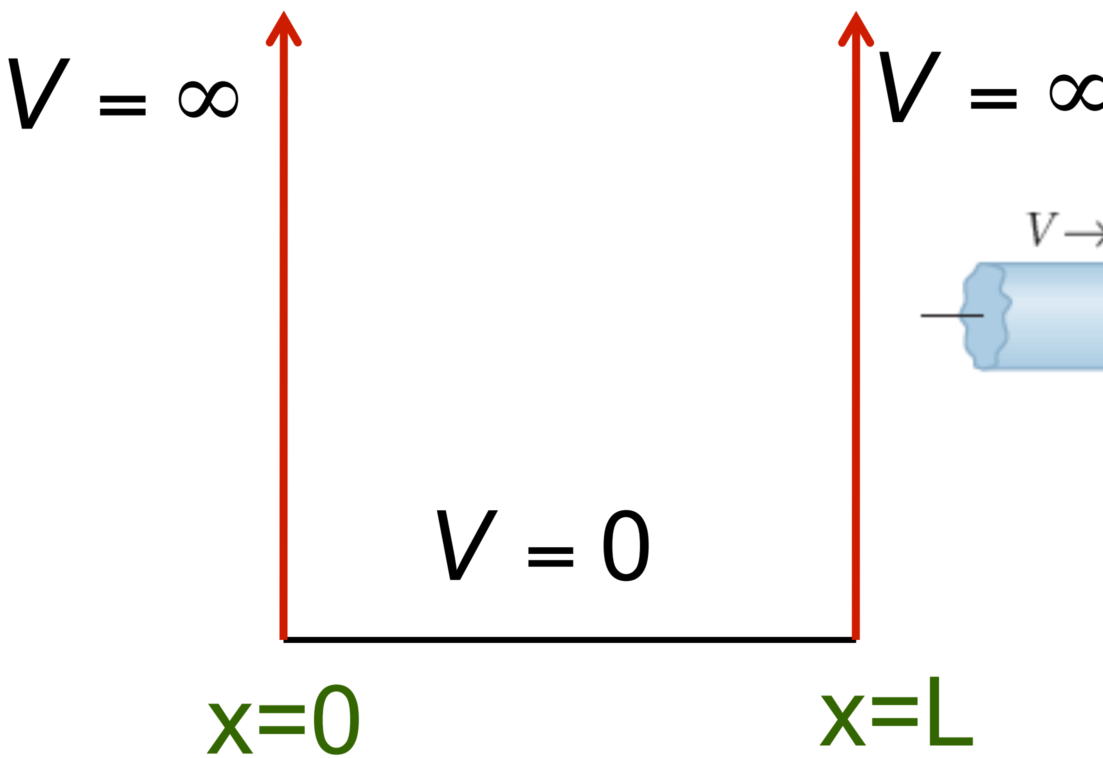
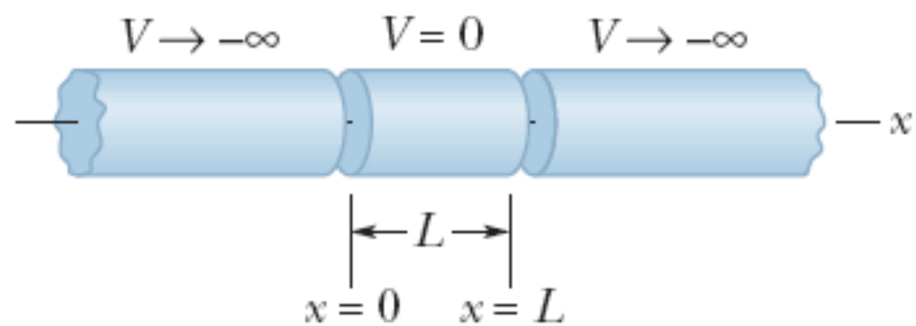
Particle in a rigid box (Infinite potential well) :

Deviations from results of classical physics

Particle in a rigid box (Infinite potential well)

$$
\begin{aligned}
V(x) &= 0 \quad \text{for } 0 < x < L \\
&= \infty \quad \text{for } x < 0 \text{ or } x > L
\end{aligned}
$$





Schrodinger Eqn. Solution

$\psi(x)=0$ For $x<0$ and $x>L$

$$\frac{d^2\psi(x)}{dx^2}+\frac{2mE}{\hbar^2}\psi(x)=0$$

$$\frac{d^2\psi(x)}{dx^2}=-\frac{2mE}{\hbar^2}\psi(x)$$

For $0<x<L$

The general solution of this equation is

$$\psi(x)=A\sin kx+B\cos kx;\ \ k^2=\frac{2mE}{\hbar^2} \qquad (1)$$

(Note that k is real as E is positive)

Boundary Conditions

The wave function must be continuous. This implies that

$$\psi(0) = \psi(L) = 0$$

$$\psi(0) = 0 \Rightarrow A\sin 0 + B\cos 0 = 0$$

$$This\ gives\ B = 0$$

$$\psi(L) = 0 \Rightarrow A\sin kL = 0$$

Quantization Conditions

This is possible only when

$$kL = n\pi$$

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi \Rightarrow E = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

n=4

n=3

n=2

n=1

A simple experimental verification of particle in a box problem: Colour difference of CdS nano particles of two different sizes

Important Notes

- We had two unknowns with three equations (including normalization condition). The additional equation quantized the energy levels.
- The values of n can only be positive and non-zero.
- The lowest energy is non-zero (zero-point energy).

Consequences

- The lowest energy corresponding to $n=1$ for an electron in a box of 1Å comes out to be 37.6 eV.
- For a marble of 0.01 kg in 0.1m box it is 5.488×10^{-64}J. It would take 10^{20} years to move one mm. The energy difference between two adjacent levels is negligibly small & hence the energy appears continuous.

What about the wave functions ?

Substituting the value of k in (1), with B = 0,

$$\psi_n(x) = A \sin\left(\frac{n\pi\pi}{L}\right)$$

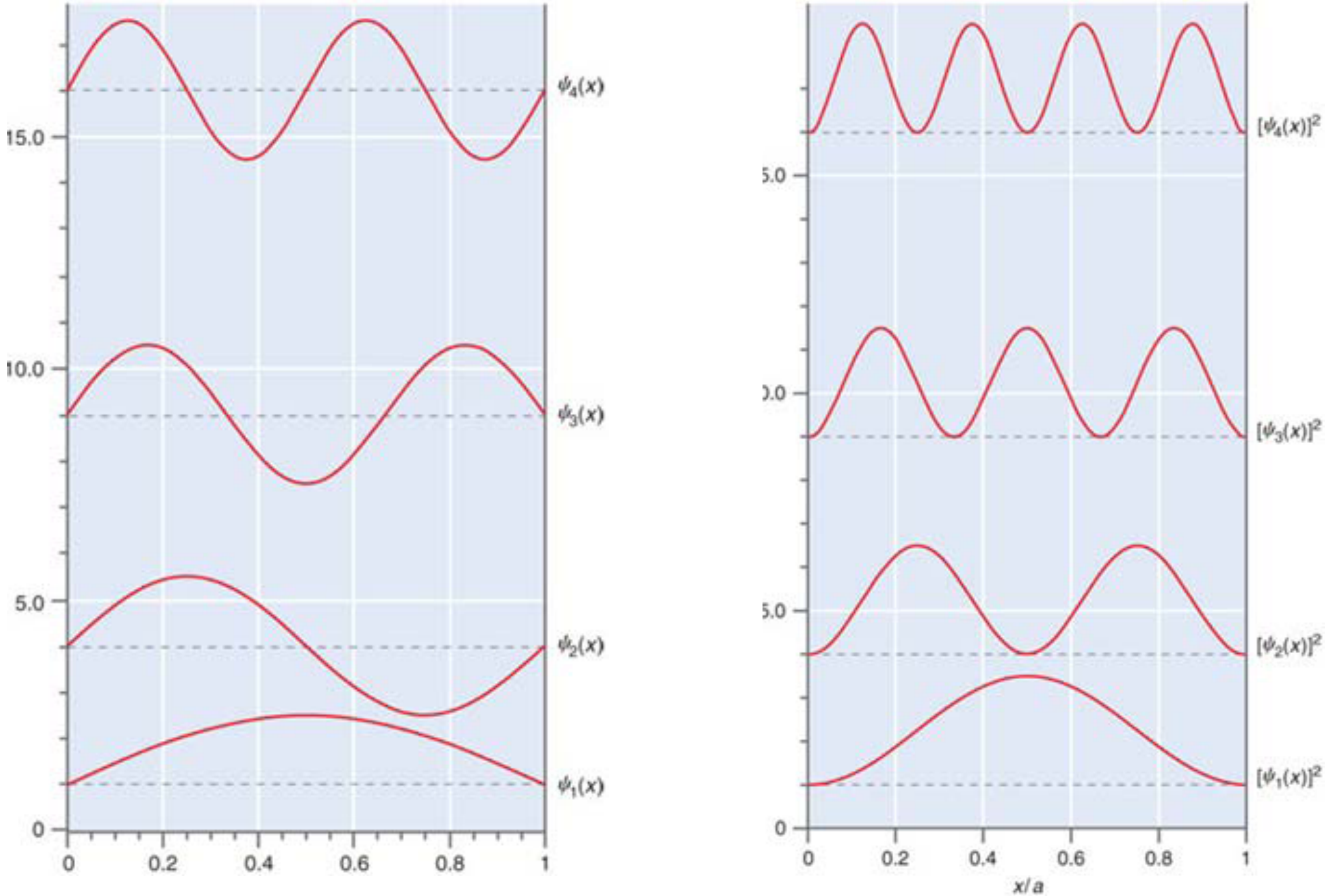
This has to be normalized,

$$i.e., \int_0^L |\psi_n(x)|^2 dx = 1 \Rightarrow \int_0^L A^2 \sin^2\left(\frac{n\pi\pi}{L}\right) = 1$$

$$\text{This gives } A = \sqrt{\frac{2}{L}}$$

$$\therefore \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi\pi}{L}\right)$$

Wave functions and corresponding probabiliy densities



Expectation values of x and x^2

$$\langle x \rangle = \int_0^L \psi_n(x)^* x \psi_n(x) dx = \int_0^L x |\psi_n(x)|^2 dx$$

$$\Rightarrow \left(\frac{2}{L}\right) \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) x dx = \frac{L}{2} (for\ any\ n)$$

$$Similarly, \langle x^2 \rangle = \frac{L^2}{3}\left[1 - \frac{3}{2n^2\pi^2}\right]$$

$$Note\ that\ \langle x \rangle^2 \neq \langle x^2 \rangle$$

Expectation values of p and p^2

$$\langle p_x \rangle = \int_0^L \psi_n(x)^* \, p_x \psi_n(x) dx = -i\hbar \int_0^L \psi_n(x)^* \frac{\partial}{\partial x} \psi_n(x) dx = 0$$

$$For\ any\ n, \langle p_x \rangle = 0$$

$$Similarly, \langle p_x{}^2 \rangle = \left(\frac{n\pi\hbar}{L} \right)^2 = 2mE_n$$

$$Note\ that\ \langle p_x \rangle^2 \neq \langle p_x{}^2 \rangle$$

Uncertainty product

$$\Delta p_x = \sqrt{\left\langle p_x^2 \right\rangle - \left\langle p_x \right\rangle^2}$$

$$= \frac{n\pi\hbar}{L}$$

$$\Delta x = \sqrt{\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2}$$

$$= \sqrt{\frac{L^2}{12n^2\pi^2}\left[n^2\pi^2 - 6\right]}$$

Contd.

$$\Delta x \Delta p_x = \hbar\sqrt{\frac{n^2\pi^2 - 6}{12}}$$

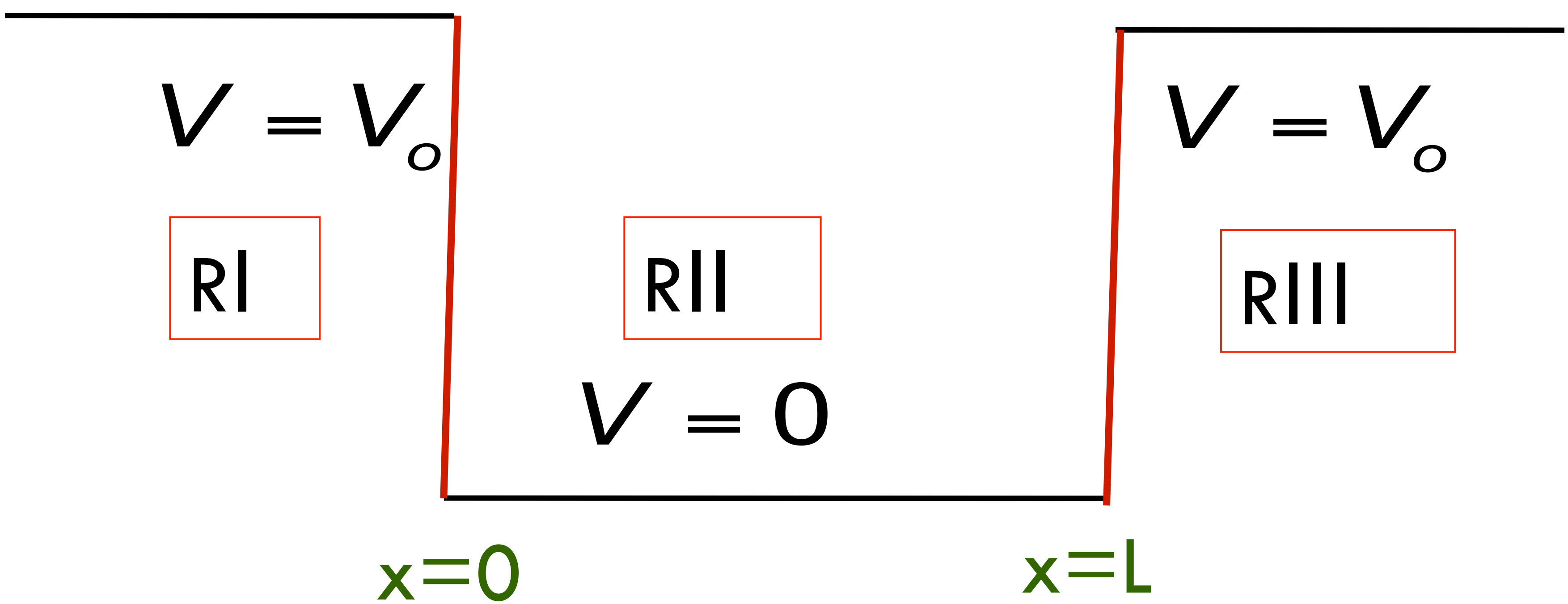
$$= 0.57\hbar \text{ for n=1}$$

$$=1.67\hbar \text{ for n=2}$$

Finite, Semi-infinite potential well
Deviations from results of classical physics

Particle in a Finite Potential Well

$$V(x) = 0 \quad \text{for } 0 < x < L$$
$$= V_o \quad \text{for } x < 0 \text{ or } x > L$$



Take E<V_o for the bound state problem.

$$\frac{d^2\psi_I(x)}{dx^2}+\frac{2m}{\hbar^2}\left(E-V_0\right)\psi_I(x)=0$$ Region 1

$$\frac{d^2\psi_{II}(x)}{dx^2}+\frac{2m}{\hbar^2}E\psi_{II}(x)=0$$ Region 2

$$\frac{d^2\psi_{III}(x)}{dx^2}+\frac{2m}{\hbar^2}\left(E-V_0\right)\psi_{III}(x)=0$$ Region 3

Note that E is positive and (E-V_0) is negative

General solutions for the three regions

$$\psi_I(x) = Ae^{\alpha x} + Be^{-\alpha x} \qquad \alpha = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$$\left.\begin{aligned} \psi_{II}(x) &= C\sin kx + D\cos kx \\ or \quad &= C'e^{ikx} + D'e^{-ikx} \end{aligned}\right\} \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\psi_{III}(x) = Ge^{\alpha x} + Fe^{-\alpha x} \qquad \alpha = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

(Note that α and k are positive)

Comments

Since it is not possible to have large probability density when x tends to - ∞ or $+\infty$, the coefficients B and G should definitely vanish.

Or, if B and G are non-zero, then we cannot Normalize the wave function in regions I and III respectively.

Well-behaved Wave Functions

$$B = 0 \qquad G = 0 \ \mathit{yields}$$

$$\psi_I(x) = Ae^{\alpha x}$$

$$\psi_{II}(x) = C\sin kx + D\cos kx$$

$$\psi_{III}(x) = Fe^{-\alpha x}$$

Invoke acceptability conditions

$$\psi_I(0) = \psi_{II}(0) \qquad \Rightarrow A = D$$

$$\frac{d\psi_I(0)}{dx} = \frac{d\psi_{II}(0)}{dx} \qquad \Rightarrow A\alpha = Ck$$

$$\psi_{II}(L) = \psi_{III}(L) \qquad \Rightarrow C\sin kL + D\cos kL = Fe^{-\alpha L}$$

$$\frac{d\psi_{II}(L)}{dx} = \frac{d\psi_{III}(L)}{dx} \Rightarrow Ck\cos kL - Dk\sin kL = -\alpha Fe^{-\alpha L}$$

4 unknowns and 4 equations

Solving the Equations

Express all constants in terms of A.

$$D = A$$

$$C = \frac{\alpha}{k} A$$

$$\frac{\alpha}{k} A \sin(kL) + A\cos(kL) = Fe^{-\alpha L}$$

$$\frac{\alpha}{k} Ak\cos(kL) - Ak\sin(kL) = -F\alpha e^{-\alpha L}$$

Divide the last two equations.

$$\frac{\alpha\cos(kL) - k\sin(kL)}{\alpha\sin(kL) + k\cos(kL)} = -\frac{\alpha}{k};$$

$$\hbar\alpha = \sqrt{2m(V_o - E)}$$

$$\hbar k = \sqrt{2mE}$$

The above equation governs the allowed energy levels.

Quantization of energy

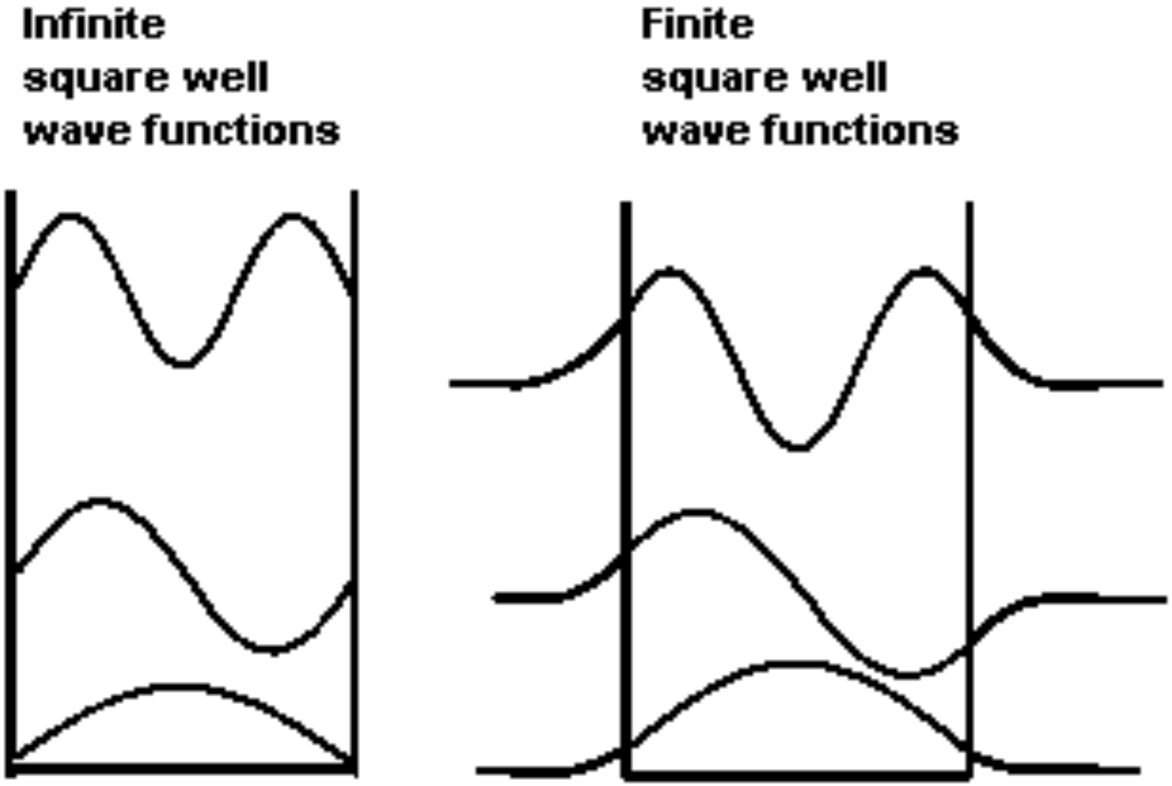
$$kL + \sin^{-1}\left(\frac{k}{\sqrt{k^2+\alpha^2}}\right) = n\pi, \qquad (k^2+\alpha^2 = 2mV_0/\hbar^2\ )$$

* There will be at least one bound state for any low value of V_0 or L (shallow or narrow well).

* As V_0 tends to infinity (for any L), the result becomes that of infinite square well.

* As V_0 tends to infinity and L tends to zero, there will be only one bound state.

Comparison between finite and infinite wells



Classically Forbidden Region

- There is a non zero probability of finding the particle in the classically forbidden region.
- This probability decreases exponentially.

- However the uncertainty principle prohibits one to localize the particle in the classically forbidden region and measure its kinetic energy.
- Since the wavelengths are more than those of the infinite well, the p values are less. Hence $(E_n)_{\text{finite well}} < (E_n)_{\text{infinite well}}$ (for the same width L)

Example of tunneling in classical physics

Barrier penetration in classical optics too.

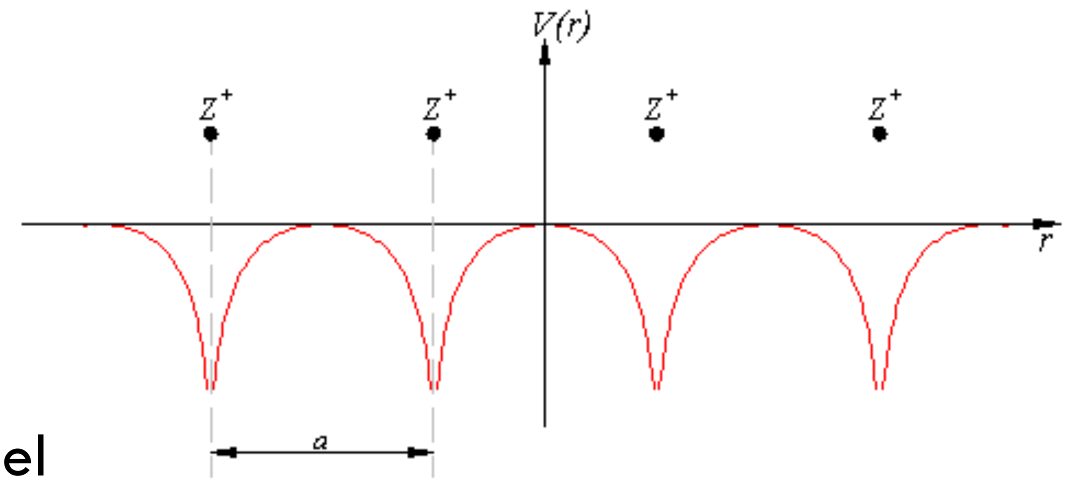
Frustrated total internal reflection

Frustrated Total Internal Reflection

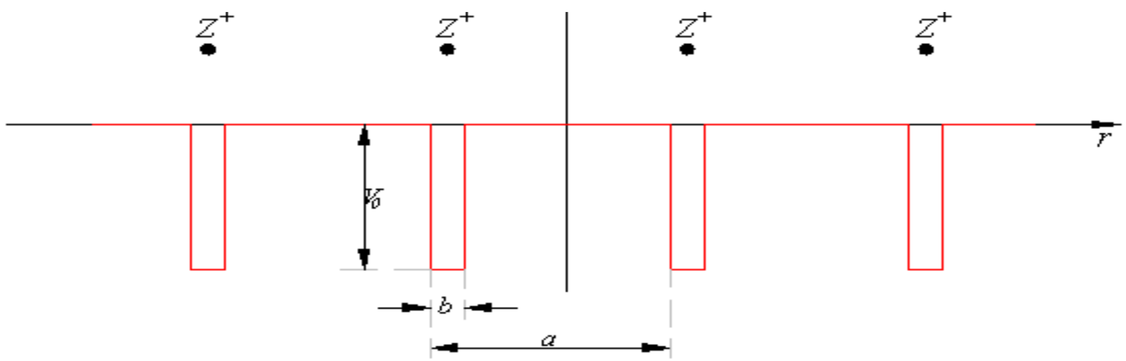
(a) (b)

Application of finite potential well

A simple application of finite well.
One dimensional periodic potential of a solid

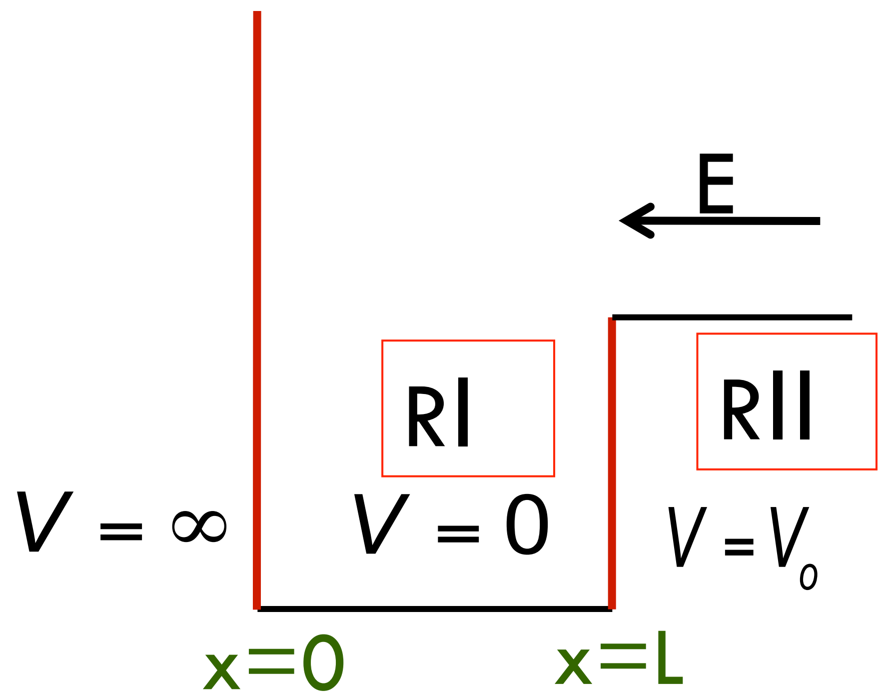


Kronig Penney model



Another example: free state vs. bound state

Semi-Infinite Square Well



Free State ($E>V_0$)

$$\frac{d^2\psi_I(x)}{dx^2}+\frac{2m}{\hbar^2}E\psi_I(x)=0$$ Region 1

$$\frac{d^2\psi_{II}(x)}{dx^2}+\frac{2m}{\hbar^2}\left(E-V_0\right)\psi_{II}(x)=0$$ Region 2

Note that E and ($E-V_0$) are positive

RI

$$\psi_I(x) = A\sin k_1 x + B\cos k_1 x \qquad k_1 = \sqrt{\frac{2mE)}{\hbar^2}}$$

RII

$$\psi_{II}(x) = Ce^{ik_2x} + De^{-ik_2x} \qquad k_2 = \sqrt{\frac{2m\left(E - V_0\right)}{\hbar^2}}$$

$$Boundary\ conditions\ demand$$

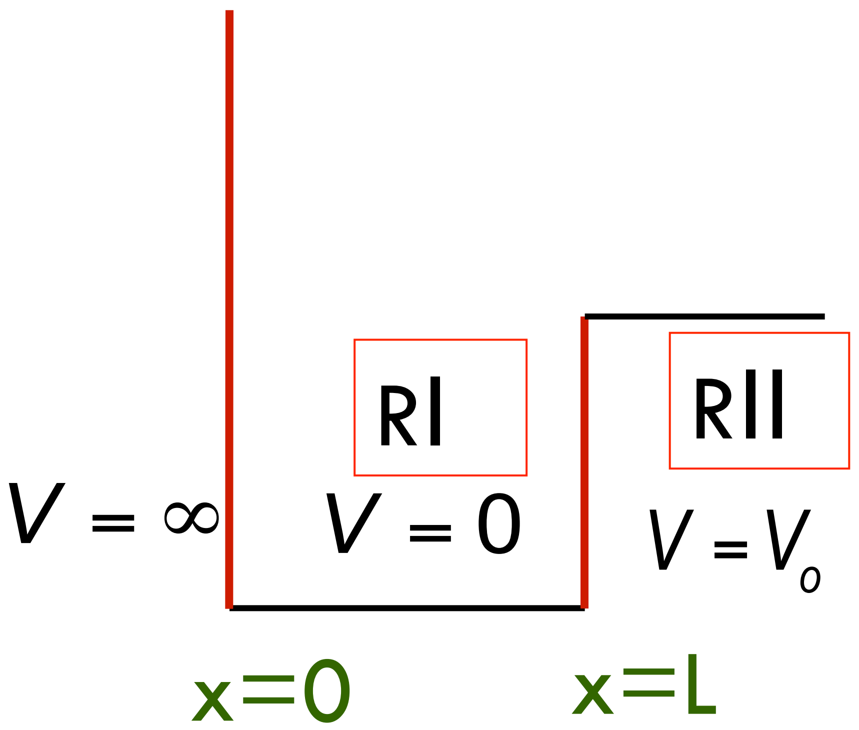
$$B = 0\,\textbf{(as in infinite well)}$$

$$A\sin k_1 L = Ce^{ik_2L} + De^{-ik_2L}$$

$$Ak_1\cos k_1 L = ik_2\left(Ce^{ik_2L} - De^{-ik_2L}\right)$$

Bound State ($E<V_0$)

$E<V_0$(bound)



$$\frac{d^2\psi_I(x)}{dx^2} + \frac{2m}{\hbar^2}E\psi_I(x) = 0 \qquad \text{Region 1}$$

$$\frac{d^2\psi_{II}(x)}{dx^2} + \frac{2m}{\hbar^2}\left(E - V_0\right)\psi_{II}(x) = 0 \qquad \text{Region 2}$$

Note that E is positive and (E-V_0) is negative

$$\psi_I(x) = A\sin kx + B\cos kx \qquad k = \sqrt{\frac{2mE)}{\hbar^2}}$$

$$\psi_{II}(x) = Ce^{\alpha x} + De^{-\alpha x} \qquad \alpha = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

B has to be zero, as in the case of infinite well.

C has to be zero as the wave function must be finite at large positive values of x (or x=+∞). This region does not contain - ∞ and hence no condition on D at this stage.

Boundary Conditions at x=L

$$A\sin kL = De^{-\alpha L}$$

$$Ak\cos kL = -\alpha De^{-\alpha L}$$

$$\therefore \cot kL = -\frac{\alpha}{k}$$ **(Quantization Condition)**

Special Case: $E=V_0$

$$\alpha = \frac{\sqrt{2m\left(V_o - E\right)}}{\hbar} = 0$$

$$k = \frac{\sqrt{2mE}}{\hbar} = \frac{\sqrt{2mV_o}}{\hbar}$$

Boundary Conditions at x=L

The boundary conditions now become

$$A\sin kL = D$$
$$Ak\cos kL = 0$$

Direct derivation for E=V$_0$

$$\psi_I(x) = A\sin kx + B\cos kx \qquad k = \sqrt{\frac{(2mE)}{\hbar^2}}$$

$$\psi_{II}(x) = Cx + D$$

B has to be zero, as in the case of infinite well.

C has to be zero as the wave function must be finite at large positive values of x (or x=+∞).

$$A\sin kL = D$$

$$Ak\cos kL = 0$$

$$\therefore \cos kL = 0$$

as we obtained earlier.

Since A cannot be zero, it implies

$$\cos kL = 0 \text{ or } kL = (2n+1)\frac{\pi}{2}$$

$$\frac{\sqrt{2mV_o}}{\hbar}L = (2n+1)\frac{\pi}{2}$$

$$V_o = \frac{\hbar^2\left[(2n+1)\frac{\pi}{2}\right]^2}{2mL^2}$$

Bound States

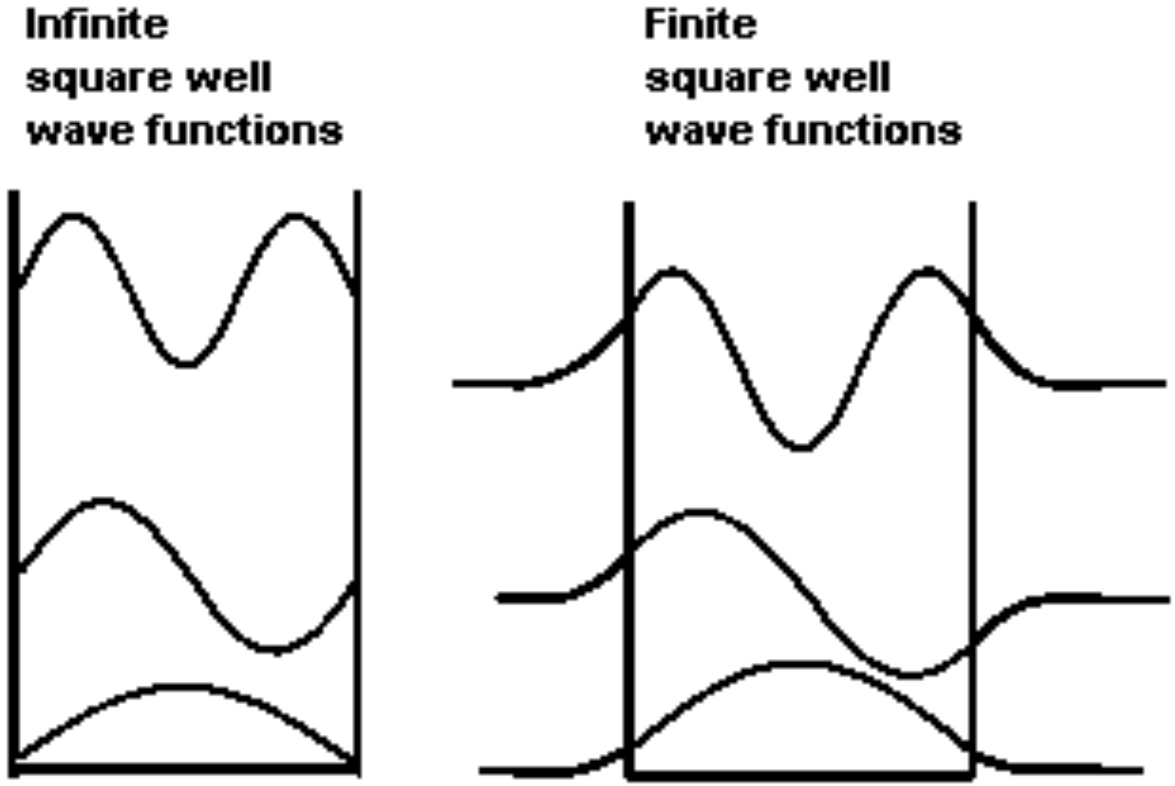
There will be no bound state (i.e., n=0), if

$$V_o < \frac{\hbar^2 \pi^2}{8mL^2}$$

There will be only one bound state (n=1) if

$$\frac{\hbar^2 \pi^2}{8mL^2} < V_o < \frac{9\hbar^2 \pi^2}{8mL^2}$$

Comparison between finite and infinite wells



Semi-infinite vs. Infinite square well

$$kL = (2n+1)\frac{\pi}{2}$$

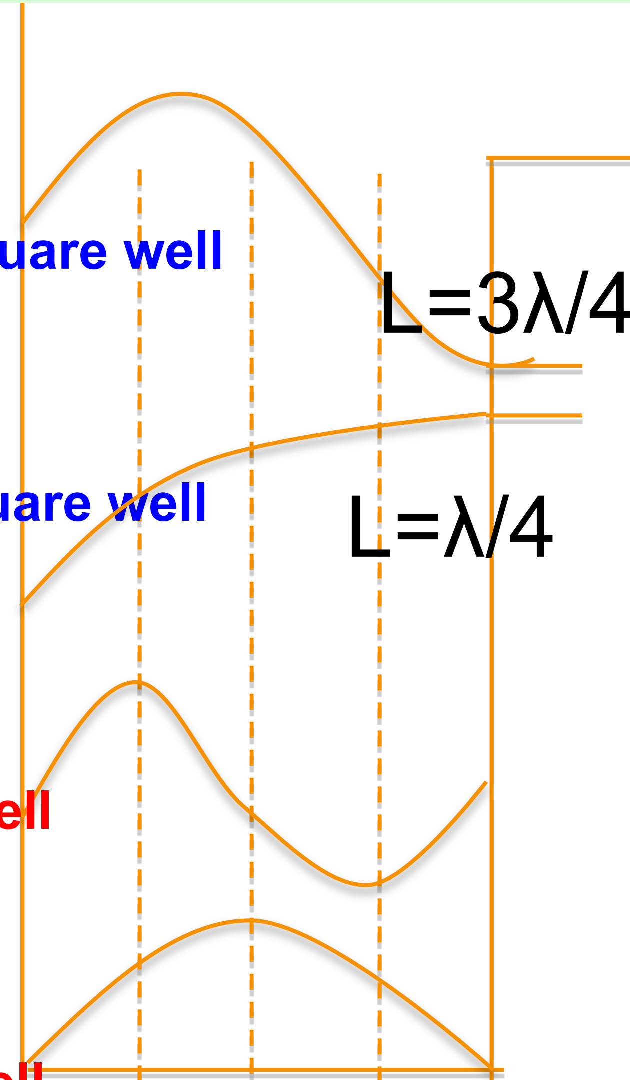
✔ **n=2, semi-infinite square well**

✔ **n=1, semi-infinite square well**

✖ **n=2, infinite square well**

$$kL = n\pi$$

✖ **n=1, infinite square well**



For the first allowed state for the semi-infinite well, because of the boundary condition

$$\mathrm{L}=\frac{\lambda}{4} \Rightarrow k=\frac{\pi}{2L}$$

$$E(=V_0)=\frac{\hbar^2 k^2}{2m}=\frac{\pi^2\hbar^2}{8mL^2}$$

Bound States

For getting the next bound state for the semi-infinite well,

$$\text{L}=\frac{\lambda}{2}+\frac{\lambda}{4}=\frac{3\lambda}{4}\Rightarrow k=\frac{3\pi}{2L}$$

$$E(=V_0)=\frac{\hbar^2 k^2}{2m}=\frac{9\pi^2\hbar^2}{8mL^2}$$

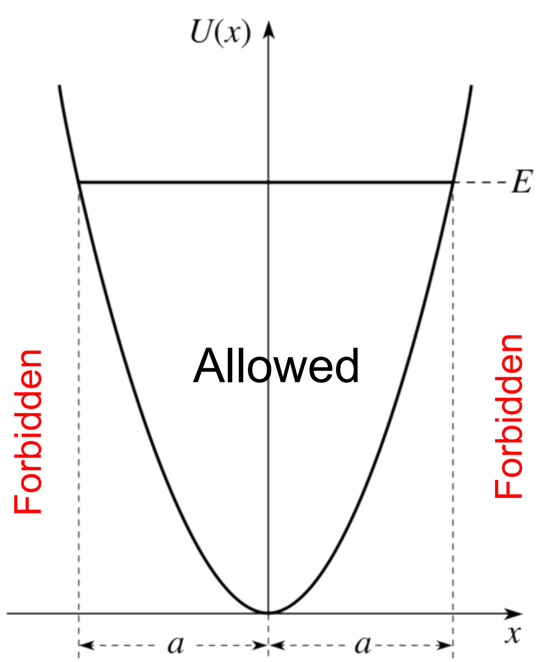
Number of bound states

- There will not be any bound state, for values of V_0 below a critical value, for a fixed L.
- As V_0 increases (depth of the well increases), more bound states become possible.

Compare this result with the finite square well, in which you will always get at least one bound state for any low value of V_0 for a fixed L value.

1D harmonic oscillator

Quantum mechanics of a 1-D simple harmonic oscillator



Trial Solution

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}kx^2\right]\psi(x) = 0$$

Try the following solution for the above equation.

$$\psi(x) = Ae^{-\alpha x^2}$$

Substitute in Schrödinger Equation

$$(-2A\alpha)\exp(-\alpha x^2)[1-2\alpha x^2]$$

$$+\frac{2m}{\hbar^2}(E-\frac{1}{2}kx^2)A\exp(-\alpha x^2)=0$$

$$[-2\alpha+4\alpha^2x^2]+\frac{2m}{\hbar^2}(E-\frac{1}{2}kx^2)=0$$

$$\left[\frac{2m}{\hbar^2}E-2\alpha\right]+\left[4\alpha^2-\frac{mk}{\hbar^2}\right]x^2=0$$

Identity condition

If the equation has to be satisfied for all values of x then we must have the following.

$$\left[\frac{2m}{\hbar^2}E - 2\alpha\right] = 0$$

$$\left[4\alpha^2 - \frac{mk}{\hbar^2}\right] = 0$$

This gives the following.

$$\alpha = \frac{\sqrt{mk}}{2\hbar}$$

$$E = \frac{\alpha\hbar^2}{m} = \frac{\hbar}{2}\sqrt{\frac{k}{m}} = \frac{1}{2}\hbar\omega$$

Normalization constant A turn out to be

$$A = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Harmonic Oscillator (1^{st} excited state)

$$\psi(x) = Bxe^{-\alpha x^2}$$

Substituting this solution in S.E. yields,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}kx^2\right]\psi(x) = 0$$

$$E = \frac{3}{2}\hbar\omega$$

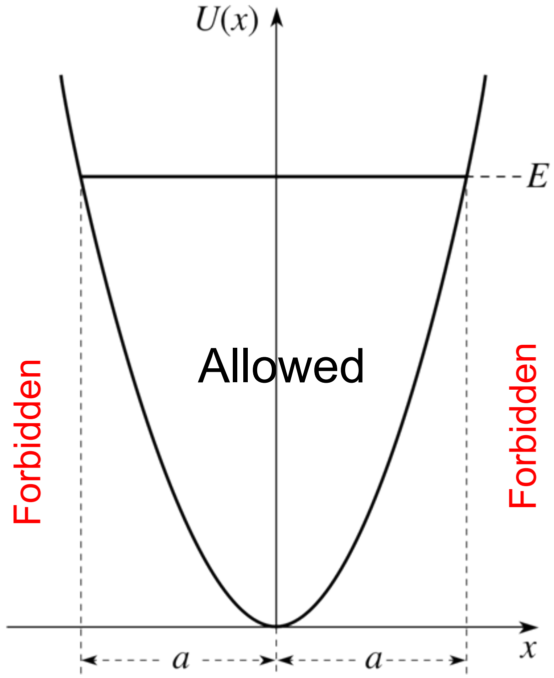
And,

$$B = \left(\frac{32\alpha^3}{\pi}\right)^{1/4}$$

General Solution

In general, $$\psi_n(x) = A_n f_n(x) e^{-\alpha x^2/2}$$

This results in wave functions similar to standing wave in the Classically allowed region joining smoothly to the falling exponential in the classically forbidden region



First four polynomials are:

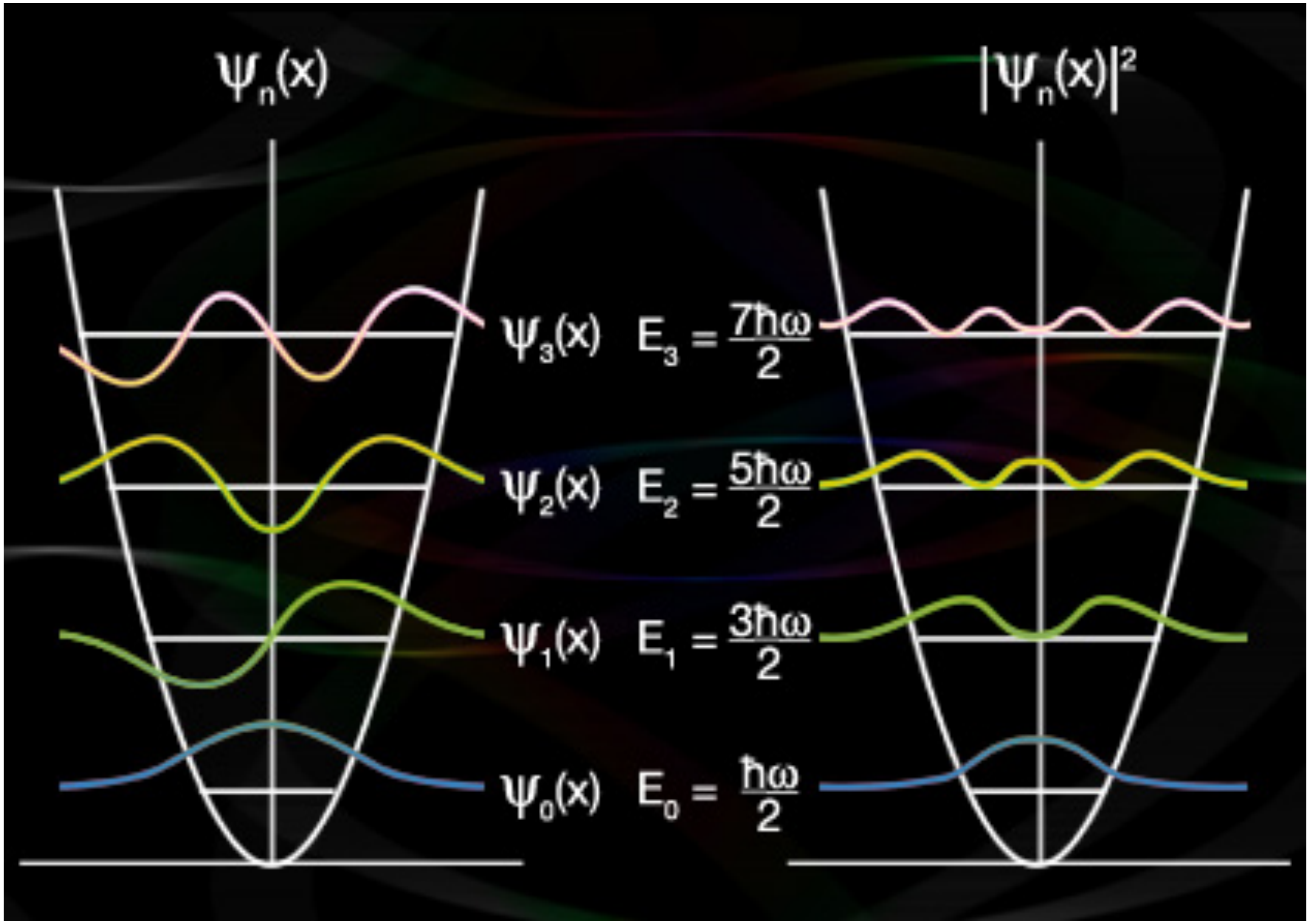
$$f_0(x) = 1$$

$$f_1(x) = 2\sqrt{\alpha}.x$$

$$f_2(x) = 2 - 4\alpha x^2$$

$$f_3(x) = 12\sqrt{\alpha}.x - 8\alpha\sqrt{\alpha}.x^3$$

Wave functions and the probability densities



Classically forbidden region and Turning pt.

Classically forbidden regions are where

$$E < \frac{1}{2} m\omega^2 x^2 .$$

$\therefore$ The classical turning points of the motion are

$$\frac{1}{2}\hbar\omega = \frac{1}{2} m\omega^2 x^2 \Rightarrow x = \pm\sqrt{\frac{\hbar}{m\omega}} = \pm\sqrt{\frac{1}{2\alpha}}$$

Uncertainty

$$For\ any\ state\ with\ quantum\ number\ 'n',$$

$$\langle x \rangle = 0 \qquad \langle x^2 \rangle = \frac{\hbar}{2m\omega}(2n+1)$$

$$\langle p_x \rangle = 0 \qquad \langle p_x{}^2 \rangle = \frac{m\hbar\omega}{2}(2n+1)$$

$$\therefore \Delta x \Delta p_x = \left(n + \frac{1}{2} \right)\hbar$$

Summary

- Various simple examples show the distinct differences that quantum mechanics offers.
- Many of these quantum effects have strong fundamental and applied interests.