

# 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 modern 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.*

Paul Dirac<sup>1</sup>

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

<sup>1</sup> 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

In 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

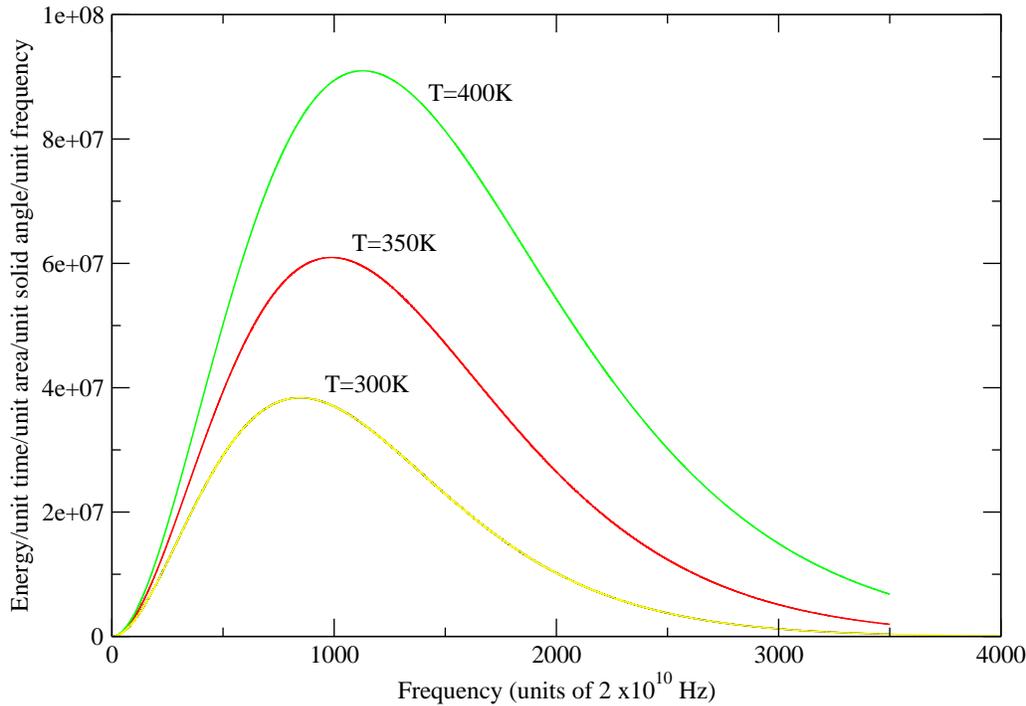
We shall now have a look at each of these.

#### The ultraviolet catastrophe

The ultraviolet catastrophe was the name given to the unsuccessful *Rayleigh–Jeans formula*—cf. ?? below—provided by classical physics for the radiation emitted by a black body.<sup>1</sup>

<sup>1</sup> 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  $\nu$  of the radiation and is a smooth curve rising to a single maximum at a particular frequency cf. figure ?? 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*.<sup>2</sup>



**Fig. 1: Experimental measurements of black body radiation**

However the theoretical calculation<sup>3</sup> for this emitted radiation  $I(\nu, T)$  gave the formula (known as the Rayleigh–Jeans formula)

$$I(\nu, T) = \frac{2\nu^2}{c^2} kT \quad (1.1)$$

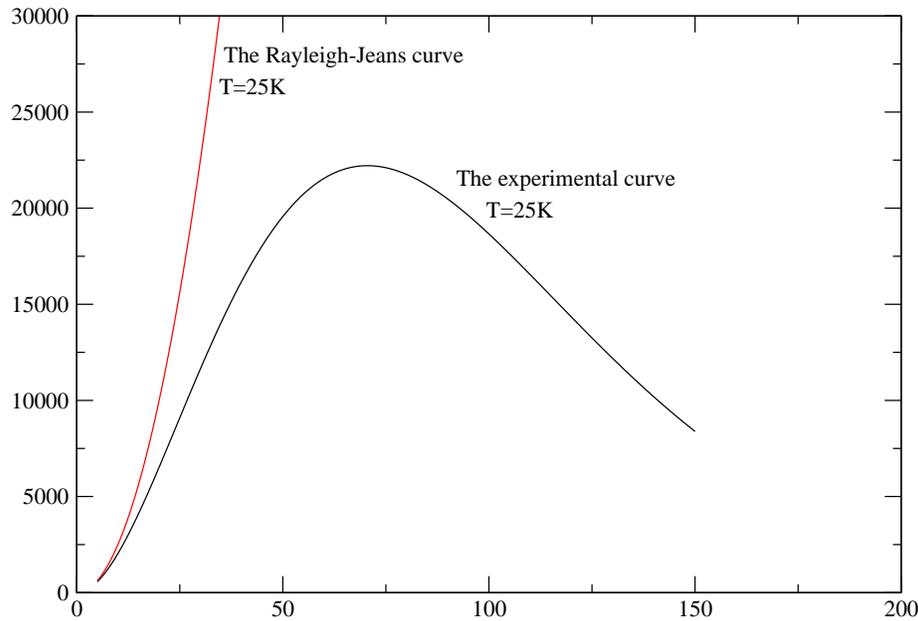
*The  
Rayleigh–  
Jeans for-  
mula*

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

<sup>2</sup> 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.

<sup>3</sup> 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).

*The failure of the Rayleigh–Jeans formula*



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

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

*Quantisation makes its first appearance in physics*

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

- (i) He postulated that electromagnetic radiation of energy  $E$  and frequency  $\nu$  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*<sup>4</sup>) whose value is given by  $h = 6.6260638 \times 10^{-34} \text{Js}$ . Note that the notation  $\hbar = h/2\pi$  is also very frequently used.

We write this as

$$E = nh\nu, \quad n = 1, 2, 3, \dots \quad (1.2)$$

(ii) He guessed<sup>5</sup> the correct form of the function  $I(\nu, T)$  giving it as

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

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  $\nu$ , we find that

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

*Rayleigh–Jeans only works for small  $\nu$*

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

<sup>4</sup> 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 ( $G = 6.674 \times 10^{-11} \text{m}^3 \text{kg}^{-1} \text{s}^{-2}$ ,  $c = 2.997 \times 10^8 \text{m s}^{-1}$ ,  $\hbar = \frac{h}{2\pi}$ )

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

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

$$T_H = \frac{\hbar c^3}{8\pi G M k}$$

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

<sup>5</sup> 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

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

tells us that the maximum occurs at the value of  $\nu$  where

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

and by actually plotting the graph of this function we find that the maximum occurs at  $\nu = \nu_*$  where<sup>6</sup>

$$\nu_* = 2.82 \frac{kT}{h} \quad (1.9)$$

and the temperature of such a body is therefore given by<sup>7</sup>

$$T = \nu_* \frac{h}{2.82k} \quad (1.10)$$

We can apply this formula **?.?** for  $\nu_*$  to a heated body which is beginning to glow *red hot*: actual experimental measurement will tell us that a red hot body has temperature

$$T \simeq 1000^0 K \quad (1.11)$$

*A red hot  
black body*

So we then compute that

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

<sup>6</sup> This result **?.?**, when stated in terms of wavelength rather than frequency, becomes the well known *Wien's displacement law* which is

$$\lambda_{max} = \frac{C}{T} \quad (1.7)$$

where  $\lambda_{max}$  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  $\nu$  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

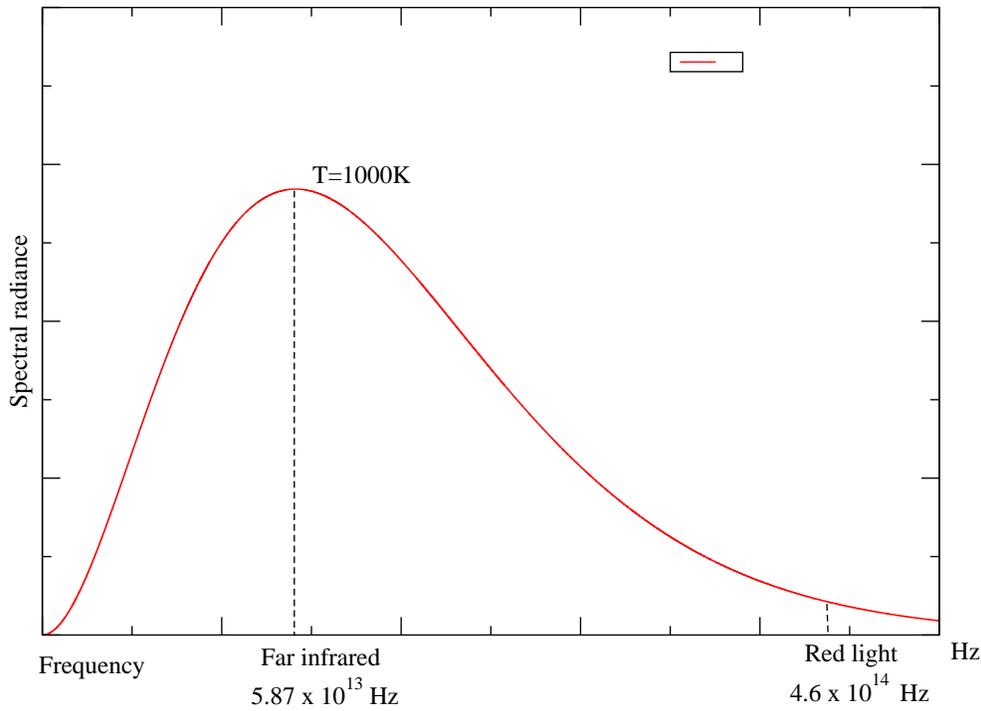
$$J = \sigma T^4, \quad \sigma \text{ a constant} \quad (1.8)$$

<sup>7</sup> 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

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

and this value is outside the visible spectrum<sup>8</sup> 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 ?? . If one increases the temperature to  $5000^0K$  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

$$2.7^0 K \quad (1.14)$$

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

$$1.89 \text{ mm} \quad (1.15)$$

*The microwave black body radiation left over after the Big Bang*

<sup>8</sup> The range of visible light is about 400–700 nm;  $1 \text{ nm} = 10^{-9}m$ .

which is in the microwave<sup>9</sup> 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*  $\nu$ ; in addition Einstein's explanation of the photoelectric effect only works if one accepts Planck's hypothesis that light of frequency  $\nu$  is made up of individual *photons* each with energy  $E$  where

$$E = h\nu \quad (1.16)$$

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

$$W \quad (1.17)$$

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.<sup>10</sup> If a photon of energy  $E$  ejects an electron thereby giving it a kinetic energy<sup>11</sup>

$$\frac{1}{2}mv^2 \quad (1.18)$$

then one has

$$E = W + \frac{1}{2}mv^2 \quad (1.19)$$

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

$$h\nu = W + \frac{1}{2}mv^2 \quad (1.20)$$

So

$$\frac{1}{2}mv^2 = h\nu - W \quad (1.21)$$

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

$$\frac{1}{2}mv^2 > 0 \quad (1.22)$$

<sup>9</sup> Microwaves are taken to have wavelengths lying in the range of roughly 1 mm to 1 m.

<sup>10</sup> For sodium one has  $W = 2.75 \text{ eV}$ .

<sup>11</sup> 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

$$\begin{aligned} h\nu - W &> 0 \\ \Rightarrow \nu &> \frac{W}{h} \end{aligned} \tag{1.23}$$

So clearly a light beam of frequency  $\nu$  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  $\nu$  and  $v$  for a range of values and uses 1.21 to plot the kinetic energy  $mv^2/2$  versus the frequency  $\nu$ . The result is a straight line graph whose slope Planck's constant  $h$ —cf. figure ?? .

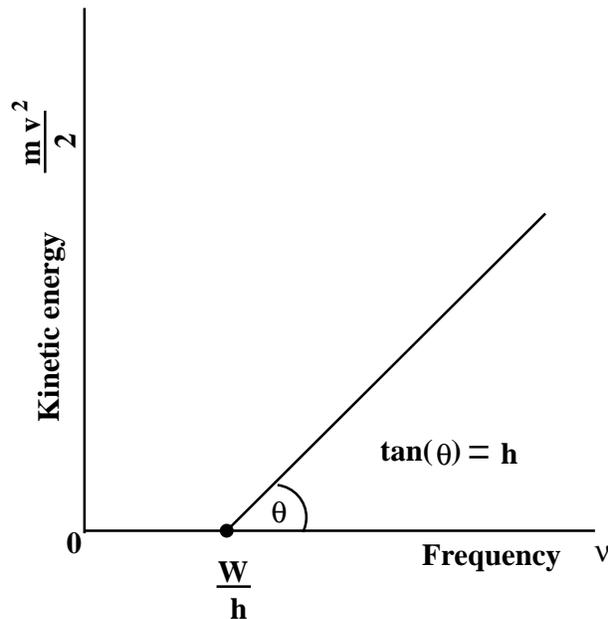


Fig. 4: The photoelectric effect graph with slope  $h$

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 Fraunhofer and others had used diffraction gratings to measure the frequencies of light emitted from the Sun<sup>12</sup> 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  $\nu_n$  emitted could be fitted to the formula

*The Balmer series*

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

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

$$B = 3.28 \times 10^{15} \text{ s}^{-1} \quad (1.26)$$

This series of frequencies  $\nu_n$   $n = 3, 4, \dots$  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.

<sup>12</sup> 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

$$L = n \frac{h}{2\pi}, \quad n = 1, 2, \dots \quad (1.27)$$

*Bohr quantisation*

where  $h$  is Planck's constant.

The great success of Bohr's quantisation rule ?? 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<sup>13</sup>

$$\begin{aligned} \frac{mv^2}{r} &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2} \\ \Rightarrow v &= \sqrt{\frac{e^2}{4\pi\epsilon_0 mr}} \end{aligned} \quad (1.28)$$

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

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

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

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

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

$$\begin{aligned} mvr &= n \frac{h}{2\pi}, \quad \text{using ??} \\ \Rightarrow mr \sqrt{\frac{e^2}{4\pi\epsilon_0 mr}} &= n \frac{h}{2\pi}, \quad \text{using ??} \\ \Rightarrow r &= \frac{n^2 h^2 \epsilon_0}{\pi e^2 m} \end{aligned} \quad (1.31)$$

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

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

<sup>13</sup> 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. ?? 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

$$\begin{aligned} r_1 &= \frac{h^2 \epsilon_0}{\pi e^2 m} = 0.529 \times 10^{-10} m, & \text{(The Bohr radius of hydrogen)} \\ &= 0.529 \text{ \AA}, & \text{(in Angstroms)} \end{aligned} \quad (1.33)$$

*The size of an atom*

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

$$\begin{aligned} E_n &= -\frac{C}{n^2}, \quad \text{where } C = \frac{e^4 m}{8\epsilon_0^2 h^2} \\ n &= 1, 2, 3, \dots \end{aligned} \quad (1.34)$$

*A discrete spectrum for hydrogen obtained*

The obtaining of this expression ?? 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  $\nu$  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

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

*Emission and absorption understood*

i.e. that<sup>14</sup>

$$\begin{aligned} h\nu &= -\frac{C}{m^2} - \left(-\frac{C}{n^2}\right) \\ \Rightarrow \nu &= -\frac{C}{h} \left\{ \frac{1}{m^2} - \frac{1}{n^2} \right\} \\ &= \nu_{mn}, \quad \text{say} \end{aligned} \quad (1.36)$$

so that the emitted frequencies  $\nu_{mn}$  given by ?? are indeed quantised, as found in experiments<sup>15</sup>.

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

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

*The Balmer series derived*

<sup>14</sup> Note that this equation ?? 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  $\nu$  and *drops down* to the energy level  $E_n$ , or, that an electron of energy  $E_n$  *absorbs* a photon of frequency  $\nu$  and *moves up* to the energy level  $E_m$ .

<sup>15</sup> On a point of nomenclature, which we only mention in case the reader has come across it, the quantity

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

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

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

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

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

*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  $\mu$  ( $\mu$  is called the *reduced mass*) where

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

where  $M$  is the proton mass.<sup>17</sup> For the proton mass  $M$  we have

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

and if we replace  $m$  by  $\mu$  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

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

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  $\mu$  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*.

*We can't  
completely  
ignore  
(kinemat-  
ically) the  
presence of  
the proton*

*Notice the  
third dec-  
imal place  
has now  
changed*

*High preci-  
sion the rule  
nowadays*

<sup>16</sup> We have not yet given the values of  $e, m$  and  $\epsilon_0$ , 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.

<sup>17</sup> The reason that this replacing of  $m$  by  $\mu$  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  $\mu$ . 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  $\nu_{mn}$  we have obtained a much *larger* set of possible frequencies namely:  $\nu_{mn}$  where  $m = 1, 2, 3, \dots$  and  $n = 1, 2, 3, \dots$  the point is that most of these frequencies are not in the visible region but the Balmer series frequencies  $\nu_{n2}$  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.

*Failings of the Bohr-Sommerfeld model*

### § 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  $\nu$  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.

*If light can behave like a particle, can electrons behave like waves?*

The far reaching idea of de Broglie was very simple: he wanted to associate a *wave*  $\psi$  to each particle of non-zero mass  $m$ . The wavelength  $\lambda$  of this wave  $\psi$  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

$$E^2 - \mathbf{p}^2 c^2 = 0 \quad (1.44)$$

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

$$\begin{aligned} E &= h\nu \\ \Rightarrow |\mathbf{p}| &= \frac{h\nu}{c} \\ \text{i.e. } |\mathbf{p}| &= \frac{h}{\lambda} \end{aligned} \quad (1.45)$$

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

$$\begin{aligned} E &= h\nu \\ \mathbf{p} &= \frac{h}{\lambda} \mathbf{n}, \quad \mathbf{n}^2 = 1 \end{aligned} \quad (1.46)$$

*Particles of positive mass  $m$  have a wavelength  $\lambda$*

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

*Experiment confirms the wave nature of electrons: they diffract*

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

$$|\mathbf{p}| = \frac{h}{\lambda} \quad (1.47)$$

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*.

*Wave-particle duality*

## § 6. The hydrogen spectrum explained: Heisenberg and Schrödinger

The spectrum of hydrogen was finally properly explained by both Heisenberg, in 1925, and Schrödinger<sup>18</sup> in 1926.

*Heisenberg and Schrödinger both cracked the problem*

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, 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])

*Heisenberg replaces classical physical quantities by operators in quantum mechanics*

*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

$$xp \neq px \quad (1.48)$$

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

$$xp - px = i\hbar I \quad (1.49)$$

<sup>18</sup> 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

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

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  $\psi$  introduced by de Broglie. Note, that, from now on we shall give  $\psi$  its modern name which is the *wave function*.

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

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

which we abbreviate to

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

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  $\psi$  by solving the simpler equation

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

and if we substitute  $??$  for the RHS of the Schrödinger equation  $??$  above we obtain the important equation

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

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  $??$  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

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

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

*The famous commutation relation for position and momentum appears*

*Here is the famous Schrödinger wave equation*

*The time independent Schrödinger equation*

*The Schrödinger equation for hydrogen*

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

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 ?? ; 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  $\psi_n$  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  $\psi$  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  $\psi$  has is as follows: the probability of finding the particle, whose wave function is  $\psi$ , in the small interval

$$dx \mathbf{i} + dy \mathbf{j} + dz \mathbf{k} \quad (1.57)$$

about the location

$$x \mathbf{i} + y \mathbf{j} + z \mathbf{k} \quad (1.58)$$

at time  $t$ , is

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

*Probability enters at the foundation of physics*

Thus, through the wave function  $\psi$ , 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<sup>19</sup> to Max Born,

4. Dezember 1926

Lieber Born

<sup>19</sup> 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

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.

*Heisenberg's  
uncertainty  
principle*

## § 10. Some motivation for the Schrödinger equation

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

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

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

$$\frac{m\mathbf{v}^2}{2} + V = E \quad (1.61)$$

where  $V$  is the potential energy. But

$$\begin{aligned} \mathbf{p} &= m\mathbf{v} \\ \Rightarrow \frac{\mathbf{p}^2}{2m} &= \frac{m\mathbf{v}^2}{2} \end{aligned} \quad (1.62)$$

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

$$E = \frac{\mathbf{p}^2}{2m} + V \quad (1.63)$$

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

$$\left. \begin{aligned} \frac{-\hbar^2}{2m} \nabla^2 \psi &= E\psi \\ E &= \frac{\mathbf{p}^2}{2m} \end{aligned} \right\} \text{for a free particle} \quad (1.64)$$

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

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

*A plane wave*

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  $\psi$  by writing

$$\mathbf{p} = \frac{h}{\lambda} \mathbf{n}, \quad E = h\nu \quad (1.66)$$

and, on substituting this data into our expression for  $\psi$ , we find that

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

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

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

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

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

and also that

$$i\hbar \frac{\partial}{\partial t} \psi = E\psi \quad (1.70)$$

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

$$\begin{aligned} -i\hbar\nabla\psi &= \mathbf{p}\psi \\ i\hbar\frac{\partial\psi}{\partial t} &= E\psi \end{aligned} \quad (1.71)$$

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

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

But for a *free particle*

$$E = \frac{\mathbf{p}^2}{2m} \quad (1.73)$$

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \quad (1.74)$$

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

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

*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

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

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

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

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  $\psi$  satisfies the equation

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi \quad (1.78)$$

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

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

which we recognise as the full Schrödinger equation [1.54](#) above.

## § 11. Operators are introduced

Finally since, according to [1.54](#), the differential operator

$$\frac{-\hbar^2}{2m}\nabla^2 + V \quad (1.80)$$

applied to the wave function  $\psi$  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

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

*The Hamiltonian is introduced*

Recall, too, that in [1.71](#) we saw that the operator

$$-i\hbar\nabla \quad (1.82)$$

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<sup>20</sup> perhaps) by  $p$  so that one writes

$$p = -i\hbar\nabla \quad (1.83)$$

*The momentum operator defined*

So  $-i\hbar\nabla$  gives  $\mathbf{p}\psi$  when applied to *any wave function*  $\psi$ , 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  $\psi$  is given by the equation

$$-i\hbar\nabla\psi = \mathbf{p}\psi \quad (1.84)$$

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

$$-i\hbar\frac{d}{dx} \quad (1.85)$$

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.

<sup>20</sup> 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]

### References

1. Planck M., Über das Gesetz der Energieverteilung im Normalspectrum (On the law of energy distribution in normal spectra), *Ann. der Phys.*, **309**, 553–563, (1901).
2. Einstein A., Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt (On a heuristic viewpoint concerning the production and transformation of light), *Ann. der Phys.*, **322**, 132–148, (1905).
3. Bohr N., On the constitution of atoms and molecules, *Phil. Mag.*, **26**, 1–25, (1913).
4. Bohr N., On the constitution of atoms and molecules, *Phil. Mag.*, **26**, 476–502, (1913).
5. Bohr N., On the constitution of atoms and molecules, *Phil. Mag.*, **26**, 857–875, (1913).
6. Sommerfeld A., Zur Quantentheorie der Spektrallinien (On the quantum theory of spectral lines), *Ann. der Phys.*, **356**, 1–94, (1916).
7. de Broglie L., Radiations—Ondes et quanta (Radiation—waves and quanta), *Comptes Rendus*, **177**, 507–510, (1923).
8. Heisenberg W., Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen (Quantum theoretical reinterpretation of kinematic and mechanical relations), *Zeit. für Phys.*, **33**, 879–893, (1925).
9. Born M. and Jordan P., Zur Quantenmechanik (On quantum mechanics), *Zeitschrift für Physik*, **34**, 858–888, (1925).
10. Born M., Heisenberg W. and Jordan P., Zur Quantenmechanik II (On quantum mechanics II), *Zeit. für Phys.*, **35**, 557–615, (1925).
11. Dirac P., The fundamental equations of quantum mechanics, *Proc. Roy. Soc. Lond.*, **A109**, 642–653, (1925).
12. Dirac P., The physical interpretation of the quantum dynamics, *Proc. Roy. Soc. Lond.*, **A113**, 621–641, (1927).

13. Schrödinger E., Quantisierung als Eigenwertproblem (Quantisation as an eigenvalue problem), *Ann. der Phys.*, **384**, 361–376, (1926).
14. Schrödinger E., Quantisierung als Eigenwertproblem (Quantisation as an eigenvalue problem), *Ann. der Phys.*, **384**, 489–527, (1926).
15. Schrödinger E., Der stetige Übergang von der Mikro-zur Makromechanik (The continuous transition from micro- to macromechanics), *Die Naturwissenschaften*, **14**, 664–666, (1926).
16. Schrödinger E., Über das Verhältnis der Heisenberg-Born-Jordanschen Quantenmechanik zu der meinen (On the relation between Heisenberg-Born-Jordan quantum mechanics and mine), *Ann. der Phys.*, **384**, 734–756, (1926).
17. Schrödinger E., Quantisierung als Eigenwertproblem (Quantisation as an eigenvalue problem), *Ann. der Phys.*, **385**, 437–490, (1926).
18. Schrödinger E., Quantisierung als Eigenwertproblem (Quantisation as an eigenvalue problem), *Ann. der Phys.*, **386**, 109–139, (1926).
19. Schrödinger E., An undulatory theory of the mechanics of atoms and molecules, *Phys. Rev.*, **28**, 1049–1070, (1926).
20. Born M., Zur Quantenmechanik der Stossvorgänge (On the quantum mechanics of collision processes), *Zeit. für Phys.*, **37**, 863–867, (1926).
21. Born M., Zur Quantenmechanik der Stossvorgänge (On the quantum mechanics of collision processes), *Zeit. für Phys.*, **38**, 803–827, (1926).
22. Heisenberg W., Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik (On the concreteness contained in the quantum theoretical kinematics and mechanics), *Zeit. für Phys.*, **43**, 172–198, (1927).
23. Dirac P., The quantum theory of the electron, *Proc. Roy. Soc. Lond.*, **A117**, 610–624, (1928).
24. van der Waerden B. L. (ed.), *Sources of quantum mechanics*, Dover, (1967).
25. Born M. and Einstein A., *The Born–Einstein letters 1916–1955*, Macmillan, (2005).
26. Bell J., On the Einstein Podolsky Rosen Paradox, *Physics*, **I**, 195–200, (1964).
27. Aspect A., Dalibard J. and Roger G., Experimental test of Bell’s inequalities using time-varying analyzers, *Phys. Rev. Lett.*, **49**, 1804–1807, (1982).