangle}$$
$$= \langle \psi | A \psi \rangle, \quad \text{since } A \text{ is self-adjoint} \tag{3.53}$$

confirming that $\langle \psi | A \psi \rangle$ is indeed always real.

The reasonableness of this definition of expectation value can be seen by examining a few examples.

Example *Expectation when ψ is an eigenstate*

First of all if the state ψ of system is already an eigenstate of A with eigenvalue λ, say—i.e. one has

$$A\psi = \lambda\psi \tag{3.54}$$

then the expectation of A in the state ψ is just then the eigenvalue

The expec-
tation of A
in an eigen-
state is just
the corre-
sponding
eigenvalue
λ—i.e. the
measured
value of A

$$\lambda \tag{3.55}$$

since one immediately finds that

$$\langle \psi | A \psi \rangle = \lambda \langle \psi | \psi \rangle$$
$$= \lambda, \quad \text{since } \langle \psi | \psi \rangle = 1 \tag{3.56}$$

So, for this example, the expectation of A in the state ψ is just the value we get on measuring A.

Example *Expectation can be an arithmetic mean*

For our next example we take a simple quantum system with a *finite* number of energy eigenstates $\{\psi_1, \psi_2, \ldots \psi_n\}$ which we take to be an orthonormal basis. Then if the system is in a state ψ which is an *equally distributed* linear combination of these n eigenstates one has

$$\psi = \frac{\psi_1}{\sqrt{n}} + \frac{\psi_2}{\sqrt{n}} + \cdots + \frac{\psi_n}{\sqrt{n}} = \sum_{i=1}^{n} \frac{\psi_i}{\sqrt{n}} \tag{3.57}$$

where the denominator factors $\sqrt{n}$ ensure that $\langle \psi | \psi \rangle = 1$—i.e. that ψ is normalised to unity. Now one readily calculates that the expectation of the energy E in the state ψ i.e. the quantity

$$\langle \psi | H \psi \rangle \tag{3.58}$$

is given by

In this example the expectation value is an arithmetic mean

$$\begin{aligned}
\langle \psi | H \psi \rangle &= \frac{1}{n} \sum_{i,j=1}^{n} \langle \psi_i | H \psi_j \rangle \\
&= \frac{1}{n} \sum_{i,j=1}^{n} E_j \langle \psi_i | \psi_j \rangle = \frac{1}{n} \sum_{i,j=1}^{n} E_j \, \delta_{ij} \\
&= \frac{1}{n} \sum_{i=1}^{n} E_i = \frac{E_1 + E_2 + \cdots + E_n}{n}
\end{aligned} \tag{3.59}$$

which we recognise as the ordinary *arithmetic mean* of the energy eigenvalues. Thus in this simple case of the state ψ being equally distributed among a finite number of eigenstates we see that the expectation value corresponds to the arithmetic mean.

Example *Expectation: the most general situation*

Moving now to the general case let us take a physical system with an infinite orthonormal basis of eigenstates ϕ_i, say, of some observable A which is in a completely general state ψ. So one has

$$\text{Basis of } \mathcal{H} = \{\phi_1, \phi_2, \ldots\}, \quad \text{and } A\phi_i = \lambda_i \phi_i, \quad (\lambda_i \text{ are the eigenvalues of } A)$$

$$\psi = \sum_{i=1}^{\infty} \alpha_i \phi_i, \quad (\text{remember } \langle \psi | \psi \rangle = 1) \tag{3.60}$$

With this information we find that

$$\begin{aligned}
\langle \psi | A \psi \rangle &= \sum_{i,j=1}^{\infty} \bar{\alpha}_i \alpha_j \langle \phi_i | A \phi_j \rangle \\
&= \sum_{i,j=1}^{\infty} \lambda_j \bar{\alpha}_i \alpha_j \langle \phi_i | \phi_j \rangle = \sum_{i,j=1}^{\infty} \lambda_j \bar{\alpha}_i \alpha_j \, \delta_{ij} \\
\Rightarrow \langle \psi | A \psi \rangle &= \sum_{i=1}^{\infty} \lambda_i |\alpha_i|^2
\end{aligned} \tag{3.61}$$

The general meaning of $\langle \psi | A \psi \rangle$.

In other words the expectation value of A in the state ψ is the sum over all possibilities of the probability the system being in the state ϕ_i (i.e. the number $|\alpha_i|^2$) times the value of the A in that state (i.e. the number λ_i).

This is a perfect definition and indeed is precisely the definition used by probability theorists for the definition of the expectation value of a random variable A.

§ 6. Position and momentum

For simplicity let us consider the case of a single particle in one space dimension whose mass is m. Let the particle be in a state whose wave function is

$$\psi(x,t) \tag{3.62}$$

Momentum is now associated to an operator p where [3]

$$p = -i\hbar \frac{d}{dx} \tag{3.63}$$

Position is taken to the operator $\hat{x}$ given by simply multiplying ψ by the coordinate x in other words we have

$$\hat{x}\psi = x\psi \tag{3.64}$$

Note carefully that, because the position operator is so simple, we find it convenient to discard the 'hat' over the x in $\hat{x}$ and just write x for the position operator, no confusion should result.

The position and momentum operators x and p *do not commute*: for we see that, if we select any state ψ then

$$p\psi = -i\hbar \frac{d\psi}{dx}$$
$$\Rightarrow xp\psi = -ix\hbar \frac{d\psi}{dx}$$

But
$$x\psi = x\psi, \quad \text{(nothing much happened!)} \tag{3.65}$$
$$\Rightarrow px\psi = -i\hbar \frac{d(x\psi)}{dx}$$
$$= -ix\hbar \frac{d\psi}{dx} - i\hbar\psi$$

So
$$xp \neq px \tag{3.66}$$

Instead we find that

$$(xp - px)\psi = -ix\hbar \frac{d\psi}{dx} + ix\hbar \frac{d\psi}{dx} + i\hbar\psi$$
$$\Rightarrow (xp - px)\psi = i\hbar\psi \tag{3.67}$$

which, using the commutator notation $[x,p] = xp - px$, we write as

$$[x,p] = i\hbar I \tag{3.68}$$

---

[3] We shall sometimes write p_x for $-i\hbar(\partial/\partial x)$ instead of p: for example when we need to distinguish between the other momentum components $p_y = -i\hbar(\partial/\partial y)$ and $p_z = -i\hbar(\partial/\partial z)$.

where I denotes the identity operator or matrix.

It is now important to note that the commutation relation for $[x, p]$ *cannot be satisfied* by matrices or operators in ordinary *finite dimensional* vector spaces: one needs to go to infinite dimensions and use Hilbert spaces $\mathcal{H}$.

An infinite dimensional space is needed for the commutation relation to be valid.

This is because if we take the trace of both sides of the commutation relation 3.68 above we get

$$\text{tr}\left([x, p]\right) = i\hbar \, \text{tr}\left(I\right) \qquad (3.69)$$

Now if the operators x and p are matrices on a finite dimensional vector space of dimension n then we immediately know from 2.26 above that the trace of any commutator is zero so that

$$\text{tr}\left([x, p]\right) = 0 \qquad (3.70)$$

However we also know that, in n dimensions,

$$\text{tr}\left(I\right) = n \qquad (3.71)$$

Hence 3.69 states that

$$0 = i\hbar \, n \qquad (3.72)$$

which is patently *false*.

The resolution of this contradiction is that x and p act as matrices on a Hilbert space $\mathcal{H}$ which is *infinite dimensional*. In $\mathcal{H}$, the Hilbert space, $\text{tr}\left([A, B]\right)$ is *not always zero*: it can have any value, even infinity as is the case for $\text{tr}\left([x, p]\right)$.

$[x, p] = i\hbar$ only possible if x and p act as infinite dimensional matrices

This means that if we redo the above calculation then 3.72 changes to the *non-contradictory* statement $\infty = \infty$. Do not worry too much about the the details of how this contradiction is resolved: the main point is to realise that x and p cannot be matrices in finite dimension but must act in infinite dimensions.

§ 7. The Heisenberg uncertainty principle
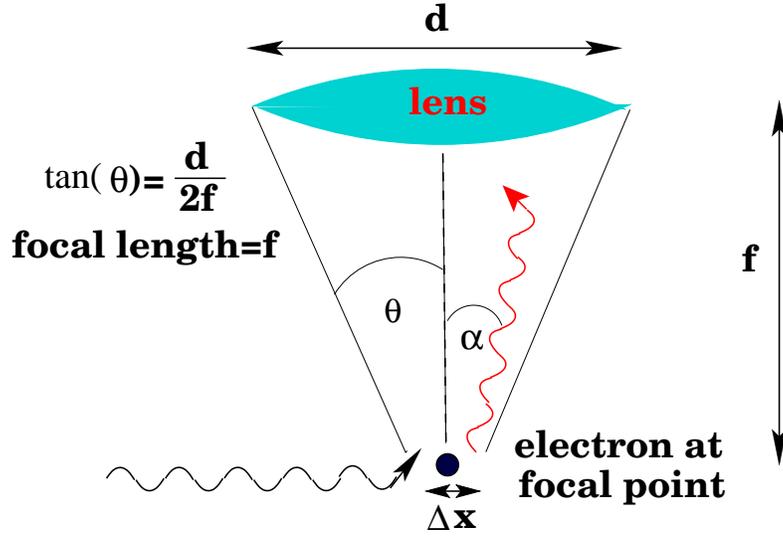
The uncertainty principle

Heisenberg is responsible for what is called the *Heisenberg uncertainty principle* which points out that it is impossible to *simultaneously measure* some physical quantities with *arbitrary accuracy*.

We now describe the most well known application of the uncertainty principle which places fundamental limits on the accuracy of simultaneous measurements of the position and momentum of a particle.

Planck's constant picks out the quantum system

The main idea is that to measure anything in a physical system means to disturb the system slightly thus changing the values the quantities being measured. Of course this idea applies both to classical and quantum systems: but in classical systems one can keep on making the errors of (simultaneous) measurements smaller and smaller; whereas we shall see that in *quantum systems* (the non-zero value of) Planck's constant $\hbar$ *prevents the errors from being made (simultaneously) arbitrarily small.*

Fig. 5: The Heisenberg γ-ray microscope

It is helpful to use Heisenberg's idealised description[4] of measuring the position of a particle—we shall take it to be an electron—using a microscope.

In figure 5 we show an electron, positioned at the focal point of a microscope[5], being hit by a photon which is then scattered back to the lens—rather than being scattered so that it misses the lens: the electron is therefore observed by the person looking through the lens.

Standard physical optics says that diffraction limits the smallest object that can be resolved by a microscope to have size s, and this size is determined by the relation

$$2s\sin(\theta) = \lambda \tag{3.73}$$

where λ is the wavelength of the radiation entering the microscope, and θ is its angular aperture as shown in figure 5.

This size s is therefore an uncertainty Δx in the position of the object being observed so, using the notation Δx rather than s, we have

$$2\Delta x\sin(\theta) = \lambda$$
$$\Rightarrow \Delta x = \frac{\lambda}{2\sin(\theta)} \tag{3.74}$$

Let the electron be at rest and the incoming photon be travelling parallel to the x-axis with wavelength λ so that it has x-momentum

$$\frac{h}{\lambda} \tag{3.75}$$

---

[4] These idealised descriptions, which are not accounts of actual experiments, are often called *thought experiments*. Such experiments are invariably backed up by real experiments carried out in a laboratory.

[5] An electron is so small that it would have to be a γ-ray microscope to be able to resolve small enough distances. So Heisenberg is being rather idealised here: that is why we call this a thought experiment.

Hence initially one has

$$p_{electron} + p_{photon} = 0 + \frac{h}{\lambda} \tag{3.76}$$

After the scattering some momentum is imparted to the electron so that the total momentum in the x-direction is now

$$p_x + \frac{h}{\lambda}\sin(\alpha) \tag{3.77}$$

where α—cf. figure 5—is the inclination of the scattered photon to the vertical. Momentum conservation then says that the total initial and final momentum are equal so we have

$$p_x + \frac{h}{\lambda}\sin(\alpha) = \frac{h}{\lambda}$$
$$\Rightarrow p_x = \frac{h}{\lambda} - \frac{h}{\lambda}\sin(\alpha) \tag{3.78}$$

However, for the electron to be observed, the angle α of the scattered photon must lie between $\mp\theta$—i.e.

$$-\theta \leq \alpha \leq \theta \tag{3.79}$$

which means that the electron momentum p_x lies between

$$\frac{h}{\lambda} - \frac{h}{\lambda}\sin(\theta) \text{ and } \frac{h}{\lambda} - \frac{h}{\lambda}\sin(-\theta) \tag{3.80}$$

Hence, subtracting these two quantities, we see that there is an uncertainty, Δp_x, in p_x given by

$$\Delta p_x = \frac{2h\sin(\theta)}{\lambda} \tag{3.81}$$

Now if we multiply Δp_x by Δx using 3.74 we find that

$$\Delta x \, \Delta p_x = \frac{\lambda}{2\sin(\theta)} \frac{2h\sin(\theta)}{\lambda} \tag{3.82}$$

which means that we have obtained the celebrated result that

$$\Delta x \, \Delta p_x = h \tag{3.83}$$

We see from this result that we *cannot* make Δx and Δp_x *simultaneously* very small—for example they cannot both be smaller than $\sqrt{h}$: we can make one of them very small but then the other has to become large so as to satisfy eq. 3.83.

Limitations on simultaneous measurement of position and momentum.

Since Planck's constant h determines the limits on the accuracy of the measurements, then the smallness [6] of h explains why this limit was never noticed before the advent of quantum mechanics. This smallness also means that we don't have to worry about the uncertainty principle in many measurement situations.

---

[6] Remember the minute value of Planck's constant: $h = 6.6260638 \times 10^{-34}\,Js$.

Actually, as we may show later if we have time, one can improve[7] on our result $\Delta x \, \Delta p_x = h$: it turns out that h may be replaced by $h/(4\pi) = \hbar/2$. Using a simple calculation with wave functions, standard deviations and the fact that $[x, p_x] = i\hbar I$, one can show that Δx and Δp_x obey the inequality

$$\Delta x \, \Delta p_x \geq \frac{\hbar}{2} \tag{3.84}$$

and this result is the best possible in the sense that there exist wave functions ψ for which 3.84 becomes an *equality*.

Still more is true: if we take any two observables A and B with commutator $[A, B]$ one can show that the uncertainties $\Delta_\psi A$ and $\Delta_\psi B$ of A and B, in any state ψ, obey the inequality

$$\Delta_\psi A \, \Delta_\psi B \geq \frac{\langle \psi | \, [A, B] \, | \psi \rangle}{2} \tag{3.85}$$

where the uncertainty $\Delta_\psi A$ of an observable A in a state ψ has been defined to be its *standard deviation*[8] in the state ψ—i.e. we have defined $\Delta_\psi A$ by writing

$$\Delta_\psi A = \sqrt{\langle \psi | \, A^2 \, | \psi \rangle - |\, \langle \psi | \, A \, | \psi \rangle \, |^2} \tag{3.86}$$

and we call this (slightly loosely) a standard deviation because we think of the expectation values $\langle \psi | \, A^2 \, | \psi \rangle$ and $\langle \psi | \, A \, | \psi \rangle$ as the averages of those quantities—cf. the definition 3.50 above of expectation values if your memory needs refreshing—incidentally, purely on a point of terminology, the quantity $\Delta_\psi^2 A = \langle \psi | \, A^2 \, | \psi \rangle - |\, \langle \psi | \, A \, | \psi \rangle \, |^2$ is called the *variance* but we shall not need to make use of this term.

Note carefully that, if ψ is eigenstate of A—or equivalently of B—then the uncertainty relation 3.85 just reduces to the trivial statement[9]

$$0 \geq 0 \tag{3.88}$$

and so we learn nothing of any value in the case where ψ is an eigenstate of A or B.

Next notice that if the observables A and B *commute* so that

$$[A, B] = 0 \tag{3.89}$$

---

[7] Note that a shortcoming in our derivation is that we have not taken in to account the fact that the photon loses some energy to the electron on being scattered—cf. a description of what is known as *Compton scattering*. Since $E = h\nu$ this means that the scattered photon has a smaller frequency and hence a *larger wavelength* than that of the incident photon. Hence the equation $\Delta p_x = 2h \sin(\theta)/\lambda$ should be replaced by $\Delta p_x = 2h \sin(\theta)/\lambda'$ where $\lambda' > \lambda$; this in turn means that Δp_x is *smaller* than the value quoted above and so the product $\Delta x \, \Delta p_x$ can be made a bit smaller than h as we have just pointed out.

[8] In Hannabuss' book $\Delta_\psi A$ is called the *dispersion* rather than the standard deviation.

[9] The reader should easily be able to see this by checking that

$$A \, |\psi\rangle = \lambda \, |\psi\rangle \Rightarrow \begin{cases} \Delta_\psi A = 0 \\ \langle \psi | \, [A, B] \, | \psi \rangle = 0 \end{cases} \tag{3.87}$$

Don't forget here, that A and B, being observables are self-adjoint operators.

then the inequality reduces to just

$$\Delta_\psi A \, \Delta_\psi B \geq 0 \tag{3.90}$$

which just says that the product of the two non-negative numbers $\Delta_\psi A$ and $\Delta_\psi B$ is non-negative: something we knew without doing any manipulations with them; in addition we see that $\Delta_\psi A \, \Delta_\psi B \geq 0$ also permits

$$\Delta_\psi A = \Delta_\psi B = 0 \tag{3.91}$$

and precisely this—i.e. $\Delta_\psi A = \Delta_\psi B = 0$—happens when ψ is an eigenstate of either A and B as takes only a moment to verify.

Hence the uncertainty principle is only a constraint (on the accuracy of simultaneous measurement) of pairs of *non-commuting* observables.

The uncertainty principle says nothing important about $\Delta_\psi A$ and $\Delta_\psi B$ when $[A, B] = 0$

CHAPTER IV

The harmonic oscillator

§ 1. Introduction

W e are now going to solve the Schrödinger equation for a very important and well known example: the harmonic oscillator. We shall work in one space dimension so that our wave functions will be of the form

$$\psi(x,t) \tag{4.1}$$

with no y or z dependence.

To have a harmonic oscillator [1] means that a particle of mass m is subject to the potential V where

The potential for a harmonic oscillator

$$V = \frac{1}{2}m\omega^2 x^2 \tag{4.4}$$

In complete generality the Hamiltonian H is given by

$$H = \frac{\mathbf{p}^2}{2m} + V \tag{4.5}$$

$$(\mathbf{p} = -i\hbar\nabla)$$

However, in one dimension,

$$-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{4.6}$$

---

[1] Recall that in *classical mechanics* a harmonically oscillating particle has energy

$$T + V = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}m\omega^2 x^2 \tag{4.2}$$

Thus its equation of motion is

$$m\frac{d^2x}{dt^2} = -m\omega^2 x$$

$$\Rightarrow \frac{d^2x}{dt^2} + \omega^2 x = 0 \tag{4.3}$$

and this is, of course, the extremely well known SHM equation for an oscillation of angular frequency ω.

Hence the *harmonic oscillator Hamiltonian* H is given by

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V$$
$$= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

$$(4.7)$$

We would like to find the possible energies E_n, say, and their associated eigenfunctions ψ_n, of this quantum system. This means that our task is to solve the time independent Schrödinger equation with H given by 4.7, i.e. to solve the equation

$$H\psi_n = E_n\psi_n \tag{4.8}$$

which, on using the explicit form of the Hamiltonian, becomes the differential equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi_n = E_n\psi_n \tag{4.9}$$

We can solve this differential equation directly by standard methods [2] but there is also a very beautiful, and simple, algebraic solution method using what are called *creation and*

---

[2] The standard method of solving 4.9 is to extract a factor of function e^{-ax^2} from $\psi_n(x)$ by writing

$$\psi_n(x) = e^{-ax^2}\phi_n(x) \tag{4.10}$$

and substituting this expression into 4.9. If $a = m\omega/(2\hbar)$ the equation, for $\phi_n(x)$, that results is

$$\frac{d^2\phi_n}{dx^2} - \frac{2m\omega}{\hbar}x\frac{d\phi_n}{dx} + \left(\frac{2mE_n}{\hbar^2} - \frac{m\omega}{\hbar}\right)\phi_n = 0 \tag{4.11}$$

Finally if we change variable from x to $y = cx$ where $c = \sqrt{2m\omega/\hbar}$ then we obtain the equation

$$\frac{d^2\phi_n(y)}{dy^2} - y\frac{d\phi_n(y)}{dx} + \left(\frac{E_n}{\hbar\omega} - \frac{1}{2}\right)\phi_n(y) = 0 \tag{4.12}$$

which we recognise as Hermite's equation

$$\frac{d^2 H_\lambda(y)}{dy^2} - y\frac{dH_\lambda(y)}{dy} + \lambda H_\lambda(y) = 0 \tag{4.13}$$

with $\lambda = \frac{E_n}{\hbar\omega} - \frac{1}{2}$. But the $H_\lambda(y)$ are polynomials of degree λ when $\lambda = 0, 1, 2, \ldots$ and, writing $\lambda = n$ means that we have

$$\frac{E_n}{\hbar\omega} - \frac{1}{2} = n$$
$$\Rightarrow E_n = (n + 1/2)\hbar\omega, \quad n = 0, 1, 2, \ldots$$

$$(4.14)$$

and these are the quantised energies of the harmonic oscillator that we shall derive much more painlessly by algebraic methods below—cf. 4.52—we see too that the energy eigenfunctions $\psi_n(x)$ are given by

$$\psi_n(x) = e^{-ax^2}H_n(cx), \quad \text{where } a = \frac{m\omega}{2\hbar}, \ c = \sqrt{\frac{2m\omega}{\hbar}} \tag{4.15}$$

which we can also derive by our algebraic methods—cf. 4.60.

annihilation operators. We shall use this latter method and turn to it in the section that follows.

§ 2. Creation and annihilation operators

Let A and B be two operators; we begin by observing the elementary fact that

$$
\begin{aligned}
(A + iB)(A - iB) &= A^2 + (iB)(-iB) + iBA - iAB \\
&= A^2 + B^2 - i[A, B] \\
\Rightarrow A^2 + B^2 &= (A + iB)(A - iB) + i[A, B]
\end{aligned}
\tag{4.16}
$$

Now turn to the harmonic oscillator Hamiltonian

$$
H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2
\tag{4.17}
$$

and choose

$$
A = -i\hbar\frac{d}{dx}, \quad B = m\omega x
\tag{4.18}
$$

so that H is then given by

$$
H = \frac{1}{2m}(A^2 + B^2)
\tag{4.19}
$$

and now if we use our 'elementary fact' 4.16 above, and remember that the momentum operator p is given by $p = -i\hbar(d/dx)$, we find that H can be written as

$$
\begin{aligned}
H &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 = \frac{1}{2m}\left(-\hbar^2\frac{d^2}{dx^2} + m^2\omega^2 x^2\right) \\
&= \frac{1}{2m}\left\{\left(-i\hbar\frac{d}{dx} + im\omega x\right)\left(-i\hbar\frac{d}{dx} - im\omega x\right) + \left[-i\hbar\frac{d}{dx}, im\omega x\right]\right\}
\end{aligned}
\tag{4.20}
$$

$$
= \frac{1}{2m}a_+a_- + \frac{i\omega}{2}[p, x], \quad \text{where} \quad \begin{cases} p = -i\hbar\dfrac{d}{dx} \\ a_+ = p + im\omega x \\ a_- = p - im\omega x, \end{cases} \quad \text{(notice that } a_+ = a_-^\dagger)
$$

But we know that the commutation relation for x and p is that

$$
[x, p] = i\hbar I
\tag{4.21}
$$

and so, since $[x, p] = -[p, x]$, our final expression for H is that

$$
H = \frac{1}{2m}a_+a_- + \frac{\hbar\omega}{2}I
\tag{4.22}
$$

It is a_+ and a_- that are called *creation and annihilation operators*; the reason for this nomenclature will become clear in §3 below.

Next we compute the commutator of a_- and a_+ and find that

$$
\begin{aligned}
[a_-, a_+] &= [p - im\omega x, \, p + im\omega x] \\
&= [p,p] - im\omega\,[x,p] + im\omega\,[p,x] + m^2\omega^2[x,x] \\
&= -2im\omega\,[x,p] \\
&= 2m\omega\hbar I, \qquad \text{using 4.21}
\end{aligned}
\tag{4.23}
$$

We shall also need below the commutator of H and a_+ so we calculate it now. We have

$$
\begin{aligned}
[H, a_+] &= \left[\left(\frac{1}{2m}a_+a_- + \frac{\hbar\omega}{2}I\right), a_+\right] \\
&= \frac{1}{2m}[a_+a_-, a_+] + 0 \\
&= \frac{1}{2m}(a_+a_-a_+ - a_+a_+a_-)
\end{aligned}
\tag{4.24}
$$

Now note that for any operators P and Q one has

$$
PQ = QP + [P, Q]
\tag{4.25}
$$

and therefore, with $P = a_-$ and $Q = a_+$, one has

$$
\begin{aligned}
a_-a_+ &= a_+a_- + [a_-, a_+] \\
\Rightarrow a_-a_+ &= a_+a_- + 2m\omega\hbar I, \qquad \text{using 4.23}
\end{aligned}
\tag{4.26}
$$

Now substitute for a_-a_+ from 4.26 into 4.24 yielding

$$
\begin{aligned}
[H, a_+] &= \frac{1}{2m}\left\{a_+(a_+a_- + 2m\omega\hbar I) - a_+a_+a_-\right\} \\
\Rightarrow [H, a_+] &= \hbar\omega\, a_+
\end{aligned}
\tag{4.27}
$$

Note that $[H, a_+] = \hbar\omega\, a_+$

which is the result we shall use below.

If we repeat the previous calculation with a_- instead of a_+ then we obtain the similar result

$$
[H, a_-] = -\hbar\omega\, a_-
\tag{4.28}
$$

Also note that $[H, a_-] = -\hbar\omega\, a_-$

a result we shall also use below.

§ 3. The harmonic oscillator spectrum

We are now ready to calculate the eigenvalues of the harmonic oscillator Hamiltonian: this is also called *the harmonic oscillator spectrum*.

So we are going to find those eigenvalues E_n and corresponding eigenfunctions ψ_n that satisfy

$$
H\,|\psi_n\rangle = E_n\,|\psi_n\rangle
\tag{4.29}
$$

The word spectrum means the set of eigenvalues

Note that we have used the Hilbert space vector notation to make the reader familiar with its use.

The first point to note is that if $|\psi_n\rangle$ is an eigenvector of H, then so is the vector

$$a_+ |\psi_n\rangle \tag{4.30}$$

This is because

$$
\begin{aligned}
Ha_+ |\psi_n\rangle &= (a_+ H + [H, a_+]) |\psi_n\rangle, \quad \text{using 4.25 with } P = H \text{ and } Q = a_+ \\
&= (a_+ H + \hbar\omega a_+) |\psi_n\rangle, \quad \text{using 4.27} \\
&= E_n a_+ |\psi_n\rangle + \hbar\omega a_+ |\psi_n\rangle, \quad \text{using 4.29} \\
&= (E_n + \hbar\omega) a_+ |\psi_n\rangle
\end{aligned}
\tag{4.31}
$$

Summarising, we have found that

$$
\begin{aligned}
H |\phi\rangle &= (E_n + \hbar\omega) |\phi\rangle \\
\text{with } |\phi\rangle &= a_+ |\psi_n\rangle
\end{aligned}
\tag{4.32}
$$

which means that $a_+ |\psi_n\rangle$ is an eigenvector of the Hamiltonian H with eigenvalue

$$E_n + \hbar\omega \tag{4.33}$$

One says that a_+ has created, from $|\psi_n\rangle$—whose energy is E_n—the state $a_+ |\psi_n\rangle$ with the *higher energy* $E_n + \hbar\omega$—this is why a_+ is called a *creation operator*.

The term creation operator explained

On the other hand if we replace a_+ by a_- in the argument begun at 4.30 above and instead consider the state

$$a_- |\psi_n\rangle \tag{4.34}$$

then a repetition of the above argument using the expression 4.28 for $[H, a_-]$ instead of that for $[H, a_+]$ shows that

$$
\begin{aligned}
H |\phi\rangle &= (E_n - \hbar\omega) |\phi\rangle \\
\text{with } |\phi\rangle &= a_- |\psi_n\rangle
\end{aligned}
\tag{4.35}
$$

In other words $a_- |\psi_n\rangle$ is an eigenvector of the Hamiltonian H with eigenvalue

$$E_n - \hbar\omega \tag{4.36}$$

So one now says that a_- has destroyed the state $|\psi_n\rangle$—whose energy is E_n—and replaced it with the state $a_- |\psi_n\rangle$ with the *lower energy* $E_n - \hbar\omega$—this is why a_- is called an *annihilation operator*.

The term annihilation operator explained

It is clear that one can keep on applying a_+ to a state $|\psi_n\rangle$ to *raise* its energy more and more or, conversely, one can keep on applying a_- to a state $|\psi_n\rangle$ to *lower* its energy more and more.

Fortunately, as we shall now go on to show, it turns out that *all the eigenstates* of the harmonic oscillator can be constructed by starting with any one eigenstate

$$|\psi_n\rangle \tag{4.37}$$

say, and successively applying a_+ and a_- to $|\psi_n\rangle$. In this way we obtain the entire harmonic oscillator spectrum of energies and their associated eigenstates.

To complete our construction of the harmonic oscillator spectrum we note that, so far, we have the following list of states and energies

State	Energy
$\vdots$	$\vdots$
$a_+^2 \,\|\psi_n\rangle$	$E_n + 2\hbar\omega$
$a_+ \,\|\psi_n\rangle$	$E_n + \hbar\omega$
$\|\psi_n\rangle$	E_n
$a_- \,\|\psi_n\rangle$	$E_n - \hbar\omega$
$a_-^2 \,\|\psi_n\rangle$	$E_n - 2\hbar\omega$
$\vdots$	$\vdots$

$$(4.38)$$

The key observation now is to realise that

$$H = \frac{\mathbf{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{4.39}$$

is a sum of the two *positive* operators $\mathbf{p}^2/(2m)$ and $m\omega^2 x^2/2$, hence all its eigenvalues must be *positive*. But, if N is large enough, then

$$E_n - N\hbar\omega \tag{4.40}$$

which is the energy of the state

$$a_-^N \,|\psi_n\rangle \tag{4.41}$$

will be negative. Hence, to prevent this happening, it must be that, for some value of N, the state $a_-^N \,|\psi_n\rangle$ vanishes—i.e. it is the zero vector: so let N be the first value of N for which

$$a_-^N \,|\psi_n\rangle = 0 \tag{4.42}$$

This means that choosing $|\phi\rangle$ to be given by

$$|\phi\rangle = a_-^{N-1} \,|\psi_n\rangle \tag{4.43}$$

we have

$$a_- \,|\phi\rangle = 0, \qquad (\text{but } |\phi\rangle \neq 0) \tag{4.44}$$

The state $|\phi\rangle$ is then the lowest energy state—or ground state—of the system since using a_- to lower its energy still more just gives the zero vector.

The term ground state introduced

We can easily compute the energy of the ground state $|\phi\rangle$ because 4.22 says that

$$H = \frac{1}{2m}a_+ a_- + \frac{\hbar\omega}{2}I \tag{4.45}$$

and so

$$H \ket{\phi} = \left(\frac{1}{2m} a_+ a_- + \frac{\hbar\omega}{2} I \right) \ket{\phi}$$

$$= \frac{1}{2m} a_+ a_- \ket{\phi} + \frac{\hbar\omega}{2} \ket{\phi} \tag{4.46}$$

$$= 0 + \frac{\hbar\omega}{2} \ket{\phi}, \qquad \text{since } a_- \ket{\phi} = 0$$

Hence

$$H \ket{\phi} = \frac{\hbar\omega}{2} \ket{\phi} \tag{4.47}$$

so that the ground state energy is $\hbar\omega/2$; and this is the lowest possible energy for the quantum mechanical harmonic oscillator.

Now we can get *all the energy eigenstates* of the harmonic oscillator by simply repeatedly applying a_+ to the ground state $\ket{\phi}$. Hence the tower of states 4.38 showing the harmonic oscillator spectrum has now become

The complete harmonic oscillator spectrum and its eigenstates

State	**Energy**
$\vdots$	$\vdots$
$a_+^n \ket{\phi}$	$(n + \frac{1}{2})\hbar\omega$
$\vdots$	$\vdots$
$a_+^2 \ket{\phi}$	$\frac{5}{2}\hbar\omega$
$a_+ \ket{\phi}$	$\frac{3}{2}\hbar\omega$
$\ket{\phi}$	$\frac{\hbar\omega}{2}$

$$\tag{4.48}$$

Hence the completely general energy eigenstate is just $a_+^n \ket{\phi}$ and it has energy $(n+1/2)\hbar\omega$. In sum we have

$$H a_+^n \ket{\phi} = (n + \frac{1}{2})\hbar\omega a_+^n \ket{\phi}, \qquad \text{for } n = 0, 1, 2, \ldots \tag{4.49}$$

We now introduce (as is the common practice) the notation $\ket{n}$ to denote the eigenstate $a_+^n \ket{\phi}$. That is we define $\ket{n}$ by writing

$$\ket{n} = a_+^n \ket{\phi}, \qquad \text{for } n = 0, 1, 2, \ldots \tag{4.50}$$

this means that 4.49 takes on the neater form

The harmonic oscillator spectrum again

$$H \ket{n} = (n + \frac{1}{2})\hbar\omega \ket{n}, \qquad \text{for } n = 0, 1, 2, \ldots \tag{4.51}$$

or, reintroducing the notation of E_n for the energy, one can write

$$H \ket{n} = E_n \ket{n}, \quad \text{with} \quad \begin{cases} E_n = (n + \frac{1}{2})\hbar\omega \\ n = 0, 1, 2, \ldots \end{cases} \tag{4.52}$$

and notice that, in this notation the ground state $\ket{\phi}$ corresponds to $\ket{0}$, in other words

$$\ket{0} = \ket{\phi} \tag{4.53}$$

It is also useful to remember that the equality $|n\rangle = a_+^n |0\rangle$ means that

$$a_+ |n\rangle = |n+1\rangle \tag{4.54}$$

§ 4. The harmonic oscillator eigenstates

Now that we have found all the eigenvalues of the harmonic oscillator Hamiltonian H we go on to find the corresponding eigenstates.

We can also easily give a completely explicit expression for the ground state[3] since 4.44 is simply a differential equation in disguise: writing $|\phi\rangle = \psi_0(x)$ and remembering that $a_- = p - im\omega x$ then 4.44 becomes the first order differential equation

$$(p - im\omega x)\psi_0(x) = 0$$
$$\text{i.e. } \left(-i\hbar\frac{d}{dx} - im\omega x\right)\psi_0(x) = 0$$
$$\Rightarrow \frac{d\psi_0(x)}{dx} = -\frac{m\omega}{\hbar}x\,\psi_0(x) \tag{4.55}$$
$$\Rightarrow \psi_0(x) = C_0 e^{-(m\omega x^2/2\hbar)}, \qquad \text{with } C_0 \text{ a constant}$$

The explicit ground state obtained using an algebraic method

The constant C_0 is fixed by imposing the standard normalisation requirement

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} \overline{\psi_0(x)}\psi_0(x)\,dx = 1$$
$$\Rightarrow |C_0|^2 \int_{-\infty}^{\infty} e^{-(m\omega x^2/\hbar)}\,dx = 1 \tag{4.56}$$
$$\Rightarrow |C_0|^2 \sqrt{\frac{\pi\hbar}{m\omega}} = 1, \qquad \text{using } \int_{-\infty}^{\infty} e^{-az^2}\,dz = \sqrt{\frac{\pi}{a}}$$

So $C_0 = (m\omega/\pi\hbar)^{1/4}$ and the correctly normalised harmonic oscillator ground state is given by

The ground state normalised to one

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-(m\omega x^2/2\hbar)} \tag{4.57}$$

and the fact that it is normalised to unity can now be compactly written as

$$\langle 0|0\rangle = 1 \tag{4.58}$$

Recall that we have an explicit algebraic formula for the eigenstates $|n\rangle$ which also can be made explicit in terms of x: since

$$\begin{cases} a_+ = -i\hbar\dfrac{d}{dx} + im\omega x \\ |0\rangle = \psi_0(x) = C_0\,e^{-(m\omega x^2/2\hbar)} \end{cases} \tag{4.59}$$

---

[3] Note that we find here precisely *one ground state*: since all higher energies can be pushed down to a ground state by a_- then the uniqueness of the ground state means that we have indeed found all the eigenvalues, together with their associated eigenstates, of the harmonic oscillator.

then these two formulae are

$$\textbf{The algebraic formula for } |n\rangle \quad \textbf{The } x\textbf{-space formula for } |n\rangle$$
$$|n\rangle = a_+^n |0\rangle \qquad\qquad |n\rangle = \left(-i\hbar \tfrac{d}{dx} + im\omega x\right)^n \psi_0(x) \qquad (4.60)$$

Using the x-space formula given in 4.60 leads very quickly to precise expressions for the wave functions $|n\rangle$. We illustrate this by calculating $|n\rangle$ for a few values of n:

The har-monic oscil-lator energy eigenstates

State	Expression
$|0\rangle$	$C_0\, e^{-(m\omega x^2/2\hbar)}$
$|1\rangle$	$(-i\hbar\dfrac{d}{dx} + im\omega x)\,|0\rangle$
	$= \left(\dfrac{2i\hbar m\omega x}{2\hbar} + im\omega x\right) C_0\, e^{-(m\omega x^2/2\hbar)}$
	$= 2im\omega C_0 x e^{-(m\omega x^2/2\hbar)}$
$|2\rangle$	$(-i\hbar\dfrac{d}{dx} + im\omega x)^2\,|0\rangle$
	$= (-i\hbar\dfrac{d}{dx} + im\omega x)\,|1\rangle$
	$= 2im\omega C_0(-i\hbar\dfrac{d}{dx} + im\omega x)x e^{-(m\omega x^2/2\hbar)}$
	$= C_0(2m\omega\hbar - 4m^2\omega^2 x^2)e^{-(m\omega x^2/2\hbar)}$
$|3\rangle$	$(-i\hbar\dfrac{d}{dx} + im\omega x)^3\,|0\rangle$
	$= (-i\hbar\dfrac{d}{dx} + im\omega x)\,|2\rangle$
	$= C_0(12im^2\omega^2\hbar x - 8im^3\omega^3 x^3)e^{-(m\omega x^2/2\hbar)}$

(4.61)

and so on. Recall, too, that $C_0 = (m\omega/\pi\hbar)^{1/4}$, cf. 4.57.

Finally we shall multiply these states $|n\rangle$ by an appropriate constant to make sure that they are normalised to unity. This can be achieved algebraically, using induction, as follows: we start with 4.22 which said that

$$H = \frac{1}{2m}a_+ a_- + \frac{\hbar\omega}{2}I \qquad (4.62)$$

But

$$a_- a_+ = a_+ a_- + [a_-, a_+]$$
$$= a_+ a_- + 2m\omega\hbar I, \qquad \text{using } [a_-, a_+] = 2m\omega\hbar I \quad (\text{cf. } 4.23) \qquad (4.63)$$
$$\Rightarrow a_+ a_- = a_- a_+ - 2m\omega\hbar I$$

Now if we substitute for $a_+ a_-$ from 4.63 into 4.62 we find that

$$H = \frac{1}{2m}a_- a_+ - \omega\hbar I + \frac{\hbar\omega}{2}I$$
$$= \frac{1}{2m}a_- a_+ - \frac{\hbar\omega}{2}I \qquad (4.64)$$
$$\Rightarrow a_- a_+ = 2m\left(H + \frac{\hbar\omega}{2}I\right)$$

Now consider the normalisation of the state $|n\rangle$. We have [4]

$$
\begin{aligned}
|n\rangle &= a_+ |n-1\rangle \\
\Rightarrow \langle n|n\rangle &= \langle n-1| \, a_- a_+ \, |n-1\rangle \\
&= 2m \langle n-1| \, (H + \frac{\hbar\omega}{2} I) \, |n-1\rangle, \qquad \text{using 4.64} \\
&= 2m \langle n-1| \, H \, |n-1\rangle + \hbar m\omega \langle n-1|n-1\rangle \\
&= 2m(n-\tfrac{1}{2})\hbar\omega \langle n-1|n-1\rangle + \hbar m\omega \langle n-1|n-1\rangle \\
&\left(\text{since } H\,|n-1\rangle = (n-\tfrac{1}{2})\hbar\omega \, |n-1\rangle, \ (\text{cf. } 4.51)\right) \\
&= 2m\hbar\omega n \langle n-1|n-1\rangle
\end{aligned}
\tag{4.66}
$$

In sum we have obtained the induction step that we wanted and it says simply that

$$
\langle n|n\rangle = 2m\hbar\omega n \langle n-1|n-1\rangle \tag{4.67}
$$

and so, by induction on n, we deduce that

$$
\begin{aligned}
\langle n|n\rangle &= 2m\hbar\omega n \langle n-1|n-1\rangle \\
&= (2m\hbar\omega)^2 n(n-1) \langle n-2|n-2\rangle \\
&= (2m\hbar\omega)^3 n(n-1)(n-2) \langle n-3|n-3\rangle \\
&\qquad\qquad \vdots \\
&= (2m\hbar\omega)^n n! \langle 0|0\rangle \\
&= (2m\hbar\omega)^n n!, \qquad \text{since } \langle 0|0\rangle = 1 \ (\text{cf. } 4.58)
\end{aligned}
\tag{4.68}
$$

So our result is that

$$
\langle n|n\rangle = (2m\hbar\omega)^n n! \tag{4.69}
$$

A simple but important formula: the value of $\langle n|n\rangle$ for the state $|n\rangle$

and since $|n\rangle$ and $|m\rangle$, being eigenstates of a Hermitian operator, are *orthogonal* when $n \neq m$ we can write that

$$
\begin{aligned}
\langle n|m\rangle &= \mu_n \, \delta_{nm}, \quad n, m = 0, 1, 2, \ldots \\
\text{where} \qquad \mu_n &= (2m\hbar\omega)^n \, n!
\end{aligned}
\tag{4.70}
$$

[4] We use the simple property of adjoints that, if A is some operator, and ϕ represents a state, then, spelling things out in complete detail, one can say that

$$
\begin{aligned}
|n\rangle &= |A\phi\rangle \\
\Rightarrow \langle n|n\rangle &= \langle A\phi| \, |A\phi\rangle \\
&= \langle A\phi| \, A \, |\phi\rangle \\
&= \langle \phi| \, A^\dagger A \, |\phi\rangle \\
&= \langle n-1| \, a_- a_+ \, |n-1\rangle, \quad \text{on setting } |\phi\rangle = |n-1\rangle \text{ and } A = a_+
\end{aligned}
\tag{4.65}
$$

and we remind the reader that (cf. 4.20) $a_+^\dagger = a_-$.

Hence the energy eigenstates which are normalised to unity are given by $|\mathbf{e_n}\rangle$ where

$$
\begin{aligned}
|\mathbf{e_n}\rangle &= \frac{1}{\sqrt{\mu_n}} |n\rangle \\
&= \frac{1}{\sqrt{\mu_n}} a_+^n |0\rangle , \quad n = 0, 1, 2, \ldots
\end{aligned}
\tag{4.71}
$$

and so the $|\mathbf{e_n}\rangle$ obey the orthonormality condition

$$
\langle \mathbf{e_n}|\mathbf{e_m}\rangle = \delta_{nm}, \quad n, m = 0, 1, 2, \ldots
\tag{4.72}
$$

§ 5. The basic operators displayed as matrices

Recall that, $\{\mathbf{e_1}, \mathbf{e_2}, \ldots \mathbf{e_n}\}$ is an orthonormal basis, then the entries M_{ij} of any $n \times n$ matrix

$$
M = \begin{pmatrix}
M_{11} & M_{12} & \cdots & M_{1n} \\
M_{21} & M_{22} & \cdots & M_{2n} \\
\vdots & & & \vdots \\
M_{n1} & M_{n2} & \cdots & M_{nn}
\end{pmatrix}_{n \times n}
\tag{4.73}
$$

are computable from the simple formula

$$
M_{ij} = \langle \mathbf{e_i}| M |\mathbf{e_j}\rangle
\tag{4.74}
$$

This also true in infinite dimensions and, applying it to the operator

$$
a_+
\tag{4.75}
$$

we see that we can write a_+ as the infinite matrix with entries a_+^{ij} given by

The operator a_+ written as an infinite matrix

$$
a_+ = \begin{pmatrix}
a_+^{00} & a_+^{01} & a^{02} & \cdots \\
a_+^{10} & a_+^{11} & a^{12} & \cdots \\
a_+^{20} & a_+^{21} & a^{22} & \cdots \\
\vdots & \vdots & \vdots &
\end{pmatrix}
\tag{4.76}
$$

$$
\text{with} \quad a_+^{ij} = \langle \mathbf{e_i}| a_+ |\mathbf{e_j}\rangle , \quad i, j = 0, 1, 2, \ldots
$$

N.B. the reader should note carefully here that the i and the j in a_+^{ij} shown in 4.76 start at 0 not 1. This is because our basis starts with an $\mathbf{e_0}$, not an $\mathbf{e_1}$, i.e. our basis is $\{\mathbf{e_0}, \mathbf{e_1}, \mathbf{e_2}, \ldots \mathbf{e_n}, \ldots\}$ and *not* $\{\mathbf{e_1}, \mathbf{e_2}, \ldots \mathbf{e_n}, \ldots\}$.

But we know that

$$
|\mathbf{e_n}\rangle = \frac{1}{\sqrt{\mu_n}} |n\rangle , \quad \text{where } \mu_n = (2m\hbar\omega)^n n!
\tag{4.77}
$$

So we compute that

$$
\begin{aligned}
a_+^{ij} &= \frac{1}{\sqrt{\mu_j \mu_i}} \langle i | \, a_+ \, | j \rangle \\
&= \frac{1}{\sqrt{\mu_j \mu_i}} \langle i | \, | j + 1 \rangle, \qquad \text{since } a_+ \, | j \rangle = | j + 1 \rangle \\
&= \frac{1}{\sqrt{\mu_j \mu_i}} \mu_i \, \delta_{i,j+1}, \qquad \text{using 4.70} \\
&= \sqrt{\frac{\mu_i}{\mu_j}} \, \delta_{i,j+1}
\end{aligned}
\tag{4.78}
$$

This means that the matrix for a_+ is *only non-zero along its subleading diagonal* and, computing the relevant non-zero number $\sqrt{\mu_{j+1}/\mu_j}$, we find that

$$
\begin{aligned}
\sqrt{\frac{\mu_{j+1}}{\mu_j}} &= \sqrt{\frac{(2m\hbar\omega)^{j+1} \, (j+1)!}{(2m\hbar\omega)^j \, j!}} \\
&= \sqrt{2m\hbar\omega} \, \sqrt{j+1}
\end{aligned}
\tag{4.79}
$$

Finally the result of displaying a_+ as an *infinite* matrix is that

The completely explicit matrix form for a_+

$$
a_+ = \sqrt{2m\hbar\omega}
\begin{pmatrix}
0 & 0 & \cdots & & & & \\
\sqrt{1} & 0 & 0 & \cdots & & & \\
0 & \sqrt{2} & 0 & 0 & \cdots & & \\
0 & 0 & \sqrt{3} & 0 & 0 & \cdots & \\
\vdots & \vdots & \ddots & \ddots & \ddots & \ddots & \cdots \\
& & & & \sqrt{n} & 0 & 0 & \cdots \\
& & & & & \ddots & \ddots & \ddots \\
& & & & & & \ddots & \ddots \\
\cdots & & & & \cdots & & &
\end{pmatrix}
\tag{4.80}
$$

where the *only non-zero entries* in the matrix are those of the form $\sqrt{1}, \sqrt{2}, \sqrt{3}, \dots$ etc. and these all lie on the subleading diagonal.

   Since

$$
a_- = a_+^\dagger
\tag{4.81}
$$

then we can take the complex conjugate [5] transpose of the matrix for a_+ in 4.80 above to get the (infinite) matrix form for a_-. Hence we find that

The explicit matrix form for a_-

---

[5] Actually the complex conjugate does nothing in this particular case since all the entries are real.

$$
a_- = \sqrt{2m\hbar\omega}
\begin{pmatrix}
0 & \sqrt{1} & \cdots & & & & \\
0 & 0 & \sqrt{2} & \cdots & & & \\
0 & 0 & 0 & \sqrt{3} & \cdots & & \\
\vdots & \ddots & \ddots & \ddots & \ddots & \cdots & \\
\vdots & & \ddots & 0 & 0 & \sqrt{n} & \cdots \\
& & & & \ddots & \ddots & \ddots \\
& & & & & \ddots & \ddots \\
\cdots & & & \cdots & & &
\end{pmatrix}
\tag{4.82}
$$

and, again, the *only non-zero entries* are those of the form $\sqrt{1}$, $\sqrt{2}$, $\sqrt{3}, \ldots$ etc. and, this time, these all lie on the superleading diagonal.

We can also give the (infinite) matrix representations of the position and momentum operators since these are just linear combinations of a_+ and a_-. To achieve this recall from 4.20 that

$$
\left.
\begin{array}{l}
a_+ = p + im\omega x \\
a_- = p - im\omega x
\end{array}
\right\}
\Rightarrow
\left\{
\begin{array}{l}
x = \frac{1}{2im\omega}(a_+ - a_-) \\
p = \frac{1}{2}(a_+ + a_-)
\end{array}
\right.
\tag{4.83}
$$

so we can straightaway calculate that

$$
x = \frac{1}{i}\sqrt{\frac{\hbar}{2m\omega}}
\begin{pmatrix}
0 & -\sqrt{1} & \cdots & & & & \\
\sqrt{1} & 0 & -\sqrt{2} & \cdots & & & \\
0 & \sqrt{2} & 0 & -\sqrt{3} & \cdots & & \\
\vdots & & \sqrt{3} & \ddots & \ddots & \cdots & \\
\vdots & & & & \ddots & 0 & -\sqrt{n} & \cdots \\
& & & & & \sqrt{n} & \ddots \\
& & & & & & \ddots & \ddots \\
\cdots & & & \cdots & & &
\end{pmatrix}
\tag{4.84}
$$

and

$$
p = \sqrt{\frac{m\hbar\omega}{2}}
\begin{pmatrix}
0 & \sqrt{1} & \cdots & & & & \\
\sqrt{1} & 0 & \sqrt{2} & \cdots & & & \\
0 & \sqrt{2} & 0 & \sqrt{3} & \cdots & & \\
\vdots & & \sqrt{3} & \ddots & \ddots & \cdots & \\
\vdots & & & & \ddots & 0 & \sqrt{n} & \cdots \\
& & & & & \sqrt{n} & \ddots \\
& & & & & & \ddots & \ddots \\
\cdots & & & \cdots & & &
\end{pmatrix}
\tag{4.85}
$$

Finally we display the Hamiltonian in matrix form—this is particularly easy since it is a diagonal matrix whose diagonal entries are simply the energy eigenvalues. In any case we know from 4.22 that

$$
H = \frac{1}{2m}a_+ a_- + \frac{\hbar\omega}{2}I
\tag{4.86}
$$

and so we then find that H is the diagonal matrix

$$H = \begin{pmatrix} \frac{\hbar\omega}{2} & 0 & \cdots & & & \\ 0 & \frac{3\hbar\omega}{2} & 0 & \cdots & & \\ 0 & 0 & \frac{5\hbar\omega}{2} & 0 & & \cdots \\ \vdots & & 0 & \ddots & & \\ & & & & (n+\frac{1}{2})\hbar\omega & \cdots \\ & \cdots & & & & \ddots \\ & & & & & \end{pmatrix} \qquad (4.87)$$

These completely explicit matrix representations for a_+, a_-, x, p and H are actually quite easy to manipulate: this means that one can readily verify that the commutators $[a_+, a_-]$ and $[x, p]$ come out correctly as well as miscellaneous other algebraic expressions involving these objects.

This brings the current chapter to a close.

CHAPTER V

Simple potentials and quantum tunnelling

§ 1. Introduction

In this chapter we solve the one dimensional Schrödinger equation for three simple but important potentials $V(x)$ and these are usually called:

  (i) The infinite square well or a particle in a box
 (ii) The finite square well
(iii) The step potential or potential barrier

The last potential—the step potential or potential barrier—is a key example with which to illustrate the phenomenon of *quantum mechanical tunnelling.*

We finish the chapter with some remarks on tunnelling and scattering

§ 2. The infinite square well or a particle in a box

The potential V for an infinite square well is defined by

$$V(x) = \begin{cases} \infty & \text{if } -\infty < x \le 0 \\ 0 & \text{if } \quad 0 < x < a \\ \infty & \text{if } \quad a \le x < \infty \end{cases} \tag{5.1}$$

where a is some positive constant. V is displayed in figure 6

The Schrödinger equation says that the eigenfunctions ψ_n and their associated energies E_n are given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} + V(x)\psi_n(x) = E_n\psi_n(x) \tag{5.2}$$

and to solve this equation it is natural to divide the x-axis up into the three ranges of x that appear in the definition 5.1 of the potential $V(x)$. Let us denote these regions by I, II and III so that we have

$$\text{I} = \{x : -\infty < x \le 0\}$$
$$\text{II} = \{x : \quad 0 < x < a\} \tag{5.3}$$
$$\text{III} = \{x : \quad a \le x < \infty\}$$

Consider first regions I and III throughout which $V = \infty$; since the product $V(x)\psi_n$ occurs in the Schrödinger equation then this product must always be *finite*, and the only way that
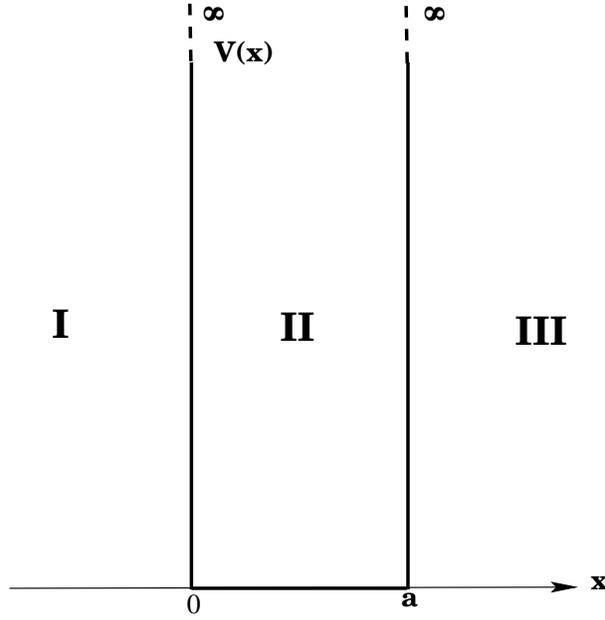
Fig. 6:   The infinite square well

this can happen is if $\psi_n(x)$ *vanishes* in these two regions. Hence we deduce the important fact that

$$\psi_n(x) = 0 \quad \text{for} \quad \left\{ \begin{array}{l} x \in \text{I} \\ x \in \text{III} \end{array} \right. \tag{5.4}$$

or, more explicitly,

$$\psi_n(x) = 0 \quad \text{for} \quad \left\{ \begin{array}{l} -\infty < x \leq 0 \\ a \leq x < \infty \end{array} \right. \tag{5.5}$$

On the other hand, in region II, we have $V(x) = 0$, so that, in region II, the Schrödinger reduces to just

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} = E_n\psi(x), \quad \text{for} \quad 0 < x \leq a \tag{5.6}$$

Thus a complete summary of what holds for all three regions I, II and III is that

$$\psi_n(x) = 0 \quad \text{for} \quad \left\{ \begin{array}{ll} -\infty < x \leq 0 & \text{(I)} \\ a \leq x < \infty & \text{(III)} \end{array} \right.$$
$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} = E_n\psi(x), \quad \text{for } 0 < x < a \quad \text{(II)} \tag{5.7}$$

This is now very easy to solve and we find that the solutions to the Schrödinger equation—which is just the SHM equation—are given by

$$\psi_n(x) = A\cos(\omega_n x) + B\sin(\omega_n x), \quad \text{with} \quad \left\{ \begin{array}{l} A, B \text{ constants} \\ \omega_n^2 = \dfrac{2mE_n}{\hbar^2} \end{array} \right. \tag{5.8}$$

But $\psi_n(x)$ must vanish in regions I and III and, more particularly, it must vanish [1] at the two points $x = 0$, a. Thus we have

$$\psi_n(0) = 0 \Rightarrow A = 0$$
$$\psi_n(a) = 0 \Rightarrow A\cos(\omega_n a) + B\sin(\omega_n a) = 0 \tag{5.9}$$

Thus 5.9 has just provided us with two simultaneous equations whose solutions are

$$\begin{cases} A = 0 \\ \sin(\omega_n a) = 0 \end{cases} \Rightarrow \omega_n a = n\pi, \ n \in \mathbf{Z} \tag{5.10}$$

Notice that $n = 0$ will only give us the trivial solution $\psi_n(x) \equiv 0$ and so we exclude it; also changing n to $-n$ only changes the sign of $\psi_n(x)$ and so can be absorbed into B, hence we shall lose no generality by taking n to be *positive* which we now do.

Finally since the relation 5.8 between the energies E_n and ω_n is that $\omega_n^2 = 2mE_n/\hbar^2$ then we find that the energies E_n are indeed quantised and given by

$$E_n = \frac{n^2\hbar^2\pi^2}{2ma^2}, \ n = 1, 2, \ldots \tag{5.11}$$

The energies for a particle in an infinite square well

Notice that the lowest energy E_1 is *positive* rather than zero as it typical for quantum mechanical systems.

Finally we point out that since any wave function $\psi(x)$ for this problem vanishes outside the region $0 < x < a$ then a particle moving under this potential is *confined* to this region— it has zero probability to be for its position to be measured anywhere else This situation is sometimes referred to as a particle in a (one dimensional) box. There are also two dimensional and three dimensional versions of the particle in a box where the particle is confined to a two dimensional rectangle, or a three dimensional box, by a potential which is infinite at the boundaries of the box.

The terminology 'particle in a box' explained

We move on to our next problem.

§ 3. The finite square well

A finite square well has a potential V given by

$$V(x) = \begin{cases} V_0 & \text{if} \quad -\infty < x \leq 0 \\ 0 & \text{if} \quad 0 < x < a \\ V_0 & \text{if} \quad a \leq x < \infty \end{cases} \tag{5.12}$$

where a and V_0 are positive constants. A graph of $V(x)$ is shown in figure 7.

The underlying physical problem is that of a particle beam

One can think of this problem physically as being that of a particle beam travelling along the x-axis towards a target represented by the potential in the region $0 < x < a$.

In region II the Schrödinger equation is the same as it is for the infinite well, namely

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} = E_n\psi(x), \quad \text{for} \ \ 0 < x < a \tag{5.13}$$

---

[1] Note that $\psi_n(x)$ it would also be discontinuous—and so not even differentiable—at the points $x = 0$, a if it didn't vanish there.
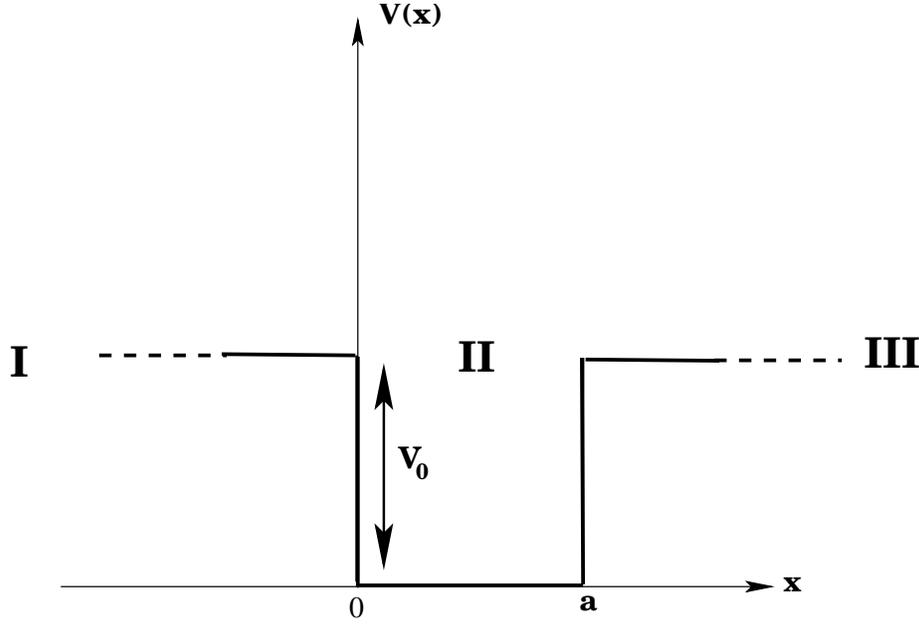
Fig. 7: The finite square well

while in regions I and III we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} + V_0\psi_n(x) = E_n\psi(x), \quad \text{for} \quad \begin{cases} -\infty < x \le 0 \\ a \le x < \infty \end{cases} \tag{5.14}$$

We deal with regions I and III first. The equation we have to solve is

$$\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} - (V_0 - E_n)\psi_n(x) = 0 \tag{5.15}$$

i.e.

$$\frac{d^2\psi_n(x)}{dx^2} - \kappa^2\psi_n(x) = 0, \quad \text{where } \kappa = \sqrt{\frac{2m(V_0 - E_n)}{\hbar^2}} \tag{5.16}$$

Next we *assume*[2] that

$$E_n < V_0 \tag{5.17}$$

so that

$$\kappa^2 > 0 \Rightarrow \kappa \text{ is real} \tag{5.18}$$

---

[2] If this is not true—i.e. if $E_n \ge V_0$—the reader can easily adjust the argument here to construct the solutions. However all these states will be *scattering states* with $\langle\psi|\psi\rangle = \infty$ rather than quantised, or bound, states with $\langle\psi|\psi\rangle < \infty$. For the case where $E_n > V_0$, then κ will then be pure imaginary: $\kappa = i\theta$, with $\theta \in \mathbf{R}$, and the two solutions $\psi_n(x)$ are oscillatory functions of the form $e^{\pm i\theta}$. Finally when $E_n = V_0$ $\kappa = 0$, and $\psi_n(x)$ just takes on the simple form $\psi_n(x) = A + Bx$.

We lose no generality by taking

$$\kappa > 0 \tag{5.19}$$

so we do so. This means that the solution to the Schrödinger equation in regions I and III can be written as

$$\psi_n(x) = \begin{cases} A_I\, e^{\kappa x} + B_I\, e^{-\kappa x}, & x < 0 \\ A_{III}\, e^{\kappa x} + B_{III}\, e^{-\kappa x}, & x > a \end{cases} \quad (\kappa > 0) \tag{5.20}$$

where A_I, A_{III}, B_I and B_{III} are constants. Now since

$$\lim_{x \to \mp\infty} \psi_n(x) \longrightarrow \infty \quad \text{is forbidden} \tag{5.21}$$

because it breaks normalisability and makes

$$\langle \psi_n | \psi_n \rangle = \int \overline{\psi_n(x)}\, \psi_n(x)\, dx\, dy\, dz = \infty \tag{5.22}$$

then we must set

$$B_I = 0 \quad \text{in region I} \quad \text{and} \quad A_{III} = 0 \quad \text{in region III} \tag{5.23}$$

In sum we have deduced that

$$\psi_n(x) = \begin{cases} A_I\, e^{\kappa x}, & \text{for} \quad x < 0 \quad \text{(region I)} \\ B_{III}\, e^{-\kappa x}, & \text{for} \quad x > a \quad \text{(region III)} \end{cases} \tag{5.24}$$

Coming now to region II we know that $\psi_n(x)$ satisfies equation 5.13 above which we write as

$$\frac{d^2\psi_n(x)}{dx^2} + \omega_n^2 \psi_n(x) = 0, \quad \text{with} \quad \omega_n^2 = \frac{2mE_n}{\hbar^2} \tag{5.25}$$

and so, as in the infinite well problem, we have the solution

$$\psi_n(x) = C\cos(\omega_n x) + D\sin(\omega_n x), \quad \text{for } 0 < x < a \quad \text{(region II)} \tag{5.26}$$

with C and D constants.

Finally we must match up the solution in region II to those in regions I and III. This is done by imposing [3] the condition that

$$\psi_n(x) \text{ and } \frac{d\psi_n(x)}{dx} \text{ are continuous where the regions join: i.e.. at } \begin{cases} x = 0 \\ x = a \end{cases} \tag{5.27}$$

On imposing these matching conditions we obtain the equations

$$\left. \begin{array}{ll} A_I = C & (i) \\ B_{III}e^{-\kappa a} = C\cos(\omega_n a) + D\sin(\omega_n a) & (ii) \end{array} \right\} \quad \text{continuity of } \psi_n(x) \text{ at } x = 0,\, a \tag{5.28}$$

[3] That this condition is reasonable follows immediately from the fact that every Schrödinger equation contains the second derivative term $d^2\psi/dx^2$ whose very existence requires continuity of ψ and $d\psi/dx$.

$$\left. \begin{array}{ll} \kappa A_{\mathrm{I}} = D\omega_n & (i) \\ -\kappa B_{\mathrm{III}}\, e^{-\kappa a} = \omega_n\left(-C\sin(\omega_n a) + D\cos(\omega_n a)\right) & (ii) \end{array} \right\} \text{ continuity of } \frac{d\psi_n(x)}{dx} \text{ at } x = 0,\, a$$

$$(5.29)$$

It is very straightforward to solve 5.28 and 5.29: first one uses 5.28 (i) in 5.29 (i) thereby deducing that

$$D = \frac{C\kappa}{\omega_n} \tag{5.30}$$

Then one substitutes this expression for D in 5.28 (ii) and 5.29 (ii) yielding the pair of equations

$$B_{\mathrm{III}}\, e^{-\kappa a} = C\cos(\omega_n a) + \frac{C\kappa}{\omega_n}\sin(\omega_n a)$$

$$\tag{5.31}$$

$$-\kappa B_{\mathrm{III}}\, e^{-\kappa a} = \omega_n\left(-C\sin(\omega_n a) + \frac{C\kappa}{\omega_n}\cos(\omega_n a)\right)$$

Now we multiply the first equation of 5.31 by κ and add it to the second. The result of this is the equation

$$0 = 2\kappa C\cos(\omega_n a) + C\left(\frac{\kappa^2}{\omega} - \omega_n\right)\sin(\omega_n a) \tag{5.32}$$

which we can instantly rewrite to read

$$\tan(\omega_n a) = -\frac{2\kappa C}{C\left(\dfrac{\kappa^2}{\omega_n} - \omega_n\right)} \tag{5.33}$$

$$= \frac{2\,\kappa\,\omega_n}{\omega_n^2 - \kappa^2}$$

But κ and ω_n are not independent: indeed, from their definitions in 5.16 and 5.25, we have that

$$\kappa^2 = \frac{2m(V_0 - E_n)}{\hbar^2}, \quad \omega_n^2 = \frac{2mE_n}{\hbar^2}$$

$$\Rightarrow \kappa^2 = \frac{2mV_0}{\hbar^2} - \omega_n^2 \tag{5.34}$$

$$\Rightarrow \kappa = \sqrt{\frac{2mV_0}{\hbar^2} - \omega_n^2}$$

and so if we use this value for κ in 5.33 above we find that

$$\tan(\omega_n a) = \frac{2\omega_n\sqrt{\frac{2mV_0}{\hbar^2} - \omega_n^2}}{2\omega_n^2 - 2mV_0/\hbar^2} \tag{5.35}$$

that is

$$\tan(\omega_n a) = \frac{\omega_n\sqrt{\frac{2mV_0}{\hbar^2} - \omega_n^2}}{\omega_n^2 - mV_0/\hbar^2}, \quad \text{where } \omega_n^2 = \frac{2mE_n}{\hbar^2} \tag{5.36}$$

Here is the quantisation condition for the finite square well energies E_n

So 5.36 gives the energies E_n of the finite square well which we see are quantised. These energies E_n have to be found numerically or graphically as there is no simple formula for ω_n coming from 5.36. Let use $g(\omega_n)$ to denote the RHS of 5.36 so that

$$g(\omega_n) = \frac{\omega_n \sqrt{\frac{2mV_0}{\hbar^2} - \omega_n^2}}{\omega_n^2 - mV_0/\hbar^2} \qquad (5.37)$$

then we show how a value of ω_n arises graphically in figure 8. The point is that the *intersection points* of the two functions are solutions to 5.36 and hence values of $\omega_n a$ giving a quantised energy E_n; note that there are four of these in figure 8.

There will always be a finite number of such quantised E_n since E_n is required to satisfy $E_n < V_0$, also there will always be at least one positive E_n as long as V_0 is non zero. Recall, too, that states with $E_n > V_0$ are not normalisable states but scattering states.

Notice that a finite square well has only a finite number of bound states

The intersection of $\tan(\omega_n a)$ and $g(\omega_n)$
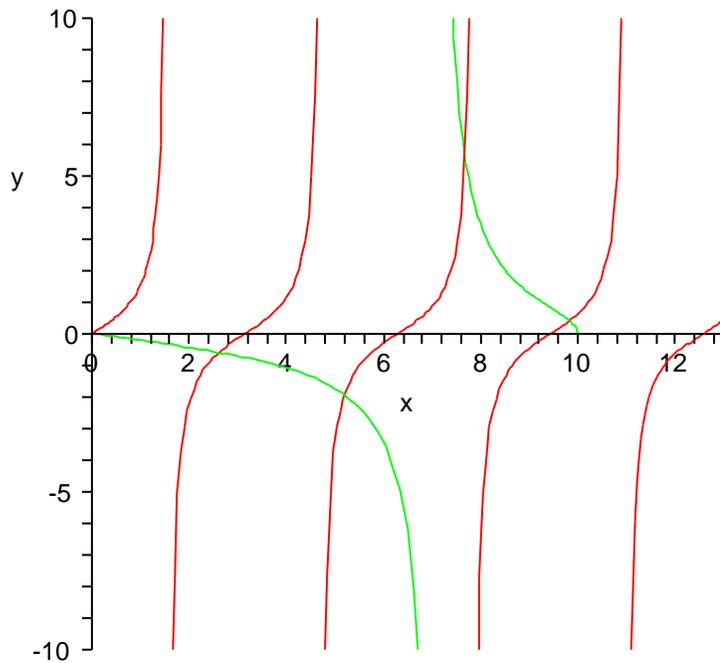
Fig. 8: Energy values for a finite square well $(a = 1,\ x = \omega_n,\ 2mV_0/\hbar^2 = 100)$

We close this section with some pictures of the energy level structure for various potentials.
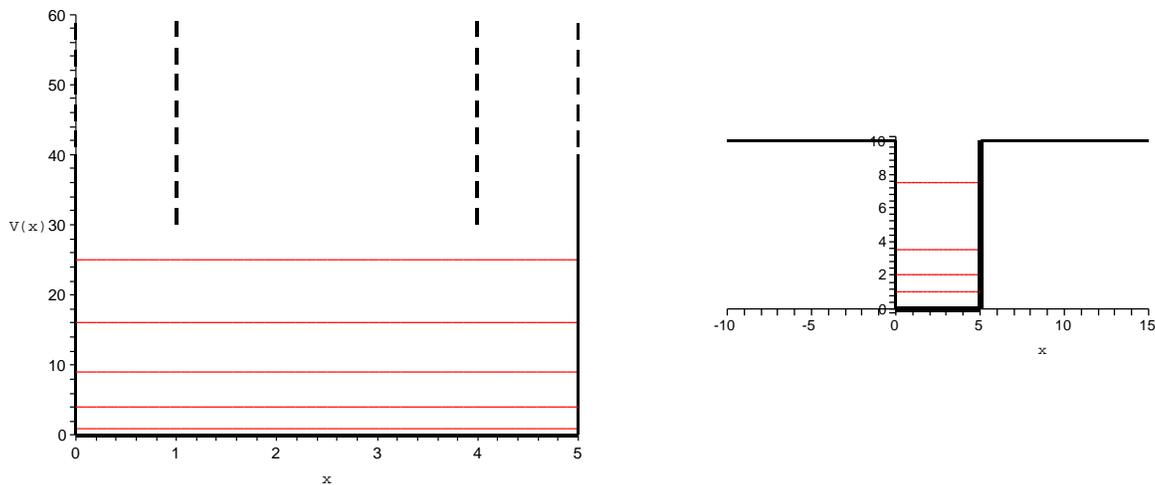
Fig. 9:   Energy levels for an infinite and a finite potential well
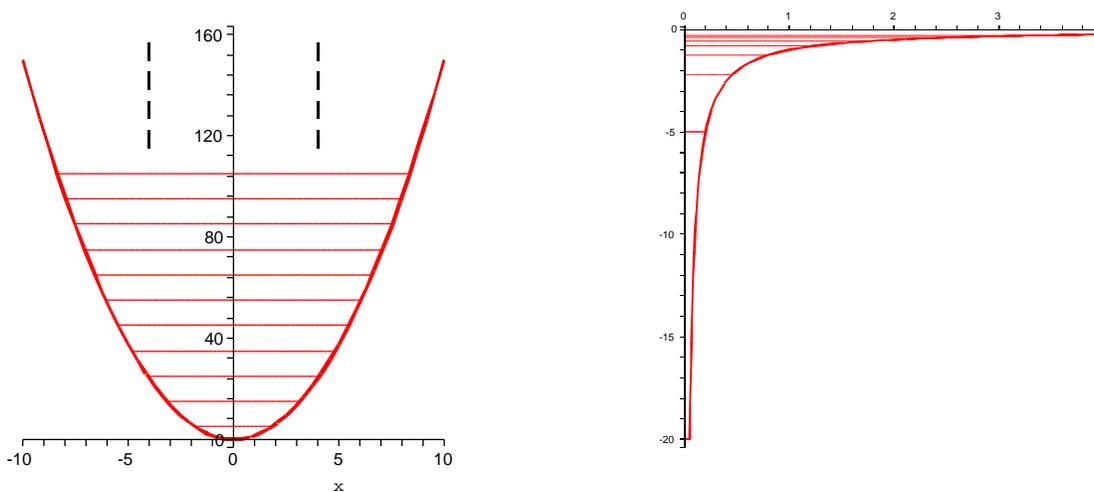
Fig. 10:   Energy levels for the harmonic oscillator and the hydrogen atom

§ 4. A potential step or potential barrier

A step potential or potential barrier $V(x)$ is defined by

$$V(x) = \begin{cases} 0 & \text{if } -\infty < x \leq 0 \\ V_0 & \text{if } \quad 0 < x < a \\ 0 & \text{if } \quad a \leq x < \infty \end{cases} \tag{5.38}$$

and is displayed in figure 11.

We see that there are similarities to the finite potential well problem of the preceding section and also we still have precisely the same regions I, II and III of the x-axis that we defined for the finite potential well. This means that we will be able to draw on the calculation done there to deduce what happens in the present problem.
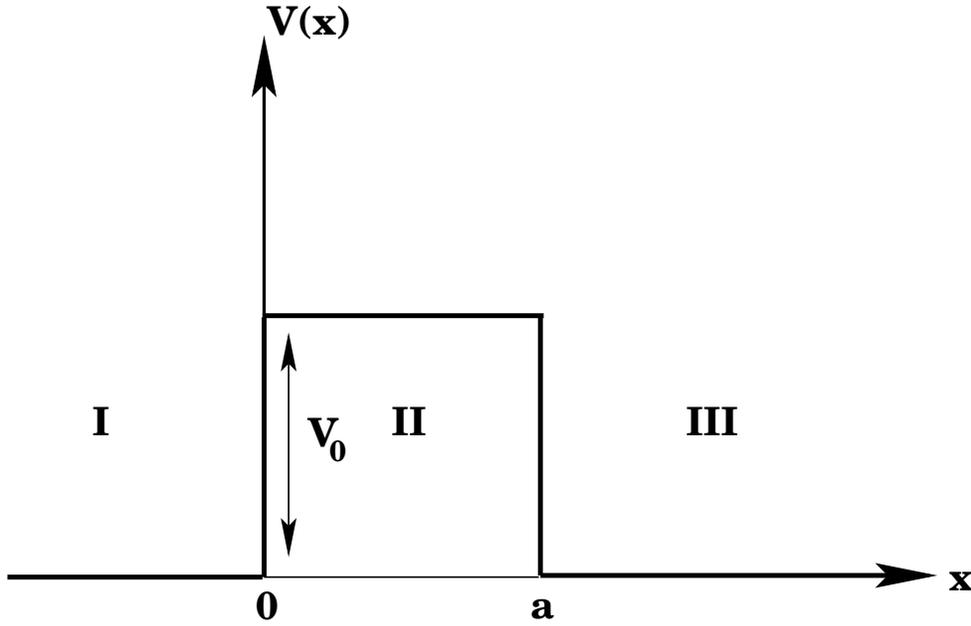
Fig. 11:   The step potential or potential barrier

The most interesting case—and this is the one that gives rise to what is called
tunnelling—is when

$$E < V_0 \tag{5.39}$$

which we now assume.

First consider a classical free particle with energy $E < V_0$ moving along the negative
x-axis so as to encounter the barrier at $x = 0$; such a particle will never penetrate into the
barrier since it requires energy $E > V_0$ to do so [4] . However quantum mechanically this is
false: such a particle can not only penetrate the barrier but also move through it to the
other side where $x > a$. The particle is said to *tunnel* through the barrier.

---

[4] Think of a ball with kinetic energy E moving towards the bottom of a hill of height h. If the ball has
mass m, and manages to get to the top of the hill, it will have potential energy V_0, where $V_0 = mgh$. But
if $E < V_0$ it will never get to the top: it will only get part of the way up.

Notice, too, that in the quantum mechanical problem the analogy is with a hill of infinite slope since
the potential jumps discontinuously from the value 0 to the value V_0 at $x = 0$. This discontinuous jump is
not necessary and is an idealisation, which would not happen in nature where the jump would be gradual:
the only reason we have it here is because the mathematics is more simple if the potential is made up of
vertical and horizontal straight line pieces.

It is quite easy to see why this is so: we shall calculate that a particle incident on the barrier from the *left* has a wave function $\psi(x)$ which is *non zero on the right* of the barrier and so has a non zero probability of being measured there—in fact the wave function ψ is non zero in all three regions I, II and III.

Now for the calculation of the wave function ψ. In region I the potential $V(x)$ is zero and so the Schrödinger equation is just

$$\frac{d^2\psi(x)}{dx^2} + \omega^2\psi(x) = 0, \quad \text{with } \omega^2 = \frac{2mE}{\hbar^2} \quad \text{for } -\infty < x < 0 \tag{5.40}$$

and so we have oscillatory solutions which we can take to be combinations of $\cos(\omega x)$ and $\sin(\omega x)$ or $e^{i\omega x}$ and $e^{-i\omega x}$ the latter being more convenient for the present problem. Hence we can write [5]

$$\begin{aligned}\psi(x) &= C\cos(\omega x) + D\sin(\omega x)\\ \text{or} \quad \psi(x) &= Ae^{i\omega x} + Be^{-i\omega x} \text{ (more convenient here)}\end{aligned} \quad \text{for } -\infty < x < 0 \tag{5.41}$$

The reason for the exponentials $e^{i\omega x}$ and $e^{-i\omega x}$ being more convenient is that $e^{i\omega x}$ represents a wave travelling from left to right and $e^{-i\omega x}$ a wave travelling from right to left [6] The expression $Ae^{i\omega x}$ represents a (plane) wave incident on the barrier from the left and $Be^{-i\omega x}$ represents a wave which is *reflected* by the barrier.

Take note that the reflected wave must be included despite the fact that the particle can penetrate the barrier; one has to remember that, though there is a non vanishing probability for transmission through the barrier, not all particles will pass through the barrier some will be *reflected* and the probability for reflection is also non vanishing.

In any case, in region I, we have

$$\psi(x) = Ae^{i\omega x} + Be^{-i\omega x}, \quad \text{for } -\infty < x < 0 \tag{5.42}$$

with A and B constant.

Passing now to region II—inside the barrier—we have, as in 5.16,

$$\frac{d^2\psi(x)}{dx^2} - \kappa^2\psi(x) = 0, \quad \text{where } \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}, \quad 0 < x < a \tag{5.43}$$

But

$$E < V_0 \Rightarrow \kappa \text{ is real} \tag{5.44}$$

and so we have

$$\psi(x) = Ce^{\kappa x} + De^{-\kappa x}, \quad 0 < x < a \tag{5.45}$$

---

[5] Notice that we write E instead of E_n and ω instead of ω_n. This is because the energy can vary continuously here: the potential does not trap the particle since it is not a well but a step, there is no energy quantisation.

[6] To see this recall (cf. 3.33) that the time dependence of ψ can be supplied by multiplying $\psi(x)$ by the factor $e^{-iEt/\hbar}$ giving here the two possibilities $\psi(x,t) = e^{\mp i\omega x}e^{-iEt/\hbar} = e^{\mp i\omega x - iEt/\hbar}$, an expression which we see represents the pair of waves mentioned above.

with C and D constant.

Finally in region III, $a < x < \infty$ we have, as in region I,

$$\frac{d^2\psi(x)}{dx^2} + \omega^2\psi(x) = 0, \quad \text{with } \omega^2 = \frac{2mE}{\hbar^2}, \quad a < x < \infty \tag{5.46}$$

from which we shall select only the right travelling solution since we know that there are no particles incident from infinity on the right. Hence we write

$$\psi(x) = Ee^{i\omega x}, \quad a < x < \infty \tag{5.47}$$

with E constant.
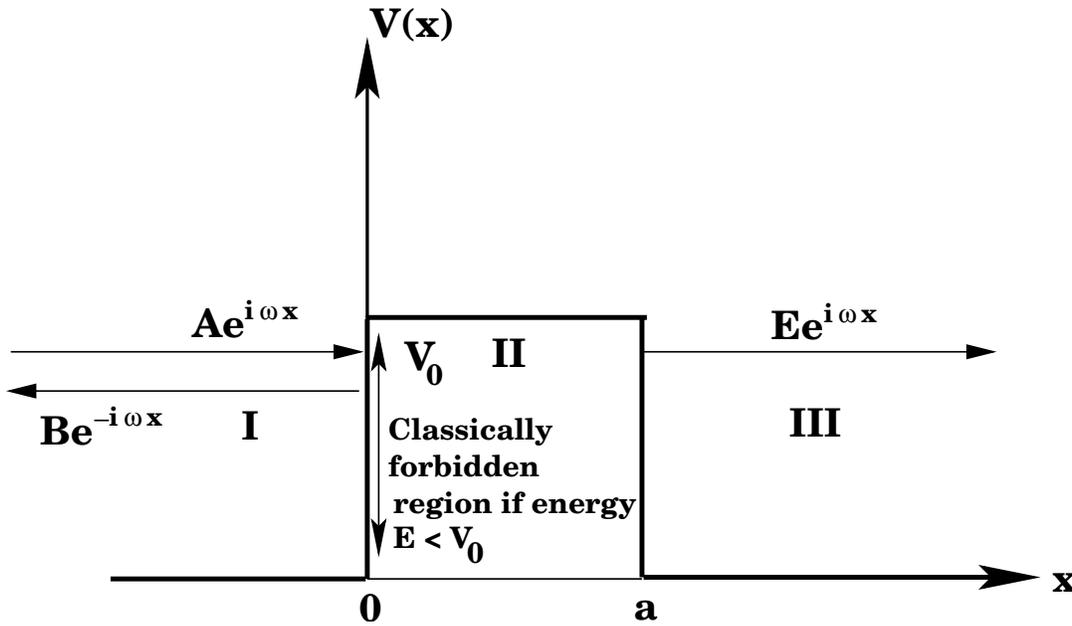
Fig. 12: The potential barrier and its incident, reflected and transmitted waves

The solution for $\psi(x)$ in all three regions just requires us to determine the unknown constants A, B, C, D, E. This simply means applying the boundary conditions of continuity for $\psi(x)$ and $d\psi(x)/dx$ at $x = 0, a$, just as had to be done for the finite well—cf. 5.27 above. The details vary slightly of course—in any case we find that we obtain

The bound- ary condi- tions for the barrier problem

$$
\begin{array}{llll}
A + B = C + D & (i) & i\omega(A - B) = \kappa(C - D) & (iii) \\
Ce^{\kappa a} + De^{-\kappa a} = Ee^{i\omega a} & (ii) & \kappa(Ce^{\kappa a} - De^{-\kappa a}) = i\omega Ee^{i\omega a} & (iv)
\end{array}
\tag{5.48}
$$

We shall solve for these details in the next section where we calculate the tunnelling probability.

§ 5. The tunnelling probability

The numerical measure of the tunnelling is the fraction of the incident particles—whose wave function is $\psi_{incident}(x) = Ae^{i\omega x}$—which are transmitted through the barrier—where the wave function is $\psi_{transmitted}(x) = Ee^{i\omega x}$. This is simply the ratio of the probability density of the transmitted beam to that of the incident beam: in other words it is

$$\frac{|\psi_{transmitted}(x)|^2}{|\psi_{incident}(x)|^2} = \frac{|Ee^{i\omega x}|^2}{|Ae^{i\omega x}|^2} = \frac{|E|^2}{|A|^2} \tag{5.49}$$

The tunnelling probability

and this is called the *tunnelling probability* and we shall denote it by T writing

$$T = \frac{|E|^2}{|A|^2} \tag{5.50}$$

T denotes the tunnelling probability

We must now finish off by solving the equations of 5.48 to get an expression for the tunnelling probability. Eliminating B from 5.48 (i) and (iii), dividing 5.48 (iv) by κ, and then adding and subtracting the resulting equation to 5.48 (ii) yields the three equations

$$A = \frac{1}{2}\left(1 + \frac{\kappa}{i\omega}\right)C + \frac{1}{2}\left(1 - \frac{\kappa}{i\omega}\right)D$$

$$Ce^{\kappa a} = \frac{1}{2}\left(1 + \frac{i\omega}{\kappa}\right)Ee^{i\omega a} \tag{5.51}$$

$$De^{-\kappa a} = \frac{1}{2}\left(1 - \frac{i\omega}{\kappa}\right)Ee^{i\omega a}$$

Now if we substitute for C and D from the second and third equations of 5.51 into the first we immediately discover that

$$\frac{E}{A} = \frac{4i\omega\kappa e^{-i\omega a}}{(\kappa^2 - \omega^2 + 2i\omega\kappa)e^{-\kappa a} + (-\kappa^2 + \omega^2 + 2i\omega\kappa)e^{\kappa a}}$$

$$= \frac{4i\omega\kappa e^{-i\omega a}}{(\kappa + i\omega)^2 e^{-\kappa a} - (\kappa - i\omega)^2 e^{\kappa a}} \tag{5.52}$$

Thus T is given by [7]

The full expression for T

$$T = \frac{|E|^2}{|A|^2} = \frac{16\omega^2\kappa^2}{|(\kappa + i\omega)^2 e^{-\kappa a} - (\kappa - i\omega)^2 e^{\kappa a}|^2} \tag{5.53}$$

and so we have our expression for the tunnelling probability T which we see is non-zero.

A useful fact to remember is that T becomes very small when the width of the barrier is large enough. [8]

---

[7] Another widely used name for T is the *transmission coefficient.*

[8] Note that if the width the barrier is very large and such that

$$\kappa a >> 0 \tag{5.54}$$

As well as tunnelling through the barrier particles can be *reflected*: the reflected wave is just $\psi_{reflected}(x)$ where

$$\psi_{reflected}(x) = Be^{-i\omega x} \tag{5.56}$$

and the *reflection probability*, which we denote by R, is then defined by [9]

$$R = \frac{|\psi_{reflected}(x)|^2}{|\psi_{incident}(x)|^2} = \frac{|Be^{-i\omega x}|^2}{|Ae^{i\omega x}|^2} = \frac{|B|^2}{|A|^2} \tag{5.57}$$

Now particles must be either reflected or transmitted, and since probability is conserved, it must be that

$$R + T = 1 \tag{5.58}$$

One can easily verify this: a very similar calculation to that done above for T shows that the reflection probability is given by

$$R = \frac{|(\kappa^2 + \omega^2)(e^{\kappa a} - e^{-\kappa a})|^2}{|(\kappa + i\omega)^2 e^{-\kappa a} - (\kappa - i\omega)^2 e^{\kappa a}|^2} \tag{5.59}$$

and a little algebra then readily allows us to verify that

$$R + T = 1 \tag{5.60}$$

as claimed.

An important fact to note about reflection is that *classically* reflection *only happens* if $E < V_0$ but quantum mechanically reflection can occur—that is $R \neq 0$—both when $E < V_0$ *and* when $E \geq V_0$.

Here is a comparison of the classical and quantum mechanical situations:

then we may drop the $e^{-\kappa a}$ in the denominator of 5.53 above, since it is then very small, and write

$$T = \frac{|E|^2}{|A|^2} \simeq \frac{16\omega^2 \kappa^2}{|-(\kappa - i\omega)^2 e^{\kappa a}|^2} = \frac{16\omega^2 \kappa^2 e^{-2\kappa a}}{(\omega^2 + \kappa^2)^2}$$
$$= \frac{16E(V_o - E)}{V_0^2} e^{-2(\sqrt{2m(V_0 - E)})(a/\hbar)} \qquad \text{valid when } \kappa a >> 0 \tag{5.55}$$

an expression which can be useful (in the last line we have re-expressed ω and κ in terms of E and V_0).

Finally a point to remember *only* if the reader ever goes on to study the (special) relativistic version of quantum mechanics known as *quantum field theory*. If we examine T in the limit as Planck's constant $\hbar \to 0$ we find that $T \to 0$ very rapidly because it contains a factor of the form $e^{-c/\hbar}$, $c > 0$. This means that $T \to 0$ more rapidly than any power of $\hbar$ and so cannot be calculated by perturbation theory in $\hbar$. So tunnelling cannot be seen in quantum field theory by using perturbation theory rather it has to do with special non-perturbative effects known as *instantons*.

[9] R is also referred to as the *reflection coefficient*.

Energy E	Classically	Quantum mechanically $(R+T=1)$
$E < V_0$	$R = 1,\ T = 0$	$R \neq 0,\ T \neq 0$
$E = V_0$	$R = 0,\ T = 0$	$R \neq 0,\ T \neq 0$
$E > V_0$	$R = 0,\ T = 1$	$R \neq 0,\ T \neq 0$

The quantum and the classical barrier compared

Notice that, in the *classical case*, when $E = V_0$, one has $R = T = 0$. This means that the particle just comes to a halt at the barrier; if one uses the hill analogy given in the footnote on p. 74 it means that the particle comes to rest at the top of the hill.

Tunnelling and the STEM

Tunnelling enables one to understand the process of alpha decay. It is also the physical mechanism used by the *scanning tunnelling electron microscope* or STEM where electrons can tunnel across the gap between a sample and an ultra fine tungsten needle whose tip is one atom across: individual atoms can then be seen easily.

Tunnelling and other areas of physics

Tunnelling is important in many other parts of physics, for example: nuclear physics, solid state physics and the physics of superconductors (the *Josephson junction*). [10]

We finish here.

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[10] The Josephson junction consists of a thin insulator between two superconductors. Electrons can tunnel across the insulator and many interesting phenomena occur. The Josephson junction plays a crucial part in measuring magnetic fields very accurately using a device called a SQUID, where the acronym stands for *superconducting quantum interference device.*

Contents

CHAPTER III

CHAPTER IV

CHAPTER V