

# Wavefunctions

Wavefunctions are...

... “Matter Waves”

From classical physics,

$$\psi(x) = \exp(i2\pi x/\lambda) = \cos(2\pi x/\lambda) + i \sin(2\pi x/\lambda)$$

is a wave propagating in the positive  $x$  direction.

Using de Broglie's relation for a particle,  $\lambda = h/p$

$$\psi(x) = \exp(ipx/\hbar) \qquad \hbar = h/2\pi$$

## ... Solutions of the Schrödinger Equation

The wavefunction  $\Psi(\mathbf{r},t)$  for a system is a solution of the Schrödinger equation, a differential equation for the spatial ( $\mathbf{r}$ ) and temporal ( $t$ ) behaviour of de Broglie waves.

$\Psi$  contains all information about the dynamical properties of the system. In principle, all observable properties may be deduced by performing the appropriate mathematical operation on  $\Psi$ .

$\Psi(\mathbf{r},t)$  is a function of time and all the coordinates of all the particles that make up the system.

$\Psi(\mathbf{r},t)$  can be interpreted as the amplitude of the probability density for the spatial description of the system.

# Properties of Wavefunctions

For a single particle wavefunction ,  $\psi(r)$

the probability density of the particle at  $r$  is  $|\psi|^2 = \psi^* \psi$

i.e. **probability of finding particle in region**  $dx$  is  $\psi^*(x)\psi(x)dx$

or volume  $d\tau$  is  $\psi^*(\tau)\psi(\tau)d\tau$

An acceptable wavefunction is ...

**continuous** usually also  $\partial\psi/\partial q$

**single valued** actually  $\psi^* \psi$

**finite everywhere**  $\int \psi^* \psi d\tau = 1$

These limitations force  $\psi$  to obey **boundary conditions**  
which result in **quantization**

i.e. only some solutions of the Schrödinger equation survive.

A wavefunction is **normalized** if  $\int \psi^* \psi d\tau = 1$

Two wavefunctions  $\psi_1$  and  $\psi_2$  are **orthogonal** if  $\int \psi_1^* \psi_2 d\tau = 0$

# The Schrödinger Equation

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \Psi + V\Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

or  $\hat{H}\Psi = i\hbar \frac{\partial}{\partial t} \Psi$

del squared  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} =$  **the Laplacian**

Assume  $\Psi(r, t) = \psi(r)\phi(t)$  and  $V = V(r)$

then  $-\frac{\hbar^2}{2m} \nabla^2 \psi(r)\phi(t) + V(r)\psi(r)\phi(t) = i\hbar \psi(r) \frac{d\phi(t)}{dt}$

i.e.  $-\frac{\hbar^2}{2m\psi} \nabla^2 \psi + V(r) = \frac{i\hbar}{\phi} \frac{d\phi}{dt}$

This equation is **separable** in  $\psi$  and  $\phi$  :

$$\left. \begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \\ i\hbar \frac{d\phi}{dt} = E\phi \end{aligned} \right\} \begin{aligned} \hat{H}\psi = E\psi \\ \text{The time-independent S equation} \\ \phi(t) = Ce^{-iEt/\hbar} \end{aligned}$$

$\Psi(r, t) = C\psi(r)e^{-iEt/\hbar}$  is a **stationary** state, because:

$\Psi^* \Psi = C^2 \psi^* \psi$  is independent of time

# The Free Particle

The translational motion of a single free particle moving in 1 dimension is described by

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

An operator.

Set  $V=0$  in Schrödinger eqn.

$$\hat{H}\psi_n = E_n \psi_n$$

$n$  labels different solutions

$$\frac{d^2\psi_n}{dx^2} = \left( \frac{-2mE_n}{\hbar^2} \right) \psi_n$$

$$\psi_n = Ce^{ikx}, \quad k^2 = 2mE_n / \hbar^2 = p_n^2 / \hbar^2$$

$$\psi_n = Ce^{\pm ip_n x / \hbar}$$

or in general,  $Ae^{+ip_n x / \hbar} + Be^{-ip_n x / \hbar}$

This represents an oscillation with wavelength  $h/p$ , since

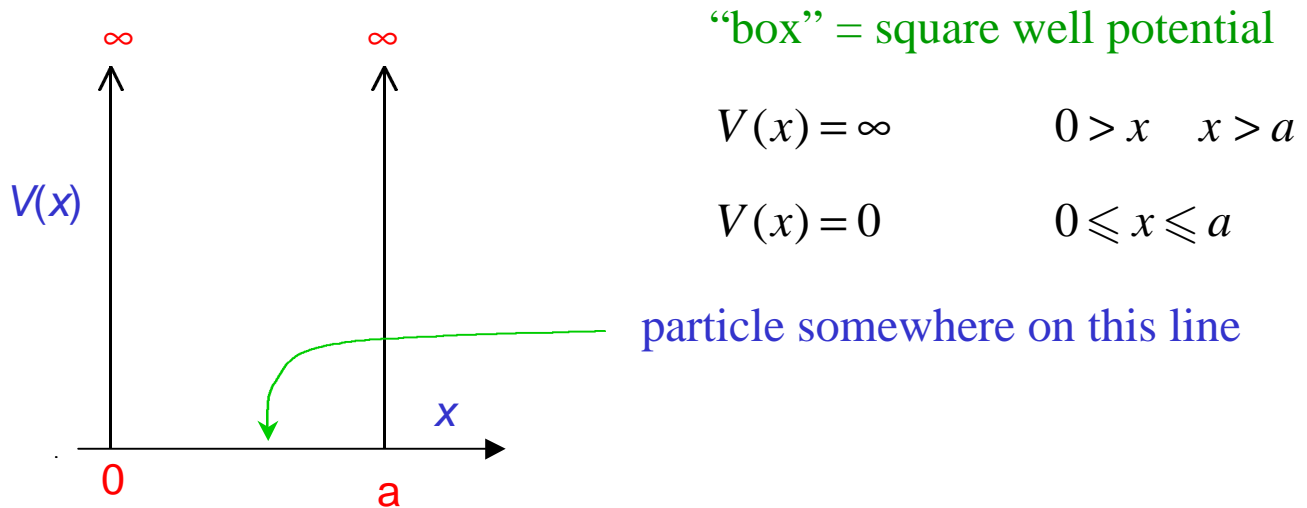
$$\exp\{\pm ipx / \hbar\} = \cos(2\pi x / \lambda) \pm i \sin(2\pi x / \lambda), \quad \lambda = h / p$$

For a given energy,  $E_n$ ,  $\psi^* \psi = C^2$  a constant.

Momentum,  $p$ , is associated with the first derivative of  $\psi$

Kinetic energy,  $E$ , with the second derivative of  $\psi$

# The Particle in a 1-D Box



$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

By extrapolation from the free particle wavefunction,

$$\psi = C \exp\left\{i\left[2m(E - V)\right]^{1/2} x / \hbar\right\} \quad \text{inside the box}$$

$$= C \exp\left\{-\left[2m(V - E)\right]^{1/2} x / \hbar\right\} \quad \text{for } V > E \quad \text{outside the box}$$

$\rightarrow 0$  as  $V \rightarrow \infty$

$\Rightarrow$  The particle is confined to the box (potential well).

Within the walls the situation is identical to the free particle...

i.e.,  $\psi_n = Ae^{+ip_n x / \hbar} + Be^{-ip_n x / \hbar}$  or  $C \cos(p_n x / \hbar) + D \sin(p_n x / \hbar)$

... until boundary conditions are applied.

## The Particle in a 1-D Box **continued**

$$\psi_n = C \cos(p_n x / \hbar) + D \sin(p_n x / \hbar)$$

$$\text{At } x=0, \psi=0 \quad \Rightarrow \quad C=0$$

$$\text{At } x=a, \psi=0 \quad \Rightarrow \quad D \sin(p_n x / \hbar) = 0 ; \text{ i.e. } p_n a / \hbar = n\pi$$

$$\psi_n = D \sin(n\pi x / a) \quad n = 1, 2, 3, \dots \quad n \text{ is called the quantum number}$$

$$E_n = \frac{p_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad n = 1, 2, 3, \dots$$

Boundary conditions impose quantization.

The value of  $D$  is found by **normalizing** the wavefunction:

$$\int \psi_n^* \psi_n \, d\tau = 1$$

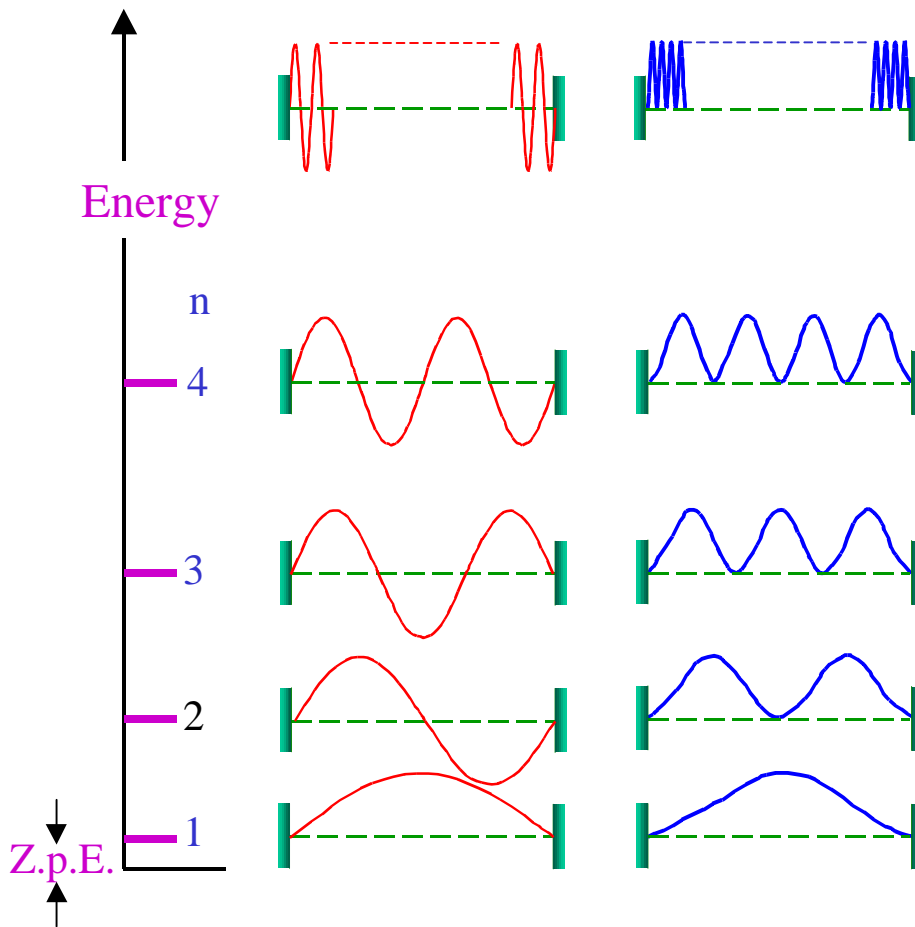
$$D^2 \int_0^a \sin^2(n\pi x / a) \, dx = \frac{1}{2} a D^2 = 1$$

$$\Rightarrow D = \left( \frac{2}{a} \right)^{1/2}$$

$$\underline{\psi_n = \left( \frac{2}{a} \right)^{1/2} \sin\left( \frac{n\pi x}{a} \right)}$$

# The Particle in a 1-D Box – Solutions

Energy Levels  $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$   $n = 1, 2, 3, \dots$



As  $a \rightarrow \infty$ ,

$$\Delta E = E_{n+1} - E_n \rightarrow 0,$$

$E$  becomes a continuous function

If  $a$  decreases,  $E$  and  $\Delta E$  become larger

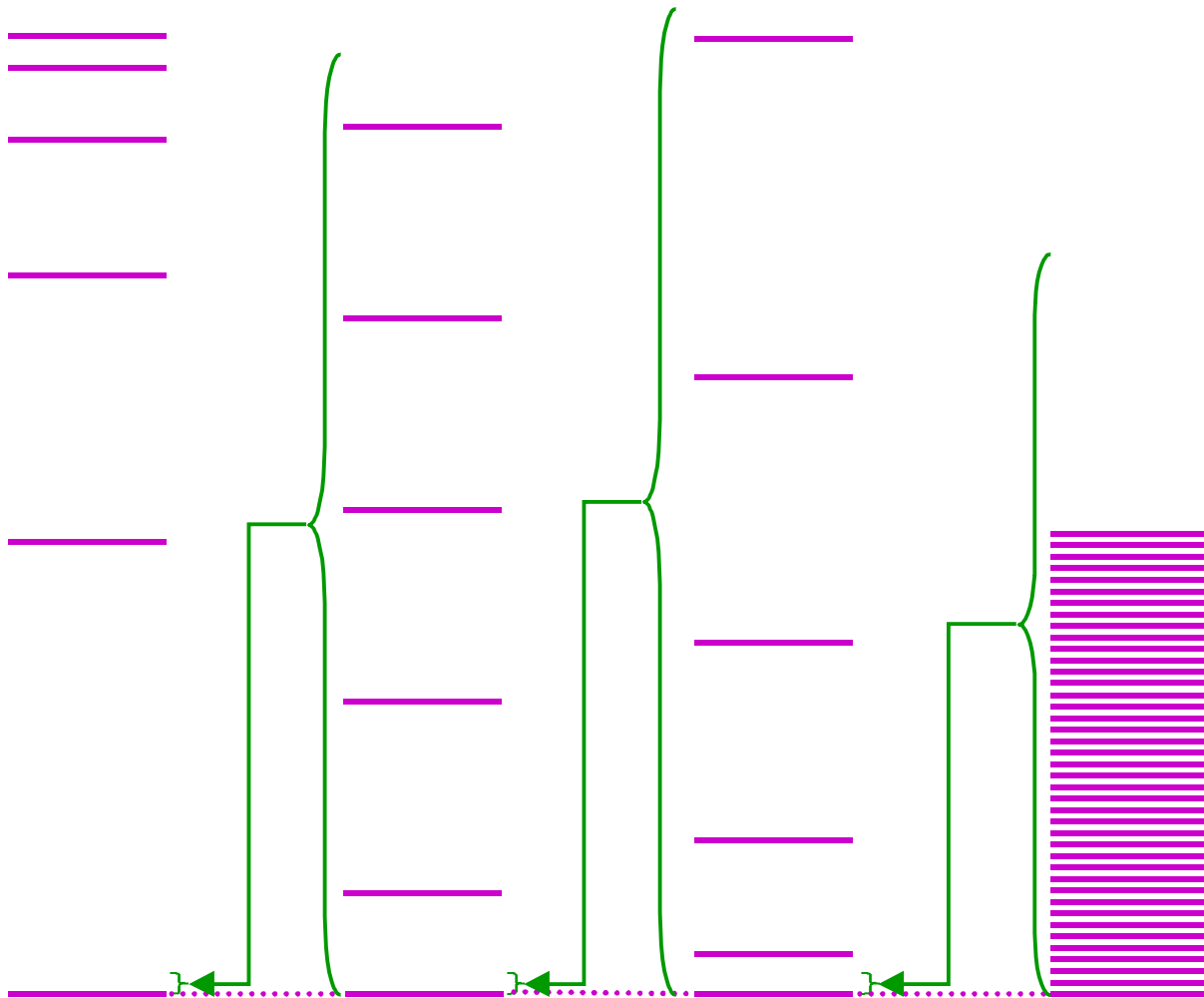
Wavefunctions  $\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$

Larger  $n$  and/or smaller  $a$  means sharper “wiggles”  
 $\rightarrow$  higher momentum and kinetic energy.

Wavefunctions of different energy (different  $n$ ) are **orthogonal**.

e.g.  $\int_0^a \psi_1 \psi_2 dx = \left(\frac{2}{a}\right) \int_0^a \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) dx = 0$

# Molecular Energy Levels



Electronic

Vibrational

Rotational

Translational

UV + visible

IR

microwave

$\sim 0$

$\lambda$ :  $10^{-9}$  -  $10^{-6}$  m

$10^{-6}$  -  $10^{-4}$  m

$10^{-4}$  -  $10^{-2}$  m

$\rightarrow \infty$

very long  $\lambda$  used in radio frequency spectroscopy  NMR

very short  $\lambda$  gamma rays used to probe nuclear energy levels





# Spectroscopy – Fundamentals

Frequency  $\nu$  Hz ( $\text{s}^{-1}$ )

$$\omega = 2\pi\nu \text{ rad s}^{-1}$$

Wavelength

$$\lambda = \frac{c}{\nu} \text{ m}$$

$$1 \text{ micron} = 1 \mu\text{m} = 10^{-6} \text{ m}$$

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

Wavenumber

$$\begin{aligned} \bar{\nu} &= 1/\lambda \text{ cm}^{-1} \\ &= \frac{\nu}{c} \text{ (Hz)} \\ &= \frac{\nu}{c} \text{ (cm s}^{-1}\text{)} \end{aligned}$$

$$c = 2.998 \times 10^{10} \text{ cm s}^{-1}$$

Emission and absorption spectroscopy are resonant processes.

$$\hbar\omega = h\nu = \Delta E$$

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

$$\hbar = h/2\pi$$

The intensities of spectral lines depend on...

population of states

Boltzmann distribution

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp(-\Delta E / kT)$$

transition probability

specific selection rules often depend on symmetry

path length and concentration

Beer-Lambert Law

$$\frac{I}{I_0} = \exp(-\epsilon[M]l)$$