2 Introduction to Quantum Mechanics [8 lectures]

2.1 Historical setting

This is a brief resume as the material of this introduction has been covered in the modern physics section of the 1st year physics course.

By the end of the 19th century, the scientific discipline of physics had developed to a truly monumental edifice to modern civilisation. The awesome predictive power and clarifying insight into nature generated by the theories of physics inspired an arrogant confidence that physics was an almost complete theory. No less did the subsequent technological advances and concomitant improvement in human quality of life re-inforce this opinion, not only amongst scientists, but also in the general population.

Thermodynamics	Carnot cycle, entropy (engines, refrigeration)
Newtonian Mechanics	All motions (astronomy, transport, machines)
Maxwell's Equations	Electricity, magnetism, EM-waves (electrification of cities, transport, X-rays, radio-communication)

Table 1: Examples of major physics theories, spectacularly successful by the end if the 19th century, and some of the technological advances they led to.

It was surmised that the few remaining unexplained phenomena, as well as the remaining inadequacies of theory, would soon yield to concentrated effort, and the final textbooks could then be written.

However, one of the most innocuous seeming of the unexplained phenomena was to change the course of scientific history, and usher in a totally new perception of nature.

The unexplained phenomenon in question was the *black body radiation* emitted by a body hotter than its surroundings. If the theories of table 1 were so satisfactory, then it should have been possible to describe the black body radiation spectrum from the foundation of existing theories in a microscopic way. The manifestation of heat as thermal motion of the molecules of the heated material was quantitatively specified by ideas from thermodynamics and Newtonian mechanics. Maxwell's equations would then quantitatively determine the radiation spectrum from these molecular oscillators. The Rayleigh-Jeans theory of black body radiation was one such example of a failed classical theory.

The failure of classical mechanics to account for black body radiation lead Max Planck to approach the problem from another direction. That is : find a mathematical expression that could account for the black body radiation spectrum, and then seek to derive this spectrum from a new equation, hitherto unknown.

This lead to the phenomenological postulation of Planck's Radiation Law for the spectral energy density of black body radiation in 1900.

$$u(\nu, T)\, d\nu = \frac{8\pi h}{c^3} \frac{\nu^3\, d\nu}{e^{h\nu/kT} - 1} \tag{1}$$

In order to "fit" the observations (see figure 1), the new constant h, termed Planck's constant, would have to have the very curiously small magnitude of

$$h = 6.626 \times 10^{-34} \text{ J.s} \tag{2}$$

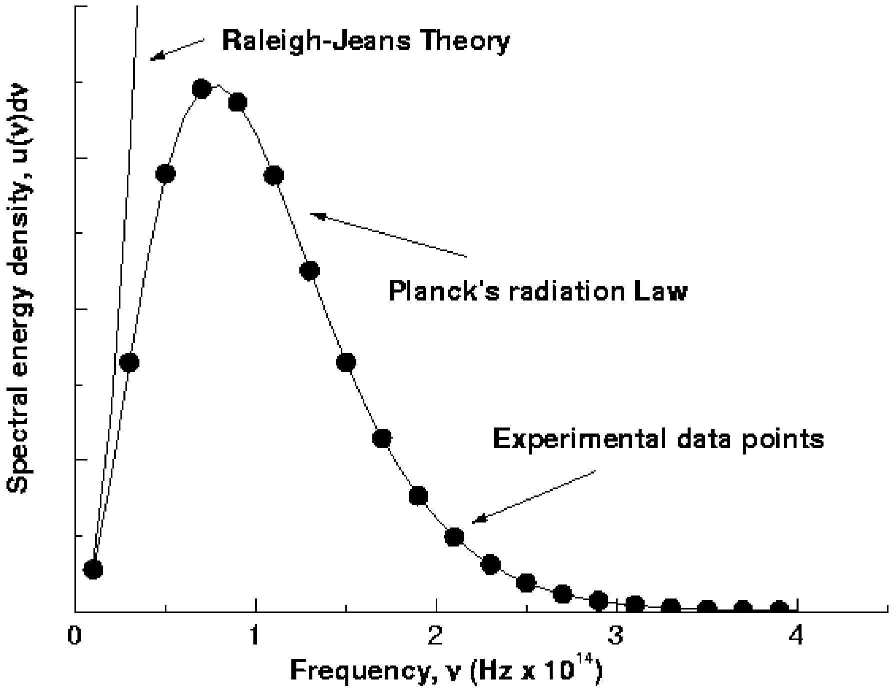

Figure 1: The black body radiation spectrum described by Planck's Radiation Law.

The new physics information which allowed Planck's Radiation Law to be derived was that the energies of the molecular oscillators must be quantised, not continuous, as it had been considered to be the case until then.

$$\epsilon = nhv \qquad n = 0, 1, 2, 3, \cdots \tag{3}$$

Each discrete bundle of energy was called a **quantum** from the Latin word for "how much".

Exercise 2.1
Show that the Rayleigh-Jeans formula

$$u(\nu, T)\, d\nu = \frac{8\pi kT}{c^3}\nu^2\, d\nu \tag{4}$$

is recovered as the low frequency limit of Planck's Radiation Law.
(Hint : note that in the low frequency limit $\frac{h\nu}{kT} \ll 1$.)

Einstein made the additional bold assertion that photons themselves had a quantised energy (not just the molecular oscillators). In this case, each photon represented a packet of energy, given by $E_\gamma = hv$ and would therefore be better described as a particle rather than an electro-magnetic wave. These particles of light were called photons.

The Photo-electric Effect, Compton Effect and Pair Production could all be well described by considering the photon (particle) theory of light rather than the wave theory of light.

Thus light could display either particle-like or wave-like properties. 19 years later (in 1924) de Broglie proposed that particles might also display wave-like properties. He postulated the de Broglie relation, (the derivation of which was the subject of Exercise 1.15) connecting the wave and particle properties together via Planck's constant. This relation identifies the de Broglie "wavelength" associated with a particle.

$$\lambda = h/p = h/(mv) \qquad \text{Planck's constant} = h = 6.626 \times 10^{-34}\ \text{J.s} \tag{5}$$

Wave theory	Particle Theory
EM-Wave theory (Maxwell's Equations)	Photo-electric Effect
Propagation of EM-waves at speed c (Hertz experiment etc)	Compton Effect
Young's double slit experiment (interference phenomena)	Pair Production
Diffraction	Gravitational red-shift

Table 2: Evidence for either the particle or the wave nature for light.

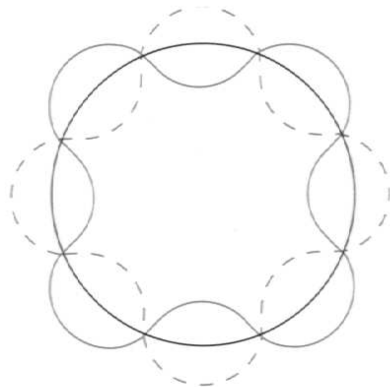

Figure 2: An example of the quantisation condition for the Bohr model of the atom. Here, four de Broglie waves are accommodated in the circumference of the electron orbit around the nucleus.

The wave nature of particles was not so incredible, as it could could provide an explanation for the quantisation of energy levels in the Bohr model of the atom. In 1913, Bohr had postulated that the angular momentum of the electron orbits in the Rutherford model of the atom would be quantised :

$$L = n\frac{h}{2\pi} \qquad n = 0, 1, 2, 3, \cdots \tag{6}$$

The Bohr model could successfully account for the stability of atoms, predict ionisation energies and sizes of hydrogenic atoms, and provide insight into line emission/absorption spectra. Using the de Broglie relation, Bohr's quantisation condition could now be written as the requirement that an integral number of de Broglie waves for the electron should be accommodated in the electron orbit of radius r.

$$2\pi r = n\lambda \qquad n = 0, 1, 2, 3, \cdots \tag{7}$$

Exercise 2.2
Recover Bohr's quantisation condition from this requirement.

More direct evidence of the wave nature of the electron was soon to come. By 1927, in a direct analogue of Young's double slit experiment for photons, an interference pattern for electrons traversing a crystal was obtained.

We may summarise the early results pointing to a quantum theory:

- Electro-magnetic waves may behave sometimes like particles (photons).
- Particles may behave sometimes like waves (de Broglie waves with $\lambda = h/p$).
- The energy of waves is quantised in such a way that $E = hf$.

- The extremely small size of Planck's constant $= h = 6.626 \times 10^{-34}$ J.s sets the scale for quantum effects.

2.2 Young's double slit experiment - Quantum mechanical behaviour

Young's double slit experiment represents the observation of an interference pattern consistent with a wave nature for objects that traverse the apparatus. This is emphasised in the figures 3 and 4 The diffraction and interference effects appear at first sight to be due to the beam of

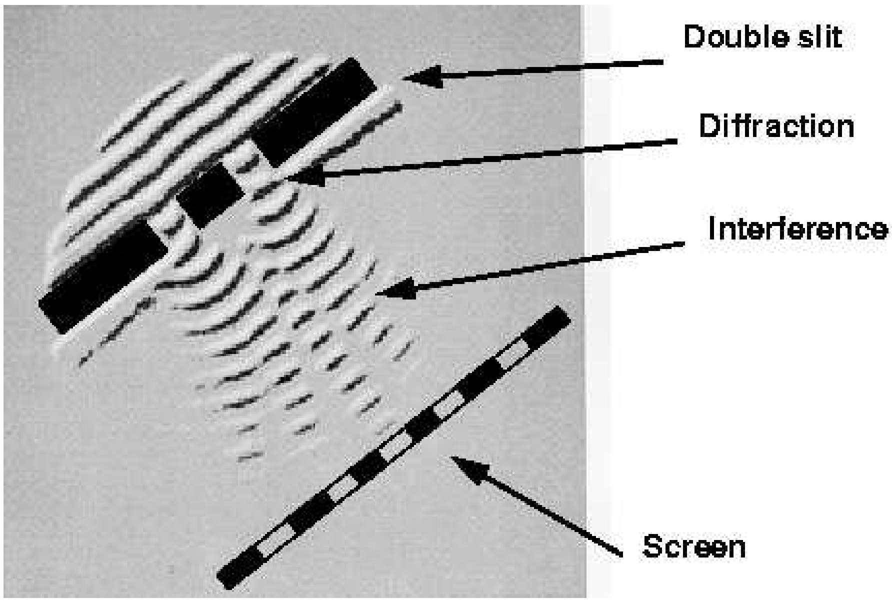

Figure 3: Young's double slit experiment with water waves.

electrons, interfering with each other. However, the interference pattern still results even if only one electron traverses the apparatus at a time. In this case, the pattern is built up gradually from the statistically correlated impacts on many electrons arriving independently at the detection system. This effect is evidenced in figure 5. We see that the electron must in some sense pass through both slits at once and then interfere with itself as it travels towards the detector. Young's double slit experiment has been performed many times in many different ways with electrons (and other particles). The inescapable conclusion is that each electron must be delocalised in both time and space over the apparatus.

Considering the analogies between Young's double slit experiment performed with water waves, electro-magnetic waves and with electrons, and considering the material of the foregoing section, we can now specify some properties for a new theory of mechanics, termed *wave mechanics.*

1. There must be a wave function $\Psi(\boldsymbol{r}, t)$ describing some fundamental property of matter. (We leave further physical interpretation of the wave function open to continuous debate through-out the course.)

2. As with the intensity pattern on the screen for water waves and light waves, the "observable" associated with the wave function indicating the probability of detection of the particle will be the intensity (square of the amplitude) of the wave. Mathematically, this is $|\Psi(\boldsymbol{r}, t)|^2 = \Psi(\boldsymbol{r}, t)\Psi^*(\boldsymbol{r}, t)$

3. The wavelength in the wave function will be related to the de Broglie wavelength of the particle $\lambda = h/p$.

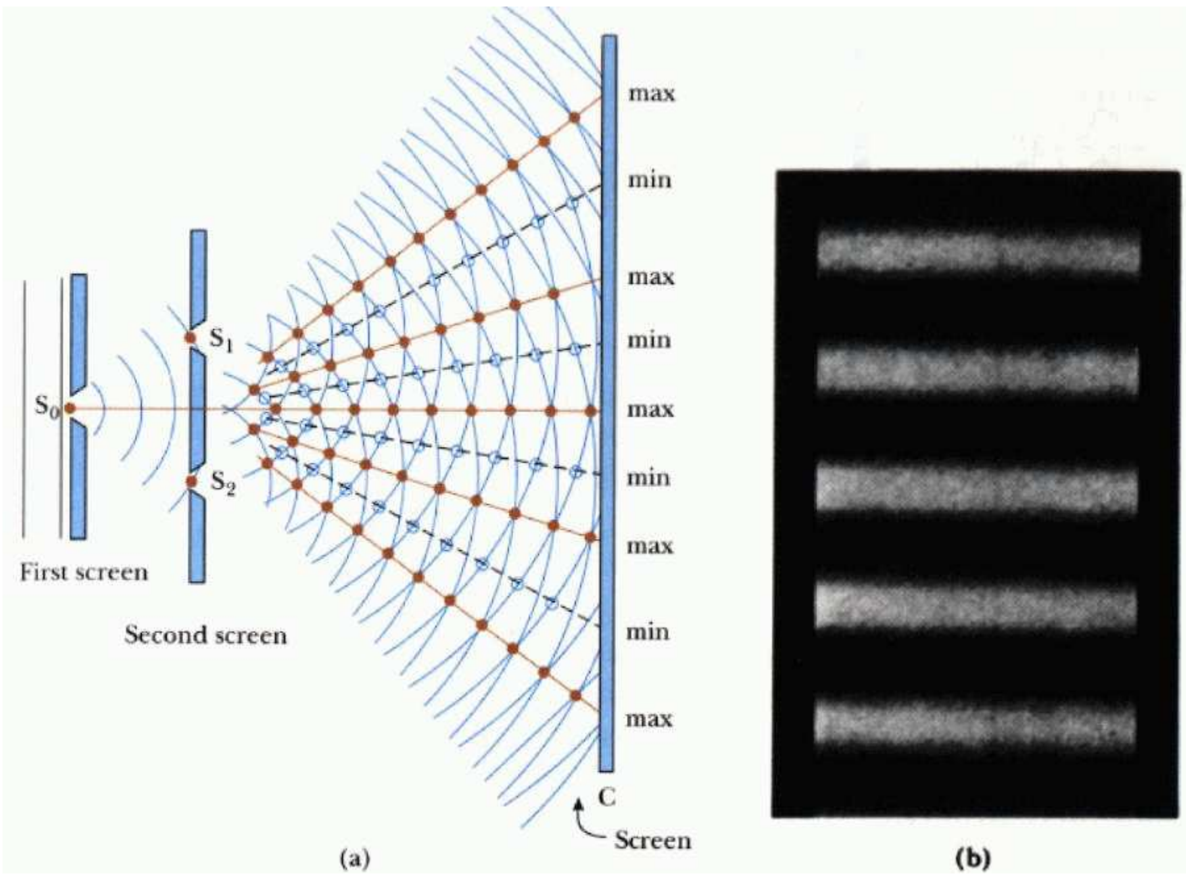

Figure 4: Young's double slit experiment, performed with either light or electrons leads to an interference pattern.

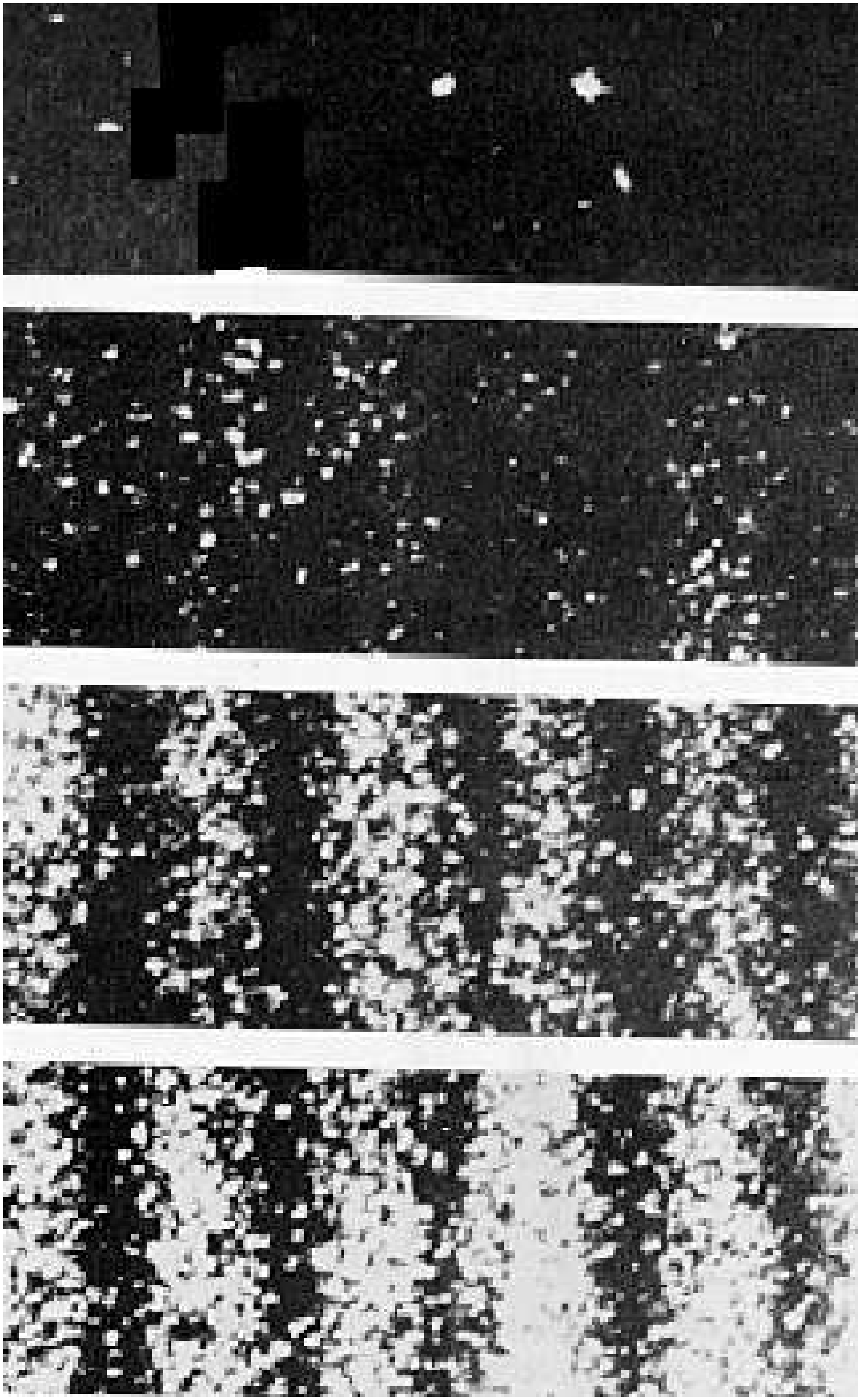

Figure 5: Young's double slit experiment, performed with electrons in such a way that only one electron is present in the apparatus at any one time.

4. We would like to be able to proceed to develop a differential equation which would specify the time evolution of the wave function, consistent with the conservation of energy and momentum of physical systems.

5. The quantisation of energy should arise in a natural way from this formalism, just as it does for other bounded systems that support oscillations.

6. Then we must develop the formalism to enable other observables than simple the probability of detection "position of the particle" to be determined. Examples would be the energy and momentum of the particle.

7. Note the judicious use of the word observable. The actual wave function itself has never yet been observed.

It is clear that an improved understanding of waves in physics is now necessary. To this end, some results from wave motion in physics are reviewed.

A transverse wave train, travelling on a string in the $+x$-direction (as in figure 6) may be represented by

$$y(x,t) = A \cos 2\pi\nu \left(t - \frac{x}{v_p}\right) \tag{8}$$

where ν is the frequency of the wave and v_p is its *phase velocity.* The phase velocity is the velocity with which a point on the wave maintaining the same phase appears to be transported.

$$v_p = \lambda\nu \tag{9}$$

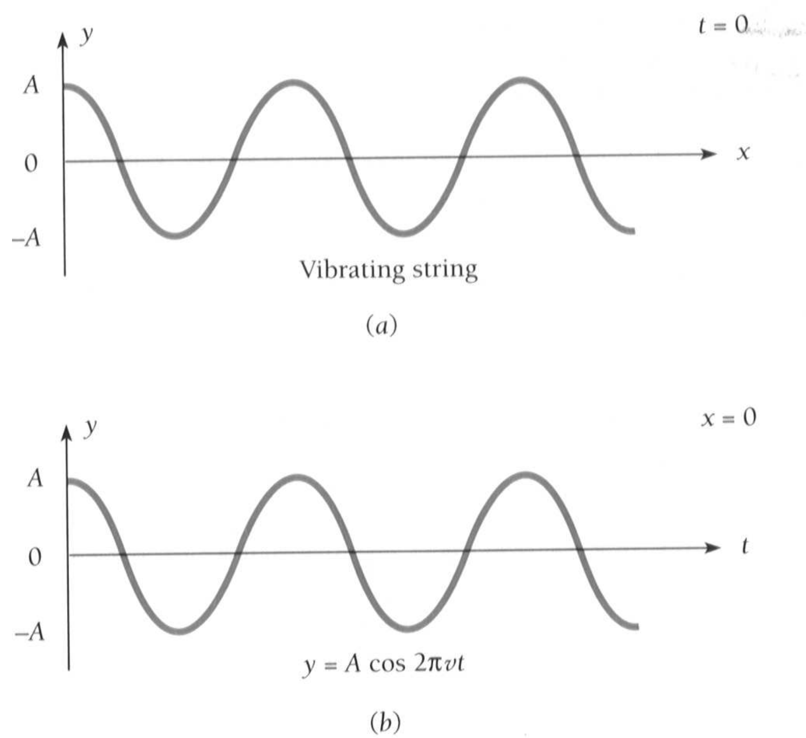

Figure 6: A transverse wave train, travelling on a string in the $+x$-direction.

It is more common to define the angular frequency (frequency in radians/sec rather than cycles/sec)

$$\omega = 2\pi\nu \tag{10}$$

and the wavenumber

$$
\begin{aligned}
k &= \frac{2\pi}{\lambda} \qquad \text{(by definition)} \\
&= \frac{\omega}{v_p} \qquad \text{(substitution with the last two equations)} \\
&= |p|/\hbar \qquad \text{(using de Broglie's relation)}
\end{aligned} \tag{11}
$$

where $\hbar = h/2\pi$. The wave equation for the wave moving in the $+x$-direction can now be written :

$$y(x,t) = A\cos(\omega t - kx) \tag{12}$$

In three dimensions, this equation would be

$$y(\mathbf{r},t) = A\cos(\omega t - \mathbf{k}.\mathbf{r}) \tag{13}$$

It turns out that in quantum mechanics, a particle will be described as a *wave packet*. By this, we mean a group of (usually infinitely many) waves which mutually interfere, creating a new wave form which exhibits some localisation. This can be illustrated by considering only two waves,

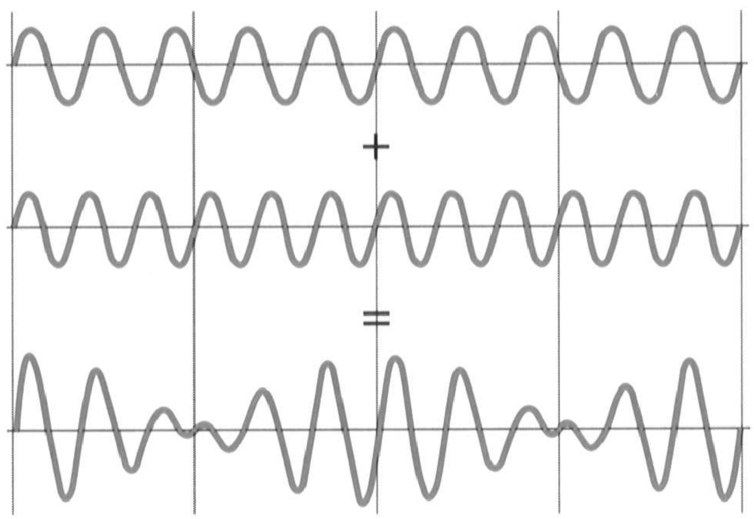

Figure 7: Two waves of nearly equal wavenumber combined coherently.

of nearly equal wavenumber ($k \pm \Delta k$), and combining them coherently as in figure 7. Clearly, performing this process with many more waves would achieve a better localisation of the wave packet, as illustrated in figure 8. We find that

$$
\begin{aligned}
y &= y_1 + y_2 \\
&= A\cos[(\omega + \Delta\omega/2)t - (k\Delta k/2)x] + A\cos[(\omega - \Delta\omega/2)t - (k - \Delta k/2)x] \\
& \;\; \ldots . \qquad \text{use trigonometric double angle formulae} \\
&= 2A\cos(\omega t - kx)\cos(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x)
\end{aligned} \tag{14}
$$

The combined wave train exhibits the phenomenon of "beats" as shown in figure 7 where an amplitude modulation envelope is superimposed no the original wave train. The amplitude modulation envelope will clearly have the frequency Δw, wavenumber Δk and hence the velocity $v_g = \Delta w/\Delta k$.

Figure 8: Localisation of a wave packet by combination of many waves.

Exercise 2.3
Confirm the derivation of the combined wave by filling in the missing steps above.

The velocity of the localised group of waves (or beat) is known as the group velocity.

$$v_g = \frac{d\omega}{dk} \tag{15}$$

This must be compared to the phase velocity of each wave train making up the wave packet

$$v_p = \frac{\omega}{k} \tag{16}$$

Exercise 2.4
Show the group and phase velocities of a de Broglie wave for a relativistic particle are given by

$$v_g = v \qquad \text{and} \qquad v_p = c^2/v \tag{17}$$

Thus the de Broglie wave group associated with a moving particle travels with the same velocity as the particle. The de Broglie waves in the packet have superluminal velocities, however, these do not represent the motion of the particle, and therefore the special relativity is not violated.

Finally, the form of the wave equation, yielding the above expression for for a wave train is

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \tag{18}$$

Exercise 2.5
Verify that $y(x,t) = A\cos(\omega t - kx)$ is indeed a solution of the wave equation. Clearly $y(x,t) = -iA\sin(\omega t - kx)$ is also a solution of the wave equation. It follows that

$$y(x,t) = Ae^{-i(\omega t - kx)} \tag{19}$$

is also a solution of the wave equation. This can be verified by direct substitution, or by exploiting the fact that any linear combination of solutions of the wave equation is itself a solution of the wave equation
(Hint: $e^{-i\theta} = \cos\theta - i\sin\theta$.)

Exercise 2.6
In fact a second order differentaial equation should have two constants of integration, which are determined by the boundary conditions of the specific problem. Show that for the equation 18 above, we could write

$$y(x,t) = A\cos(\omega t - kx) + B\sin(\omega t - kx) \tag{20}$$

or

$$y(x,t) = Ce^{-i(\omega t - kx)} + De^{+i(\omega t - kx)}. \tag{21}$$

Also find the relationship between the two sets of coefficients. We will use the former set when discussing standing waves (like a guitar string), and the latter set when discussing travelling waves (like a ripple on a large pond). Make sure you appreciate this point.

2.3 Wave Functions, Operators

Experiments have guided our intuition in developing a new theory for quantum objects.

Intuition	Implementation
Young's double slit experiment for particles and for waves yield similar interference patterns.	Postulate a wave function associated with quantum particles particle $\longrightarrow \Psi(x,t)$.
The interference pattern is observed via intensity variations on a screen. The intensity of a wave is its amplitude squared.	Postulate that the probability of finding a quantum particle at a given position and time is related to the mod squared of its wave function. $P(x,t) \propto \|\Psi(x,t)\|^2$.
We need to respect energy quantisation as prompted by the study of black body radiation.	For quantum particles $E = h\nu$.
The wave nature of particles is evidenced by the de Broglie relation.	For quantum particles $\lambda = h/p$.

The simplest wave function is the wave function of a free-particle (absence of forces acting on the particle). The particle can be considered to be moving in the $+x$-direction. A logical way to postulate wave function for a free particle is then :

$$\Psi(x,t) = Ae^{-(i/\hbar)(Et-px)} \tag{22}$$

where we have used our previous expression for wave motion in the $+x$-direction. To emphasize the applicability of this expression to a quantum particle, we have also incorporated the identities

$$E = h\nu = \frac{h}{2\pi} 2\pi\omega = \hbar\omega \tag{23}$$

which expresses the quantisation of energy and

$$\frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k = p \tag{24}$$

which is de Broglie's relation linking particle and wave properties. The energy E and momentum p are now part of the description of the wave function for the free particle. Energy and momentum are termed *observables* in Quantum Mechanics, because we can "measure" or "observe" them.

We need to develop a mathematical procedure that allows us to calculate observables from the wave function. The first step towards this is to note that

$$\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial x} = p\,\Psi(x,t) \tag{25}$$

and

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = E\,\Psi(x,t). \tag{26}$$

Exercise 2.7
Verify these equations.

Because the momentum and energy can be "extracted" from the wave function by "operating" on it appropriately, we define the energy and momentum "operators" as

$$\text{Momentum operator} \qquad \mathsf{p} = \frac{\hbar}{i}\frac{\partial}{\partial x} \tag{27}$$

and

$$\text{Energy operator} \qquad \mathsf{E} = i\hbar\frac{\partial}{\partial t} \tag{28}$$

Note that the operator for momentum squared is

$$\begin{aligned} \mathsf{p}^2 &= \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 \\ &= -\hbar^2\frac{\partial^2}{\partial x^2} \end{aligned} \tag{29}$$

2.4 Schrödinger's Time-Dependent Wave Equation

The question is, how do we proceed to construct a dynamical equation for quantum objects which are represented by wave functions ? Clearly, we must choose a basic physical law and try to express it in terms of wave functions and operators, rather than classical concepts. Accordingly, we choose the Law of Conservation of Energy :

$$\text{Total Energy} \quad = \quad \text{Kinetic Energy} + \text{Potential Energy} \tag{30}$$

Expressed classically

$$E = \frac{p^2}{2m} + U(x,t) \tag{31}$$

and expressed quantum mechanically, using wave functions and operators

$$\mathsf{E}\Psi = \frac{\mathsf{p}^2}{2m}\Psi + U(x,t)\Psi \tag{32}$$

or

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + U(x,t)\Psi \tag{33}$$

Generalising to three dimensions, we achieve finally -
Schrödinger's Time Dependent Wave Equation :

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi + U(x,y,z,t)\Psi. \tag{34}$$

In general, the procedure for studying physical systems with Schrödinger's time dependent wave equation is as follows:

Determine the Potential Energy function $U(x,y,z,t)$.
Insert it into Schrödinger's time dependent wave equation.
Solve the resulting equation to obtain the wave function for the particle in the specified potential.
Calculate observables using the wave function.

Because Schrödinger's wave equation determines the mechanical behaviour of quantum particles, the new physics that results is known as Quantum Mechanics.

You may feel that we have simply assumed a wave function for a free particle ($U(x, y, z, t) =$ const) and then used this to write down a quantum mechanical form of the law of conservation of energy using operators. This is correct, we can only assume. Schrödinger's wave equation cannot be derived. It is postulated (with some intuition !). It is nearly a century of success in describing known physics and vastly improved insight into hitherto undreamt of phenomena that has given a good measure of confidence in Quantum Mechanics.

2.5 Calculating Observables

The modulus squared of the wave function is interpreted as the probability per unit volume per unit time of finding the particle at position and time $(\boldsymbol{r}, t)$

$$P(\boldsymbol{r}, t) = |\Psi(\boldsymbol{r}, t)|^2 \, d^3\boldsymbol{r} \;\; dt. \tag{35}$$

This is ensured by always requiring the normalisation condition

$$\int_{-\infty}^{+\infty} |\Psi(\boldsymbol{r}, t)|^2 \, d^3\boldsymbol{r} \;\; dt = 1 \tag{36}$$

It follows that the expectation value of any quantity is therefore

$$\langle G \rangle = \int_{-\infty}^{+\infty} G(\boldsymbol{r}, t) |\Psi(\boldsymbol{r}, t)|^2 \, d^3\boldsymbol{r} \;\; dt \tag{37}$$

We call $|\Psi(\boldsymbol{r}, t)|^2$ the *probability density.*

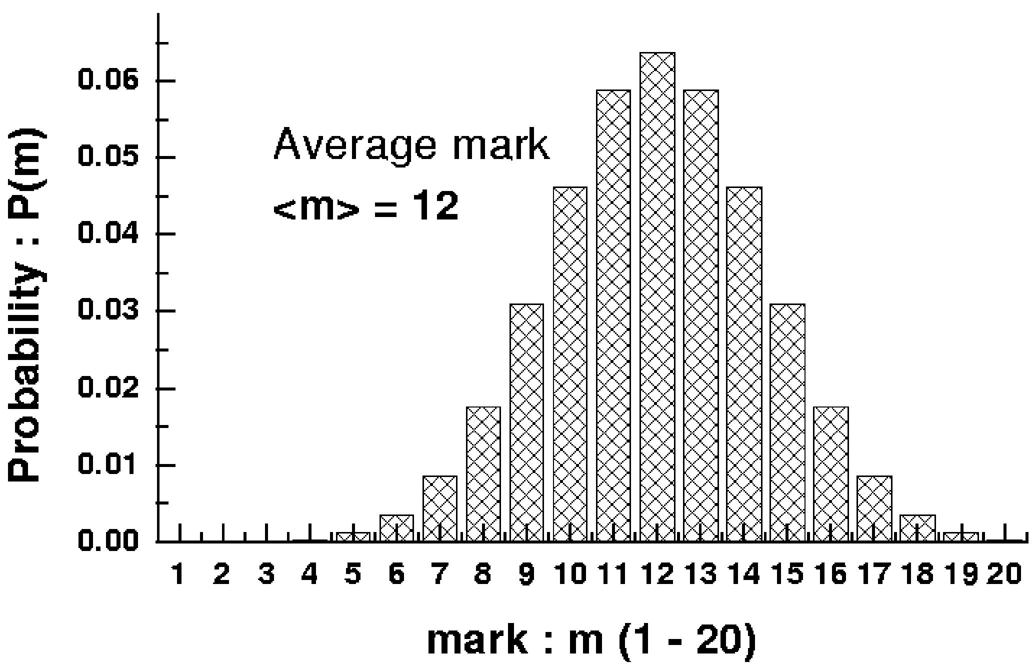

Figure 9: Normalised frequency distribution for student marks in a test out of 20 marks.

This procedure is in fact self-evident.

To illustrate it, we consider the marks of a class of students in a test. The test is marked out of a maximum of 20 marks. The performance of the students is evaluated. The frequency of each mark for the class is plotted as a probability distribution, as in figure 9. (Count the number of times a given mark m is obtained, divide this by the total marks obtained summed over the whole class). The area under this distribution will now be unity, as expected for a probability distribution.

$$\sum_{m=1}^{20} P(m) = 1 \tag{38}$$

The average mark (expectation value of m) is calculated as

$$\langle m \rangle = \sum_{m=1}^{20} mP(m) \tag{39}$$

If the set of possible marks m were now to belong to a continuous distribution represented by the variable x rather than the discrete distribution represented by the variable m ($m \longrightarrow x$), then the summation would be replaced by an integration ($\sum \longrightarrow \int$), so that

$$\langle x \rangle = \int_{-\infty}^{+\infty} xP(x)\, dx. \tag{40}$$

Now, having accepted one can calculate the expectation value of x in this way, the result is easily generalised to any function $G(\boldsymbol{r}, t)$ where the probability distribution of the variables $(\boldsymbol{r}, t)$ is $P(\boldsymbol{r}, t) = |\Psi(\boldsymbol{r}, t)|^2\, d^3\boldsymbol{r}\, dt$.

For example, calculating the expectation value of position at a given time is

$$\langle \boldsymbol{r}(t) \rangle = \int_{-\infty}^{+\infty} \boldsymbol{r}\, |\Psi(\boldsymbol{r}, t)|^2\, d^3\boldsymbol{r} \tag{41}$$

2.6 Schrödinger's Time-Independent Wave Equation

Suppose the potential did not depend explicitly on time (as in all the cases we will study).

$$U(x, y, z, t) \equiv U(x, y, z) \tag{42}$$

It is then possible to simplify Schrödinger's wave equation using the method of *separation of variables* into two equations viz., a time-dependent part and a time-independent part. We start by assuming a trial wave function

$$\Psi(x, y, z, t) = \psi(x, y, z) f(t) \tag{43}$$

which has the space and time time part "separated" out by factorisation. We now re-insert this *ansatz* back into Schrödinger's wave equation

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} [\psi(x, y, z) f(t)] &= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) [\psi(x, y, z) f(t)] \\ &\quad + U(x, y, z) \psi(x, y, z) f(t). \end{aligned} \tag{44}$$

Now we note that

$$\frac{\partial}{\partial t} [\psi(x, y, z) f(t)] = \psi(x, y, z) \frac{\partial}{\partial t} f(t) \tag{45}$$

and

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2} \right) [\psi(x, y, z) f(t)] = f(t) \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z). \tag{46}$$

This enables a re-arrangement of terms so that the L.H.S of the equation is only a function of time, and the R.H.S. of the equation is only a function of position.

$$\frac{1}{f(t)} i\hbar \frac{\partial}{\partial t} f(t) = - \frac{1}{\psi(x,y,z)} \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x,y,z) + U(x,y,z) \tag{47}$$

If the equality is to hold for all values of $\boldsymbol{r} = (x, y, z)$ and for all values of t, then both the L.H.S. and the R.H.S must be equal to the same constant k.

$$\frac{1}{f(t)} i\hbar \frac{\partial}{\partial t} f(t) = k \tag{48}$$

and

$$-\frac{1}{\psi(x,y,z)} \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x,y,z) + U(x,y,z,t) = k \tag{49}$$

This constant is known as the constant of separation.

We can immediately solve the time dependent part. We rewrite it as

$$\frac{\partial}{\partial t} f(t) = -i \frac{k}{\hbar} f(t) \tag{50}$$

It is now easy to verify that

$$f(t) = e^{-(ik/\hbar)t} \tag{51}$$

is a solution.

Note that the separation constant k has the dimensions of energy. It is also the same time dependence as for the quantum particle in free space (plane wave : $\Psi(x,t) = Ae^{-(i/\hbar)(Et-px)}$) if we make the identification the the separation constant is in fact the energy of the system $k = E$. Therefore

$$\Psi(x,y,z,t) = \psi(x,y,z) e^{-(iE/\hbar)t} \tag{52}$$

The remaining time-independent part is known as **time-Independent wave equation** and is written

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x,y,z) + U(x,y,z)\psi(x,y,z) = E\psi(x,y,z) \tag{53}$$

As we solve Schrödinger's time-independent wave equation in various situations (this means by specifying different potentials $U(x, y, z, t)$ for the different physical systems), we will see that not just one solution, but a family of solutions for the wave function arises.

$$\psi(x,y,z) \longrightarrow \psi_n(x,y,z) \tag{54}$$

Each wave function form the family of wave functions is called an *eigenfunction*. Corresponding to the n^{th} eigenfunction $\psi_n(x, y, z)$, there will be a related *eigenvalue*

$$E \longrightarrow E_n \tag{55}$$

The family of energy eigenvalues represent the quantisation of the energy spectrum. The family of eigenfunctions represent the states of the system (ground state, excited states). The label n has the significance of a *quantum number* labelling the various wave functions (states) and discretised energies.

2.7 Simple Quantum Systems

It is usually a very difficult problem to solve Schrödinger's wave equation. However, there are three simple scenarios :

1. the particle in a box,
2. the finite potential well,
3. barrier penetration and tunneling,

which are readily solvable. These examples turn out not only to be instructive, but also to have tremendous application to the understanding of matter in general and semi-conductivity in particular (for electrical engineers). It will be seen later that semi-conductivity is a *purely quantum phenomenon*. There is *no classical road* towards an understanding of semi-conductivity. Classical physics alone would never have lead to the discovery of semi-conductivity. It is worthwhile noting that the vast edifice of *modern electronics* rests entirely on a proper understanding of quantum mechanics. In fact, this is true to such an extent, that history records that it was two theoreticians who initiated the fabrication of the first semi-conducting device (see figure 10). This was based on the predictions of quantum mechanics. Thus it was, that the most tremendous improvement in our quality of life through technology of the last century was the result quantum mechanics - the highest level of abstraction achieved during the last century.

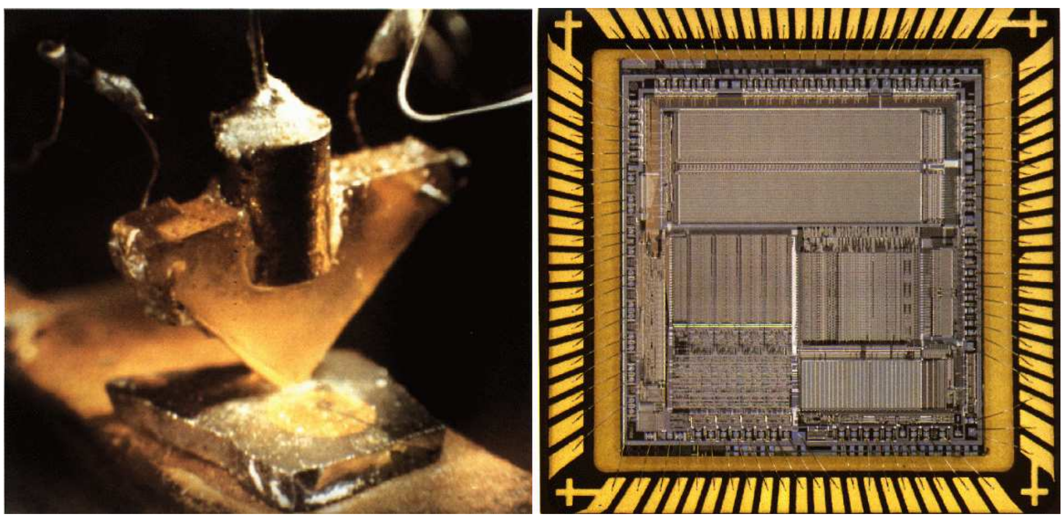

Figure 10: a) The first semi-conducting device - a point contact diode.
b) A modern large scale integrated device (100 MB memory chip).

2.7.1 The particle in a box

When studying this section, keep in mind that the simplest and earliest system taught, the particle in a box, is still an excellent model (with various adjustments) illuminating the behaviour of electrons in a metal, nucleons in a nucleus, plasma in a star, amongst other systems.

Considering just a one-dimensional box of length L, we see that we have the potential

$$U(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \leq x \leq L \\ \infty & x > L \end{cases} . \tag{56}$$

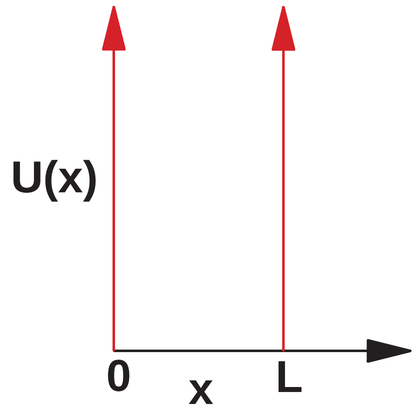

Figure 11: The box in one dimension : a square potential well with infinitely high walls.

In one dimension, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x) = E\psi(x) \tag{57}$$

However, in the case of a particle confined between infinitely high walls, we see that the particle will be restricted to the potential free region $0 \leq x \leq L$ between the walls. This is because the particle cannot have infinitely high potential energy behind the walls. Classically, the particle could have any energy, moving back and forth making elastic collisions with the walls of the box. Quantum mechanically, we must solve for the wave function that satisfies the equation

$$\left[\frac{\partial^2}{\partial x^2} + \frac{2m}{\hbar^2}E\right]\psi(x) = 0 \tag{58}$$

subject to the appropriate boundary conditions. Clearly, on the boundaries, we must require

$$\psi(x) = 0 \text{ for } x = 0 \text{ and } x = L. \tag{59}$$

The general solution of equation 58 is

$$\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x \tag{60}$$

as can be verified by back substitution. There are two constants A and B. These are effectively the two "constants of integration" which result from the solution (by integration) of the 2nd order differential equation. The value of one of the constants, as well as the value of E are determined by application of the boundary conditions. The value of the other constant is determined by the normalisation condition

$$\int_{-\infty}^{\infty} |\psi(x)|^2\, dx = \int_0^L |\psi(x)|^2\, dx = 1. \tag{61}$$

The normalisation condition is chosen so that $|\psi(x)|^2$ represents a probability density.

The boundary conditions clearly require that the coefficient of the cosine term is zero ($B = 0$). So we now have

$$\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x \tag{62}$$

Applying the boundary conditions again to the remaining sine term, we have to insist

$$\frac{\sqrt{2mE}}{\hbar}L = n\pi \qquad \text{n=1,2,3....} \tag{63}$$

There are therefore many (discrete) values of E which will satisfy the boundary conditions. Quantisation of energy has therefore arisen in a natural way,

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad \text{n=1,2,3....} \tag{64}$$

Note that this is very different to the classical case, where any energy values were possible.

The unnormalised solution is

$$\psi_n(x) = A\sin\frac{\sqrt{2mE_n}}{\hbar}x = A\sin\frac{n\pi x}{L} \tag{65}$$

Now applying the normalisation requirement

$$\begin{aligned}\int_{-\infty}^{\infty}|\psi(x)|^2\,dx &= \int_0^L|\psi(x)|^2\,dx \\ &= A^2\int_0^L\sin^2\frac{n\pi x}{L}\,dx \\ &= A^2\frac{L}{2} \\ &= 1.\end{aligned} \tag{66}$$

Therefore

$$A = \sqrt{\frac{2}{L}}. \tag{67}$$

Exercise 2.8
Verify the integration

Finally, the normalised wave functions for the particle in a one-dimensional box of length L are

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad \text{n=1,2,3...} \tag{68}$$

The first three wave functions $\psi_n(x)$ for $n = 1, 2, 3$ are displayed in figure 12 with the corresponding probability densities. Note that the wave function $\psi_n(x)$ may be positive as well as negative. The corresponding probability density $|\psi_n(x)|^2$ is always positive. The probability density of the quantum particle is dependent on the quantum number n. For example, for $n = 1$, the particle is most likely to be in the middle of the box. Note also that the quantum number n is always one less than the number of nodes. There are always nodes at the walls of the box. For a given energy state, a quantum particle may not be anywhere in the box with equal probability. In contrast, for any kinetic energy, a classical particle is equally likely to be found anywhere in the box.

The lowest energy that the particle can have is

Exercise 2.9
Find the probability that a particle trapped in a box L wide can be found between $0.45L$ and $0.55L$ for the ground and first excited states.

Exercise 2.10
Find the expectation value $\langle x\rangle$ of a particle trapped in a box L wide.

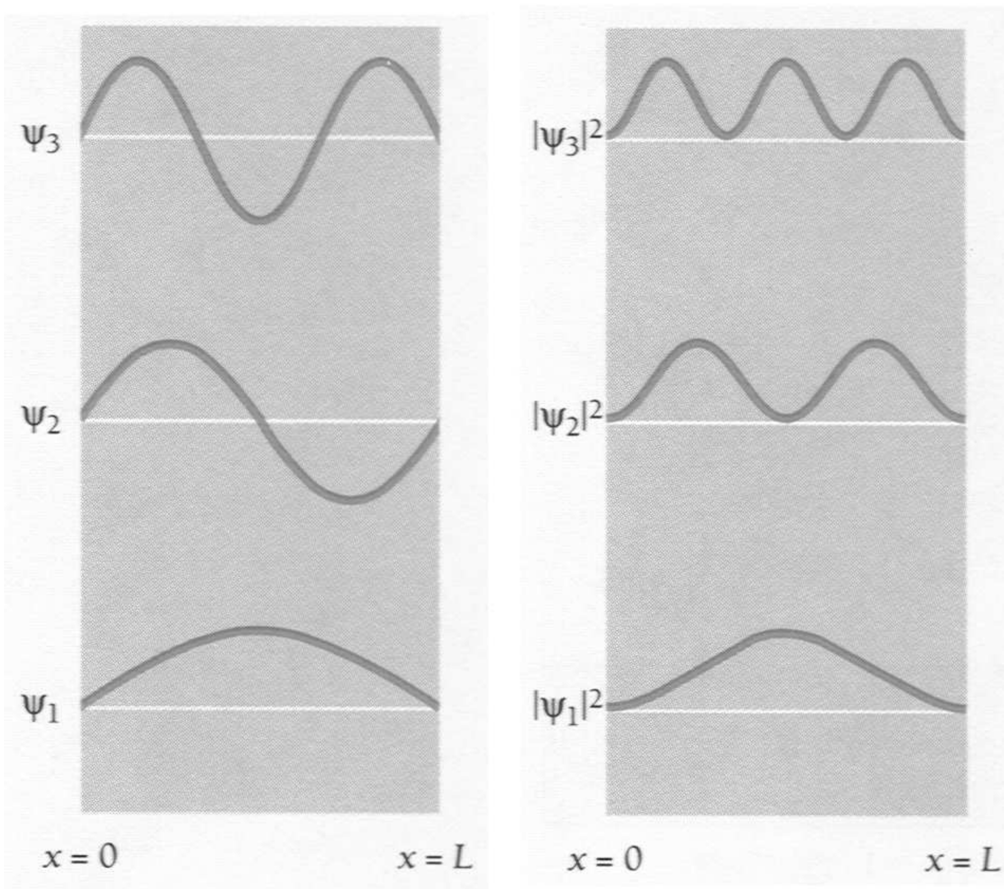

Figure 12: a) The first three wave functions and b) the correspond probability densities for a quantum particle in a box.

2.7.2 The finite potential well

A more realistic potential is the finite potential well (figure 13).

$$U(x) = \begin{cases} U & x < 0 & \text{region I} \\ 0 & 0 \leq x \leq L & \text{region II} \\ U & x > L & \text{region III} \end{cases} . \tag{69}$$

Note that the walls of the square well are infinitely thick, but of finite height.

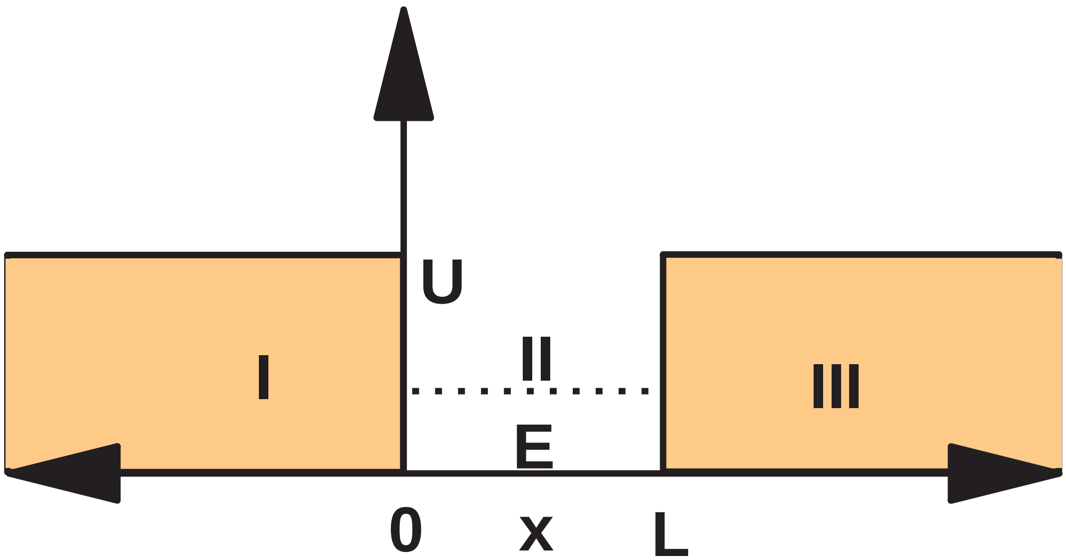

Figure 13: A particle trapped in a square potential well with barriers of finite height U, but infinitely thick.

In this case, we will see that a particle trapped in the well with energy $E < U$ may have probability density in the classically disallowed regions, I and III. In solving Schrödinger's equation,

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x) = E\psi(x) \tag{70}$$

we have to consider each of the three regions separately. In regions I and III we have

$$\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2m}{\hbar^2}(E - U)\psi(x) = 0 \tag{71}$$

or

$$\frac{\partial^2}{\partial x^2}\psi(x) - a^2\psi(x) = 0 \quad \begin{cases} x & < & 0 \\ x & > & L \end{cases} \tag{72}$$

where

$$a = \frac{\sqrt{2m(U - E)}}{\hbar}. \tag{73}$$

Now, because we are considering trapped states for the particle in the well, $E < U$. Therefore a is a real positive number $a > 0$. Accordingly, the solutions of equation 72 are given by

$$\psi_I = Ae^{ax} + Be^{-ax} \tag{74}$$
$$\psi_{III} = Ce^{ax} + De^{-ax} \tag{75}$$

Applying the boundary conditions will determine some of the constants. Both ψ_I and ψ_{III} must be finite everywhere, and this includes for $x = \pm\infty$. We therefore have to have $B = C = 0$, so that

$$\psi_I = Ae^{ax} \tag{76}$$
$$\psi_{III} = De^{-ax} \tag{77}$$

The wave functions therefore die away exponentially inside the classically non-allowed region, from the internal boundaries of the well outwards. What about inside the well in region II ? Here the potential is zero $U = 0$. The Schrödinger equation is therefore

$$\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2m}{\hbar^2}E\psi(x) = 0. \tag{78}$$

This may be written

$$\frac{\partial^2}{\partial x^2}\psi(x) - a'^2\psi(x) = 0 \quad \text{for } 0 \leq x \leq L \tag{79}$$

where

$$a' = i\frac{\sqrt{2mE}}{\hbar}. \tag{80}$$

Because a' is imaginary, the solutions of equation 78 will now be oscillatory :

$$\psi_{II} = E\sin\frac{\sqrt{2mE}}{\hbar} + F\cos\frac{\sqrt{2mE}}{\hbar}. \tag{81}$$

The boundary conditions must be applied again, at the interfaces between regions I and II and at the interfaces between regions II and III. The solutions of the Schrödinger wave equation should match smoothly from one region to another. This means that both the function value, as well as its slope should match. These conditions are written :

$$\psi_I(x=0) = \psi_{II}(x=0) \tag{82}$$

$$\frac{\partial}{\partial x}\psi_I(x=0) = \frac{\partial}{\partial x}\psi_{II}(x=0) \tag{83}$$

and the same for $x = L$. These equations are now more difficult to solve than in the case of the particle in a box with infinitely high walls. However, solving these equations numerically, we again find that the boundary conditions dictate a family of solutions for the wave functions and the energies,

$$\psi \longrightarrow \psi_n \tag{84}$$

$$E \longrightarrow E_n. \tag{85}$$

The first three wave functions and their energies are shown in figure 14. Note the oscillatory behaviour of the wave inside the well, and the exponential decay of the wave amplitude into the classically disallowed regions. This new effect of *barrier penetration* is a purely quantum phenomenon. There is a smooth matching of the exponential part of the wave to the oscillatory part. The corresponding probability density diagrams indicate the probability of finding the particle in the classically non-allowed regions.

2.7.3 Applications of the "particle in a box"

Despite its simplicity, the idea of a particle in a box has been applied to many situations with spectacular success. Three examples suffice.

1. The simplest example of two nucleons bound by the strong nuclear force is the deuteron. In nature, the deuteron is only barely bound, and has no excited states. Approximating the nuclear force by a radial square well as shown in figure 15 spectacularly reproduced the existing knowledge of the deuteron, and provided further insight into the nuclear force. Notice that only one state exists in the well. The oscillatory part of the wave function in the well barely "turns over" before the exponential part outside the well commences. The

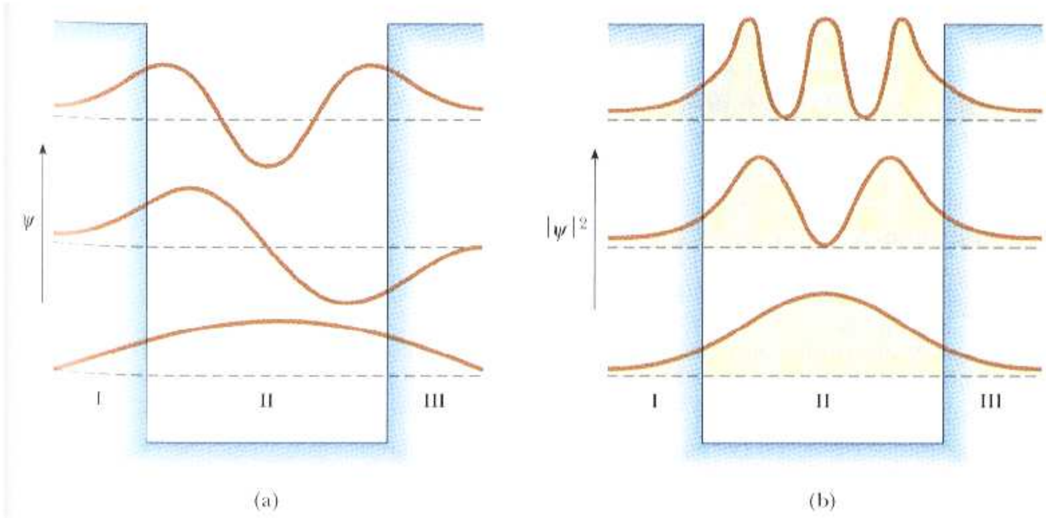

Figure 14: Wave functions and probability densities of a particle in a finite square potential well.

deuteron is indeed "barely bound" ! The well depth is 35MeV, indicating the strength of the nucleon-nucleon force. The ground state of the deuteron is a mere 2.2 MeV below the top of the well. If the nucleon-nucleon force were only slightly weaker, there would be no such thing as the deuteron, the proton to helium fusion cycle in the sun would not be possible, and the universe would not have been able evolve beyond hydrogen gas clouds to form burning stars.

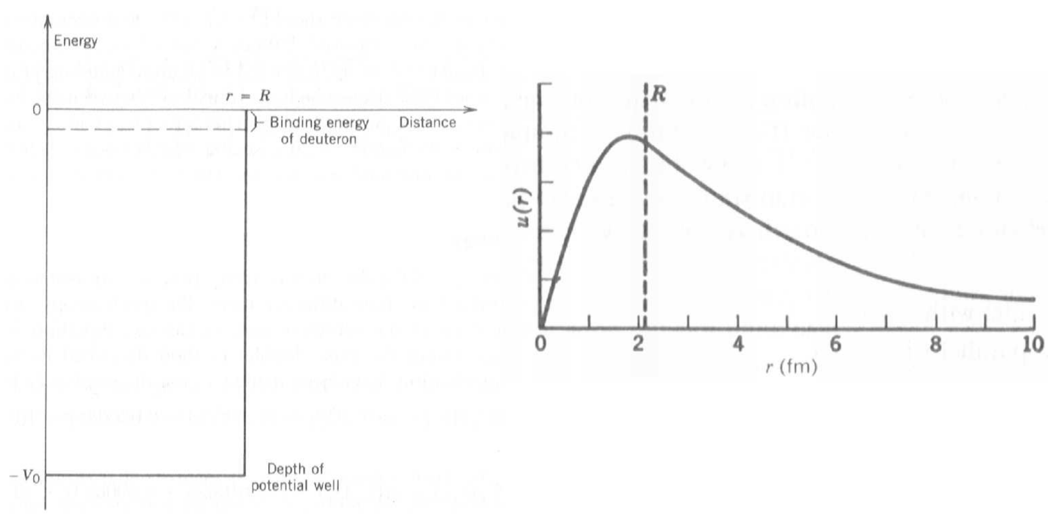

Figure 15: The deuteron radial square well, showing only one weakly bound state, and the corresponding wave function.

2. The electrons in a metal may be conceived of as particles in a box. The "background" of positive ion cores provides the attractive three dimensional well in which they move. This situation is shown schematically in figure 12. The electrons are therefore quantum particles represented by wave functions trapped in the "metal box". Their energy is given by the equation 64, adapted for a three dimensional box in an obvious way.

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n^2 = n_x^2 + n_y^2 + n_z^2 \tag{86}$$

This model is able to explain the motion of conduction electrons, their contribution to the specific heat of the metal, and their contribution to magnetism in the metal. In addition, the penetration of the electron wave function outside of the "metal box" is vital in understanding the propagation of electrons across contacts, even if there is an insulating oxide layer covering the metal, or even of the contact interface is inhomogeneous.

3. The thermodynamic equilibrium of a cold white dwarf star is modelled by balancing the behaviour of the electrons, modelled as particles in a box, with the gravitational forces. This model predicts the stellar mass threshold (Chandrasekhar limit) for final collapse of a white dwarf to a black hole.

So, the humble particle in a box has really been applied to objects varying in size from the nucleus to a star, and including also the behaviour of electrons in metals. The case of electrons in metals, especially interesting to electrical engineers, will be pursued further.

2.7.4 Barrier penetration, tunneling

In the previous example, the quantum particle could penetrate for some distance through walls which were infinitely thick. What would happen if a quantum particle were to propagate towards walls which were not infinitely thick ? The particle in fact has a finite probability of passing through such a wall. This is known as the *tunneling effect*, and it is a purely quantum phenomenon. Figure 16 depicts a particle incident from the left approaching a barrier. The height of the barrier U is larger than the energy E of the particle, $E < U$. Some of the amplitude of the quantum particle is reflected, while some passes through the barrier (non-classical behaviour), and emerges to continue travelling towards the right on the other side.

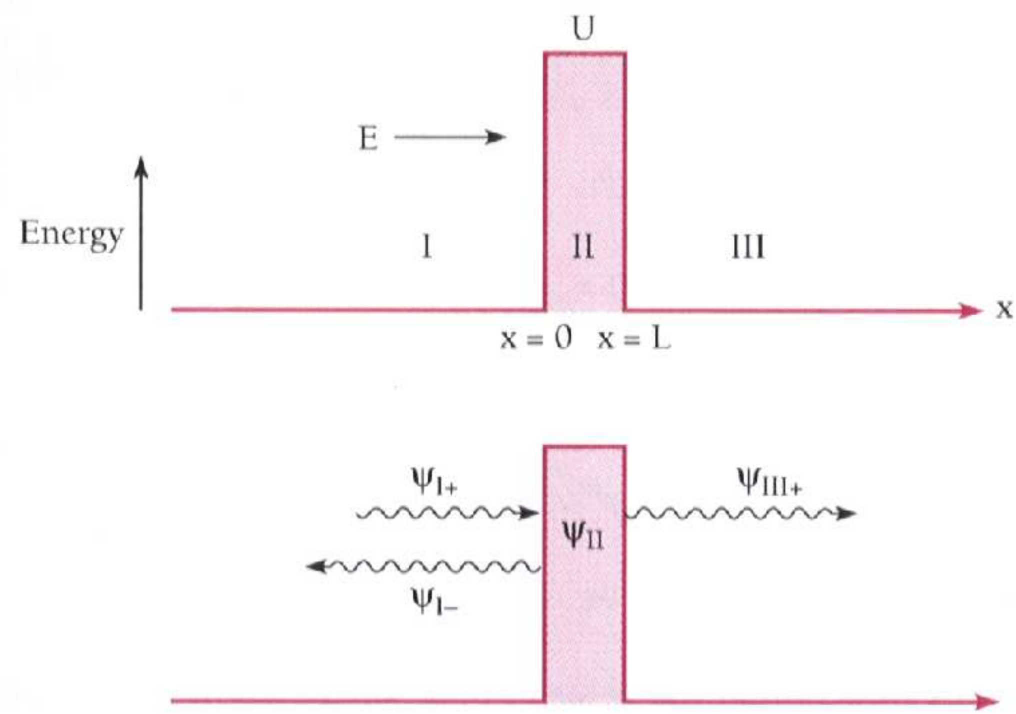

Figure 16: A particle with an energy below the barrier height approaches the barrier. Some amplitude is reflected, and some amplitude tunnels through to the other side.

The potential is :

$$U(x) = \begin{cases} 0 & x < 0 & \text{region I} \\ U & 0 \le x \le L & \text{region II} \\ 0 & x > L & \text{region III} \end{cases} \quad . \tag{87}$$

It is clear, as in the previous problem, that in the potential free areas we will have oscillatory solutions, while in the area where the particle energy is less than the barrier height $E < U$, we will have exponential solutions.

Using the identities

$$e^{i\theta} = \cos\theta + i\sin\theta \tag{88}$$

$$e^{-i\theta} = \cos\theta - i\sin\theta \tag{89}$$

we can write the oscillatory solution as

$$\psi_I = Ae^{ik_1x} + Be^{-ik_1x} \tag{90}$$

$$\psi_{III} = Fe^{ik_1x} + Ge^{-ik_1x} \tag{91}$$

where

$$k_1 = i\frac{\sqrt{2mE}}{\hbar}. \tag{92}$$

This is a more suitable form to describe wave functions moving in a particular direction. For example,

$$\psi_{I+} = Ae^{ik_1x} \qquad \text{incident wave} \tag{93}$$

is a wave function in region I incident from the left. At $x = 0$, the wave ψ_{I+} strikes the barrier and is partially reflected, as the wave function

$$\psi_{I-} = Be^{-ik_1x} \qquad \text{reflected wave.} \tag{94}$$

A classical particle would rebound off the barrier completely, not partially. However, we already know that some of the amplitude of the wave function will penetrate into the barrier in the classically non-allowed region II. Inside the barrier (region II from $0 \le x \le L$), we know that $U > E$, and therefore the Schrödinger wave equation will have not have oscillatory solutions, but exponential solutions.

$$\psi_{II} = Ce^{-k_2x} + De^{-k_2x} \tag{95}$$

where

$$k_2 = \frac{\sqrt{2m(U-E)}}{\hbar}. \tag{96}$$

If the barrier is not infinitely thick, then some amplitude may still remain on the far side of the barrier. On the far side of the barrier, in region III ($x > L$), the transmitted wave would again be moving towards the right.

$$\psi_{III+} = Fe^{ik_1x} \qquad \text{transmitted wave} \tag{97}$$

Applying the boundary conditions, we demand that the wave functions in all three regions match smoothly to each other, in both value and slope.

$$\left.\begin{aligned} \psi_I &= \psi_{II} \\ \frac{\partial}{\partial x}\psi_I &= \frac{\partial}{\partial x}\psi_{II} \end{aligned}\right\} \quad x = 0 \tag{98}$$

at the left hand side of the barrier and

$$\left.\begin{aligned} \psi_{II} &= \psi_{III} \\ \frac{\partial}{\partial x}\psi_{II} &= \frac{\partial}{\partial x}\psi_{III} \end{aligned}\right\} \quad x = L. \tag{99}$$

Specifying these conditions, we find we must solve the equations

$$\begin{aligned} A+B &= C+D \\ ik_1A - ik_1B &= -ik_2C + ik_2D \\ Ce^{-k_2L} + De^{k_2L} &= Fe^{ik_1L} \\ -k_2Ce^{-k_2L} + k_2De^{k_2L} &= ik_1Fe^{ik_1L} \end{aligned} \tag{100}$$

Considering figure 16, we can see that the interesting quantity to calculate is the amount of transmitted wave amplitude relative to the incident amplitude. This is know as the transmission coefficient $T = |\frac{F}{A}|^2$. (The steps to realise the transmission coefficient from here on are presented for your interest, and are not examinable.)

$$\begin{aligned} \frac{A}{F} &= \left[\frac{1}{2} + \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right] e^{(ik_1+k_2)L} \\ &+ \left[\frac{1}{2} - \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right] e^{(ik_1-k_2)L}. \end{aligned} \tag{101}$$

If the barrier is much higher than the particle energy, then $\frac{k_2}{k_1} > \frac{k_1}{k_2}$ so that

$$\frac{k_2}{k_1} - \frac{k_1}{k_2} \approx \frac{k_2}{k_1}. \tag{102}$$

Suppose also the barrier is wide enough so that the transmitted amplitude is weak $k_2L \gg 1$

$$e^{k_2L} \gg e^{-k_2L}. \tag{103}$$

We can now simplify the expression for the transmission probability

$$\frac{1}{T} = \left|\frac{A}{F}\right|^2 = \left|\left(\frac{1}{2} + \frac{ik_2}{4k_1}\right) e^{(ik_1-k_2)L}\right|^2. \tag{104}$$

finally

$$T = \left|\frac{F}{A}\right|^2 = \left(\frac{1}{4} - \frac{k_2^2}{16k_1^2}\right)^{-1} e^{-2k_2L}. \tag{105}$$

As the bracketed quantity is more slowly varying than the exponential, we can simplify the transmission probability further to

$$T \approx e^{-2k_2L}. \tag{106}$$

The transmission of a quantum particle through a barrier is shown in figure 17 below.

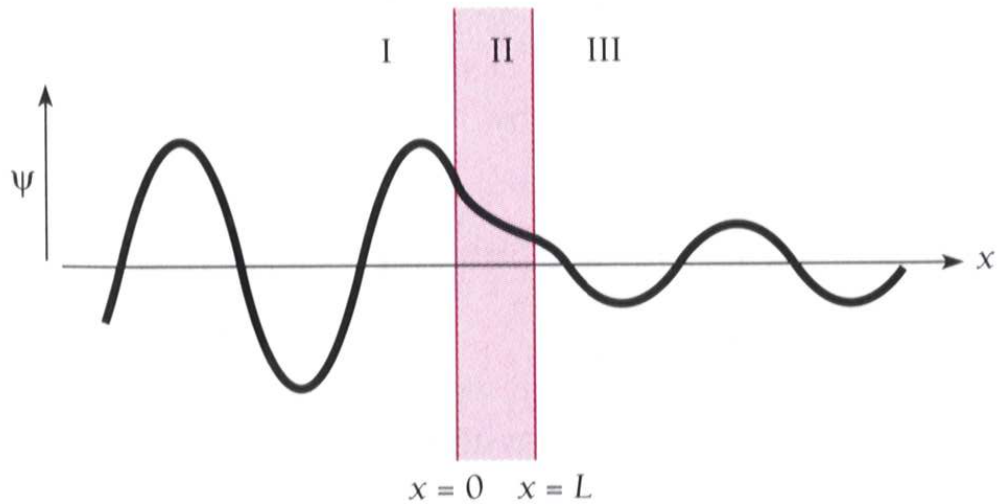

Figure 17: A quantum particle tunneling through a barrier.

2.7.5 Applications of "tunneling"

The concept of tunneling, whereby a quantum particle penetrates through a classically disallowed region, has also been applied to many situations with spectacular success. Three examples suffice.

1. **A new ultra-Microscope :** A new class of microscopes (with atomic resolution) that exploit the tunneling current between a specimen and a very sharp tip has been developed. The sequence of three figures 18, 19 and 20 below show the tunneling tip of a scanning tunneling microscope (STM), the scanning principle, and an image at atomic resolution of a silicon crystal surface.

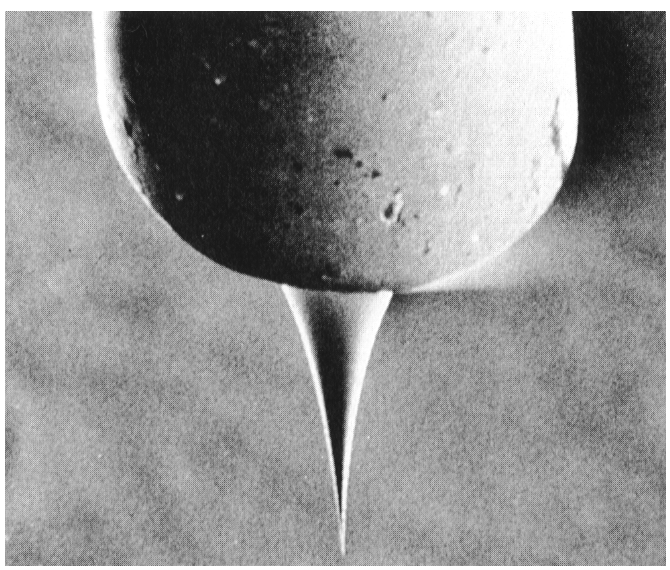

Figure 18: The tunneling tip in a tunneling microscope.

2. **Alpha particle deacy :** The explanation of alpha particle decay as the tunneling of an alpha particle out of the nucleus (figure 21) explained the tremendous variation of alpha-particle lifetimes (25 orders of magnitude, figure 22) as being due to the rather small differ-

ences in barrier parameters. This remains one of the most impressive ranges of applicability of a single theory in physics.

3. **The end of the road for the classical computer :** So far, miniturisation and very large scale integration of microchips has proceeded by pushing engineering technology boundaries. How far can we continue this game ? It turns out that the tunneling process represents a physics limit for the miniaturisation of feature size on a chip. No technological process can go beyond this boundary without changing the physical basis of the computational device. From this point on, we are in the realm of the quantum computer, and the clasical computer can go no further. The tunneling could be between neighbouring wires or across the gate

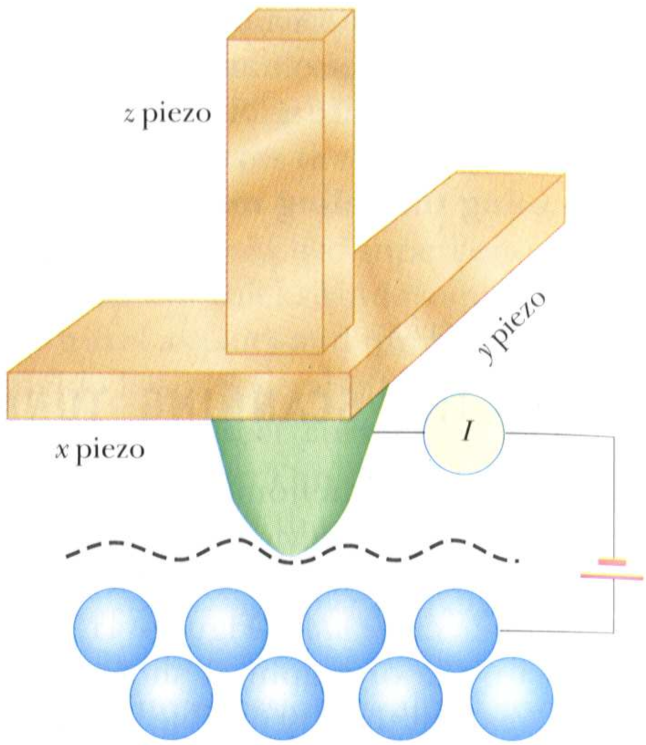

Figure 19: The tunneling tip is scanned over the specimen, producing an image of the tunneling current.

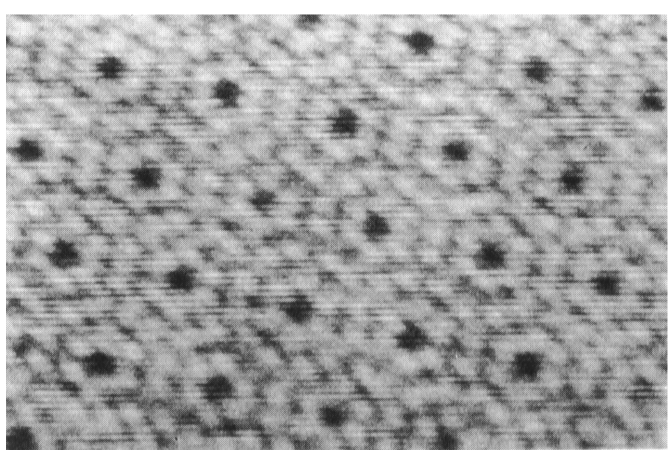

Figure 20: The tunneling tip is scanned over the specimen, producing an image of the tunneling current.An image of a silicon crystal surface produced by a STM.

of a transistor or some other feature where the quantum behaviour is manifested. Imagine that the quantum process (tunneling) should not be more likely than the classical process (thermally driven over-barrier hopping - Arrhenius Law), so that the limiting case is when

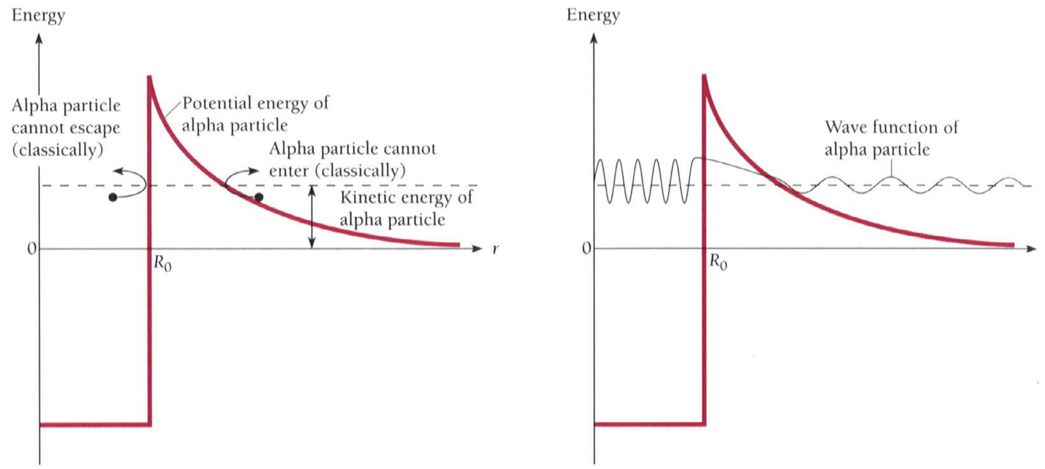

Figure 21: The representation of alpha particle decay as the tunneling of an alpha particle out of the nucleus.

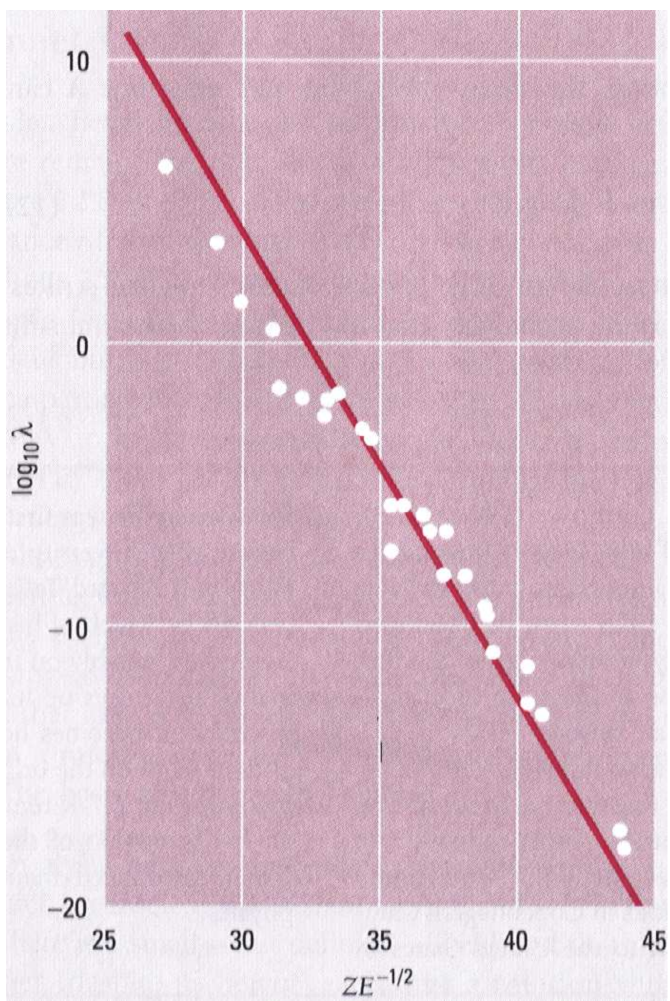

Figure 22: The large variation of alpha particle decay rates or inverse lifetimes (25 orders of magnitude) explained by tunneling theory.

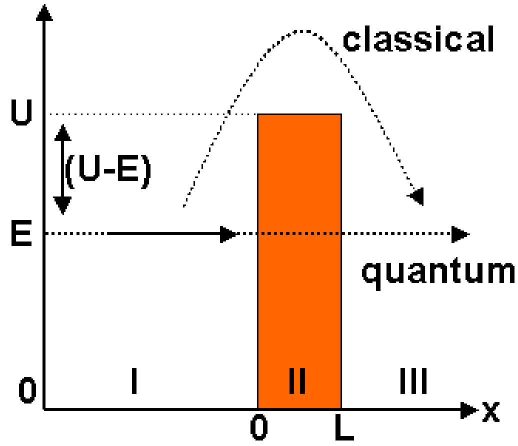

Figure 23: Classical and quantum pathways for an electron to escape its boundary.

they are equal (see figure 23).

$$\text{Transmission probability through a barrier} \qquad T = e^{-2\frac{\sqrt{2m(U-E)}}{\hbar}L}$$
$$\text{and}$$
$$\text{Thermal over-barrier hopping probability} \qquad P = e^{-\frac{(U-E)}{kT}}. \tag{107}$$

Now suppose you imagine typical values for the parameters in the formula. The hight of the barrier above the particle is $(U - E) \approx 1$ eV, and the system is at room temperature $kT = 26$ meV.

$$e^{-2\frac{\sqrt{2m(U-E)}}{\hbar}L} = e^{-\frac{(U-E)}{kT}}. \tag{108}$$

We find the value for the minimum feature size L of a conventional chip is

$$L \approx 4 \quad \text{nm}. \tag{109}$$

(Hint ; use $\hbar c = 197$ MeV.fm (or ev.nm) and $mc^2 = m_e c^2 = 511$ keV)