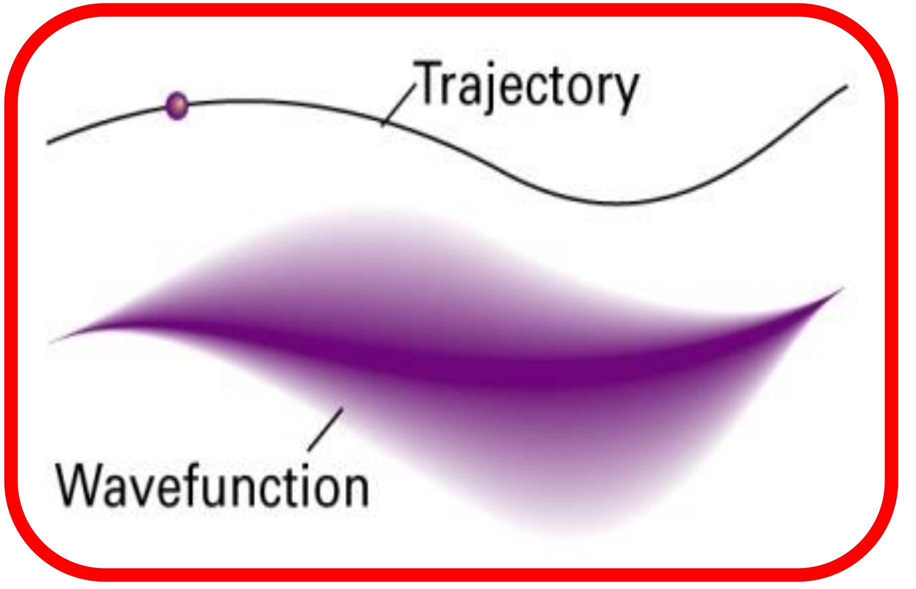
The Dynamics of microscopic systems

Description of a quantum mechanical system

- A QM particle cannot have a precise trajectory, there is only a probability.

- A particle is spread through space like a wave… There are regions where the particle is more likely to be found than others.

- To describe this distribution the concept of wavefunction ψ is introduced, in place of trajectory.



Description of a quantum mechanical system

A **Wave function** is a mathematical function that contains all the dynamical information about the state of a system.

It determines the particle's probability distribution; a kind of blurred version of trajectory

The concept of the wave function and the equation governing its change with time were discovered in 1926 by the Austrian physicist Erwin Schrodinger.

The Schrödinger Equation

For a one-particle, one-dimensional system

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}}_{\textbf{KE}} + \overbrace{V(x)}^{\textbf{PE}}\psi = \underbrace{E\psi}_{\textbf{Total Energy}} \qquad \hbar \equiv \frac{h}{2\pi}$$

Operator Form:

$$\hat{H}\psi = E\psi$$

Where, the Hamiltonian operator $\hat{H} \equiv -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2} + V(x)$

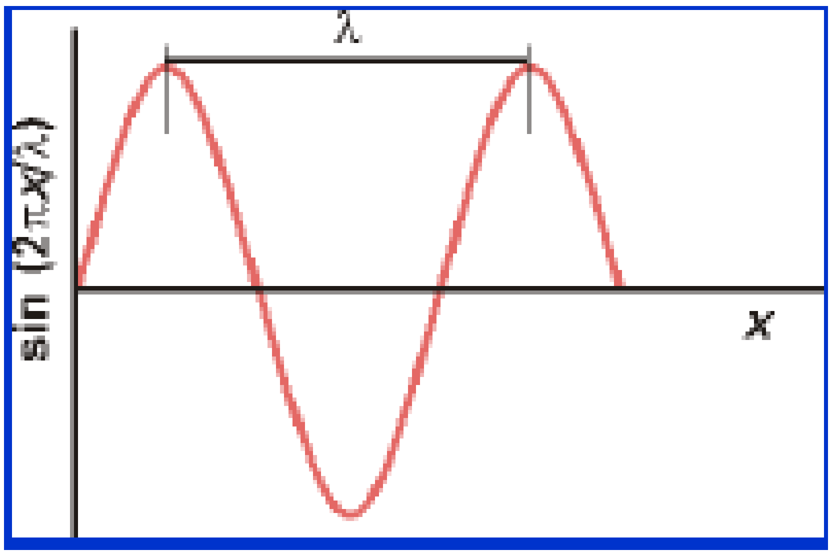
The Schrödinger Equation: Free particle

For special case with $V = 0$, SE becomes

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

Let, $k^2 = 2mE/\hbar^2$

A solution is: $\psi = \sin(kx)$ $\rightarrow$ wave with $\lambda = 2\pi/k$



Standard harmonic wave

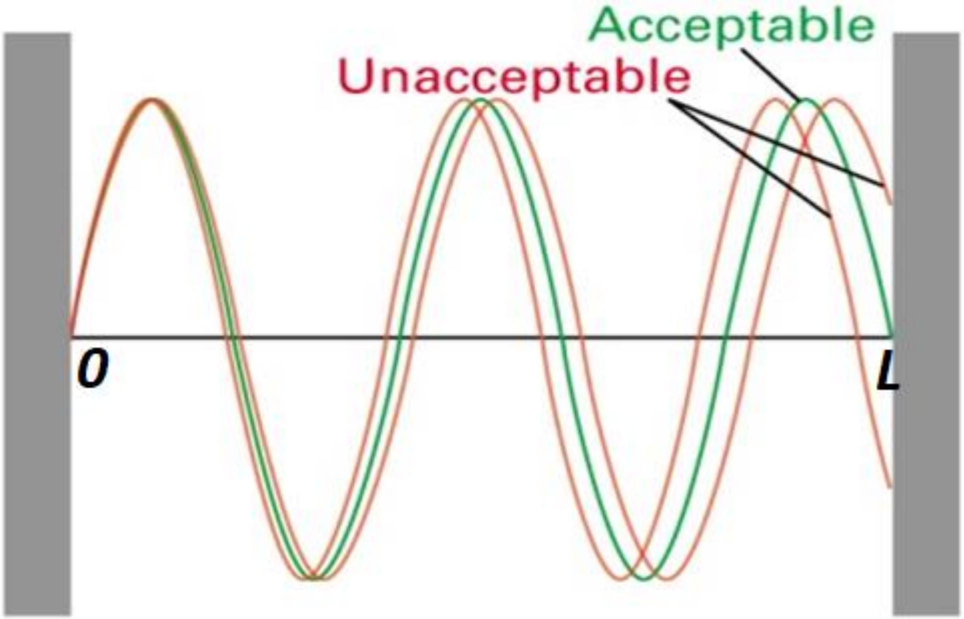
$$E = E_K = \frac{p^2}{2m} = \frac{k^2\hbar^2}{2m}$$

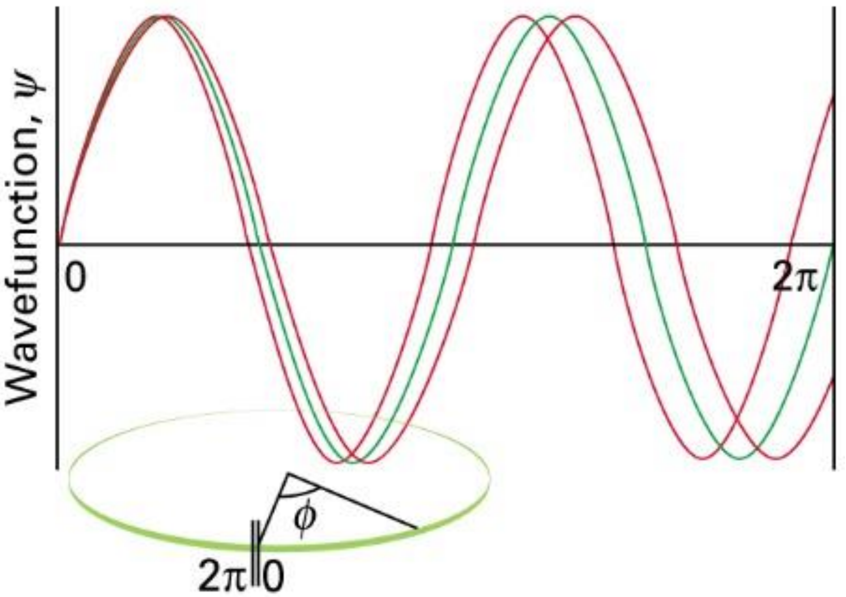
$$\boxed{p = k\hbar = \frac{h}{\lambda}}$$

Experimentally verified

Solutions of the Schrödinger Equation

- **Infinite number of solutions are possible.**
- **But, solutions which obey the boundary conditions of the system are <u>only</u> allowed.**



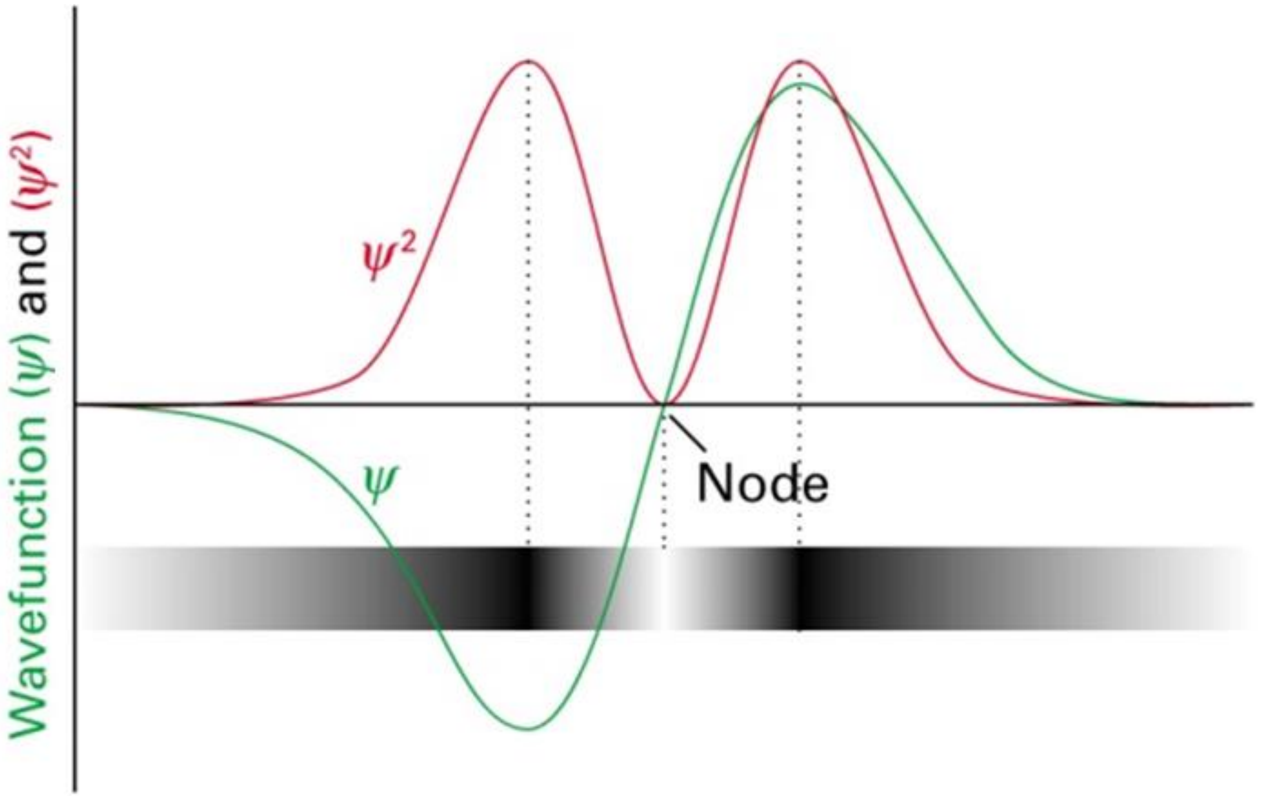


- ❑ **Each solution corresponds to a particular wavelength, and thus a particular Energy.**
- ❑ **Only certain values of Energy are acceptable, i.e. Energy is quantized.**

(Born) Interpretation of wavefunction

The Wave function Ψ contains all the dynamical information about the particle it describes.

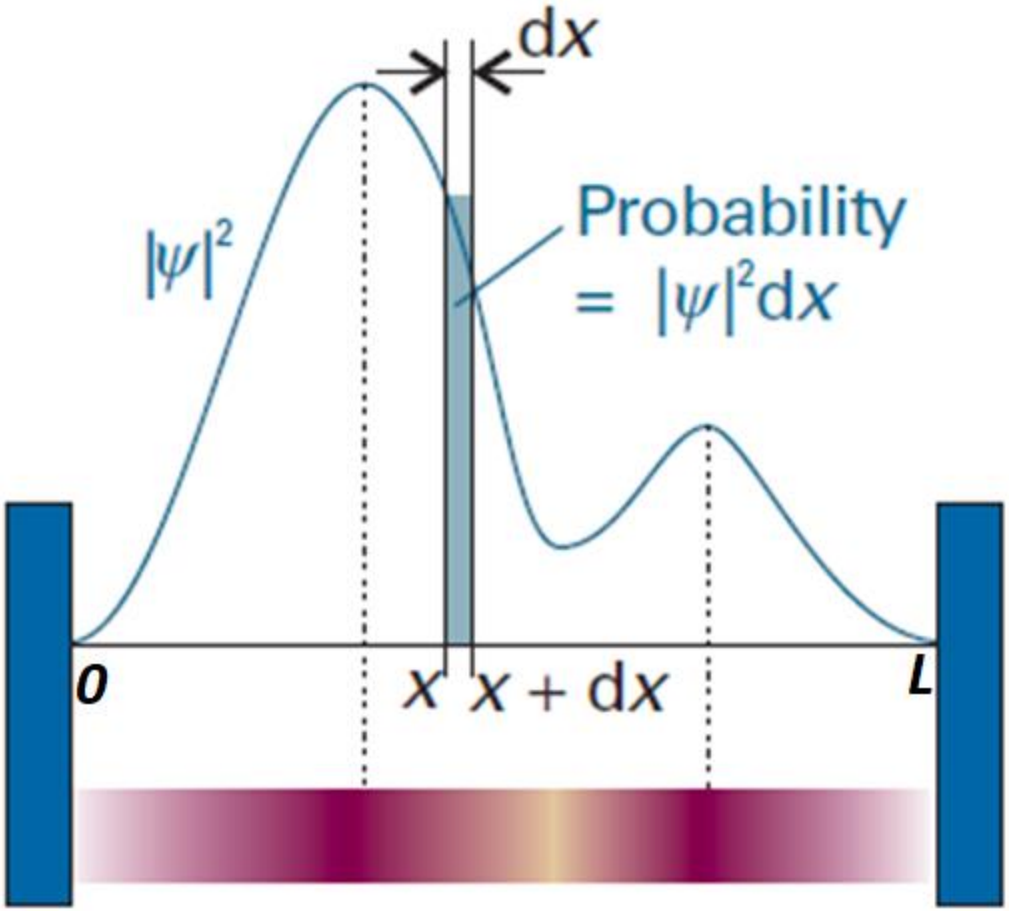
Ψ: No physical interpretation (can be complex).



Ψ^2 (or $|\Psi|^2$ if Ψ complex) is real and related to probability of finding a particle.

(Born) Interpretation of wavefunction

Probability of finding a particle in a small region of space of volume dx is proportional to $|\psi|^2\, dx$



Between 0 to L

$$Prob = \int_0^L |\psi|^2 dx$$

- ❑ ψ^2 is probability density
- ❑ ψ is probability amplitude

Acceptable wavefunction

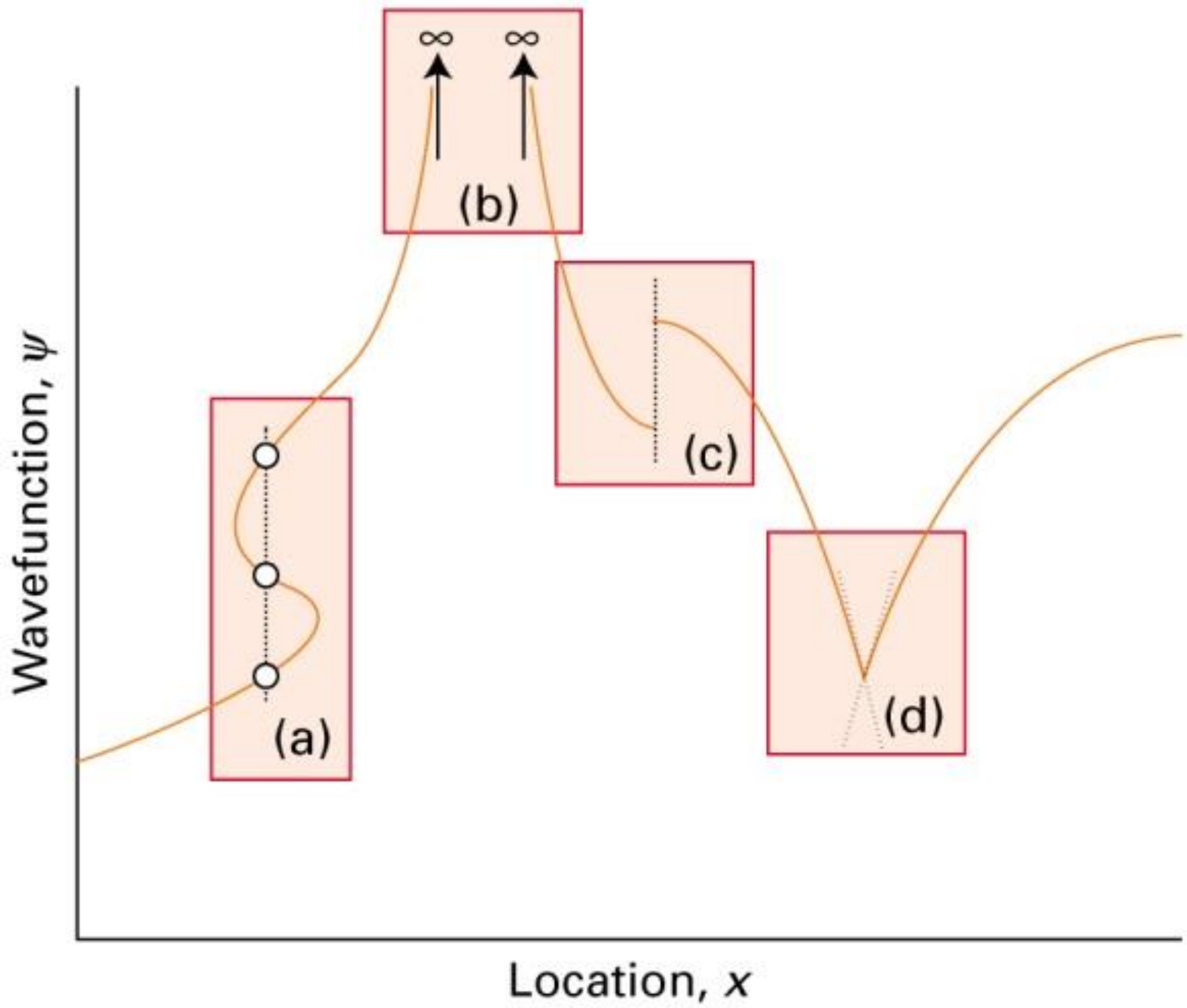
Must be:

a) single valued

b) finite

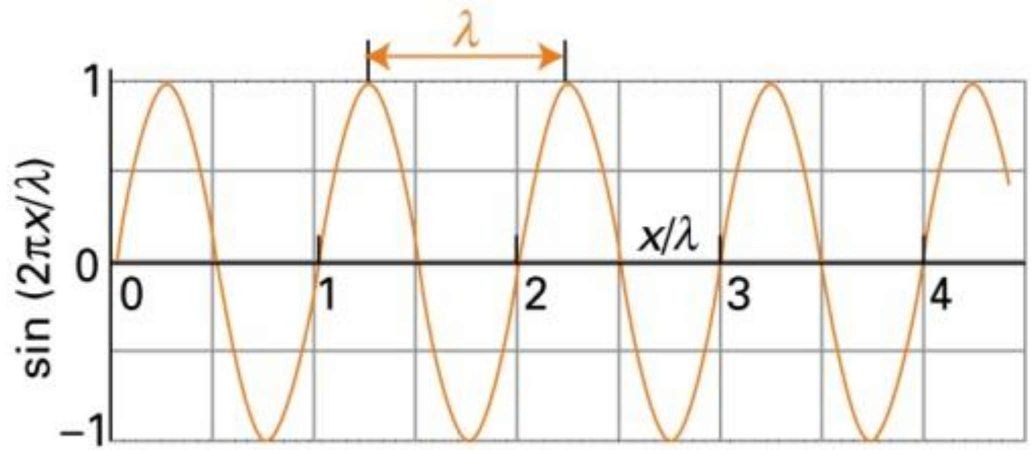
c) Continuous

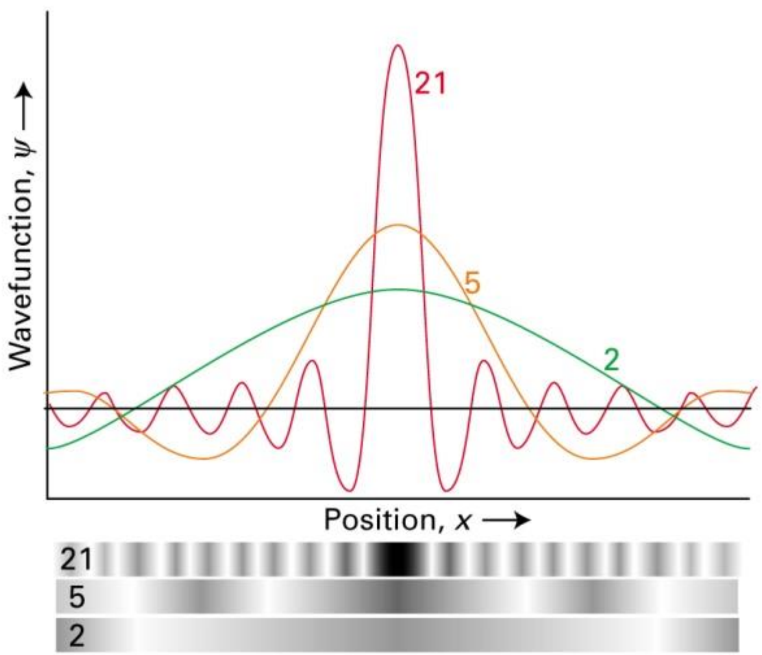
d) continuous slope

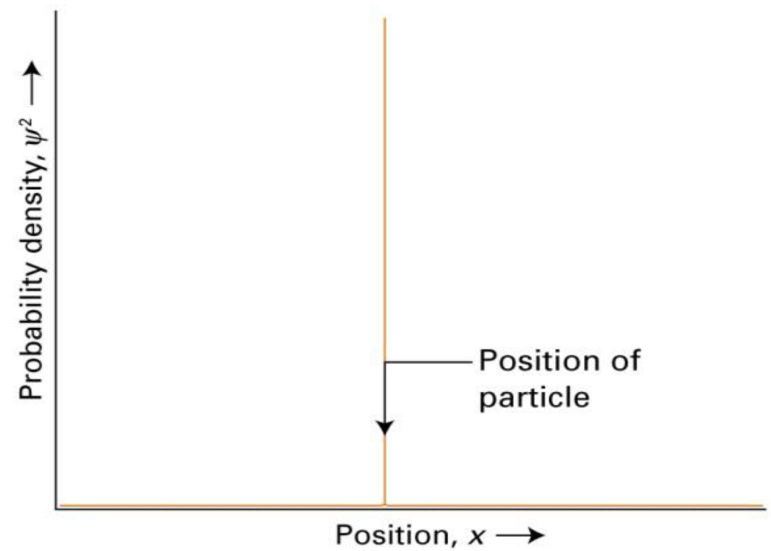


The uncertainty principle

The wave
$\psi = \sin(2\pi x/\lambda)$
corresponds to
$p = h/\lambda$ but with no
precise position!







An infinite no. of waves (momenta) are needed to create the ψ of a well-defined particle.

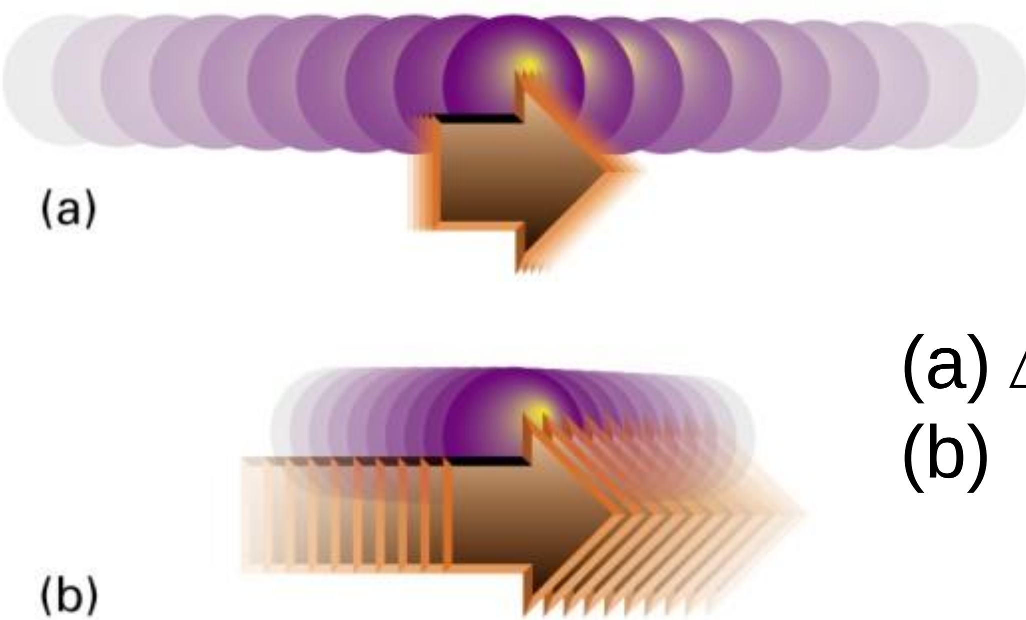
The (Heisenberg) uncertainty principle

It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

$$\Delta p_x \, \Delta x \geq \hbar / 2$$

Position-momentum uncertainty relation

$\Delta x, \Delta p_x$: uncertainty in position and momentum



Sphere: x, Arrow: p

(a) Δp small, Δx uncertain

(b) Δx small, Δp uncertain

Implications of uncertainty principle

- *Position and momenta are complementary (i.e not simultaneously specifiable !)*

- *We can specify position at the expense of momentum, or vice-versa*

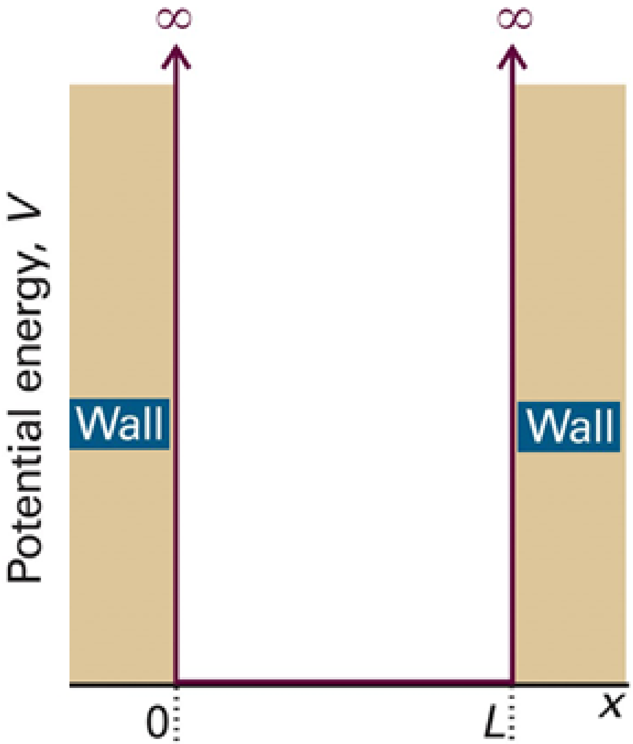
- *The concept of "Orbit" (a precise position & momentum of electron) is ruled out.*

Applications of quantum mechanics

1. Translation
2. Vibration

Translation: Particle in a box

Consider a particle with constant potential energy confined in a one-dimensional region (Box of length *L*)



Potential

Inside box:

V = const. = 0

Wall potential = ∞

Due to impenetrable walls, Ψ(x) = 0 at x < 0 and x > L

For continuity of Ψ:

Ψ(x) = 0 at x = 0 and x = L **(Boundary conditions)**

Solution of the Schrödinger Equation

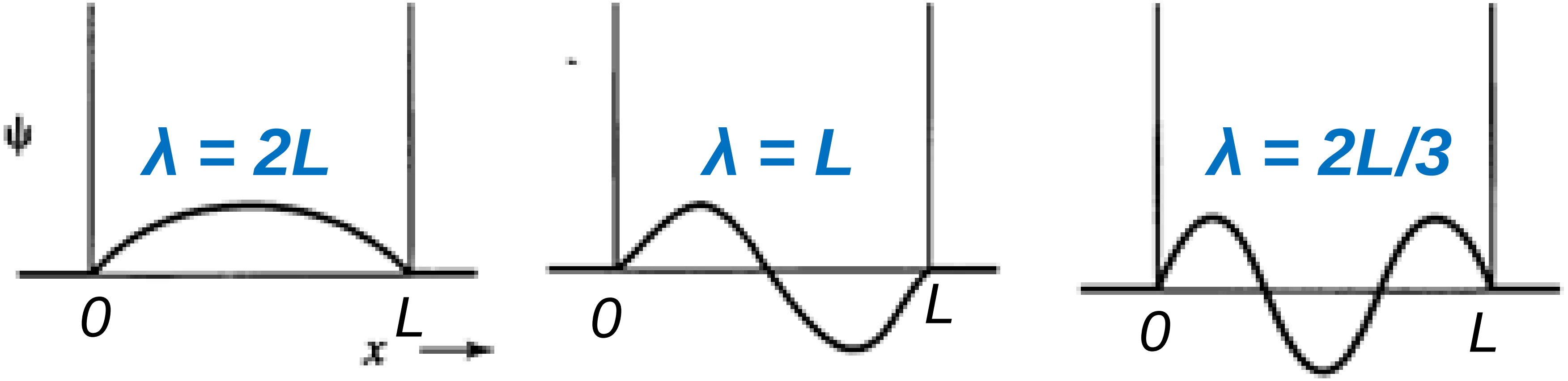
SE for V = 0: $$\frac{d^2\psi}{dx^2}+k^2\psi=0$$ where, $k^2 = 2mE/\hbar^2$

A solution is: $\psi = \sin(kx)$ $\rightarrow$ wave with $\lambda = 2\pi/k$

Ψ needs to satisfy the boundary conditions,

Ψ(x) = 0 at x = 0 and x = L

i.e. each acceptable Ψ must fit inside the box exactly



In general, $\lambda = 2L/n, \quad n = 1, 2, 3\cdots$

The Schrödinger Equation: Solution

With $V = 0$ $\quad \frac{d^2\psi}{dx^2} + k^2\psi = 0$ $\quad$ where, $k^2 = 2mE/\hbar^2$

A solution is $\psi = \sin(kx) \longrightarrow$ wave with $\lambda = 2\pi/k$

With the boundary condition, $\lambda = 2L/n,\ n = 1, 2, 3\cdots$

$$\boxed{k = 2\pi/\lambda = \pi n/L}$$

$$E_n = \frac{k^2\hbar^2}{2m} = \frac{(\pi n/L)^2(h/2\pi)^2}{2m} = \frac{n^2h^2}{8mL^2}$$

$$\psi_n(x) = N\sin(n\pi x/L), \quad n = 1, 2\cdots$$

N: Normalization constant

Normalization constant (N) is chosen such that the total probability of finding the particle is <u>one</u>

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

Normalization

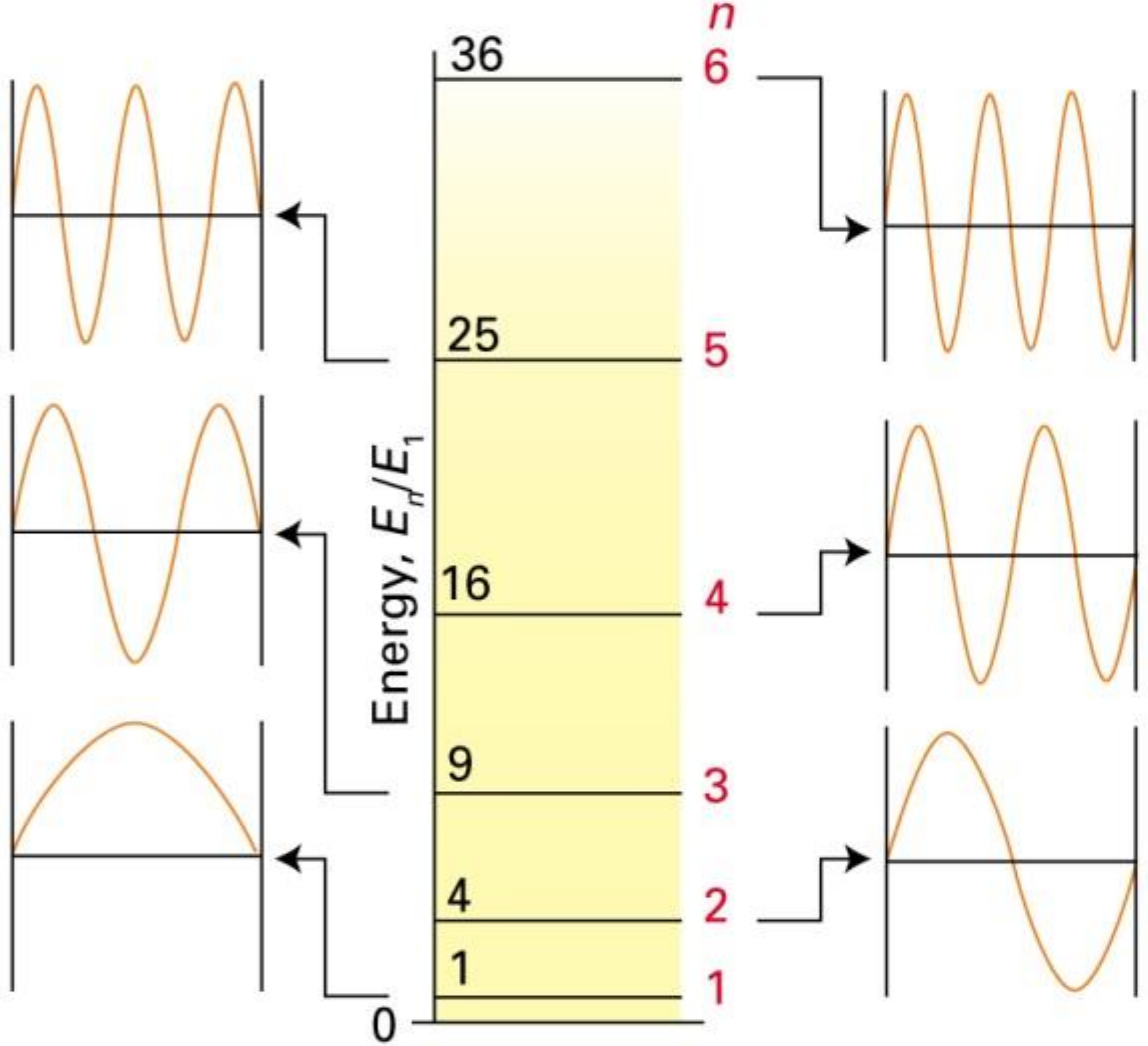
$$1 = N^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = N^2 \left(\frac{L}{2}\right) \Rightarrow N = \left(\frac{2}{L}\right)^{1/2}$$

$$\int \sin^2(ax)dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} + const$$

$$\boxed{\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2 \cdots}$$

Permitted Energy levels & wavefunctions

$$\psi_n = \sqrt{(2/L)}\sin(n\pi x/L) \qquad n = 1,2,3,\cdots \qquad E_n = n^2h^2/(8mL^2) = n^2E_1$$



Zero-point energy

- Lowest irremovable energy

$$E_1 = \frac{h^2}{8mL^2}$$

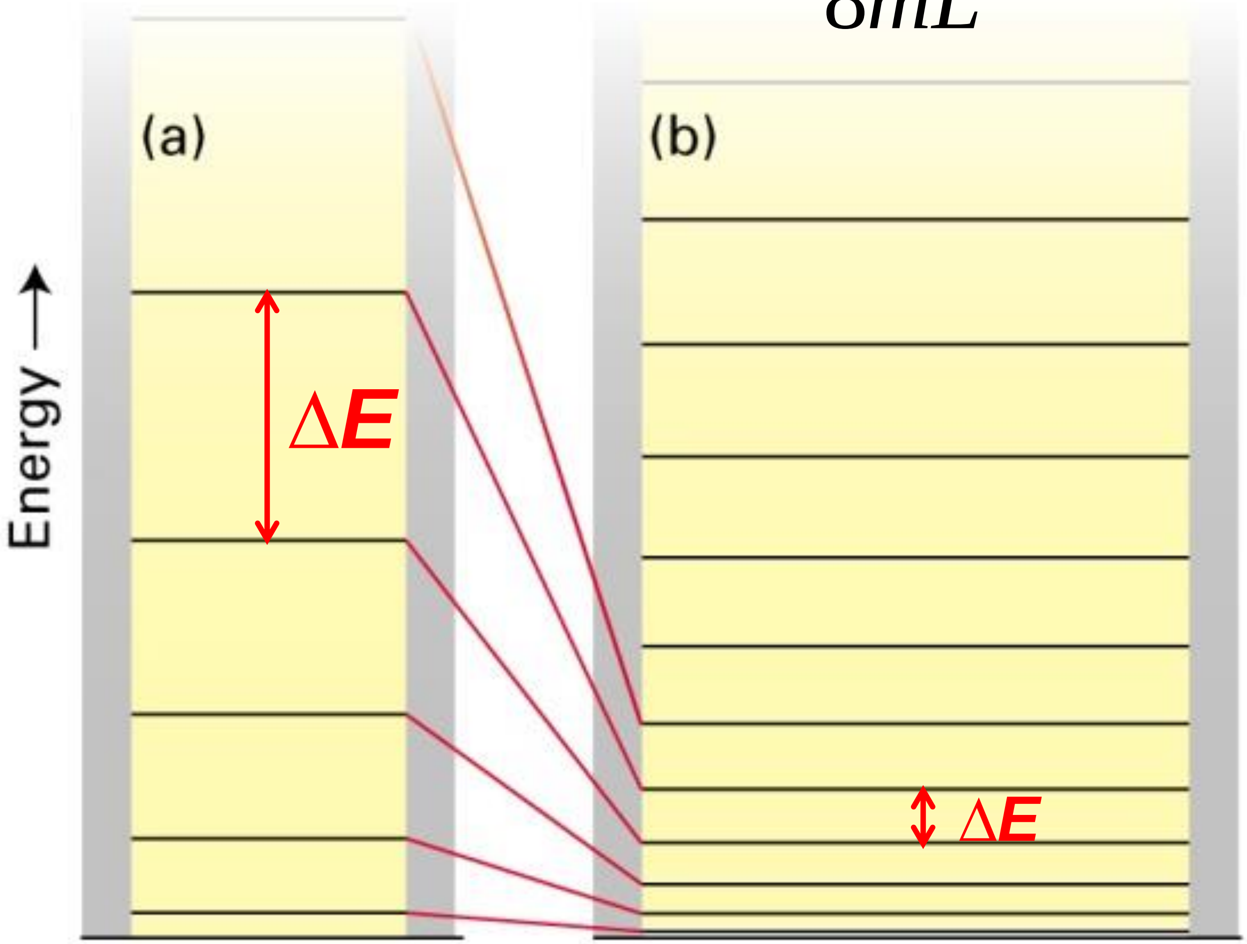
- Existence is in consistent with uncertainty principle

No. of Nodes: *n* - 1

Energy difference between adjacent levels

$$\Delta E = E_{n+1} - E_n = (2n+1)\frac{h^2}{8mL^2}$$

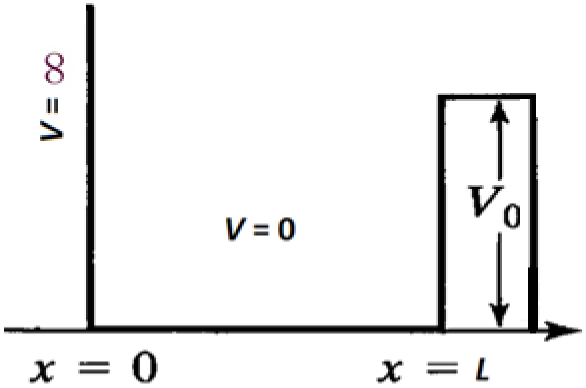
Smaller *Size*



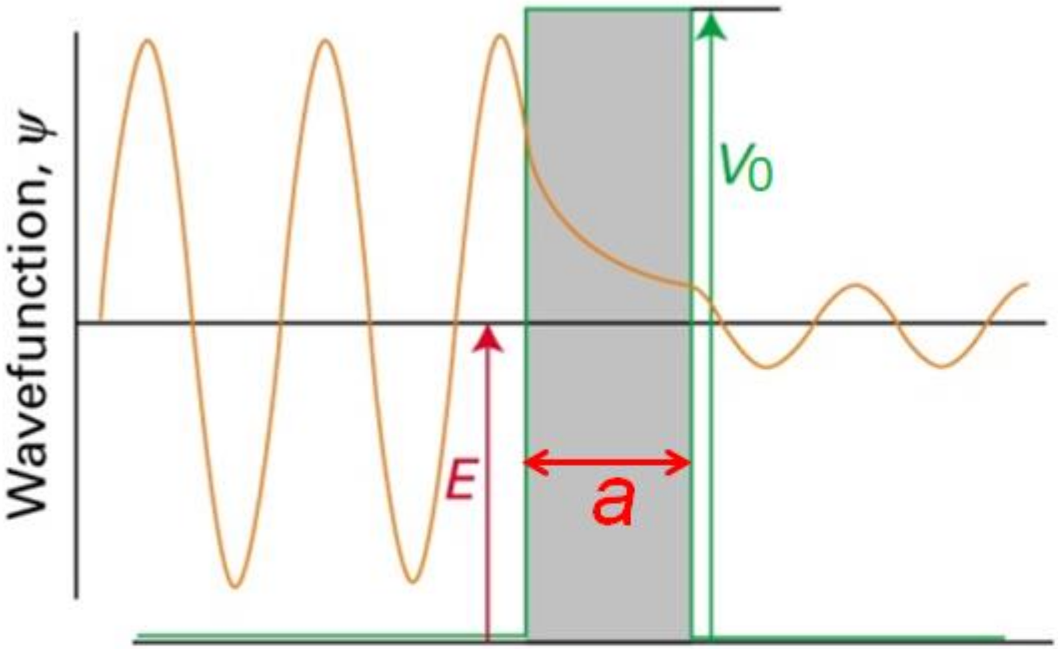
Larger *Size*

Greater **the** **size/mass** **of the system, less important are the effects of quantization**

Particle-in-a-box with finite barrier



Let E < V_0
(i.e. classically the particle can not escape the container)



Although E < V_0, the probability of finding particle outside the container is NOT zero. Such leakage by penetration into or through classically forbidden region is called tunnelling.

Transmission probability:

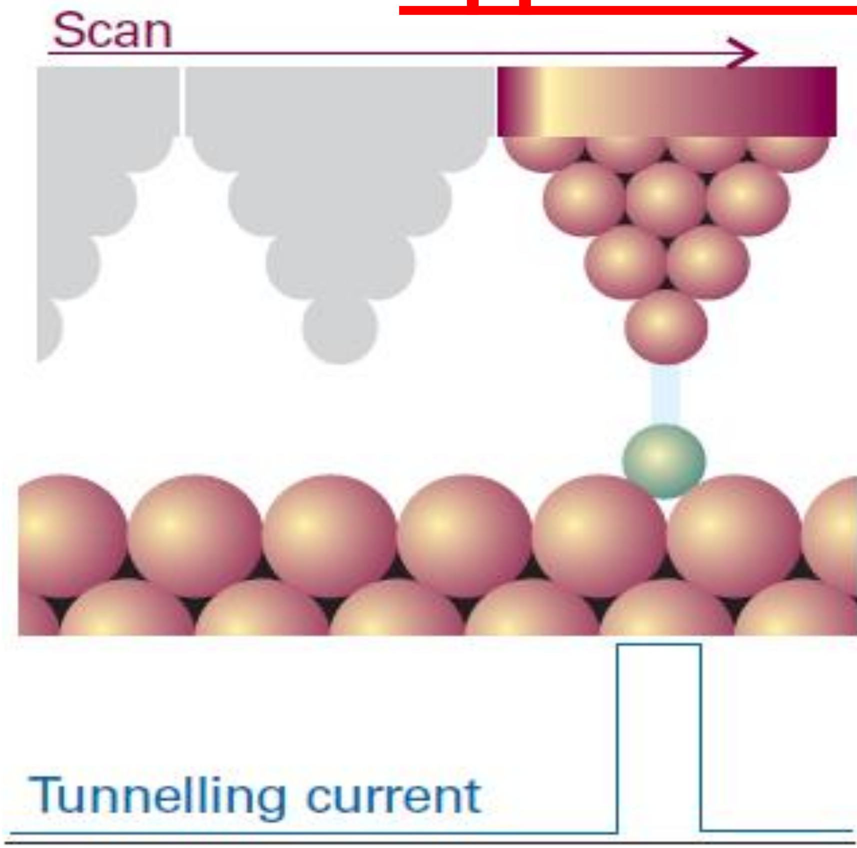
$$T \approx 16\varepsilon(1-\varepsilon)e^{-2\kappa a}$$

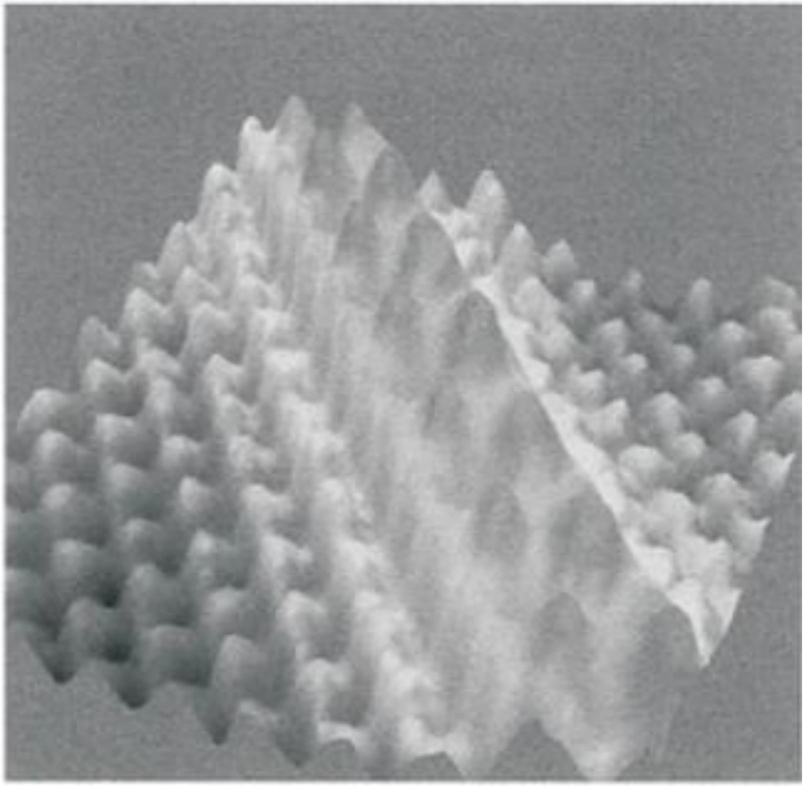
$$\kappa = \sqrt{2m(V_0 - E)}/\hbar$$

$$\varepsilon = E/V_0$$

Particles of low *mass* are more able to tunnel through barrier than heavy ones:
more important for electrons, moderate important for protons, and negligible for most other heavier particles.

Application of Tunnelling





A scanning tunnelling microscope makes use of the current of electrons that tunnel between the surface and the tip.

An STM image of caesium atoms on a gallium arsenide surface

Translation: Motion in two dimensions

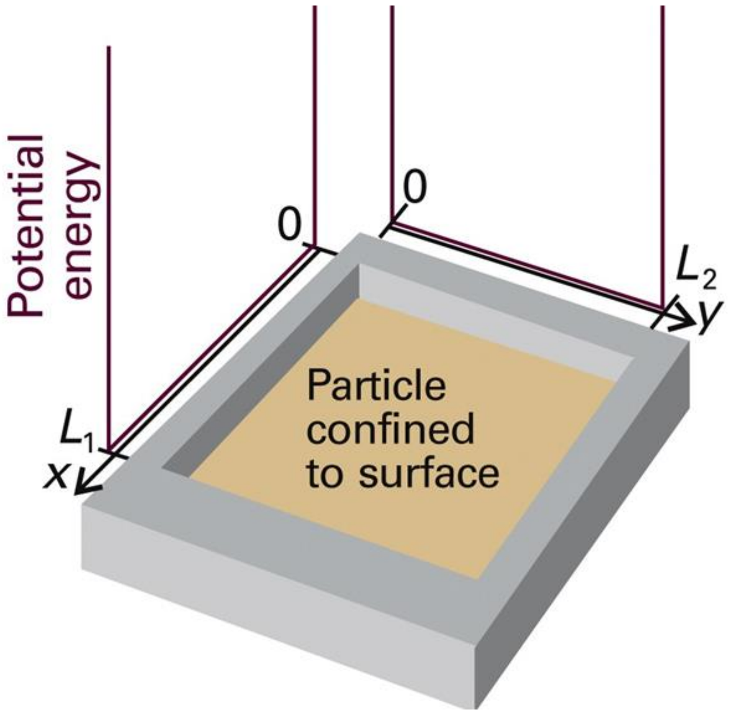
A particle with constant potential energy in a two-dimensional region with impenetrable walls at both sides

Potential

Inside 2D box:

V = const. = 0

Wall Potential: = ∞



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

Separation of variables technique, which divides the equation into two ordinary differential equations, one for each variable.

Translation: Motion in two dimensions

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

$$\psi(x,y)=X(x)Y(y)$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}=E_XX$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=E_YY$$

$$E=E_X+E_Y$$

$$X_{n_1}(x)=\left(\frac{2}{L_1}\right)^{1/2}\sin\frac{n_1\pi x}{L_1}$$

$$Y_{n_2}(y)=\left(\frac{2}{L_2}\right)^{1/2}\sin\frac{n_2\pi y}{L_2}$$

$$0\le x\le L_1 \quad n_1=1,2,\ldots$$

$$0\le y\le L_2 \quad n_2=1,2,\ldots$$

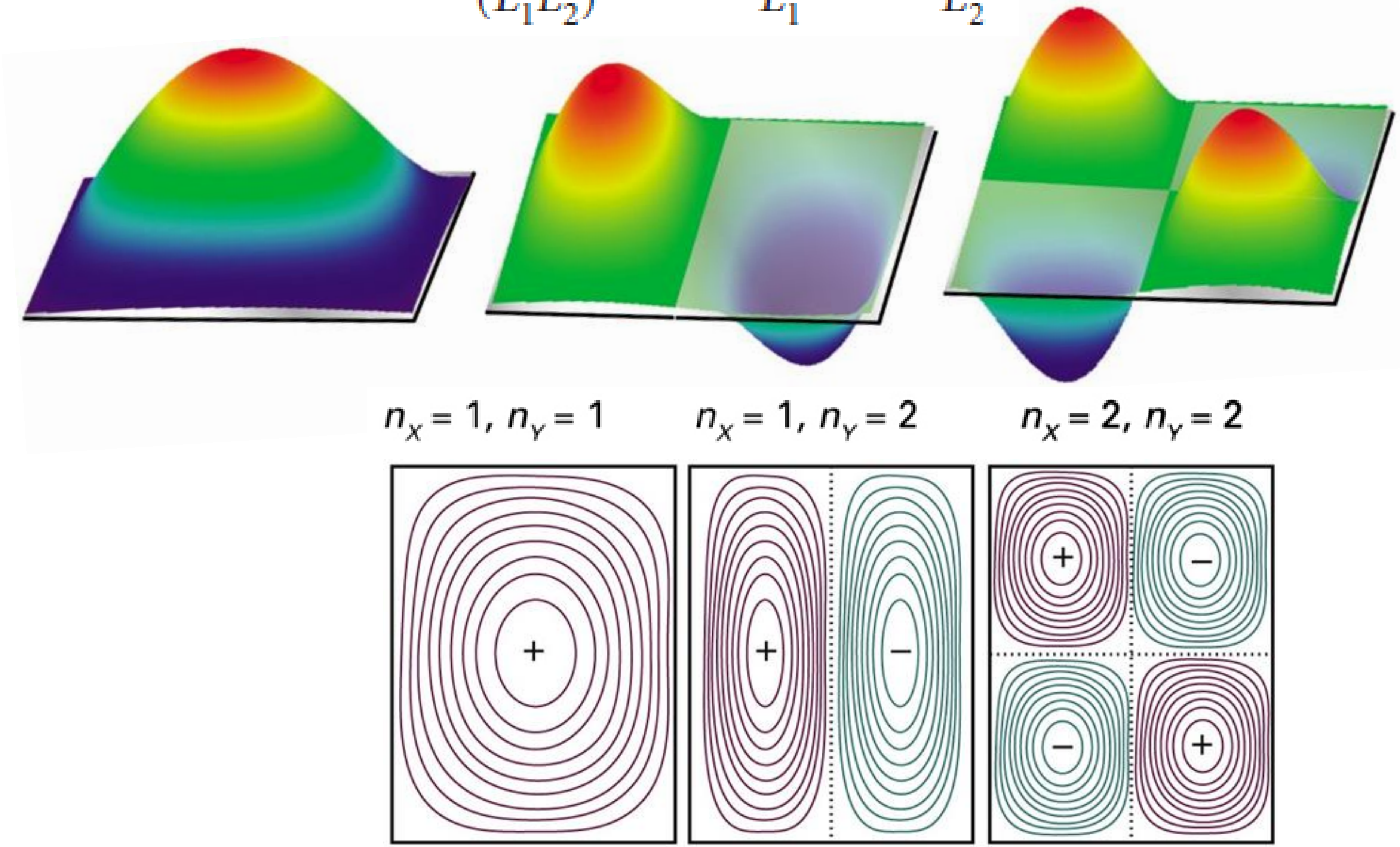
because $\psi=XY$ and $E=E_X+E_Y$, we obtain

$$\psi_{n_1,n_2}(x,y)=\frac{2}{(L_1L_2)^{1/2}}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2}$$

$$E_{n_1n_2}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m}$$

Wavefunctions…

$$\psi_{n_1,n_2}(x,y) = \frac{2}{(L_1L_2)^{1/2}} \sin\frac{n_1\pi x}{L_1} \sin\frac{n_2\pi y}{L_2}$$



Degeneracy

$$E_{n_1 n_2} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m} \qquad \psi_{n_1,n_2}(x,y) = \frac{2}{(L_1 L_2)^{1/2}} \sin\frac{n_1 \pi x}{L_1} \sin\frac{n_2 \pi y}{L_2}$$

$$n_1 = 1, 2, \ldots \text{ and } n_2 = 1, 2, \ldots$$

with $L_1 = L_2 = L$ (square plane surface):

$$E_{n_1 n_2} = (n_1^2 + n_2^2)\frac{h^2}{8mL^2} \qquad \psi_{n_1,n_2}(x,y) = \frac{2}{L} \sin\frac{n_1 \pi x}{L} \sin\frac{n_2 \pi y}{L}$$

Consider the cases:

$n_1 = 1$, $n_2 = 2$

and

$n_1 = 2$, $n_2 = 1$

$$\psi_{1,2} = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L} \qquad E_{1,2} = \frac{5h^2}{8mL^2}$$

$$\psi_{2,1} = \frac{2}{L}\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L} \qquad E_{2,1} = \frac{5h^2}{8mL^2}$$

- Although the wavefunctions are different, they correspond to the same energy (**degenerate**).
- The occurrence of degeneracy is related to the symmetry of the system.

Vibration: The harmonic oscillator

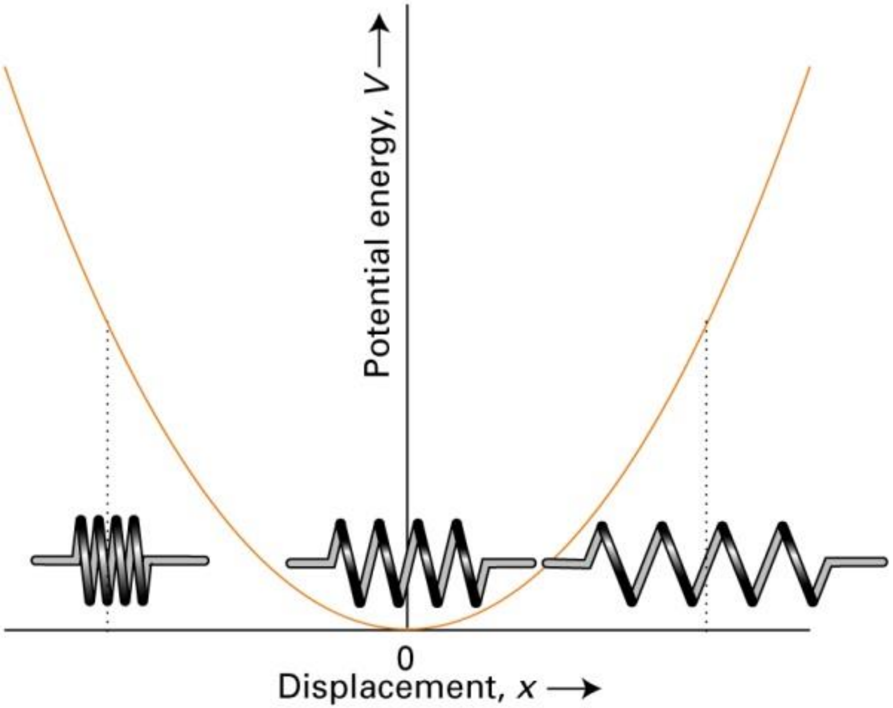
Harmonic vibration follows Hooke's Law of force

Restoring force, F = -*k x*

k: is the force constant,
x: is the displacement

$$\because F = -\frac{dV}{dx}$$

$$\Rightarrow V = \frac{kx^2}{2}$$



Parabolic potential: characteristic of a harmonic Oscillator
Positive displacement: extension

The harmonic oscillator: Solution

Potential energy varies with coordinate. SE becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{1}{2}kx^2\psi=E\psi$$

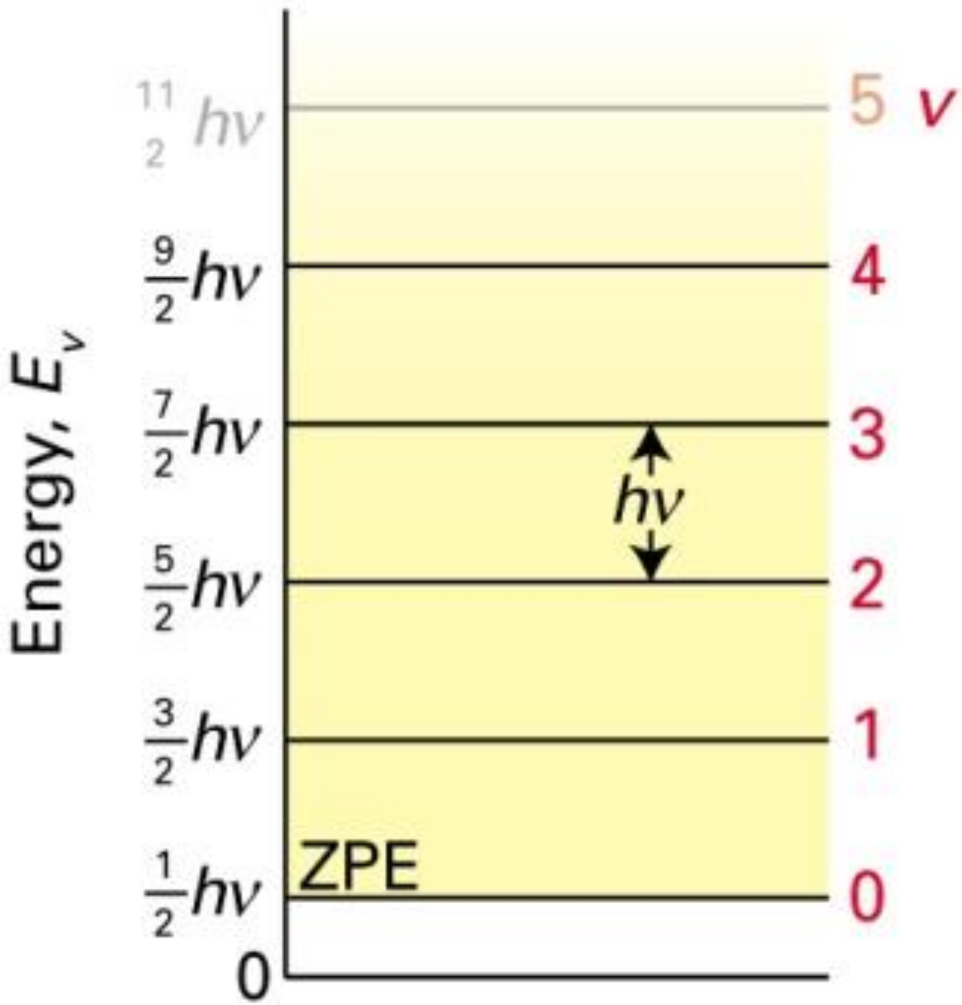
Energy Levels:

$$E_\upsilon=(\upsilon+\frac{1}{2})h\nu$$

$$\upsilon=0,1,2\cdots$$

$$\nu=\frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$\boxed{\Delta E=E_{\upsilon+1}-E_\upsilon=h\nu}$$

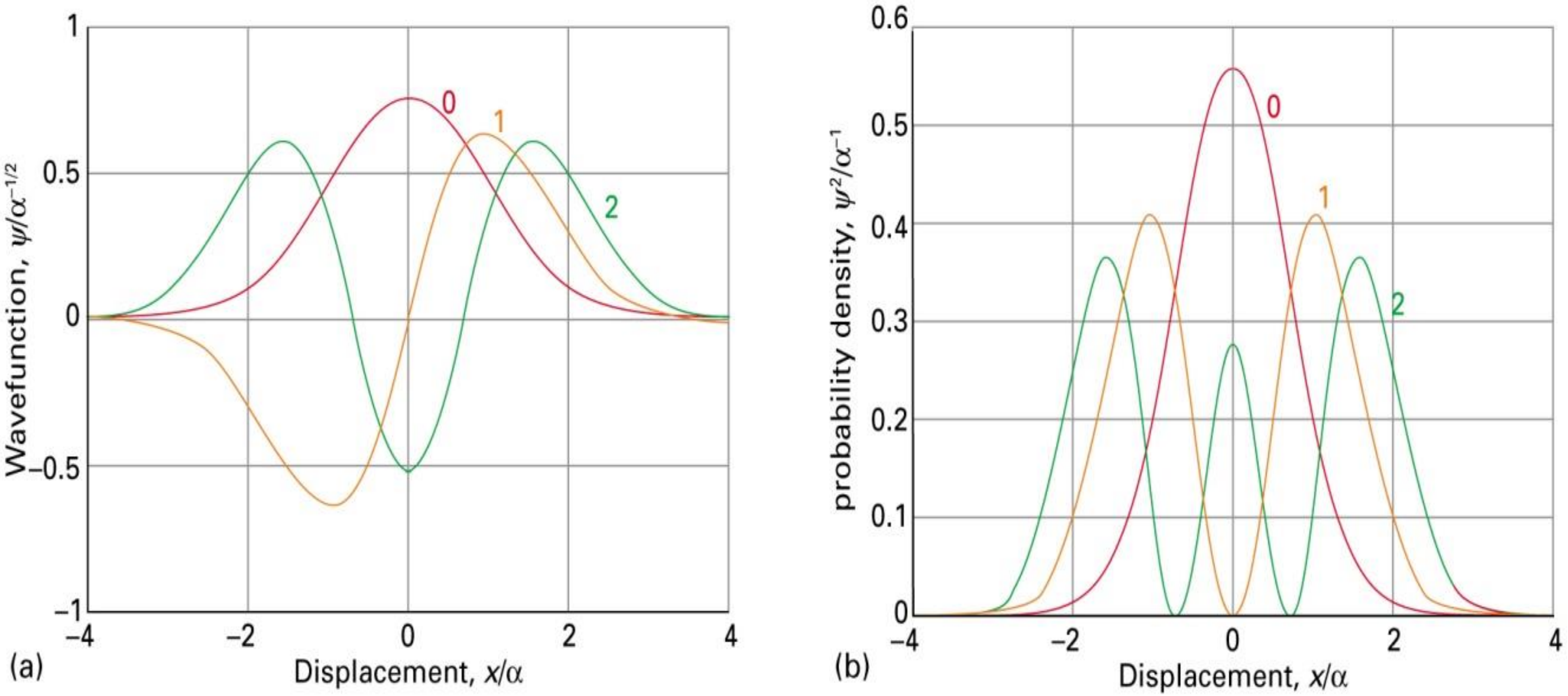


The harmonic oscillator: Solution

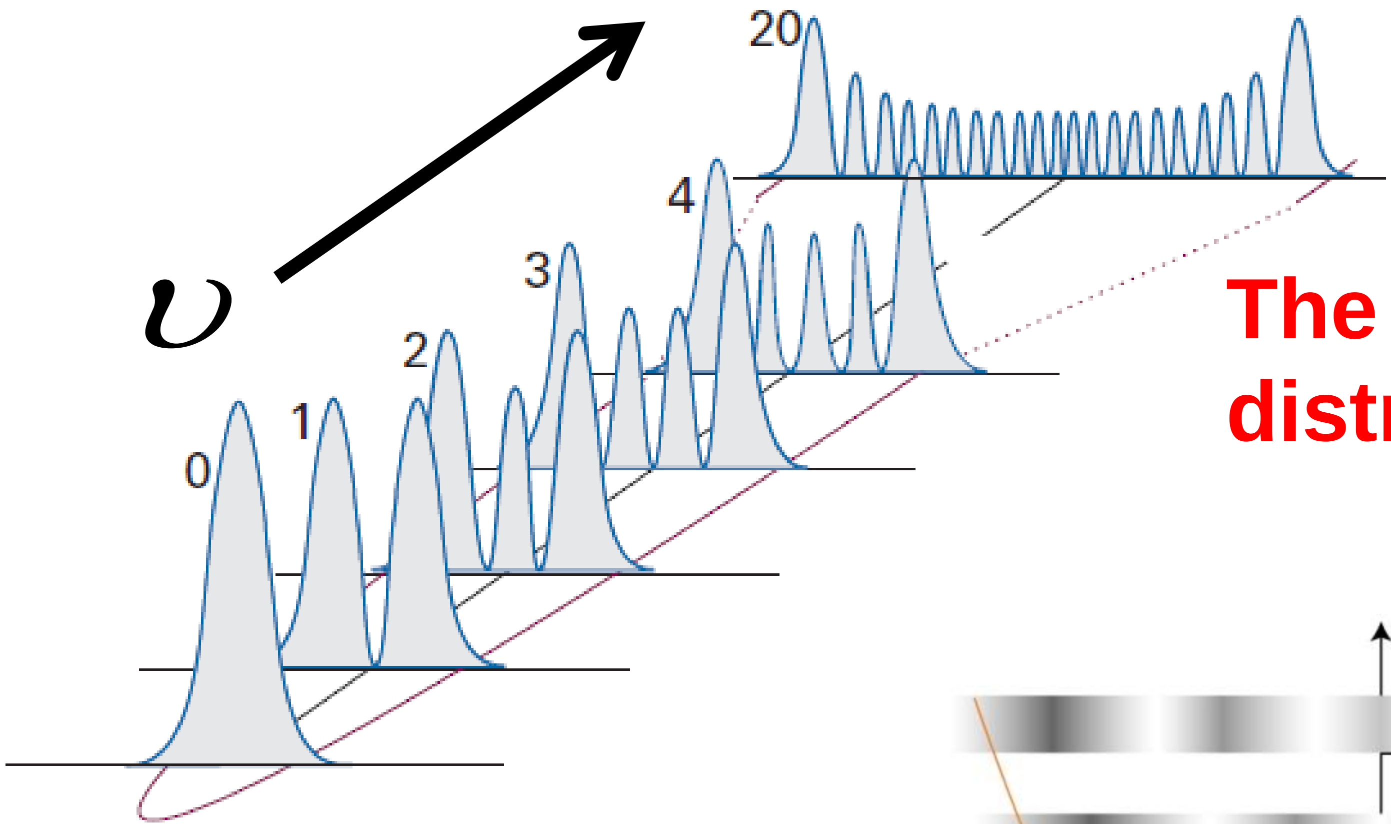
Wavefunctions are given as Hermite polynomials

$$\psi_0 = (\alpha/\pi)^{1/4} e^{-\alpha x^2/2} \qquad \alpha \equiv 2\pi\nu m/\hbar$$

$$\psi_1 = (4\alpha^3/\pi)^{1/4} x e^{-\alpha x^2/2} \qquad \psi_2 = (\alpha/4\pi)^{1/4}(2\alpha x^2 - 1) e^{-\alpha x^2/2}$$



No. of nodes: ν



The probability distributions

Tunnelling →