Unit II – Quantum Mechanics of simple systems

Topics covered under this unit

1. **The Schrodinger's wave equation**

   a. **Time dependent wave equation**
   b. **Time independent wave equation**

2. **Solutions of the wave equation to interpret a moving free particle**

3. **Solutions of the wave equation to interpret a moving particle encountering a potential step**

   a. **Energy of the particle greater than the potential step**
   b. **Energy of the particle less than the potential step**

4. **Solutions of the wave equation to interpret a moving particle encounter a potential barrier**

   a. **Barrier tunneling**
   b. **Radioactive alpha decay as a case of barrier tunneling**

5. **Solutions of the wave equation to interpret a moving particle confined to a region with infinite potentials at the boundaries**
   a. **One dimensional potential well**
   b. **Two dimensional potential well**
   c. **Three dimensional potential well**

6. **Qualitative discussions of the solutions of the wave equation to describe a moving particle confined to a region with finite potentials at the boundaries**

7. **Solutions of the wave equation to interpret a system if two particles connected with a bond as a harmonic oscillator**

8. **Discussions of the wave functions of a hydrogen atom**

Schrodinger's Wave equation

The moving particle is described by a wave function and there is a need to have a wave equation which can describe this moving particle. Schrodinger's approach to describe the motion in terms of a differential equation is one of the most popular methods. (Dirac's operator mechanics with vector spaces is another method of describing the moving particle and is a computational friendly method.)

The one dimensional time dependent Schrodinger's wave equation

The most general method of describing a system involves evaluating the system in terms of the state variables of position and time.

The total energy of a system is equal to the sum of kinetic energy and potential energy (which are observables of the system)

The energy expression can be written as   E = KE + V

Multiplying throughout with the wave function ψ we get

$$E\psi(x,t) = KE\psi(x,t) + V\psi(x,t) \qquad \text{......... (1)}$$

This equation can be written in terms of the corresponding operators as

$$\widehat{E}\psi(x,t) = \widehat{KE}\psi(x,t) + V\psi(x,t)$$

which is an eigen value equation for the total energy of the system.

The total energy operator is $\left\{i\hbar\frac{\partial}{\partial t}\right\}$, the kinetic energy operator is $\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\}$.

replacing the total energy and the kinetic energy terms with the respective operators we can rewrite the expression (1) as

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

Schrödinger equation

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2\nabla^2}{2m} + V(\vec{r})\right]\Psi(\vec{r},t)$$

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THE
PHYSICAL REVIEW

The Nobel Prize in Physics 1933
Erwin Schrödinger, Paul A.M. Dirac

The Nobel Prize in Physics 1933 was awarded jointly to Erwin Schrödinger and Paul Adrien Maurice Dirac "for the discovery of new productive forms of atomic theory."

AN UNDULATORY THEORY OF THE MECHANICS OF ATOMS AND MOLECULES

By E. SCHRÖDINGER

ABSTRACT

The paper gives an account of the author's work on a new form of quantum theory. §1. The Hamiltonian analogy between mechanics and optics. §2. The analogy is to be extended to include real "physical" or "undulatory" mechanics instead of mere geometrical mechanics. §3. The significance of wave-length;

or $$\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + i\hbar\frac{\partial\Psi}{\partial t} - V\Psi = 0 \qquad \text{....(2)}$$

which is the Schrödinger's time dependent wave function since $\Psi(x,t)$ is a function of both position and time.

The solution of the differential equation yields the wave function $\mathbf{\Psi}$ which is the state function of the system.

The one dimensional time independent Schrodinger's wave equation

Generally any system in the steady state is time invariant and hence the wave function could be independent of time. In such a case we can write the wave function can be written as the product of two functions one that is position dependent and the other time dependent.
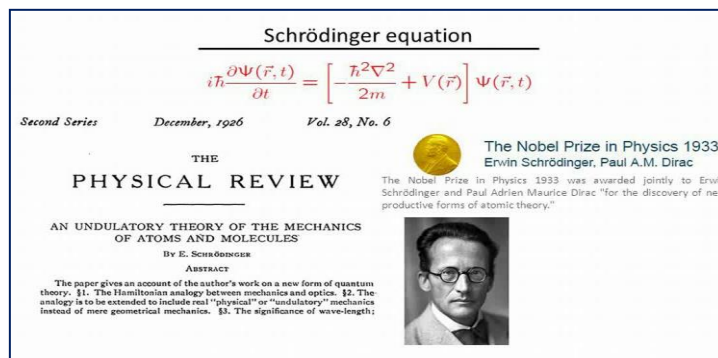
Ie., $\Psi(x,t) = Ae^{\frac{i}{\hbar}(px)}.e^{-\frac{i}{\hbar}(Et)} = \psi(x).\phi(t)$

where $\psi(x) = Ae^{\frac{i}{\hbar}(px)}$ is the position dependent part and $\phi(t) = e^{-\frac{i}{\hbar}(Et)}$ is the time dependent part.

Substituting $\Psi(x,t) = \psi(x).\phi(t)$ in equation (2) we get

$\frac{\hbar^2}{2m}\frac{\partial^2\psi(x).\phi(t)}{\partial x^2} + i\hbar\frac{\partial\psi(x).\phi(t)}{\partial t} - V\psi(x).\phi(t) = 0$

The total energy E of the steady state system being a constant, the total energy operator can be replaced by the value E with no loss of sense.

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x).\phi(t)}{dx^2} + E\psi(x).\phi(t) - V\psi(x).\phi(t) = 0$$

The above equation can be written as $\left\{\frac{\hbar^2}{2m}\frac{d^2\psi(x).}{dx^2} + E\psi(x) - V\psi(x)\right\} * \phi(t) = 0$

We recognize that the product of two functions is zero and since $\phi(t) \neq 0$

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x).}{dx^2} + E\psi(x) - V\psi(x) = 0 \quad \dots\dots\dots\dots\dots(3)$$

This is the Schrödinger's time independent one dimensional wave equation. The solutions of the Schrodinger's wave equation yield the wave function $\psi(x)$ which describes the physical state of the system.

The solution so obtained has to be checked for continuities at any boundaries and normalized to get the exact wave function of the system.

In general the Hamiltonian form of this equation is written as

$$\mathbf{H\Psi = E\Psi}$$

Where the Hamiltonian operator $\widehat{H} = \widehat{KE} + \widehat{PE} = \left\{\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V\right\}$

[Three dimensional Schrodinger's wave equation.

The Schrodinger's wave equation for a 3D can be evolved by looking at the problem as three one dimensional problem in the independent variables *x,y and z*. The wave function of such a system can be written as

$\Psi(x, y, z) = \psi(x)\psi(y)\psi(z)$ where $\psi(x)$, $\psi(y)$ and $\psi(z)$ are the three mutually independent wave functions of the particles in the orthogonal co-ordinate system.

The derivatives of the wave function can be written as partial derivatives of the wave function.

The SWE then can be written as

$$\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x, y, z) + (E - V)\Psi(x, y, z) = 0$$

which can be simplified as

$$\frac{\hbar^2}{2m}\nabla^2\Psi(x, y, z) + (E - V)\Psi(x, y, z) = 0$$

where $\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$ is the Laplacian operator

$\nabla^2 = \nabla.\nabla$ and the operator $\nabla = \hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$]

[Linear superposition of wave functions from SWE.

The wave function $\psi(x)$ which is the solution of the differential equation $\frac{\hbar^2}{2m}\frac{d^2\psi(x).}{dx^2} + E\psi(x) - V\psi(x) = 0$ is a state function. Since a system could have multiple states the solution of the wave equation can give us multiple wave functions $\psi(x)$. If $\psi_1(x)$ represents a state 1 andf $\psi_2(x)$ represents a state 2 of the system then it can be seen that a linear combination of $\psi_1(x)$ and $\psi_2(x)$ is also a solution of the SWE. Thus $\psi_{12}(x) = n.\psi_1(x) + m.\psi_2(x)$ will also be a solution of the SWE. It is obvious that the superposition of two waves is a wave packet and can represent the state of a system.

It is also evident that the probability densities however do not add to give the probability density of the new state and has to be estimated from the new wave function]

Template for solving problems in quantum mechanics using the Schrödinger's wave equation

The Schrodinger's wave equation can be applied to any physical system and the solution of the wave equation yields the wave function of the system. The wave function is probability amplitude and contains information about the physical state (observables of the system). The wave function has to be a well behaved wave function to represent a moving particle.

The template for solving the Schrodinger's wave equation is:

1. *Define / set up the physical system (define particle nature, boundaries of potential, total energy of the particle etc)*

2. *Write the Schrodinger's wave equation and apply the known conditions*

3. *Obtain the general form of the wave function*

4. *Check / verify the wave function for it's characteristics*
   - *finiteness, discreteness and continuity of ψ and its derivatives,*
   - *normalization of the wave functions*

5. *Interpret the solution and get the implications on the quantum system.*

Problem no 1. Free Particle solution

A particle is said to be a free particle when it experiences no external forces.

Thus the force given by $F = -\frac{dV}{dx} = 0$. This implies that either V is zero or V is a constant.

The simplest case then could be when the particle is moving in a region of zero potential i.e., V=0.

The Schrödinger's time independent one dimensional wave equation for the system simplifies to

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x).}{dx^2} + E\psi(x) = 0 \quad \text{or} \quad \frac{d^2\psi(x).}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

$$\frac{d^2\psi(x).}{dx^2} + k^2\psi = 0 \text{ where } k = \sqrt{\frac{2mE}{\hbar^2}} \text{ is the propagation constant.}$$

The solution of this differential equation is $\psi = Ae^{ikx} + Be^{-ikx}$ where A and B are constants.

As a general concept the first part describes a forward moving wave packet (in increasing x direction) and the second part describes a backward moving wave packet (decreasing x direction)

The energy of the particle is given by $E = \frac{\hbar^2 k^2}{2m}$.

Since the free particle is moving in a zero potential region and there is no restriction on wave number or the energy of the particle, we conclude that the total energy of the particle is kinetic in nature with no implications of quantization.

This could the quantum description of a classical free particle.

**Energy interaction of particles with fields**

Consider a simple arrangement of two highly conducting hollow tubes perfectly aligned along the axes and electrically separated by an

extremely small distance. Let the first tube be connected to ground so that the potential on the surface of the tube is V=0.

The second tube is connected to a constant potential V=V₀ with respect to ground.

Consider a particle with energy E incident along the axis of the first tube. Since the potential on the surface of the tube is zero, there is no effect on the particle's motion inside the first segment. As the particle leaves the first segment and tries to enter the second segment, there is a forward acceleration (deceleration) of the particle as it enters the second segment. Once inside the second segment the radial forces on the particle add up to zero and the particle continues to move through the segment with energy $E \pm V$. We treat this as an interaction of the particle with the field where it has gained (or lost) energy with the potential field.
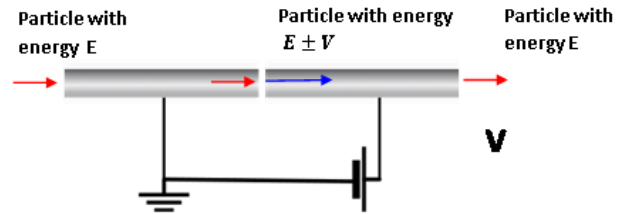
As the particle reaches the end of the second segment, the interaction is reversed. The particle can now be decelerated (or accelerated) which results in the particle giving away the energy it gained (or lost) back to the field.

This experiment reveals two aspects – a particle moving in force fields where the forces are zero since $\frac{dV}{dx}$ is zero in both segments of the tube. However, there can be an exchange of energy with the field as the particle enters or as the particle leaves the second part of tube where there exists a constant potential.

Thus, in general it can be concluded that a particle moving in a field can interact with the field and exchange energy with the field at the boundaries. This concept is quite useful in understanding the particle's motion in a field.

Problem no. 2 - Potential Steps

The behavior of a moving particle when it encounters a potential field along its path is the first step in solving problems in Quantum Mechanics. In reality the potential field varies inversely as the distance from the source of the potential (i.e., $V \propto \frac{1}{r}$). However, the solution of the Schrödinger's wave equation becomes difficult if the actual potential variations are considered. It is therefore necessary and sufficient if the potentials are approximated to simpler (solvable) systems.

This leads to the concept of potential steps where the potential energy vs. distance graphs show a discrete jump from a zero value to a constant value V_0. However the behavior of the wave function (representing the particle) can have different responses depending on the energy of the particle as compared to the energy of the potential step. The energy of the particle can be greater or less than the energy of the potential step.
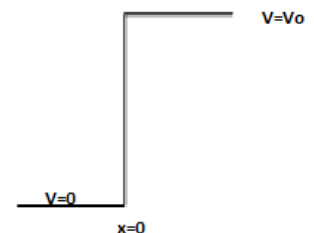
The problem can be divided as a two region problem, region I in which the potential V=0 and the region II in which the potential V= V₀.

The Schrödinger's wave equation $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$

for the region I with V=0 this becomes $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$

The solution of the equation in region I is given by

$$\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}$$

where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$ and the debroglie wavelength $\lambda_1 = \frac{h}{\sqrt{2mE}}$

The component with the positive exponent represents the oncoming wave and the negative exponent represents the reflected wave at the boundary x=0

In region II the nature of the wave function will depend on the energy E of the particle in comparison to the energy of the potential step.

Case I. If the energy E of the particle is greater than the energy of the potential (E>V$_o$) step then the Schrödinger's wave equation for the region II can be written as

$$\frac{\partial^2 \psi_{II}}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_o)\psi_{II} = 0$$

with the solution being $\psi_{II} = Ce^{-ik_{II}x} + De^{ik_{II}x}$ where $k_{II} = \sqrt{\frac{2m(E-V_o)}{\hbar^2}}$. The nature of the wave function remains the cyclic and the particle propagates in region II with reduced kinetic energy (E-V$_o$). The first term of the wave function is non existing since there cannot be a reflection after x>0 as there is no disruption in the potential.
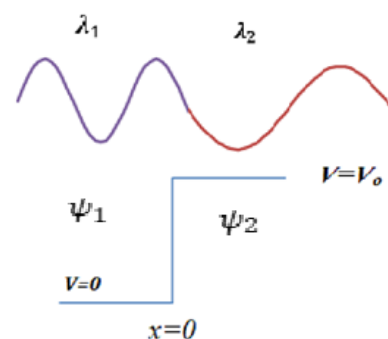
The momentum in the second region is given by

$\hbar k_{II} = \sqrt{2m(E - V_o)}$ and the corresponding debroglie wavelength $\lambda_{II} = \frac{h}{\sqrt{2m(E-V_o)}}$ which is longer than the debroglie wavelength in region I.

In this case the constants B and D can be found in terms of A by applying the boundary condition that the wave function and its derivatives are finite and continuous at *x = 0*.

$at\ x = 0\quad \psi_{I(x=0)} = \psi_{II(x=0)}\ gives\ A + B = D$

$at\ x = 0\quad d\psi_{I(x=0)} = d\psi_{II(x=0)}\ gives\ (A - B)k_I = Dk_{II}$

Solving the simultaneous equations we get $D = 2A * \left(\frac{k_I}{k_I\ and\ k_{II}}\right)$

$D = 2A * \left(\frac{k_I}{k_I + k_{II}}\right)$ and $B = A * \left(\frac{k_I - k_{II}}{k_I + k_{II}}\right)$

It is seen that the coefficient B of the reflected component is non zero implying that there is a small probability of reflection at x=0 even if the energy of the particle is greater than the potential step V$_o$.

The flux of incident particles is given by $\psi_1^*\psi_1 \times v_1 = A^*A\,v_1$

The reflection coefficient can be written as $R = \frac{reflected\ flux}{incident\ flux} = \frac{B^*B\,v_1}{A^*A\,v_1} = \left(\frac{k_I - k_{II}}{k_I + k_{II}}\right)^2$

and the transmission coefficient $T = \frac{transmitted\ flux}{incident\ flux} = \frac{D^*D\,v_{II}}{A^*A\,v_I}$ where v_I and v_{II} are the velocities of the particles in the two regions.

Thus, the transmission co-efficient T = $\left(\frac{4k_I.k_{II}}{k_I + k_{II}}\right) = \frac{4\sqrt{E.(E-Vo)}}{\left(\sqrt{E} + \sqrt{E - Vo}\right)^2}$

It is observed that R+T = 1, i.e. the flux incident has to be partially reflected and partially transmitted.

R and T are the relative probabilities of reflection and transmission at the potential step.

Case II Energy of the particle < V₀.

In region I the behavior of the particle is the same at the previous case (since V=0) and the wave function will be

$$\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}$$

If the energy E of the particle is lesser than the energy of the potential step $(E < V_o)$, then the Schrödinger's wave equation for the region II can be written as

$$\frac{\partial^2 \psi_2}{\partial x^2} - \frac{2m}{\hbar^2}(V_o - E)\psi_2 = 0$$

with the solution being $\psi_2 = Fe^{-\alpha x} + Ge^{\alpha x}$ where $\alpha = \sqrt{\frac{2m(V_o - E)}{\hbar^2}}$

The second part of the wave function $Ge^{\alpha x}$, makes ψ_2 infinite for large values of **x** and hence cannot be part of the wave function. Setting the coefficient **G** to be zero the wave function reduces to

$$\psi_2 = Fe^{-\alpha x}$$

The wave function has a finite value and decays exponentially in region II. Thus there exists a finite probability for the particle to be found in region II $(since\ \psi_2{}^*\psi_2\ is\ non\ zero)$ which is unlike the classical solution.
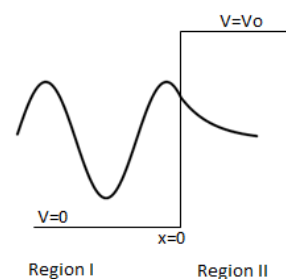
(In an exponential decay the wave function is significant till it decays to $\frac{1}{e}$ of the value at x=0. At x=0 the value of the function $\psi_2 = F$. The changes in this function $\psi_2 = Fe^{-\alpha x}$ become insignificant at some Δx.

The function evaluated at Δx gives $\psi_2(\Delta x) = Fe^{-\alpha \Delta x} = F * \frac{1}{e} = F * e^{-1}$.

This implies $\alpha * \Delta x = 1$ or $\Delta x = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_o - E)}}$).

The wave function becomes insignificant at a distance $\Delta x = \frac{\hbar}{\sqrt{2m(V_o - E)}}$ which is the penetration depth in region II. The penetration depth increases as the energy of the particle increases.

In the second region the kinetic energy of the particle is negative which implies that the particle cannot physically exist in the second region.

We conclude that when a particle (or beam of particles with identical E) is incident on a potential step, there is a quantum mechanical effect which -

- the particle can be reflected back even if the energy of the particle E > V₀.
- the particle can have a small but finite probability of being in the second region even if E<V₀.

Problem no. 3 - Potential Barrier

The potential barrier is a region in space where the potential is a constant V₀ for all 0<x<L and V=0 for the all x<0 and x>L

A particle of mass m and energy E < V₀, incident on the potential barrier is represented by a forward moving wave. Since E <V₀ classically we expect the particle to be reflected back at the potential barrier and there is no probability of finding the particle in the region beyond the barrier.

In **region I** with V=0 the Schrödinger's wave equation becomes $\frac{\partial^2\psi_I}{\partial x^2} + \frac{2m}{\hbar^2}E\psi_I = 0$ (1)

The solution of the equation in region I is given by

$$\psi_I = Ae^{ik_1x} + Be^{-ik_1x} \qquad (2)$$

where $k_I = \sqrt{\frac{2mE}{\hbar^2}}$ and the debroglie wavelength $\lambda_I = \frac{h}{\sqrt{2mE}}$

The first term in equation 2 represents the incident wave and the second term represents the reflected component.

In **region II** since E<V₀, the Schrödinger's wave equation for the region II can be written as

$$\frac{\partial^2\psi_{II}}{\partial x^2} - \frac{2m}{\hbar^2}(V_o - E)\psi_{II} = 0 \qquad (3)$$

with the solution being $\psi_{II} = De^{-\alpha x}$ where $\alpha = \sqrt{\frac{2m(V_o-E)}{\hbar^2}}$ (4)

In region II the nature of the wave function changes to an exponentially decaying function. The penetration depth is given by $\Delta x = \frac{\hbar}{\sqrt{2m(V_o-E)}}$ (5)

And in **region III,** the potential being 0, the wave equation is $\frac{\partial^2\psi_{III}}{\partial x^2} + \frac{2m}{\hbar^2}E\psi_{III} = 0$

and the wave function is given by $\psi_{III} = Ge^{ik_{III}x}$ (6)

where $k_{III} = \sqrt{\frac{2mE}{\hbar^2}}$ and the debroglie wavelength $\lambda_{III} = \frac{h}{\sqrt{2mE}}$
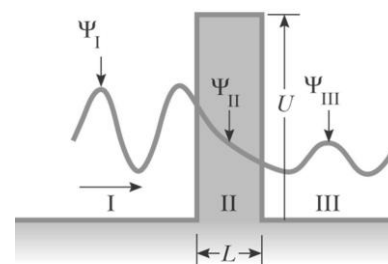
The amplitude of the reflected and transmitted waves can be evaluated in terms of the incident amplitude by applying the boundary conditions

$$\psi_I = \psi_{II}\ at\ x = 0 \quad and \quad \psi_{II} = \psi_{III}\ at\ x = L$$

and $\frac{d\psi_I}{dx} = \frac{d\psi_{II}}{dx}$ at x = 0 and $\frac{d\psi_{II}}{dx} = \frac{d\psi_{III}}{dx}$ at x = L

The transmission coefficient which gives the probability of the particles being transferred to the third region can be estimated as $T = \frac{transmitted\ flux}{incident\ flux} = \frac{G^*G\ v_3}{A^*A\ v_1}$

where v_1 and v_3 are the velocities of the particle in region I and III. Since the energy of the particle is the same in the two regions the velocities are also same and

the transmission coefficient can be evaluated approximately as

$$T = \frac{G^*G}{A^*A} \approx 16\frac{E}{V_o}\left[1-\frac{E}{V_o}\right]e^{-2\alpha L} \cong e^{-2\alpha L}$$
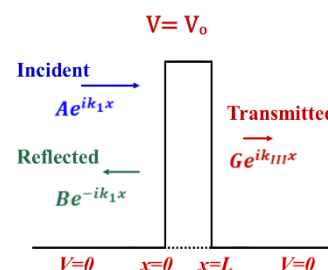
Thus the probability of transmission is more if either α or a is small. Smaller α implies smaller $(V_o - E)$. Thus particles with higher energy have higher transmission probability through the barrier.

If the width of the barrier **L is less than the penetration depth** Δx then there is a finite probability that the particle is transmitted across the barrier.

This process of transmission through a potential barrier even when the energy of the particle is lesser than the barrier potential is known as barrier tunneling or the quantum mechanical tunneling.

It is also noted that for all values of E, there is always a reflected component which is given by **R = 1 – T** which is higher than the transmitted coefficient.

[The particle in the second region has a negative Kinetic energy and this is not a physical reality. However, the particle can exchange energies with the field (potential) without violating the uncertainty principle $\Delta E.\Delta t = \frac{h}{4\pi}$. Thus the energy exchange has to happen in a time interval of $\Delta t = \frac{h}{4\pi\Delta E}$. This gives a time interval which is extremely small of the order of femto seconds. Thus, the particle has to cross the barrier almost instantaneously]

Radioactive alpha decay as a case of barrier tunneling

Emission of alpha particles (Helium nuclei) in the decay of radioactive elements can be example of tunneling.

The positive charge on the nucleus creates a nonlinear potential barrier around the nucleus. This potential barrier is estimated to be as high as 20MeV at the surface.

In the radioactive α decay of the nucleus, two protons and two neutrons are emitted as a single entity (a doubly charged He nucleus). The process of radioactive decay of α particles with low energies compared to the barrier potential could be explained as a case of barrier tunneling.

The potential which varies inversely as the distance from the surface of the nucleus can be approximated to a triangular potential. This can then be modeled as a series of rectangular potentials of thin slices of thickness Δr. The potential barrier for each of these slices


decrease by a small ΔV, which gives $\alpha_n = \sqrt{\frac{2m(V_n - E)}{\hbar^2}}$

The transmission coefficients for each of the slice of potential barrier can be evaluated with $T_n = e^{-2\alpha_n \Delta r}$ and the total transmission probability is the product of all these individual transmission probabilities. This gives a reasonable

estimate of the tunneling probabilities of alpha particles.

Tunneling rate is very sensitive to small changes in energy and size of the nucleus and account for the wide range of decay times to different radioactive nuclei.

Taking the alpha particles to be in a state of constant motion with a very high kinetic energy, the frequency of approach to the nuclear surface can be estimated to be the diameter of the nucleus divided by the velocity of the particles. This frequency when multiplied by the transmission co-efficient gives us the probability that an alpha particle is emitted out of the nucleus. The inverse of this probability is then the mean lifetime for alpha decay of the radioactive nucleus.
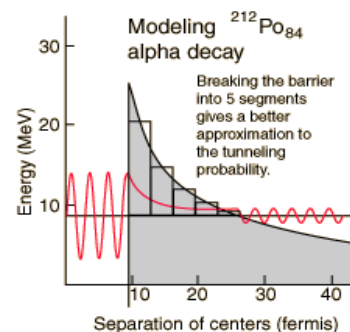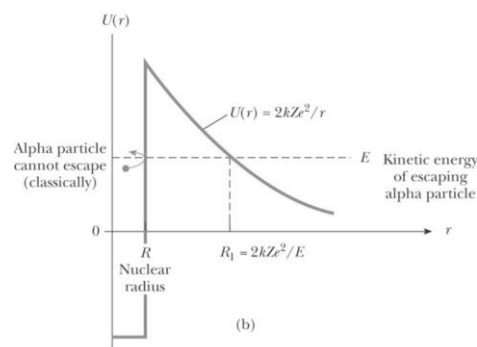
Problem no. 4 - Particle in a Box with infinite potentials at the walls

A particle with mass m and energy E is confined in a one dimensional box with infinite potential at the boundaries. Defining the boundaries to be $x = -\frac{a}{2}$ and $x = +\frac{a}{2}$ where the potential tends to infinity. The particle is confined to the region $-\frac{a}{2} < x < +\frac{a}{2}$ and cannot be found in regions outside the boundaries $x < -\frac{a}{2}$ and $x > \frac{a}{2}$. The potential inside the region $-\frac{a}{2} < x < +\frac{a}{2}$ is V=0.

The Schrödinger's wave equation $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$

in the region within the well V=0 this becomes

$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0$

$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$

The solution of the equation in region $-\frac{a}{2} < x < \frac{a}{2}$ is given by

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Applying the boundary condition that $\psi = 0$ at $x = -\frac{a}{2}$ and $x = \frac{a}{2}$

At $x = -\frac{a}{2}$ $\psi\left(x = -\frac{a}{2}\right) = A\sin\left(-k\frac{a}{2}\right) + B\cos\left(k\frac{a}{2}\right) = 0$ gives

$-A\sin\left(k\frac{a}{2}\right) + B\cos\left(k\frac{a}{2}\right) = 0$ [1]

At $x = \frac{a}{2}$ $\psi\left(x = \frac{a}{2}\right) = A\sin\left(k\frac{a}{2}\right) + B\cos\left(k\frac{a}{2}\right) = 0$ gives

$A\sin\left(k\frac{a}{2}\right) + B\cos\left(k\frac{a}{2}\right) = 0$ [2]

The two conditions imply that (since sine and cosine functions cannot be zero at the same time) if **$A = 0$ then $B \neq 0$** and **if $A \neq 0$ then $B = 0$** since when $\sin\left(k\frac{a}{2}\right) = 0$, $\cos\left(k\frac{a}{2}\right) \neq 0$ and vice versa.

Taking the first condition that $A = 0$ and $B \neq 0$ implies that when

$$\cos\left(k\frac{a}{2}\right) = 0, \quad k\frac{a}{2} = (2N-1)\frac{\pi}{2} \text{ or } k = (2N-1)\frac{\pi}{a} \text{ n odd multiple of } \frac{\pi}{a})$$

The second condition $B = 0$ then $A \neq 0$ which implies that

$$\sin\left(k\frac{a}{2}\right) = 0 \text{ or } k\frac{a}{2} = N\pi \text{ or } k = 2N\frac{\pi}{a} \text{ (an even multiple of } \frac{\pi}{a})$$

The above two conditions can be combined and generalized to give the allowed values of the propagation constant (wave number)

$$k = \frac{n\pi}{a} \text{ with } n = 1, 2, 3 \ldots$$
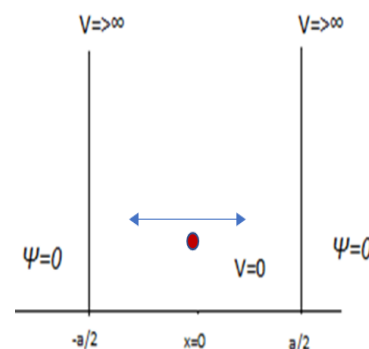
The wave function then reduces to

$$\psi(x) = A\cos(kx) \text{ for n odd and}$$
$$\psi(x) = A\sin(kx) \text{ for n even}$$

The allowed values of k give the allowed states with energy $E_n = \frac{h^2 n^2}{8ma^2}$

The wave functions can be normalized for the individual states to give the constants A and B.

The constant A can be evaluated by normalizing the wave function ie., integrating the function between limits of $-\frac{a}{2}$ and $\frac{a}{2}$ $\int \psi^* \psi dx = 1$

$$\int_{-a/_2}^{a/_2} \left[A sin \left(\frac{n\pi}{a}x\right)\right]^2 dx = \frac{A^2}{2} \int_{-a/_2}^{a/_2} \left[1 - \cos\left(\frac{2n\pi}{a}x\right)\right] dx$$

This on integration gives $\frac{A^2}{2} \left[x - \frac{L}{2n\pi}\sin\left(\frac{2n\pi}{a}x\right)\right]_{-a/_2}^{a/_2} = \frac{A^2}{2}[a - 0] = 1$

This gives a value of $A = \sqrt{\frac{2}{a}}$

The exact form of the wave function becomes

$$\psi_n(x) = \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi}{a}x\right) \quad for \; n \; odd \qquad \text{(even parity)}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \quad for \; n \; even \qquad \text{(odd parity)}$$

[Parity *of a function is determined by changing the sign of the variable. If the function remains unchanged then it is defined as an even parity functions and if the function changes sign then it is an odd parity function.*

If $\psi(-x) = \psi(x)$ then the function has an even parity and

if $\psi(-x) = -\psi(x)$ then the function has an odd parity.]

Eigen functions and Eigen values

Eigen functions are exact wave functions which represent the state of the system completely. Eigen functions are exact solutions of the Schrodinger's wave equation.

The even parity Eigen function of a particle in a infinite potential well $\psi_n = \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi}{a}x\right)$ and odd

parity Eigen function of a particle in a infinite potential well $\psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$

The first three states correspond to n=1,2 and 3
The Eigen functions are

$\psi_1 = \sqrt{\frac{2}{a}}\cos\left(\frac{\pi x}{a}\right)$

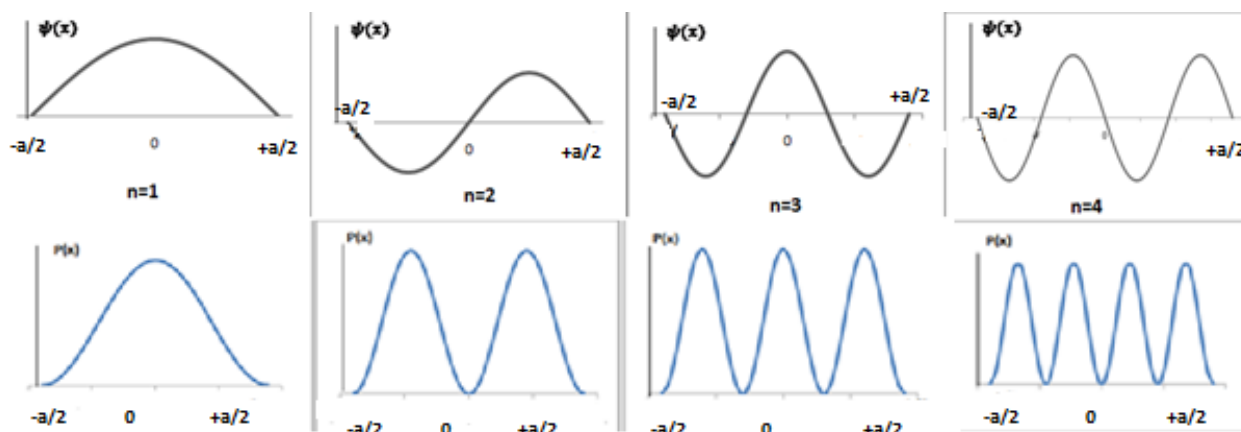$\psi_2 = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)$

$\psi_3 = \sqrt{\frac{2}{a}}\cos\left(\frac{3\pi x}{a}\right)$

Eigen values of the system are the exact values of the physical parameters of the system obtained from an Eigen function using operators.

The Eigen energy values is given function $E_n = \frac{h^2 n^2}{8mL^2}$ where n = 1,2 3…

And the Eigen values are $E_1 = \frac{h^2}{8ma^2}$ $\quad E_2 = \frac{h^2 2^2}{8ma^2}$ $\quad E_3 = \frac{h^2 3^2}{8ma^2}$

Probability density $\psi^*\psi$ for the first three states is obtained by squaring the corresponding wave functions $\psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$ or $\psi_n = \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi x}{a}\right)$. The square of the function is close to a gaussian shape.

In the first state n=1, the probability of finding the particle is maximum at $x = 0$ and the area under the curve represents the total probability of finding the particle in the ground state which is 1.00

In the second state n=2, the probability of finding the particle is maximum at $x = -\frac{a}{4}$ and $x = +\frac{a}{4}$ .The area under one segment of the curve represents the probability of finding the particle in the first excited state and is $\frac{1}{2} = 0.5$.

In the third state n=3,the probability of finding the particle is maximum at $x = -\frac{a}{3}, x = 0$ and $x = +\frac{a}{3}$ .The area under one segment of the curve represents the probability of finding the particle in the first excited state and is $\frac{1}{3} = 0.333$.

In general, the probability of finding the particle in the nth state, in a segment of length $\frac{a}{n}$ is $\frac{1}{n}$.

The probability of finding the particle between two limits in the well is given be the expression

$P = \int_{x_1}^{x_2}\left[A\cos\left(\frac{n\pi}{a}x\right)\right]^2 dx$ or $\int_{x_1}^{x_2}\left[A\sin\left(\frac{n\pi}{a}x\right)\right]^2 dx$, depending on the whether the state n is odd or even. Note that this probability will be less than 1 if the limits are not the boundaries of the well.

The Eigen values of the momentum and the $p_n = \hbar k = n\frac{h}{2a}$

Particle in a 2D well of infinite potential at the boundaries

A particle in a two dimensional well has two degrees of freedom and can move in XY plane. This can be treated as a case of particle confined in a well with infinite potentials at the boundaries of the x and y directions. The momentum **P** of a particle moving in the x y plane can be resolved into two independent momentum components **Px** and **Py** along the x and y directions.

The problem can be analyzed as two independent problems for the x and y directions and the solutions would be similar to the one dimensional infinite potential well problem.
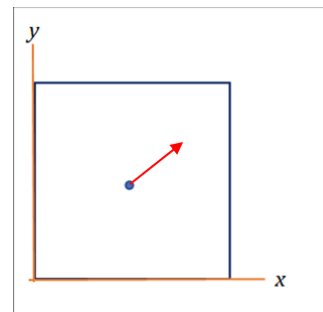
The Schrodinger's equation can be written as $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$

$\frac{\partial^2 \psi}{\partial x^2} + k_x{}^2 \psi = 0$ where $k_x = \sqrt{\frac{2mE_x}{\hbar^2}}$ and the solutions to this are

The eigen functions for the x direction

$$\psi_{n_x}(x) = \sqrt{\frac{2}{a}} \cos\left(\frac{n_x \pi}{a} x\right) \ for \ n_x \ odd \qquad \text{(even parity)}$$

$$\psi_{n_x}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a} x\right) \ for \ n_x \ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_x = \frac{h^2 n_x{}^2}{8mL^2}$ where n_x can take values 1,2,3,4,5….

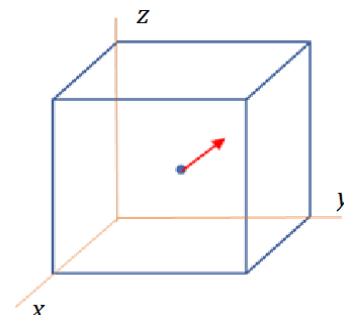The particle's movement in the y direction can be analysed similarly.

The Schrodinger's equation can be written as $\frac{\partial^2 \psi}{\partial y^2} + \frac{2m}{\hbar^2} E\psi = 0$

$\frac{\partial^2 \psi}{\partial y^2} + k^2 \psi = 0$ where $k_y = \sqrt{\frac{2mE_y}{\hbar^2}}$ and the solutions to this are

The eigen functions for the y direction

$$\psi_{n_y}(y) = \sqrt{\frac{2}{a}} \cos\left(\frac{n_y \pi}{a} y\right) \ for \ n_y \ odd \qquad \text{(even parity)}$$

$$\psi_{n_y}(y) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_y \pi}{a} y\right) \ for \ n_y \ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_y = \frac{h^2 n_y{}^2}{8mL^2}$ where n_y can take values 1,2,3,4,5….

The total energy of the system is then $E_n = E_x + E_y = \frac{h^2 n_x{}^2}{8mL^2} + \frac{h^2 n_y{}^2}{8mL^2} = \frac{h^2}{8mL^2}(n_x{}^2 + n_y{}^2)$

The allowed energy states of the particle are then decided by the allowed values of n_x and n_y.

The first allowed state is the ground state of the system and given by $E_{11} = 2\frac{h^2}{8mL^2} = 2E_o$ where $E_o = \frac{h^2}{8mL^2}$.

The second allowed state of the system is given by $E_{21} = 5E_o$ which is also the energy of the state E_{12}. There are two allowed states for the same energy value of $5E_o$. This state is then doubly degenerate.

In general, for a 2D system in when $n_x = n_y$ the energy state is a single state and when $n_x \neq n_y$ the energy state has a degeneracy factor of 2.

The separation between energy states does not increase monotonically as in the 1D system.

The wave functions of the corresponding states can be written as

$\psi_{11} = \frac{2}{a} \cos\left(\frac{\pi}{a} x\right) \cos\left(\frac{\pi}{a} y\right)$ for the first allowed state with $n_x = n_y = 1$

$\psi_{21} = \frac{2}{a} \sin\left(\frac{2\pi}{a} x\right) \cos\left(\frac{\pi}{a} y\right)$ for the second allowed state with $n_x = 2 \ and \ n_y = 1$

$\psi_{12} = \frac{2}{a} \cos\left(\frac{\pi}{a} x\right) \sin\left(\frac{2\pi}{a} y\right)$ for the allowed state with $n_x = 1 \ and \ n_y = 2$

From the wave functions we realize that the two states are different but has the energy eigen value of $5E_o$. Such states are referred to as degenerate states.

Particle in a 3D Box of infinite potential at the boundaries

A particle in a three dimensional well has three degrees of freedom and can move in 3D space. This can be treated as a case of particle confined in a box of sides L with infinite potentials at the boundaries of the x, y and z directions. The momentum **P** of a particle moving in space can be resolved into three independent momentum components **P$_x$**, **P$_y$** and **P$_z$** along the coordinate axes.

This problem can be analysed as three independent problems for the x, y and z directions and the individual solutions will be similar to the one dimensional infinite potential well problem.

The Schrodinger's equation can be written as $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0$

$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0$ where $k_x = \sqrt{\frac{2mE_x}{\hbar^2}}$ and the solutions to this are

The eigen function for the x directions

$$\psi_n(x) = \sqrt{\frac{2}{a}} \cos\left(\frac{n_x \pi}{a} x\right) \ for \ n_x \ odd \qquad (even \ parity)$$

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a} x\right) \ for \ n_x \ even \qquad (odd \ parity)$$

with the eigen values for energy as $E_x = \frac{h^2 n_x^2}{8mL^2}$ where n_x can take values 1,2,3,4,5....

The particle's movement in the y direction can be analysed.

The Schrodinger's equation can be written as $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0$

$\frac{\partial^2 \psi}{\partial y^2} + k^2\psi = 0$ where $k_y = \sqrt{\frac{2mE_y}{\hbar^2}}$ and the solutions to this are

The eigen function for the y directions

$$\psi_n(y) = \sqrt{\frac{2}{a}} \cos\left(\frac{n_y \pi}{a} y\right) \ for \ n_y \ odd \qquad (even \ parity)$$

$$\psi_n(y) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_y \pi}{a} y\right) \ for \ n_y \ even \qquad (odd \ parity)$$

with the eigen values for energy as $E_y = \frac{h^2 n_y^2}{8mL^2}$ where n_y can take values 1,2,3,4,5....

The particle's movement in the z direction can be analysed.

The Schrodinger's equation can be written as $\frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} E\psi = 0$

$\frac{\partial^2 \psi}{\partial y^2} + k_z^2\psi = 0$ where $k_z = \sqrt{\frac{2mE_z}{\hbar^2}}$ and the solutions to this are

The eigen functions for the z direction

$$\psi_n(z) = \sqrt{\frac{2}{a}} \cos\left(\frac{n_z \pi}{a} y\right) \ for \ n_z \ odd \qquad (even \ parity)$$

$$\psi_n(z) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_z \pi}{a} y\right) \quad for \ n_z \ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_y = \frac{h^2 n_y{}^2}{8ma^2}$ where n_y can take values 1,2,3,4,5….

The total energy of the system is then

$$E_n = E_x + E_y + E_z = \frac{h^2 n_x{}^2}{8ma^2} + \frac{h^2 n_y{}^2}{8ma^2} + \frac{h^2 n_z{}^2}{8ma^2} = \frac{h^2}{8ma^2}\left(n_x{}^2 + n_y{}^2 + n_z{}^2\right)$$

The allowed energy states of the particle are then decided by the allowed values of n_x, n_y and n_z.

The first allowed state is the ground state of the system and has an energy

$E_{111} = 3\frac{h^2}{8ma^2} = 3E_o$ where $E_o = \frac{h^2}{8ma^2}$.

The second allowed state of the system is given by $E_{211} = 6E_o$ which is also the energy of the state $E_{121} and E_{123}$. There are three allowed states for the same energy value of $6E_o$. This state is then triply degenerate.

The analysis of the first few states reveal that the states are non degenerate when $n_x = n_y = n_z$. The states have a degeneracy factor of 3 whenever two of the numbers n_x, $n_y \ and \ n_z$ are equal and not equal to the third.

When all the three numbers n_x, $n_y \ and \ n_z$ are unequal then the energy state would have a degeneracy of 6.

Further the separation between energy states does not increase monotonically as in the 1D system.

The wave functions of the corresponding states can be written as

for the first allowed state with $n_x = 1$, $n_y = 1 \ and \ n_z = 1$

$$\psi_{111} = \left(\frac{2}{a}\right)^{\frac{3}{2}} \cos\left(\frac{\pi}{a}x\right) \ \cos\left(\frac{\pi}{a}y\right) \cos\left(\frac{\pi}{a}z\right)$$

the second allowed state with $n_x = 2$, $n_y = 1 \ and \ n_z = 1$

$$\psi_{211} = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{2\pi}{a}x\right) \ \cos\left(\frac{\pi}{a}y\right) \cos\left(\frac{\pi}{a}z\right)$$

the allowed state with $n_x = 1$, $n_y = 2 \ and \ n_z = 1$

$$\psi_{121} = \frac{2}{a}\cos\left(\frac{\pi}{a}x\right) \ \sin\left(\frac{2\pi}{a}y\right) \cos\left(\frac{\pi}{a}z\right)$$

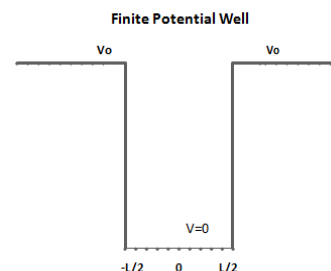for the allowed state with $n_x = 1$, $n_y = 1 \ and \ n_z = 2$

$$\psi_{112} = \left(\frac{2}{a}\right)^{\frac{3}{2}} \cos\left(\frac{\pi}{a}x\right) \ \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{n_z \pi}{a}z\right)$$

From the wave functions we realize that the three states are different but has the energy Eigen value of $6E_o$.

Problem no. 5 - Finite potential well

Finite Potential Well

The finite potential well is a closer approximation to real potentials in solids. The particle can be confined to a region with constant potential V_O at the walls $|x| > \frac{L}{2}$.. Inside the potential well region of –L/2 to +L/2 the potential is zero. In this case the SWE for the three regions can be solved to get the nature of the wave functions.

However, these do not result in an exact solution and approximation methods are used. The nature of the wave functions in the three regions can be written as

$\psi_1 = De^{\alpha x}$ where $\alpha = \sqrt{\frac{2m(V_o-E)}{\hbar^2}}$ for the region x< $^{-L}/_2$

$\psi_2 \cong A\cos(k_2 x)\ for\ odd\ values\ of\ n$ or

$\psi_2 = A\sin(k_2 x)$ for even values of n   where $k_2 = \sqrt{\frac{2mE}{\hbar^2}}$ for the region $^{-L}/_2 < x < ^{L}/_2$

The cosine solutions show even parity (symmetric when sign of the function becomes negative) and the sine solutions exhibit odd parity (anti symmetric when sign of the function becomes negative). However, it is to be noted that the wave function ψ_2 would not be zero at the boundaries of $-\frac{L}{2}\ and +\frac{L}{2}$.
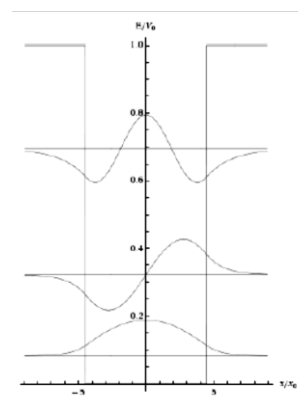
$\psi_3 = Ge^{-\alpha x}$ where $\alpha = \sqrt{\frac{2m(V_o-E)}{\hbar^2}}$ for the region x> $^{L}/_2$

The continuity of the wave functions and their derivatives at the boundaries $-\frac{L}{2}\ and +\frac{L}{2}$ gives the conditions
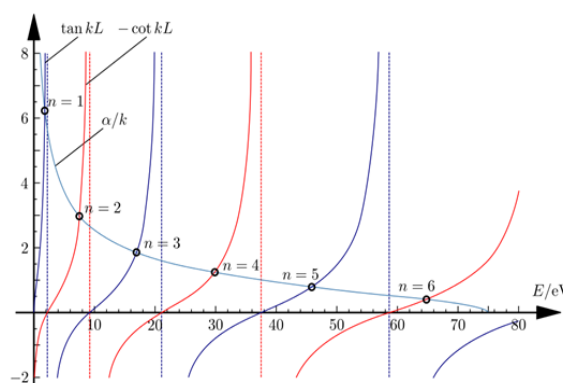
$\alpha = k\tan(k\frac{L}{2})$ or $\sqrt{(V_o - E)} = \sqrt{E}\tan\left(\sqrt{\frac{2mE}{\hbar^2}} * \frac{L}{2}\right)$ for

n=1

and

$\alpha = -k\cot(k\frac{L}{2})$ or $\sqrt{(V_o - E)} = -\sqrt{E}\cot\left(\sqrt{\frac{2mE}{\hbar^2}} * \frac{L}{2}\right)$

for n=2

It can be seen that the right-hand side and left-hand side of the equations contain the same variable E and the nature of variations of the functions on either sides are quite different and hence an exact solution do not exist. (Equations of this type are called transcendental equations.)

The energy values of the particle inside the well region can be found from graphical or approximate methods. The variation of the left-hand side and the right-hand side could be plotted on the same graph as a function. The points of intersection of the LHS and RHS plots are the solutions as the values of E satisfy both the equations.

Thus, the different energy states could be evaluated.

Since the particle is in the finite potential well, at least one solution to the problem exists. Or one energy state exists for the particle in the finite potential well. The number of solutions would obviously depend on the height of the finite potential V_o.

From the expression for the energy of an infinite potential well we can write the energy of the particle in a finite potential well as

$$E_{infinite} = \frac{\hbar^2\pi^2 n^2}{2mL^2} = \frac{\hbar^2 n^2}{2m(width\ of\ the\ well\ where\ \psi \to 0)^2}$$

In the case of the finite potential well we can define the effective width of the well as the points where the wave function becomes insignificant. Thus, the effective width of the well is the width of the well plus twice the penetration depth of the particle in that energy state. The penetration depths in the regions of the potential V_o is given by $\Delta x = \frac{h}{\sqrt{2m(V_o - E_x)}}$ which is a function of E_x.

The effective width of the box (defined approx as the points at the wave function becomes insignificant of zero) is then larger and can be approximated as $L + 2\Delta x$

In the case of the finite potential well the energy of the particle can be written as

$$E_{finite} = \frac{\hbar^2\pi^2 n^2}{2m(width\ of\ the\ well\ where\ \psi \to 0)^2} = \frac{\hbar^2\pi^2 n^2}{2m(L + 2\Delta x)^2}$$

Hence the energy values are less than the energy values for the corresponding states of an infinite potential well of the width L.

Problem no. 6 - Harmonic Oscillator

Harmonic oscillator is one of the most fundamental systems in quantum mechanics which gives insight to a variety of problems such as the vibrational molecular spectroscopy.

The classical harmonic oscillator is a bound particle subjected to oscillations about a mean position. However, a restoring force that is proportional to the displacement of the particle from a mean position keeps the amplitude of the oscillations within limits. The force equation of such a system in classical physics is $\mathbf{F} = \mathbf{ma} = \mathbf{m}\frac{d^2 x}{dt^2} = -\mathbf{kx}$ where k is the force constant given by

$m\omega^2$ where $\omega = \sqrt{\frac{k}{m}}$ is the frequency of vibration and m is the mass of the system.

The potential energy of the system is evaluated as

$$\mathbf{V} = -\int \mathbf{Fdx} = \int \mathbf{kdx} = \frac{1}{2}\mathbf{kx^2} = \frac{1}{2}\mathbf{m\omega^2 x^2}.$$

Consider a diatomic molecule with the masses of the atoms as m_1 and m_2 bound by a bond that is springy in nature. This can be studied as a spring mass system with spring constant (which basically depend on the bond strength). In this case the effective mass μ of the system will

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

decide the frequency of oscillations $\omega = \sqrt{\frac{k}{\mu}}$ and the potential energy of the system can be written as

$$V(x) = \frac{1}{2}\mu\omega^2 x^2.$$

Using this form of the potential in the Hamiltonian $\mathbf{H\psi}$ we get
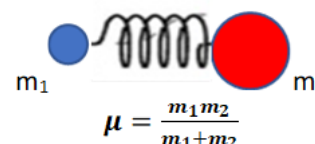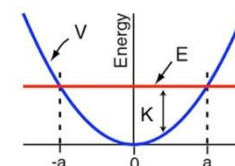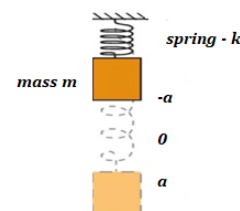
$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + V\psi(x) = -\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}\mu\omega^2x^2 = E\psi(x)$$

The Schrodinger wave equation can be written as

$$\frac{d^2\psi(x)}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}\mu\omega^2x^2\right)\psi(x) = 0$$

Notice the term $E - \frac{1}{2}\mu\omega^2x^2$ is positive since V(x) cannot increase infinitely.

A solution to this can be attempted by substituting $\xi = \gamma x$ (ξ *is pronounced as zai*) and $\gamma = \sqrt{\frac{\mu\omega}{\hbar}}$

The eigen function is of the form $\psi_n(x) = N_n H_n(\gamma x)e^{-\frac{1}{2}(\gamma x)^2}$

where n=0,1,2,3,4... $N_n = \sqrt{\left[\frac{\gamma}{2^n n!\sqrt{\pi}}\right]}$ and

$H_n(\xi)$ **are** the Hermite polynomials described by

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \text{ for n} \geq 1$$

The first two terms of the Hermite polynomial are $H_0(\xi) = 1$ and $H_1(\xi) = 2\xi$ which can be used to find the successive terms.

$$\psi_0(x) = N_0 H_0(\xi)e^{-\frac{1}{2}\xi^2} = \left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\frac{\mu\omega}{\hbar}x^2}$$

$$\psi_1(x) = N_1 H_1(\xi)e^{-\frac{1}{2}\xi^2} = \sqrt{\frac{2}{\sqrt{\pi}}}\cdot\left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{3}{4}}\cdot x\cdot e^{-\frac{1}{2}\frac{\mu\omega}{\hbar}x^2}$$

The solutions yield the Eigen energy values of the system as

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

This gives the allowed energy states as $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \dots\dots$

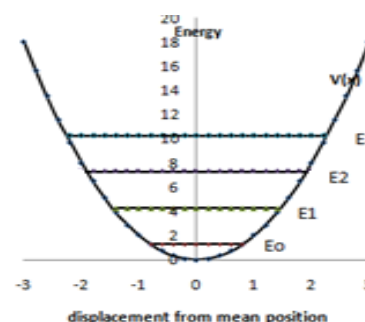Thus, the minimum energy state of the system is a non-zero $= \frac{1}{2}\hbar\omega$ where ω is the fundamental frequency of vibration. The higher energy states are then equally spaced at $\hbar\omega$ which is unlike the energy of states in the particle in a box solution.

[To verify that the wave functions are solutions of the SWE, we can substitute $\psi_0(x)$ and the corresponding energy $E_o = \left(\frac{1}{2}\right)\hbar\omega$ in the Schrodinger's wave equation.

$$\frac{d}{dx}\{\psi_0(x)\} = \frac{d}{dx}\left\{\left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\frac{\mu\omega}{\hbar}x^2}\right\} = \left\{-\left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{1}{4}}\cdot\frac{\mu\omega}{\hbar}xe^{-\frac{1}{2}\frac{\mu\omega}{\hbar}x^2}\right\} = -\frac{\mu\omega}{\hbar}x\psi_0(x)$$

Differentiating once again $\frac{d}{dx}\left[-\frac{\mu\omega}{\hbar}x\psi_0(x)\right] = -\left(\frac{\mu\omega}{\pi\hbar}\right)\left\{\psi_0(x) - \frac{\mu\omega}{\hbar}x^2\psi_0(x)\right\}$

Substituting this in the SWE gives

$$-\left(\frac{\mu\omega}{\hbar}\right)\left\{\psi_0(x) - \frac{\mu\omega}{\hbar}x^2\,\psi_0(x)\right\} + \frac{2\mu}{\hbar^2}\left(\left(\frac{1}{2}\right)\hbar\omega - \frac{1}{2}\,\mu\omega^2 x^2\right)\psi_0(x) =$$

$$-\left(\frac{\mu\omega}{\hbar}\right)\psi_0(x) + \left(\frac{\mu\omega}{\hbar}\right)^2 x^2\,\psi_0(x) + \frac{2\mu}{\hbar^2}\left(\frac{1}{2}\right)\hbar\omega - \frac{2\mu}{\hbar^2}\frac{1}{2}\,\mu\omega^2 x^2 \psi_0(x) = 0$$

Thus, we note that $\psi_0(x)$ satisfies the SWE and hence is an eigen function of the system

Similarly, verify that $\psi_1(x)$ also satisfies the SWE with the corresponding energy $E_1 = \left(\frac{3}{2}\right)\hbar\omega$.]


The wave functions of the system can be graphically inferred by considering each of the states to be equivalent to a one-dimensional finite potential well. The width of the well corresponds to the maximum displacement in that state. Therefore, the wave functions of the finite potential well that we inferred are useful even in this case. However, each state has an increasing width and the tails of the decaying wave functions also increase as the energy of the state increases. The probability distribution functions for the first few states are also shown in the figure.
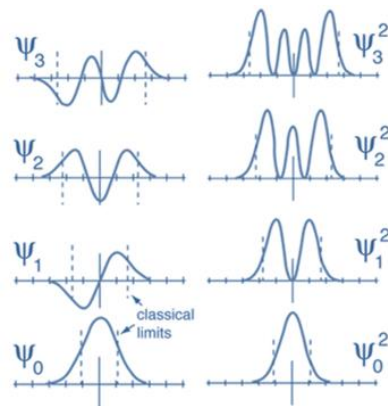
The real potential energy variations deviate from the ideal parabolic potential energy curve. The bonding results in exchange of electrons / sharing of electrons resulting in a deviation of the electrostatic interactions. The deviation is treated as a perturbation of the harmonic oscillator potential with an addition term for the potential.

The result of this variation results in energy levels which are not uniformly distributed and the separation between the energy levels decrease for larger values of **n**.

This analysis helps us understand the vibration energy states of a diatomic molecule and forms the fundamental analysis of the Infra Red absorption by the molecular. This analysis can be extended to understand the vibrational states of lattices in a crystal which leads to the concept of phonons in crystals.

Anharmonic oscillator
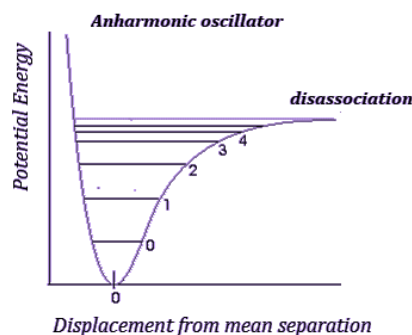
Problem 7: Discussion of the solutions to the Hydrogen atom problem.

The hydrogen atom is the simplest possible stable atom with one proton in the nucleus and one electron in the orbital. In the ground state, the system exhibits perfect spherical symmetry. Hence the possibility of looking for a solution to the Schrodinger's wave equation for the states of the electron could be attempted. Though the problem looks very simple as a case of only two particles, the mathematical analysis of the solutions is very exhaustive.

The methodology and the solutions are discussed to present a picture of how the quantum numbers of a system evolves out naturally from the solution of the differential equation in three dimensions.

The 3D SWE in cartesian co-ordinate system can be written as

$$\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z) + (E-V)\Psi(x,y,z) = 0$$

Since the hydrogen atom exhibits a spherical symmetry it is prudent to write the Schrodinger's wave equation in the spherical co-ordinate system (r, θ, φ).

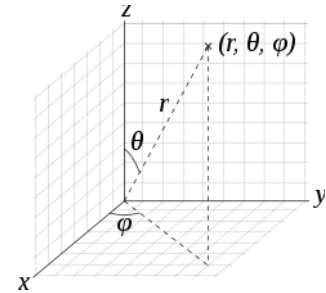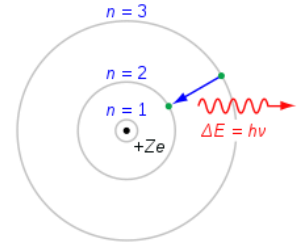[the transition to the spherical coordinate system from the cartesian coordinate system is possible with the transition relations

$x = r\sin\theta\cos\varphi$, $y = r\sin\theta\sin\varphi$ and $z = r\cos\theta$

where $r = \sqrt{x^2 + y^2 + z^2}$ is the radius vector

$\theta = \tan^{-1}\left(\frac{\sqrt{x^2+y^2}}{z}\right)$ is the polar angle (varying between 0 to 2π and

$\varphi = \tan^{-1}\left(\frac{y}{x}\right)$] is the azimuthal angle (varying between 0 to 2π]

In spherical polar co-ordinate system, the SWE can be written as

$$\frac{\hbar^2}{2\mu}\frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2\Psi}{\partial\varphi^2}\right] + (E - V(r))\Psi(r,\theta,\varphi) = 0$$

where the wave function in spherical polar co-ordinates is $\Psi(r,\theta,\varphi)$.

The potential energy term can be written as $V(r) = \frac{e^2}{4\pi\varepsilon_o r}$

The wave function can be resolved into three independent components in the three independent variables r, θ and φ.

$$\Psi(r,\theta,\varphi) = R(r).\Theta(\theta).\Phi(\varphi)$$

The Schrodinger's wave equation can be resolved into three mutually independent equations using the method of separation of variables as

$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -m_l^2$ with the solution $\Phi(\varphi) = Ae^{im_l\varphi}$ where $m_l = o, \pm1, \pm2, ...$is the magnetic quantum number (which gives the possible orientations of the quantized angular momentum of the system).

Substituting for the expression $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}$ we can separate the expressions in R and Θ as

$$\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)\right] = l(l+1)$$

where l is an arbitrary constant which an integer greater than or equal to m_l. This puts a restriction on $m_l = 0, \pm1, \pm2, \dots \pm l$

In general, $l = 0, 1, 2, 3 \dots\dots n - 1$ is the angular momentum quantum number which describes the quantized angular momentum of the orbital electron as $L = \sqrt{(l(l+1))}.\hbar$

The radial part of the wave equation

$$\frac{1}{R}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) +\right] + \frac{2\mu r^2}{\hbar^2}[E - V(r)] = l(l+1)$$

We observe that the energy of the system is dependent only on the solution of this equation which gives the radial component of the wave function as

$$R_{nl(r)} = \frac{1}{r}\rho^{l+1}e^{-\rho}.v(\rho)$$

The variable $\rho = \frac{r}{an}$ where n is an integer $n = 1, 2, 3..$ and $a \equiv \frac{4\pi\varepsilon_o\hbar^2}{\mu e^2} = 0.529 \times 10^{-10}m$ is the Bohr radius.

$v(\rho)$ is a polynomial of degree $j_{max} = n - l - 1$ given by $v(\rho) = \sum_{j=0}^{\infty}c_j\rho^j$

whose co-efficient are given by the recursion formula $c_{j+1} = \left\{\frac{2(j+l+1)-\rho_o}{(j+1)(j+2l+2)}\right\}c_j$ and $\rho_o = 2n$

The normalized radial wave function $R_{nl(r)} = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+1)!]^3}}e^{-r/na}\left(\frac{2r}{na}\right)^l$

where **n** is the principal quantum number defined by $n = 1, 2, 3\dots\dots$

The first few radial wave functions can be written as

$R_{10}(r) = 2a^{-3/2}e^{-r/a}$ for n=1 and l=0

$R_{20}(r) = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)e^{-r/2a}$ for n=2 and l=0

$R_{21}(r) = \frac{1}{\sqrt{24}}a^{-3/2}\left(\frac{r}{a}\right)e^{-r/2a}$ for n=2 and l=1

These wave functions can be shown to be solutions of the radial wave equation. Then by induction we conclude that the radial wave function is a solution of the radial part of the SWE.

The probability of finding the electron at a distance r from the nucleus can be estimated using the probability density. The plot shows the probability of locating the electron in the three states 1s, 2s and 3s.
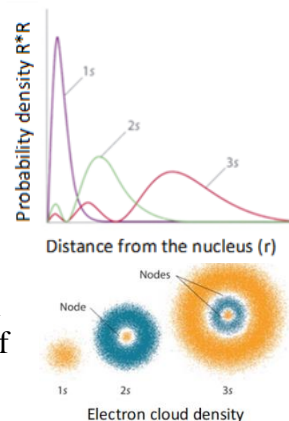
The eigen energy simplifies to $E_n = -\frac{\hbar^2 k^2}{2\mu} = -\frac{\mu e^4}{8\pi^2\varepsilon_o^2\hbar^2\rho_o^2} = -\frac{\mu e^4}{8\pi^2\varepsilon_o^2\hbar^2.4n^2}$

$$E_n = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right]\frac{1}{n^2} = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right]\frac{1}{n^2} \qquad \text{where n=1,2,3....}$$

The energy is written as negative to indicate that the system is in a bound state. This implies that when the energy of the system goes to zero the binding between the particles is broken and the particles are free particles. This happens for a large value of $n \to \infty$

The ground state energy of the system can be evaluated as $E_1 = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right] = -13.6eV$

The different allowed energy states correspond to the different values of n. This enables to estimate the energy of transition between different states, which gives us the absorption or emission spectra of the atom.

The energy difference between two states can be evaluated as

$$\Delta E = E_{n1} - E_{n2} = -\left[\left\{\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right\}\frac{1}{n_1^2} - \left\{\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right\}\frac{1}{n_2^2}\right]$$

The transitions from states with $n > 1$ to $n = 1$ result in spectral lines in the ultraviolet region which is the Lyman series.

The transitions from states with $n > 2$ to $n = 2$ result in spectral lines in the visible region which is the Balmer series.

The transitions from states with $n > 3$ to $n = 3$ result in spectral lines in the infra red region which is the Paschen series.
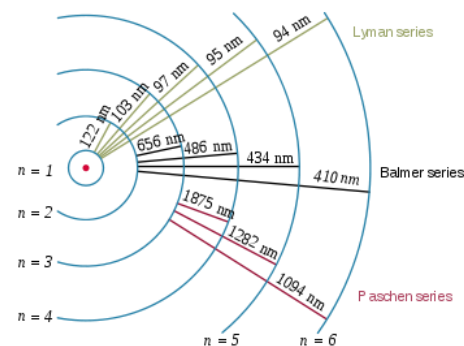
The predicted values of the wavelengths of the spectral lines of the Hydrogen atom $\left(\Delta E = \frac{hc}{\lambda}\right)$ agree with the observed wavelengths in the emission spectra of the Hydrogen atom.

The same analysis can be used to study hydrogen like atoms with a single electron in the outer most orbital such as Deuterium, doubly ionized Lithium, etc. The effective mass μ can be estimated and gives reasonably correct values of the energy of the states and hence their spectral characteristics.

[**Verification of the eigen functions of the radial equation:**

The radial part of the wave equation

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) +\right] + \frac{2\mu r^2}{\hbar^2}[E - V(r)]R = l(l+1)R$$

For the state n=2, l=0   the radial equation $R_{20}(r) = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)e^{-r/2a}$

The radial wave equation $\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial R_{20}}{\partial r}\right) +\right] + \frac{2\mu r^2}{\hbar^2}[E - V(r)]R_{20} = 0$

The energy $E_2 = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right]\frac{1}{2^2}$ and the potential $V(r) = \frac{e^2}{4\pi\varepsilon_o r}$

The first term of the Radial wave equation:

Differentiating $\mathbf{R_{20}}$ with respect to r once

$$\frac{\partial R_{20}}{\partial r} = \frac{1}{\sqrt{2}}a^{-3/2}\left(-\frac{1}{2a}e^{-r/2a} - \frac{1}{2a}e^{-r/2a} + \frac{r}{(2a)^2}e^{-r/2a}\right) = \frac{1}{\sqrt{2}}a^{-3/2}\left(-\frac{1}{a}e^{-r/2a} + \frac{r}{(2a)^2}e^{-r/2a}\right)$$

Multiplying the result with r^2 $\quad r^2\frac{\partial R_{20}}{\partial r} = \frac{1}{\sqrt{2}}a^{-3/2}\left(-\frac{r^2}{a}e^{-r/2a} + \frac{r^3}{(2a)^2}e^{-r/2a}\right)$

Differentiating the result once again with respect to r

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R_{20}}{\partial r}\right) = \frac{1}{\sqrt{2}}a^{-3/2}\left(-\frac{2r}{a}e^{-r/2a} - \frac{r^2}{a}e^{-r/2a}\times\left(-\frac{1}{2a}\right) + \frac{3r^2}{(2a)^2}e^{-r/2a} + \frac{r^3}{(2a)^2}e^{-r/2a}\times\left(-\frac{1}{2a}\right)\right)$$

$$= \frac{1}{\sqrt{2}}a^{-3/2}\left(-\frac{2r}{a}e^{-r/2a} + \frac{2r^2}{(2a)^2}e^{-r/2a} + \frac{3r^2}{(2a)^2}e^{-r/2a} - \frac{r^3}{(2a)^3}e^{-r/2a}\right)$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R_{20}}{\partial r}\right) = \frac{1}{\sqrt{2}}a^{-3/2}\left(-\frac{2r}{a}e^{-r/2a} + \frac{5r^2}{(2a)^2}e^{-r/2a} - \frac{r^3}{(2a)^3}e^{-r/2a}\right)$$

Evaluating the second term, substituting for E_2 & $V(r)$ and simplifying

$$\frac{2\mu r^2}{\hbar^2}[E_2 - V(r)] = \left[-\frac{2\mu r^2}{\hbar^2}\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right]\frac{1}{2^2} - \frac{2\mu r^2}{\hbar^2}\frac{e^2}{4\pi\varepsilon_o r}\right] = \left[-\frac{r^2}{(2a)^2} + \frac{2r}{a}\right]$$

$$\frac{2\mu r^2}{\hbar^2}[E - V(r)]\,R_{20} = \left[-\frac{2r^2}{(2a)^2} + \frac{2r}{a}\right]\times\frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)e^{-r/2a}$$

$$= \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)\left[-\frac{2r^2}{(2a)^2} + \frac{2r}{a}\right]e^{-r/2a}$$

$$= \frac{1}{\sqrt{2}}a^{-3/2}\left[-\frac{r^2}{(2a)^2} + \frac{2r}{a} + \frac{r^3}{(2a)^3} - \frac{2}{2}\frac{r^2}{a^2}\right]e^{-r/2a}$$

$$= \frac{1}{\sqrt{2}}a^{-3/2}\left[\frac{r^3}{(2a)^3} - \frac{5r^2}{(2a)^2} + \frac{2r}{a} +\right]e^{-r/2a}$$

The sum of the two terms

$$\frac{1}{\sqrt{2}}a^{-3/2}\left(-\frac{2r}{a}e^{-r/2a} + \frac{5r^2}{(2a)^2}e^{-r/2a} - \frac{r^3}{(2a)^3}e^{-r/2a}\right) + \frac{1}{\sqrt{2}}a^{-3/2}\left[\frac{r^3}{(2a)^3} - \frac{5r^2}{(2a)^2} + \frac{2r}{a} +\right]e^{-r/2a} = 0$$

Thus, $\mathbf{R_{20}}$ is a solution of the radial wave equation. It can be verified similarly for wave functions of any state.]

[Particle in a Box with infinite potentials at the walls (boundaries at x=0 to x=L

A particle in an one dimensional box is confined to be within the boundaries (x=0 and x=L) where the potential tends to infinity. The particle cannot be found outside the boundary x<0 and X>L. The potential inside the well V=0.
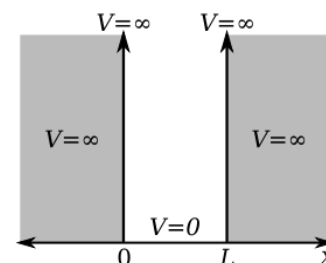
The Schrödinger's wave equation $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$

in the region within the well V=0 this becomes $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$

$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$

The solution of the equation in region 0<x<L is given by

$$\psi(x) = A sin(kx) + B cos(kx)$$

Applying the boundary condition that $\psi = 0$ at $x = 0$ and $x = L$

At x=0 $\psi(x = 0) = A sin(k0) + B cos(k0) = 0$ gives $B = 0$

The wave function then reduces to $\psi(x) = A sin(kx)$

At x=L $\psi(L) = A sin(kL) = 0$.
If A=0 the wave function does not exist and hence $kL = n\pi$

Or $k = n.\frac{\pi}{L}$, thus propagation constant can be only multiples of $\frac{\pi}{L}$

This also gives us the energy $E_n = \frac{\hbar^2 n^2}{8mL^2}$

The wave function then reduces to $\psi(x) = A sin\left(\frac{n\pi}{L} x\right)$

The constant A can be evaluated by normalizing the wave function ie., $\int_0^L \psi^*\psi \, dx = 1$

$$\int_0^L \left[A sin\left(\frac{n\pi}{L}x\right)\right]^2 dx = \frac{A^2}{2} \int_0^L \left[1 - \cos\left(\frac{2n\pi}{L}x\right)\right] dx$$

Which on integration gives $\frac{A^2}{2}\left[1 - \frac{L}{2n\pi}\sin\left(\frac{2n\pi}{L}x\right)\right]_0^L = \frac{A^2}{2}[L - 0] = 1$.

This gives a value of $A = \sqrt{\frac{2}{L}}$

The exact form of the wave function becomes $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$
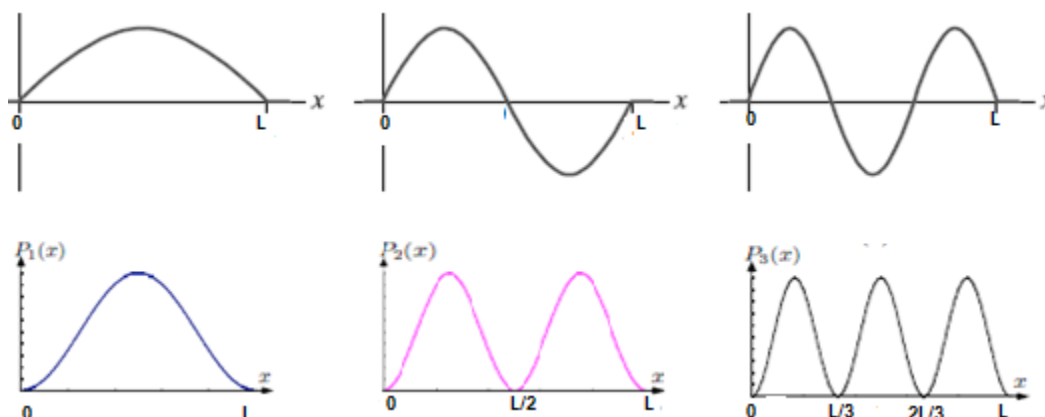
Eigen functions and Eigen values

The Eigen function of a particle in a infinite potential well $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ and the Eigen energy values is given function $E_n = \frac{\hbar^2 n^2}{8mL^2}$ where n = 1,2 3...

The first three states correspond to n=1,2 and 3

The Eigen fuctions are $\psi_1 = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$ $\psi_2 = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$ $\psi_3 = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi x}{L}\right)$

And the Eigen values are $E_1 = \dfrac{h^2}{8mL^2}$ $E_2 = \dfrac{h^2 2^2}{8mL^2}$ $E_3 = \dfrac{h^2 3^2}{8mL^2}$

Probability density $\psi^*\psi$ for the first three states is obtained by squaring the wave function

$\psi_n = \sqrt{\dfrac{2}{L}} \sin\left(\dfrac{n\pi x}{L}\right)$. The square of the function is close to a Gaussian shape.

In the first state n=1 the probability of finding the particle is maximum at $L/2$ and the area under the curve represents the total probability of finding the particle in the ground state which is 1.00

In the second state n=2 the probability of finding the particle is maximum at $L/4$ and $3L/4$ .The area under one segment of the curve represents the probability of finding the particle in the first excited state and is $1/n = 0.5$.

In the third state n=3 the probability of finding the particle is maximum at $L/6$, $L/3$ and $+5L/6$ .The area under one segment of the curve represents the probability of finding the particle in the first excited state and is $1/n = 0.333$.

In general, the probability of finding the particle in the nth state, in a segment of length L/n is $1/n$.]

Numericals

1. Electrons with energies of 4.00 eV are incident on a potential step 3.0 eV high. Find the probability of reflection at x=0 and transmission for x>0. **(Ans R=   ;T =19.20%)**

2. A proton with energy E is incident on a potential step of height 3.5eV. If the de Broglie wavelength of the particle after transmission is 1.228 nm, find the energy of the proton.

3. A beam of identical electrons is incident on a barrier 6.0 eV high and 2 nm wide. Find the energy of the electrons if 1% of the electrons are to get through the barrier.**(Ans =5.963eV)**

4. An electron and a proton with the same energy E approach a potential barrier whose height U is greater than E. Comment on their tunneling probability.

5. A current beam 10 pico amperes (of identical electrons) is incident on a barrier 5.0 eV high and 1 nm wide. Find the transmitted current strength if the energy of the electrons is 4.9ev.**(Ans = T=3.93%** Transmitted current = 10pA *.0393 = 0.393pA**)**

6. Find the normalisation constant B for the wave function $\Psi = B[sin(\pi x/L) + sin(2\pi x/L)]$ **(
   Ans $B = \sqrt{\frac{1}{L}}$)**

7. Show that the probability of finding a particle trapped in an infinite potential well between x and x+Δx is approx Δx/L and is independent of x.

8. Find the probability that a particle in a box of width L can be found between 0 and L/n when the particle is in the nth state

9. A particle in an infinite potential well of width a. Find the probability of finding the particle between a/3 and 2a/3 in the ground and third excited states. **(Ans:)**

10. What is the minimum energy of an electron trapped in a one dimensional region the size of an atomic nucleus (1 x 10^{-14} m)? **(Ans 3.77 Gev)**

11. Find the energy required to excite a particle in a box of width '**a**' from the second excited state to the fifth state. **()**