# Schroedinger wave equation

In 1926, Schroedinger provided a basis for an unifying theory which will enable us to predict and explain occurrences on an atomic scale. This was done by discovering an equation for predicting $\psi$, the wave function of a particle, in any particular circumstances. This expression includes the kinetic energy, T, associated with a particle. In general, however, a particle can also possess potential energy. For instance, it might be an electron moving in a solid; the electron not only has kinetic energy but it also moves in the field due to the lattice and thus has a space-dependent potential energy.

In general, the total energy E of a particle, V denotes the potential energy

$$E \; = \; \hbar\,\omega = T \, + V$$

- The 1D wave function becomes

$$\psi = A_o \exp[-j(Et - px)/\hbar] \qquad (1)$$

- where $\omega = 2\pi f$ and $\hbar = h/2\pi$

What equation does this generalised wave function satisfy ?
Say, $\quad \partial^2 H/\partial x^2 = \varepsilon\mu \cdot \partial^2 H/\partial t^2 \qquad\qquad (2)$

The solution of which

$H = H_o \exp[-j(\omega t - \beta x)]$

This gives the magnetic field of a plane wave propagating in a medium with permittivity $\varepsilon$ and permeability $\mu$

Try to find a wave equation similar to (2) but which has $\psi$ as its solution:

First differentiate w.r.t. t

$$\frac{\partial \psi}{\partial t} = -\frac{j}{\hbar} E \psi = \frac{-j\left(V + \frac{1}{2} m v^2\right)\psi}{\hbar} \tag{3}$$

Also differentiate $\psi$ w.r.t. x, twice

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi = \frac{-m^2 v^2}{\hbar^2}\psi \tag{4}$$

Therefore from (3)

$$-\frac{1}{2}mv^2\psi = -j\hbar\frac{\partial\psi}{\partial t} + V\psi$$

From (4)

$$-\frac{1}{2}mv^2\psi = \frac{1}{2m}\hbar^2\frac{\partial^2\psi}{\partial x^2}$$

And therefore

$$\frac{\partial^2\psi}{\partial x^2} - \frac{2m}{\hbar^2}V\psi + j\frac{2m}{\hbar}\frac{\partial\psi}{\partial t} = 0$$

This is the 1D, time-dependent Schroedinger wave equation

- governs the behaviour in 1D of all particles
- not rigorous derivation, assumed p=h/λ and E=hf
- there is no proof of the equation → like Newton's laws
- agreement with experiments is the only check as to its validity
- must be used when considering the interaction of atomic sized particles

- 3D, time dependent Schroedinger (S) equ.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} - \frac{2m}{\hbar^2}V\psi + j\frac{2m}{\hbar}\frac{\partial \psi}{\partial t} = 0$$

- applicable to any particle
- for a large class of problems in which the total particle energy is constant → bound particles or a constant current of particles → S equation can be simplified by separating out the time- and position-dependent parts

- by separation of variables, of time and position dependent parts → time independent S equation.

$$\psi = \Psi(x).\Gamma(t)$$

$$\Rightarrow \frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\Psi = 0$$

# Interpretation of the wave function

- What is the physical significance of $\psi$ ?

- Unlike the E and M fields where field vectors are oscillating as in a radio wave, or in sound waves as pressure waves. Since $\psi$ is a function of space and time coordinates, we might expect that it represents the position of a particle at some time t.

- However, in general, it is impossible to locate a particle exactly in space $\rightarrow$ see later, uncertainty principle. We can only consider the probability of a particle being at a particular point in space. $\psi$ is a solution of the S equation and is usually a complex quantity.

- In 1926, Max Born showed that the square of $\psi$'s absolute magnitude $|\psi|^2$ is proportional to the probability of a particle being in unit volume of space, centred at the point where $\psi$ is evaluated, at time t.

- Therefore, although the exact position of a particle at a particular time cannot be predicted, it is possible to find its most probable location. It follows that $|\psi|^2 \Delta V$ is proportional to the probability that a particle will be found in the volume element $\Delta V$. For example, the probability of finding a particle in the range x $\rightarrow$ x + dx, y $\rightarrow$ y = dy and z $\rightarrow$ z + dz is proportional to

- $\left|\psi(x,y,z,)\right|^2$ dx dy dz $= \psi\psi^*$ dx dy dz

- where $\psi^*$ is the complex conjugate of the wave function. Although the direct physical significance of particle waves is not clear, if we solve S's equation in particular circumstances and obtain a wave function $\psi$, the *probability density* $\left|\psi\right|^2$ can be used to predict accurately what the spatial distribution of particles will be at time t, provided that a sufficiently large number of experiments are performed.

# Normalisation

- If a particle exists at all, it is certainly located somewhere in space. It is convenient to choose the constant of proportionality such that the integral of the probability density over all space equals unity or

$$\iint \int_{-\infty}^{\infty} \psi\psi^* \, dxdydz = 1$$

- A wavefunction which satisfies this condition is said to be normalised, when normalised, $|\psi|^2 \Delta V$ = probability that a particle will be found in a volume $\Delta V$.

- the boundary conditions $\psi$ must be continuous and $\psi$ must be single valued function of position.

# Uncertainty principle

- There is a lack of precision with which the two variables E and t, p and x can be specified (measured) simultaneously.

- Suppose, for example, in a particular experiment, the energy of a particle can be measured to some accuracy $\Delta E$ and the time at which the measurement is taken is known to some accuracy $\Delta t$; then a classical theory would indicate that the precision to which these parameters can be measured is limited only by the experimental apparatus and technique.

- The uncertainty principle shows, however, that if the particle's energy is determined very accurately, so that ΔE is small, there is a proportional increase in the lack of precision in the time measurement and Δt increases.

# Uncertainty principle
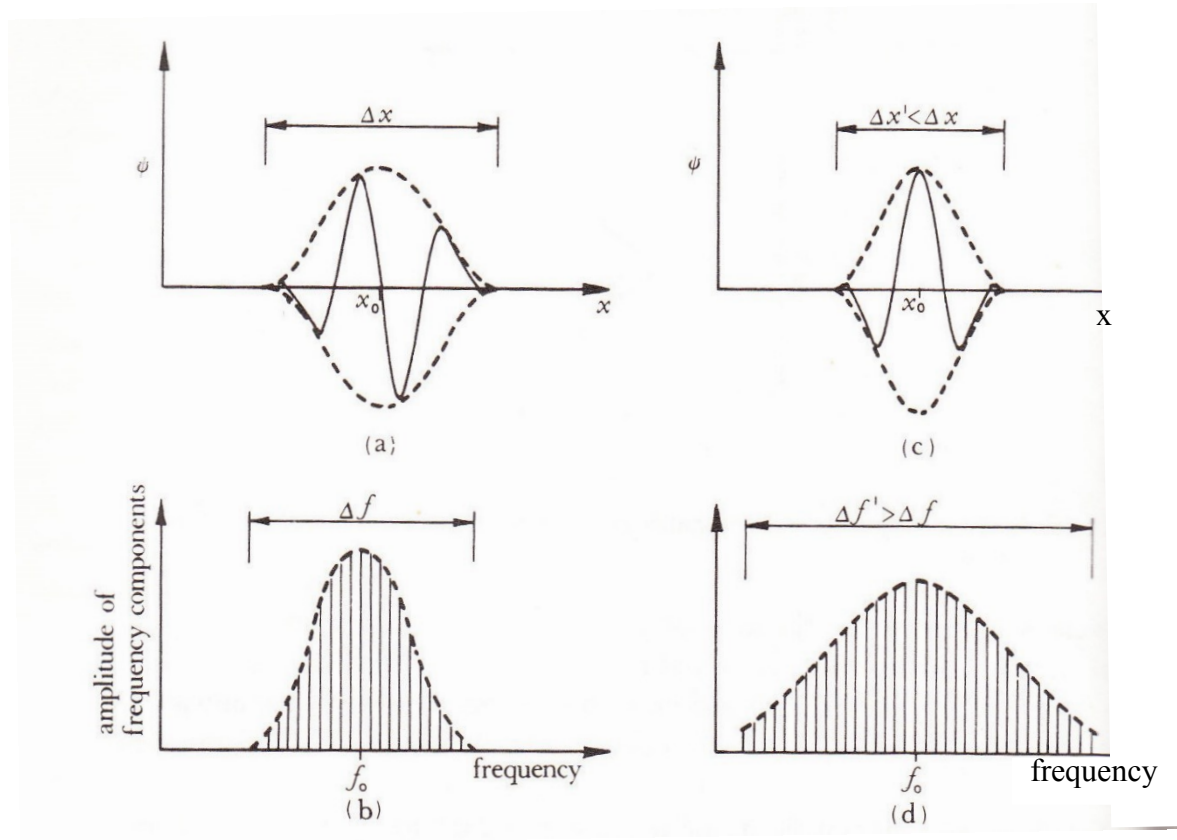
# Uncertainty principle

- $\Delta x$ represents the degree of lack of precision of locating the particle - time of arrival of the wavepacket at some particular location can only be measured to an accuracy $\Delta t$, related to $\Delta x$ by,

- $\Delta x = v.\Delta t$

# Uncertainty principle

- The amplitudes of the various components of wave can be obtained by Fourier analysis to give the frequency spectrum of the wavepacket.

- $\Delta E = h\Delta f$

- And therefore, if the accuracy in the location of x is increased, $\Delta x$ and hence $\Delta t$ is made shorter, this leads to an increased $\Delta E$, and a greater uncertainty as to the precise value of the energy of the particle.

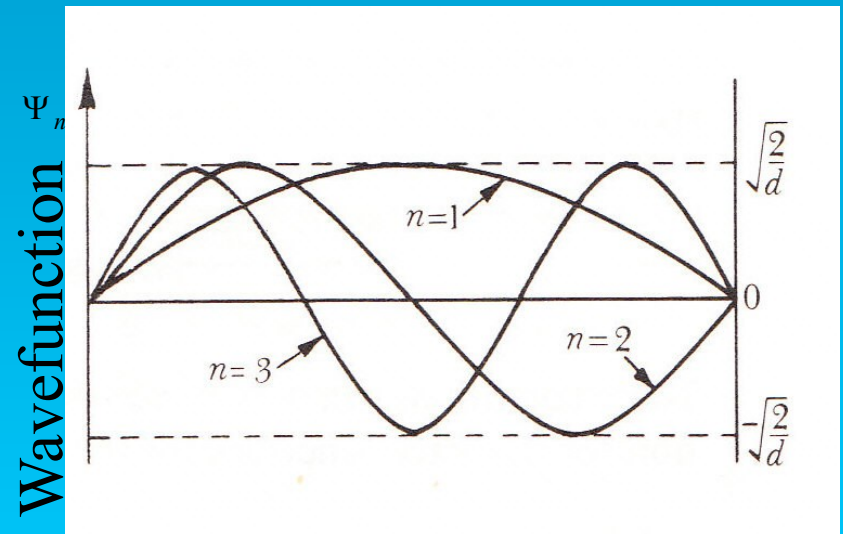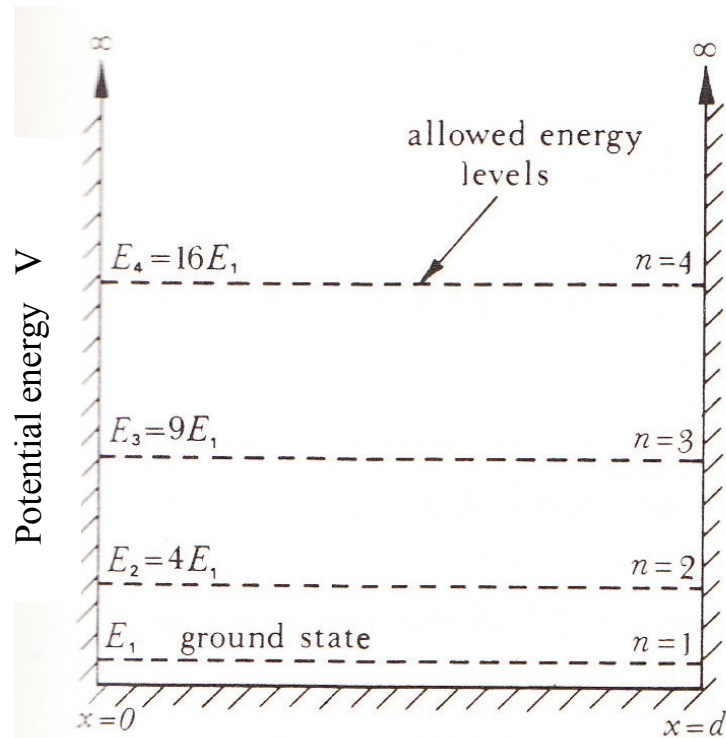- $\Delta E . \Delta t \geq \sim \hbar$

# Uncertainty principle

- Also

- $\Delta E = h\Delta f = \frac{1}{2}$ mv. $\Delta v$
  $= \frac{1}{2}$ v $\Delta p$

- Therefore,

- $\Delta p \cdot \Delta x \geq \sim \hbar/2$

# Uncertainty principle

- Fortunately, the uncertainties implicit in Heisenberg's principle need not be too restricting for normal laboratory-scale experiments since h is very small, of order $10^{-34}$. However, the limitations to accuracy become critical for atomic-sized particles, when the magnitudes of the experimental variables can become minute.

# Particle in a box potential well

- A particle of mass m and total energy E moves only in the x-direction under the boundary conditions :

Potential energy V

∞       ∞

allowed energy levels

$E_4 = 16E_1$      $n = 4$

$E_3 = 9E_1$      $n = 3$

$E_2 = 4E_1$      $n = 2$

$E_1$   ground state      $n = 1$

$x = 0$       $x = d$

Wavefunction $\Psi_n$

$\sqrt{\dfrac{2}{d}}$

$n = 1$

$0$

$n = 3$      $n = 2$

$-\sqrt{\dfrac{2}{d}}$

The S equation is:

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}E\Psi = 0$$

for $0 \le x \le d$, V=0.

The solution is:

$$\Psi = Ae^{j\beta x} + Be^{-j\beta x} \qquad (1)$$

- where

$$\beta^2 = \frac{2m}{\hbar^2} E$$

Now the particle cannot penetrate the containing walls, therefore ψ = 0 outside the well for 0 ≥ x ≥ d.

For continuity of ψ at the boundaries,

B=-A

- And

$$0 = A(e^{j\beta d} - e^{-j\beta d})$$

Or

sin βd = 0

Hence

$$\beta d = \frac{\sqrt{2mE}}{\hbar} d = n\pi \qquad \text{Where n} = 1,2,3\ldots$$

- These conditions can be substituted into equ. 1 to give a general expression for the wave function for the particle in the well:

$$\Psi = C \sin\left(\frac{n\pi x}{d}\right)$$

where C is a newly defined normalising constant whose value can be obtained by arguing that the probability that the particle is located somewhere in the well = 1.
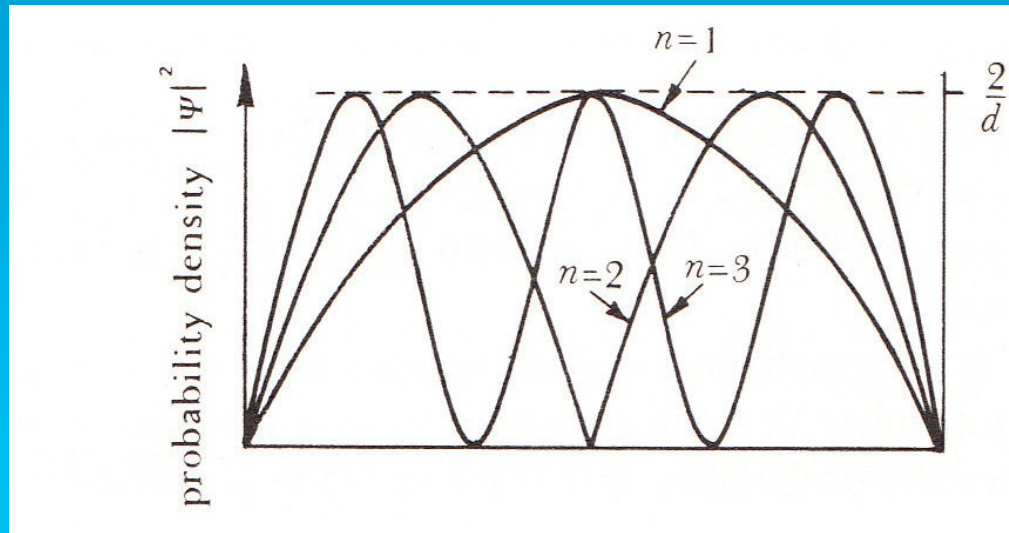
- Since the probability that it is located in length dx is $\psi\psi*dx$, then

$$\int_0^d \Psi\Psi^* \, dx = 1$$

Or

$$\int_0^d C^2 \sin^2(n\pi x/d) \, dx = 1$$

For which we find that $\qquad C = \sqrt{2/d}$

- The normalised solution for $\psi$ becomes:

$$\Psi = \sqrt{\frac{2}{d}} \sin\left(\frac{n \pi x}{d}\right)$$
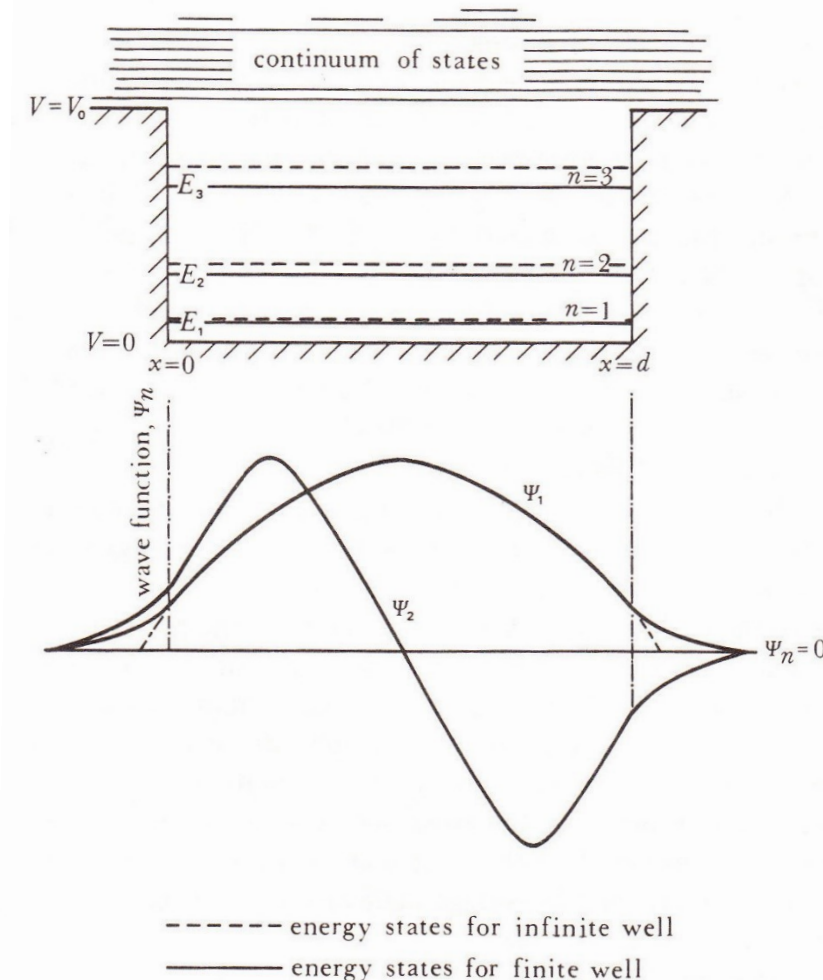
The wave function for the found particle is one set of discrete values, each corresponding to a different value of integer n.

The total energy of the bound particle has only a discrete set of allowed values:

$$E = \frac{\hbar^2 n^2 \pi^2}{2md^2} = \frac{n^2 h^2}{8md^2}$$

n = 1,2,3…

# For a finite 1D well

- Solving S.E. in 3D spherical coordinates give quantum numbers

$$\psi \quad (r, \theta, \varphi) = f_r (r). \; f_\theta (\theta). \; f_\varphi (\varphi)$$

- principle quantum no., which defines the total energy of an electron in a particular state; solution in r gives n = 1,2,3,........
- azimuthal quantum no., associated with the angular momentum of an electron, solution in θ, give  l = 0,1,2,3…….., (n-1)

- magnetic orbital quantum numbers, associated with the fact that an electron in an orbital constitutes a rotating charge and hence an electric current which has associated magnetic field and magnetic moment. The orientation of this inherent magnetic moment with an externally applied magnetic field is quantised and the quantum number m arises because of the discrete number of possible orientations. Solution in φ, give m=-l, m=0, m=+l

- spin quantum number s – Pauli's exculsion principle – no more than one electron can exist in any one quantum state

- We have seen that the particular quantum state of an electronic orbital can be specified by a set of quantum numbers (n,l,m,s). Such numbers completely define the wave functions for a given electron and are usually quoted instead of the wave function because they are less cumbersome.

- For example, Hydrogen – (1,0,0, 1s)
- Helium – (1,0,0, $1s^2$)
- s,p,d,f corresponds to angular momentum quantum number l = 0,1,2,3

# Photoluminescence from multiple quantum wells