

Elementary quantum theory.

20.1 Introduction.

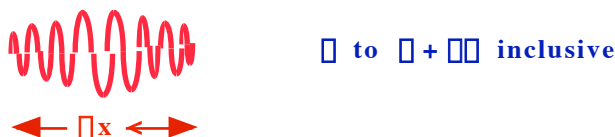
We have seen that nature is not simple and that many things come in little lumps or quantities that are limited to a set of discrete values. One reason for this is because there is a connection between the phenomena and the observer. The act of observation or measurement cannot be separated from the result. The observer interacts with the 'things' being observed and alters them. On the human scale these alterations are too small to have any obvious effect, but on the atomic scale this interaction between observer and observed is very important.

Secondly, our sense of reality on a human scale cannot be extended into the realm of the sub-atomic particle. We can never know what a particle is doing between observations. We can never know what form it takes between observations, only what we 'see' at the moment of observation. The common perception of what we call reality is something like the existence of an object such as a brick. We assume that the brick remains unchanged between observations, that is, the brick exists whether or not we see it or touch it. At the sub-atomic level this is not true. We only experience the observations and these are contradictory, since we sometimes see a wave and sometimes a particle. That is, we can only know anything from the interaction with the observer [or the instruments used]. What the 'things' consist of is a **mystery**. We have developed a mathematical model that we call a wave function but this is not a wave in the classical sense and nor does it represent anything real.

20.2 Wave-particle duality [continued, with some repetition, from chapters 17 and 18]

If electrons are waves then how can they be located in space. The answer is that if the electron is represented by a wave function that is the sum of a small range of wavelengths $\Delta\lambda$ [interfering] the result is a wave pulse looking something like the diagram below. This is a function with a speed v equal to that of the electron.

Fig20[i] A wavicle.



G.P.Thomson, son of J.J.Thomson the discoverer of the electron, found that electrons had wave like properties in 1927. The dual [wave-particle] nature of light and electrons was now established. A few years earlier in 1924, **Louis de Broglie** had put forward a theory that particles such as electrons would show wave properties and this now gave a reason for the assumptions made by N.Bohr. De Broglie postulated that the electron in atomic hydrogen, when considered as a wave, must form a circular standing wave, if the energy state of the electron was to be stable. He proposed that the wavelength of the electron or any particle was inversely proportional to it's momentum. One reason for this was that momentum is a **vector** and the only wave property related to direction was the wave number which is given the symbol **k**. In the equation for three dimensional waves **k** is a vector in the direction perpendicular to the wave front. In the equation for a wave in the **+x** direction $k = 2\pi/\lambda$. In one dimensional waves the equation is

$$y = a \sin 2\pi[ft - x/\lambda] \quad \text{or} \quad y = a \sin k[vt - x] \quad \text{eqn. [i]}$$

Also Einstein had shown much earlier that the **four momentum** of a photon, which has zero rest mass, was given by [see chapter 23 on special relativity]

$$p^2 = [E/c]^2 - p^2 = m_0^2 c^2 = 0 \quad \text{and therefore} \quad E/c = p$$

Using the energy of a photon $E = hf = hc/\lambda$ where **h** is Planck's constant and eliminating **E** we have the expression for the wavelength of a particle $\lambda = h/p$ Thus de Broglie proposed that this applied to particles as well as photons.

[i] For a particle mass m then $\lambda = h/mv$. eqn. [ii]
 For high speeds the mass m is the relativistic mass not the rest mass.

[ii] The electrons in a hydrogen atom are in a circular orbit, circumference $2\pi r$, and there must be a whole number $[n]$ of wavelengths in each circle forming a stationary wave :-

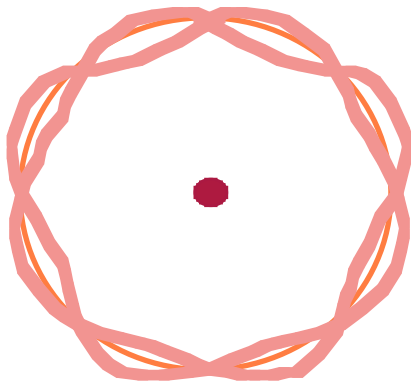
$$n\lambda = 2\pi r = nh/mv \quad \text{and therefore} \quad rmv = L = n [h/2\pi]$$

That is angular momentum is an integer multiple of some constant, which is precisely the assumption made by N.Bohr. This wave particle duality was the starting point for Schrodinger's development of quantum mechanics.

20.3 Stationary Waves.

If the electron [wave function] is trapped [held in place by an electric field] by the proton or nucleus the like other waves it becomes a stationary wave. See waves in strings and pipes in the Sound Unit. Thus in an atom the electron exists as a stationary wave function and like strings there are many modes of vibration. These modes correspond to the energy levels of the electron.

Figure 20[ii]. Electron standing waves.



Four wavelengths fitting into a circumference.

Of course the classical conditions for the orbit still apply and the permitted energy levels are as before. The difference is that now there is a **reason** for the quantisation.

Of course nothing actually oscillates the function is that of a wave but it does not represent anything physical. The function tells us the energy of the electron and the probability of finding the electron at any point.

20.4 The wave function; ψ .

One should not think of the standing wave in an atom as the actual path of a particle. The idea of a stationary wave like a string or sound wave is not quite the same, indeed the wave must be three dimensional to account for the obvious spherical nature of the atom. Today the electron is represented by a wave function and the picture is really only a representation of the wave function. The wave function is an equation, a mathematical description of reality. It was **Max Born** who proposed that the amplitude or the magnitude of the wave function being connected to the probability of finding an electron in that place.

In Bohr's theory there is no reason why the value of the quantum number **n** could not be zero. In de Broglie's theory the stationary wave has to exist because the electron is in a restricted space and the lowest value of **n** is one. Therefore the electron cannot decay in to the nucleus. This had been a problem with Bohr's model.

It seems that particles have a wavelength, which means that they should be expressed by a wave equation. Particles are not just little round objects, they diffract, interfere and generally behave like waves; and also EM waves, like light, behave as particles in many interactions. Thus today matter and radiation are grouped together and expressed as wave functions, which are given the Greek letter psi, ψ . This is a mathematical way of expressing the observed properties of, for the sake of a better word '**things**'. However, we must not forget that an electron is a point mass when it is observed or detected and so is a photon. They may exhibit wave properties when large numbers are involved, or even on their own, but when they are actually interacting with a detector they are effectively mass points. A wave function must in some way express these observed properties but the function itself need not represent a physical entity, nor does it represent a wave in the usual sense of the word. Most importantly at the macroscopic level quantum theory must agree with everyday experience and the classical laws of physics. This is known as the **correspondence principle**.

A particle is located in space at a particular point but a wave is not confined to a point and would spread out indefinitely. A wave function can be defined that is restricted to a volume of space. Such a function is the superposition of waves over a small band of wavelengths and these interfere to produce a wave packet localised in space over a small distance. This is rather like two waves interfering to produce beats in sound. If we have, not two waves, but a small band of wavelengths around a particular value they interfere as shown below. The amplitudes of these waves also varies. It can be shown that if the wavelength of a particle, determined from it's momentum, is λ and if the function is restricted to a spatial extension Δx , then the wavelengths interfering must be over a range $\Delta \lambda$ such that

$\Delta \lambda \Delta x > \lambda^2$ and the wave groups look as shown in fig.20[iii].

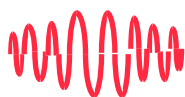
If $\lambda_2 > \lambda_1$ then $\Delta \lambda_1 \lambda_1 = \Delta \lambda_2 \lambda_2 > \lambda^2$

therefore $\Delta \lambda_1 > \Delta \lambda_2$

Fig.20[iii] Wave functions for a particle.

momentum known less precisely

λ to $\lambda + \Delta \lambda$ inclusive



position known more precisely

$\Delta \lambda > \Delta \lambda'$

same speed and momentum

$\Delta x < \Delta x'$

momentum known more precisely

λ to $\lambda + \Delta \lambda'$ inclusive



position known less precisely

20.5 Heisenberg’s uncertainty principle.

The above means that the actual wavelength we started with λ is now actually a range of wavelengths, $\Delta\lambda$. Since the momentum originally determined the wavelength, we now have a range or uncertainty for the momentum, Δp . Heisenberg considered the act of observation of a particle and concluded that there was an ultimate limit to the degree of certainty in measuring particular pairs of quantities.

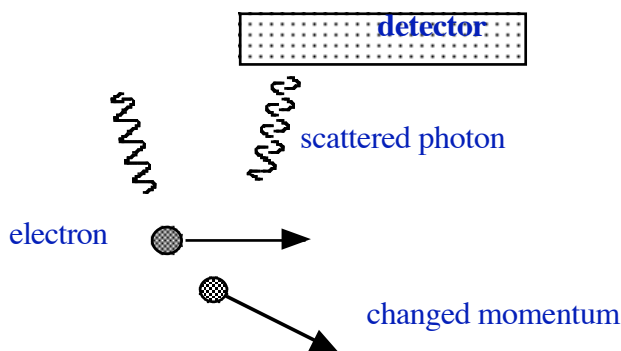
According to W.Heisenberg, if we know the momentum of a particle very precisely, then we also know the de Broglie wavelength associated with the particle precisely. This means that the spread of the wave function is really large and we therefore do not know the position of the particle very well. The uncertainty of the position is high if the uncertainty of the momentum is low. Heisenberg formalised this in his uncertainty principle, which he deduced from practical considerations and which states

“There exists a fundamental limit on the ultimate precision with which momentum and position of an object may be measured simultaneously.”

Heisenberg showed that $\Delta x \Delta p > \frac{h}{2\pi}$ eqn.[iii]

One can think about a particle at an exact position in space, but when it comes to actually measuring the position, or even looking at the object, we can never know it exactly. Nor can we know the momentum of the particle. The relation above can be understood from a non rigorous treatment of the act of observation of, say, an electron. The act of just seeing an electron would involve at least one photon striking it and then entering our detecting equipment. The photon has momentum and hence gives an impulse to the electron

Fig.20[iv]. Looking at an electron.



If we assume that the change in the momentum of the electron is at worst $\Delta p \sim \frac{h}{\lambda}$

and the error in the observed position of the electron is at worst $\Delta x \sim \lambda$

Substituting for λ we have $\Delta x \cdot \Delta p = h$ This does not mean that the uncertainty is due to the limitations of the observer and the electron is actually at a definite position and has a definite momentum. The uncertainty is a reflection of the wave-particle duality of reality.

20.6 Applications of Heisenberg’s Principle.

[i] Ionisation energy.

The uncertainty principle can be used to estimate the energy of the electron confined in the hydrogen atom. The uncertainty in the position of the electron is about one radius of an atom of hydrogen. This is approximately $\Delta x = 5 \times 10^{-11} \text{m}$

Therefore since $\Delta x \Delta p \sim \frac{h}{2\pi}$ then $\Delta x \Delta p > \frac{h}{2\pi}$ $\Delta p = 2 \times 10^{-24} \text{ kgms}^{-1}$

This gives the order of magnitude of the kinetic energy of the electron as about

$E_k = 2 \times 10^{-18} \text{ J}$ or 10 eV which is comparable with the ionisation energy of 13.6 eV

[ii] Energy and time.

His theory also shows that the energy of a particle and the time that it is somewhere, or an event happens, are related in the same way. The uncertainty in the energy of a particle dE and the interval of time dt for the observation are always such that

$$dE dt \geq \frac{h}{2\pi} \quad \text{eqn. [iv]}$$

This can be seen to be approximately true as follows. Let us assume that we wish to determine the frequency f of a photon of EM radiation in an observation lasting for an interval dt . The uncertainty in the count of the number of waves n is at best one.

frequency $f = n/dt$ and the uncertainty in the frequency is $df = 1/dt$

This gives a rough value for the uncertainty in the energy of the photon [or particle] of

$$dE = h df = h/dt \quad \text{therefore} \quad dE dt \geq h$$

You may remember that position and time form a four vector that is invariant. Momentum and energy are also related in the same way, so the above is reasonable.

[iii] The ground state of an electron.

Heisenburg's uncertainty principle also forbids a zero energy state for a bound electron. If it were permitted, we would know it's momentum exactly and its position as, somewhere within the box or atom.

That is if $dp = 0$ then $dx dp = 0$ which is impossible according to Heisenburg.

It seems the the uncertainty principle is a direct consequence of the wave-particle duality of matter. It also means that the act of observation is an integral part of the phenomenon. It means that observed things can never be all wave or all particle. It seems that nature is reluctant to reveal itself. In the double slit experiment we can now see that the photons can pass through both slits as a wave function as long as they are not observed in the act. If we detect the passage through a slit we alter the pattern and the form of the wave function.

20.6 Schrodinger's wave equation.

Around the same time E.Schrodinger developed a mathematical theory of matter described by wave functions. It should be realised that the wave function cannot be derived from first principles. It is a first principle in itself. The function must, however, satisfy all the observed phenomena.

- [i] A wave function is both positive and negative so the square of the amplitude of the wave function $|\psi|^2$ is taken to be the probability of finding the particle at any point. Thus a wave function might show a probability $P = 0.3$ that the electron is found within a region of space such as in a box but this does not mean that we can detect 30% of the electron's properties there. The whole particle will either be found or not found.
- [ii] The probability can vary between zero and one and the sum of the probabilities over the region that the particle is known to be confined must be unity.

$$\int_{-\infty}^{+\infty} |\psi|^2 dx = 1$$

eqn. [v]

The function ψ is chosen to be complex because real functions give impossible results, like a time variable probability. However, in certain cases only the real part is needed. The function must also be single valued and constant at all points in the box.

20.7 The wave function of a free electron.

A particle moving at constant speed and freely anywhere in space is represented by the equation for a progressive wave. The wave function is usually written in exponential form, which by **de Moivre's** theorem is :-

$$\psi = A e^{-2\pi i [ft - X/\lambda]} = A \cos 2\pi [ft - X/\lambda] - i A \sin 2\pi [ft - X/\lambda]$$

The real part of this is the wave equation developed in chapter one on sound waves, apart from a phase difference.

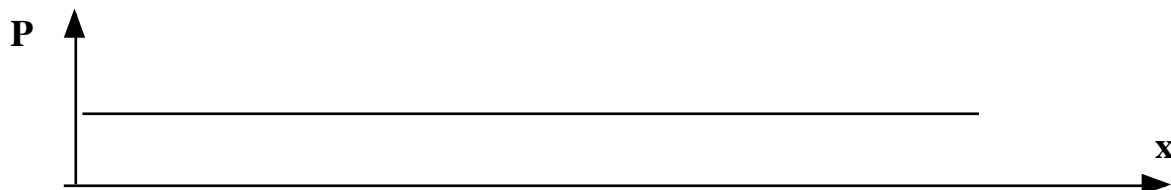
$$y = A \cos 2\pi [ft - X/\lambda] = A \sin 2\pi [ft + \pi/4 - X/\lambda]$$

The probability [p] of finding the electron anywhere is given by $p = |\psi|^2$ which is constant [the same at all points] for a free electron and where,

$$|\psi|^2 = A \cos 2\pi [ft - X/\lambda] + i A \sin 2\pi [ft - X/\lambda]$$

$$\text{and thus } |\psi|^2 = A^2$$

Fig.20[v] Probability of finding a free electron.



Using the energy of a wave pulse $E = hf$ and de Broglie's relation $\lambda = h/p$ we get the following, which is the wave function for an unconstrained electron with momentum p and energy E . The probability of finding the electron at any point is A , which in this case for a completely free electron in an infinite space is zero.

$$\psi = A e^{-2\pi i/h [Et - px]} \quad \text{eqn. [vi]}$$

20.8 Confined electrons.

At non relativistic speeds the total energy E of such an electron is the sum of its kinetic energy E_k and its potential energy V . The potential function is a scalar field that gives the force on the electron or particle in the region. The potential energy will be a function of its position $[x]$ and time $[t]$ in one dimension ; or $[x,y,z,t]$ in three [four] dimensions. The force field acts as a constraint on the motion of the electron.

$$E = E_k + V = p^2/2m + V \quad \text{and multiplying by } \psi \quad \text{we get}$$

$$E\psi = p^2\psi/2m + V\psi \quad \text{eqn. [vii]}$$

If we differentiate the wave function twice with respect to x and once with respect to time we get

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{4\pi^2 p^2}{h^2} \psi \quad \text{and} \quad \frac{\partial \psi}{\partial t} = \frac{-2\pi i E}{h} \psi$$

If we now substitute for $E\psi$ and $p^2\psi$ in the energy equation [vii] we get the Schrodinger **time dependent** wave equation in one dimension.

$$\frac{i\hbar}{2\pi} \frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{8\pi^2m} \frac{\partial^2\psi}{\partial x^2} + V\psi \quad \text{eqn. [viii]}$$

When you do a little more mathematics you will see that the three dimensional equation is simply

$$\frac{i\hbar}{2\pi} \frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{8\pi^2m} \nabla^2\psi + V\psi$$

The wave function eqn [vi] can be written as a time dependent part and a space dependent part :-

$$\psi = A e^{-2\pi i/\hbar [Et - px]} = A e^{-2\pi i/\hbar Et} e^{2\pi i/\hbar px} = \psi_x \psi_t$$

If the potential energy function V is independent of time which is usually the case even for electrons in an atom, then we only **need** a function of position ψ_x .

Hence substituting $\psi_x \psi_t$ in eqn. [vii] for ψ we get

$$\frac{i\hbar}{2\pi} \psi_x \frac{\partial\psi_t}{\partial t} = \frac{-\hbar^2\psi_t}{8\pi^2m} \frac{\partial^2\psi_x}{\partial x^2} + V\psi_x \psi_t$$

Rearranging and separating the space and time parts, we have

$$\frac{i\hbar}{2\pi} \frac{\partial\psi_t}{\partial t} = \frac{-\hbar^2}{8\pi^2m} \frac{\partial^2\psi_x}{\partial x^2} + V = E \quad \text{[necessarily a constant]}$$

The time dependent integrates to give us the time variation of the wave function

$$\psi_t = e^{-2\pi i/\hbar [Et]} \quad \text{and hence the constant } E \text{ is the total energy.}$$

The space dependent part can be rearranged and dropping the suffix x for ψ_x the differential equation for ψ_x becomes

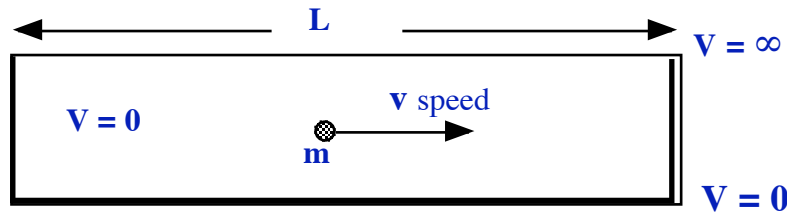
$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2m}{\hbar^2} [E - V] \psi = 0 \quad \text{eqn. [ix]}$$

This is the steady state form of Schrodinger's equation in one dimension. We can now look at the case of an electron confined in a box, which is much more simple than the electron bound to a proton in a hydrogen atom. However, this leads to the understanding of quantised energy levels and is a starting point.

20.9 An electron in a rigid box.

If we consider the wave function for a particle confined to a region of space we see that it can only have a certain set of values for its kinetic energy. These are determined by a number that is an integer. $n = 1, 2, 3$, etc. This is called the **principal quantum number** $[n]$. It determines the energy states of the electron.

Fig.20[vi]. An electron in a box.



The box has hard ends and the electron rebounds elastically at each end. Also we assume that there is no electric field inside the box. Thus we have $V = 0$ [inside] and $V = \infty$ [outside], hence we have an equation that we recognise as similar to that for simple harmonic motion and for which a solution is known

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{8\pi^2 m}{h^2} E \psi \quad \text{and} \quad \psi|' = 0 \quad \text{at the ends of the box}$$

which has as a solution

$$\psi = A \sin \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} x \quad \text{and} \quad \psi = B \cos \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} x \quad \text{eqn.[x]}$$

where $\psi = 0$ for $x = 0$ or $x = L$

Since only $\sin \psi = 0$ at $\psi = 0$ the first solution is taken and for $x = L$

$$\left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} L = n\pi \quad \text{and} \quad \frac{8\pi^2 m E}{h^2} L^2 = n^2 \pi^2$$

Therefore we have a limitation on the values that the wave function can have. The function itself is of no interest to us here, but the solutions are such that the energy of the electron is given by

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{where } n \text{ is an integer and cannot be zero.}$$

This means that the energy of the electron or any particle confined in any way can only have certain values and the energy is quantised. E.Schrodinger's wave function for a particle confined in a box also shows that there can not be a zero energy state. The number n is called the **principal quantum number**. The diagram below shows a wave function, say an electron, confined in a box. The electron moves back and forth, bouncing off the ends. The boundary of the box determines that the wave function must finish there and so the waves functions must form standing waves in the box. The wave function ψ can be found by substituting the value of E_n for E in eqn.[x].

This simplifies to $\psi_n = A \sin [n\pi x/L]$

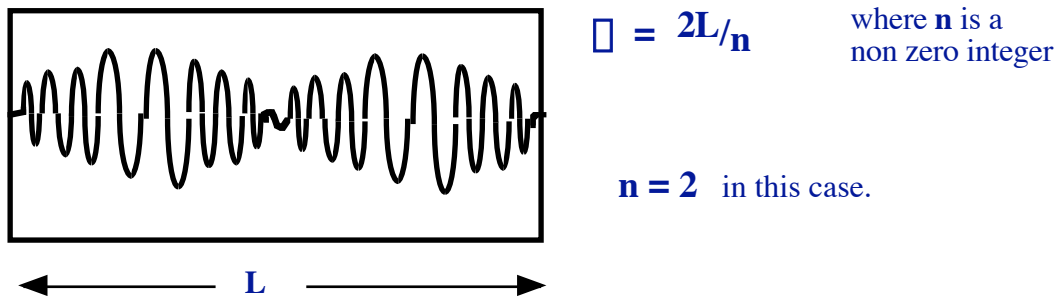
Now the probability of finding the electron inside the box is **one**. It is definitely in the box. This means that

$$\int_0^L |\psi|^2 dx = A^2 \int_0^L \sin^2 [n\pi x/L] dx = A^2 [L/2] = 1$$

Therefore $A = \left[\frac{2}{L} \right]^{1/2}$ and $\psi_n = \left[\frac{2}{L} \right]^{1/2} \sin [n\pi x/L]$

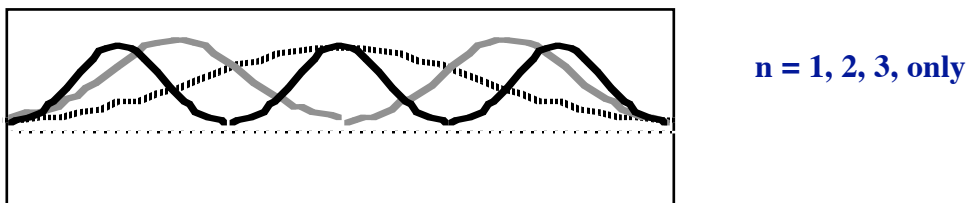
We can now calculate the probability of an electron being at any point and the function is now said to be **normalised**.

Fig.20[vii] Confined wave functions.



When $n = 1$ the probability of finding the electron gradually increases towards the centre of the box, which seems reasonable. Interestingly for $n = 2$ as shown, the probability of finding the electron at the centre of the box is zero. Higher energy states have more places where the electron is never found.

Fig.20[viii] Probability distribution for an electron in a rigid box



You may remember the equation of standing waves from Appendix 1C in the first chapter on sound waves, which is $\psi = 2a \sin [2\pi ft] \cos [2\pi x/\lambda]$. This gives a value of ψ^2 that is time dependent and we have the impossible situation of the probability of the electron, being at a position or even being in the box, varying with time between some value and zero. This is why the complex form of the equation is used. That the wave function for the confined electron is a standing wave can be seen by including the time component of Schrodinger's equation.

$$\psi = A e^{-2i\pi/h Et} \sin \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} x \quad \text{written as} \quad \psi = A e^{-t} \sin x$$

for simplicity; and using de Moivre's theorem to combine them we obtain

$$e^{ix} - e^{-ix} = 2i \sin x \quad \text{retaining the simple form.}$$

$$\psi = A/2i \left(e^{-i[x-t]} - e^{-i[x+t]} \right)$$

This is two waves travelling in opposite directions and with our limiting conditions there is a node at each end of the box. This means that the electron in the box can never be at rest, if a stationary wave exists. The fixed series of permitted wavelengths gives a series of energy levels that are quantised. This applies to an electron in an atom as well, although the mathematics is more complicated, and therefore we can see why the electrons around an atom do not spiral into the nucleus. The quantisation of the energy levels in an atom is a direct result of the wave-particle nature of reality and only a completely free electron can have a complete range of momenta and therefore energies.

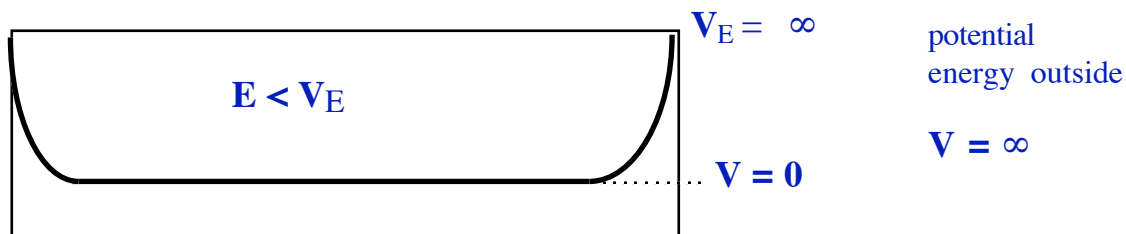
Experimental Confirmation.

In the case of an electron bound to an atom a full treatment enables the probability of a downward electron transition to be calculated. In turn we can then predict the relative brightness of the spectral lines for that element. The theory agreed with observation very well.

20.10 Electron in a non rigid box.

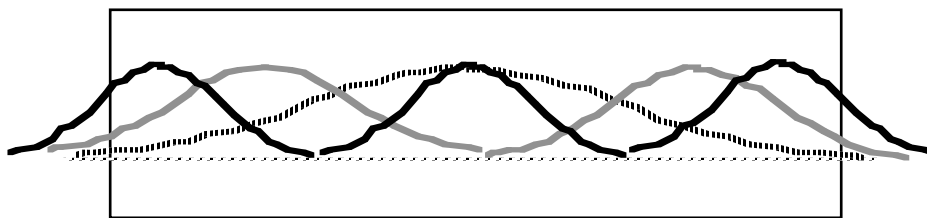
If the ends of the box are not rigid and can 'give' when the electron hits the probability functions for $n = 1, 2$ and 3 , are as shown below. Such a box would have to slow the electron gradually and then 'throw' it back instead of a sudden reversal of velocity at each end. This means that the ends of the box would have a potential function with a steep gradient at each end.

Fig.20[ix] Potential function for a non rigid box.



The potential is infinite outside in theory, but in practice it can never be such and if the energy outside is finite then there is a probability of finding an electron outside the box. This is despite its energy being less than V .

Fig.20[x] Probability distribution for a non rigid box



This is the situation for the electron bound to an atom. The boundary is not rigid and the electron could escape. In the simple case of the box, there is a probability of finding the electron **outside** the box, which is greater for the higher energy levels. This can be explained in terms of the uncertainty principle.

$$dp dx > h/2\pi$$

The uncertainty in the momentum of the particle must be infinite outside the box if the position is known to be definitely inside the box. This means that the energy of the particle outside could be infinite as well. This is impossible in practice and hence there is some chance of a particle escaping from a bound situation even if it does not have enough energy to escape according to classical physics. This explains tunnelling and alpha particle emission from radioactive nuclei.

Wave functions for more realistic situations become increasingly complex and we will stop here. The point is that classical physics does not explain the observed phenomena and quantum theory does. Three other quantum numbers arise in more detailed analysis of wave functions. These are mentioned briefly.

20.11 Orbital and Magnetic quantum numbers.

In three dimensions the restrictions on the values of the wave function due to any limits on the probability of a particle being at any point, caused by it being confined to a region of 3D space, give rise to two more quantum numbers. This should be reasonable since in 3D there are three boundary conditions. In the case of the hydrogen atom the electric field of the proton confines the electron to a set of orbits.

The mathematics of three dimensional wave functions is quite complicated and usually involves using spherical polar coordinates. It turns out that, not only is the total energy of the electron quantised, but also it's angular momentum [L]. This is a vector and is specified by both magnitude and direction. The quantum number that limits the magnitude of the angular momentum is called the orbital quantum number [l].

The direction of the angular momentum is limited by the magnetic quantum number [m_l]. This is in a way a quantisation of space since only specific axes of rotation are permitted. It is called magnetic because an electron orbiting the nucleus will have a magnetic field and be affected by an external field. This is the small effect that results in the separation of the principle lines in the spectrum into many fine lines seen in the **Zeeman** effect.

20.12 Quantum spin.

A fourth quantum number called spin [m_s] arises, when relativistic effects are included, which can only be plus or minus a half. This is not due to the electron spinning on it's own axis, which is a classical concept, but is simply a quantum number that arises due to the effect of the magnetic field of the proton on the electron. This was first explained by Dirac in 1928 using special relativity. In the frame of reference of the electron the proton is spinning around and therefore produces a magnetic field. When an external field is applied some lines split into two narrowly separated lines. Some energy levels are split even without an external field giving two spectral lines that are very close together. An example of this is the two D-lines of sodium.

All four of the quantum numbers [n, l, m, s] arise from limitations on the values of the wave function ψ produced by the boundary conditions and the fields within the region of confinement. These numbers have sets of values outlined in the table below.

Fig.20[xi] Quantum numbers.

Name	Symbol	Permitted Values
Principal	n	1, 2, 3, ... n
Orbital	l	0, 1, 2, ... [$n - 1$]
Magnetic	m_l	$-l, -(l - 1), -1, 0, +1, 2, \dots +l$
Spin	m_s	$+1/2, -1/2$, only

20.13 Stationary states.

The wave functions for the electron in an atom give a probability distribution that does not vary with time, although the wave function itself does. This means that the charge distribution of the electron is constant or static. The distribution agrees closely with the orbits of Bohr and de Broglie but since the picture is one of **stationary charge** there is no emission of EM radiation and the **problem of decaying orbits in Rutherford's classical theory is not relevant.**

20.14 The absorption and emission of radiation.

We have seen that waves can interfere or superpose and the same applies to the wave functions for electrons confined around atoms. If the wave functions for the electron in the energy levels of the hydrogen atom are say ψ_1, ψ_2, ψ_3 , etc. then if ψ_1 and ψ_2 interfere to produce $[\psi_1 + \psi_2]$ the probability distribution is not stationary.

$$[\psi_1 + \psi_2]^2 = \psi_1^2 + \psi_2^2 + 2\psi_1\psi_2$$

The last term is time dependent.

In hydrogen the function oscillates at a frequency given by

$$f = [E_2 - E_1] / h \quad \text{where } E \text{ is the energy of the electron and hence}$$

$$E_2 - E_1 = hf \quad \text{which is the expression we recognise for the Bohr atom.}$$

This superposing of wave functions occurs when a photon of this frequency is incident on the atom. The electron effectively has this frequency as one of many natural frequencies and it absorbs the photon and resonates at this frequency until all of the energy of the photon is absorbed and then it settles in the stationary state of ψ_2 . Thus only photons with frequencies equal to these non stationary states can be absorbed and hence explaining line absorption spectra.

20.15 Spontaneous emission.

The electron is not stable above the ground state and can only exist at this level for a lifetime of around 10^{-8} seconds. The transition to the ground state again involves the electron oscillating with the same frequency that is determined by the time dependent part of the superposed wave function, $\psi_2\psi_1$. This only ceases when a photon of this frequency and energy $E_2 - E_1$ is emitted. The lifetime of the electron in an excited state depends on the two superposed wave functions and primarily on the lower level. Thus if there are many possible downward transitions from say ψ_9 the most probable one is that with the shortest lifetime. Therefore some transitions occur much more than others and this accounts for the differing brightness of the spectral lines in most spectra and sodium with its two very bright yellow lines and much fainter red and green lines is a good example. Neither Bohr's theory and that of de Broglie did not explain the different brightness of the lines.

20.16 Induced emission.

If a photon with one of the natural frequencies of an excited electron passes very close to the atom it can trigger the electron to drop to the corresponding lower level, emitting a photon with the same frequency and in phase with the original photon. For example if an electron is represented by ψ_3 there are two possible natural or resonant frequencies determined by the parts of the superposed functions $\psi_3\psi_1$ and $\psi_3\psi_2$. As the photon exerts an influence on the electron, through its EM field, it sets it oscillating but this time the final state is the lower level and a second photon is emitted. If the incident photon has a different frequency nothing happens.