Consider the Following

Determining Ψ - Solving the Schroedinger Equation.

- The wavefunction clearly contains vital information – how can we extract it?
- Schroedinger showed that the wavefunction is a solution to special kind of wave equation, which we now call the Schroedinger equation

$$\boxed{\hat{H}\Psi = E\Psi}$$

- This is actually the time independent Scroedinger equation. There is a time dependent version which will not concern us here.
- The symbol '*H* hat' is the Hamiltonian operator (see below) and *E* is the energy.
- This is a type of equation known as an eigenvalue equation, of the general form

$$\hat{G}f = gf$$

- *G hat* is an operator, *f* an eigenfunction and *g* a constant called the eigenvalue of the operator *G.*

Eigenvalue Equations - Operators

- Operators (unsurprisingly) operate on a function. For example

$$f = 2x \qquad \hat{G} = x\text{x (i.e. '}x\text{ times') so} \qquad \hat{G}f = 2x^2$$

alternatively

$$f = 2x \qquad \hat{G} = \frac{d}{dx}\text{(i.e. 'differentiate wrt }x\text{')} \qquad \hat{G}f = 2$$

- But neither of these are proper eigenvalue equations, which require the result of 'operation on *f*' to be *gf*, a constant times *f* Let's try another example

$$\hat{G} = 7\frac{d}{dx} + 5 \qquad f = e^x$$

- After a little thought

Choosing the Operator

- One of the postulates of quantum mechanics is that for every observable there is a corresponding operator.
- In chemistry we are mainly interested in energy, *E*. For all the problems we will encounter the energy can be expressed in terms of momentum and position, so we need the operators for *x* and *p*.

observable	**symbol**	**Operator form**
Position	x (or y or z)	$\hat{x}$
Momentum in x direction	p_x	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
Kinetic Energy, x direction	$\frac{mv^2}{2} = \frac{p_x^2}{2m}$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Potential energy, x coord.	V	$V(x)$

Setting Up the Schroedinger Equation – Free Particle Problem

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

'H hat' is the Hamiltonian, the operator for the observable energy, *E*
The total energy is kinetic (T) plus potential (V), so classically *H = T+V*
We cast these in their quantum mechanical operator form

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad V \to V(x) \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

Thus

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = E\Psi \quad or \quad -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + [V(x) - E]\Psi = 0}$$

For a free particle V(x) = 0, so the Schroedinger equations simplifies ro

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = E\Psi$$

A differential equation, which you have to solve for Ψ

Might now be a good time to revise some maths?

Clearly some calculus is going to be needed. It will be useful to remember the following results, where *C* is a constant of integration.

Function, *f(x)*	**Differential wrt to *x***	**Integral over *x***
constant, c	0	$cx + C$
x^a	ax^{a-1}	$\frac{x^{a+1}}{a+1} + C$
$\sin ax$	$a\cos ax$	$-\frac{1}{a}\cos ax + C$
$\cos ax$	$-a\sin ax$	$\frac{1}{a}\sin ax + C$
e^{ax}	ae^{ax}	$\frac{1}{a}e^{ax}$

The log form is often useful

$$\frac{d}{dx}\ln ax = \frac{1}{x} \qquad \int \frac{dx}{x} = \ln x + C$$

In many cases we make use of definite integration

$$\int_a^b f dx = [F(x)]_{x=a}^{x=b} = F(b) - F(a) \qquad e.g. \int_2^3 x^2 dx = \left[\frac{x^3}{3}\right]_2^3 = \frac{27}{3} - \frac{9}{3} = \frac{19}{3}$$

We will also have to make use of COMPLEX NUMBERS

e.g. $z = x+iy$ in which z is complex, x the' real part', y the 'imaginary part' (both real numbers) *and* $i = \sqrt{-1}$. Generally complex numbers conform to the rules of ordinary arithmetic.

To form the complex conjugate of a function f, f^*, replace i with $-i$ wherever it occurs, so $z = x + iy$, $z^* = x - iy$

Note that $zz^* = x^2 + y^2$, so is always real (so even if a wavefunction is complex $\Psi\Psi^*$, the probability, is real).

Finally we will find Eulers relation very useful. $\boxed{e^{i\theta} = \cos\theta - i\sin\theta}$

The form of the Schroedinger equation suggests that we look at differential equations

The 2nd order homogeneous equation

$$\frac{d^2y}{dx^2} + a\frac{dy}{dx} + by = 0$$

Has solutions of the form $y = e^{\lambda x}$

By substitution we obtain

$$e^{\lambda x}\left(\lambda^2 + a\lambda + b\right) = 0$$

Which for $\lambda \neq x \neq 0$ has solutions when the quadratic in brackets = 0, thus

$$\lambda_{1,2} = \frac{1}{2}\left(-a \pm \sqrt{a^2 - 4b}\right)$$

$$y_1 = e^{\lambda_1 x} \qquad y_2 = e^{\lambda_2 x}$$

The general solution is always a combination of these two

$$\boxed{y = c_1 e^{\lambda_1 x} + c_2 e^{\lambda_2 x}}$$

A very important case is $a = 0$, $b = \omega^2$

$$\frac{d^2y}{dx^2} + \omega^2 y = 0$$

Which (see above) has the general solution

$$y = c_1 e^{i\omega x} + c_2 e^{-i\omega x}$$

Or, using Euler's relation

$$y = d_1 \cos\omega x + d_2 \sin\omega x$$

Back to the free particle problem

We found the appropriate form of the Schroedinger equation to be

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = E\Psi$$

Which we can re-write as

$$\frac{\partial^2\Psi}{\partial x^2} + k^2\Psi = 0$$

$$k^2 = \frac{2mE}{\hbar^2}$$

We now know the solution to be

$$\Psi = d_1 \cos kx + d_2 \sin kx$$

Which is fine, but we need to know values for d_1 and d_2. These can often be found by imposing boundary conditions, e.g. $\Psi = 0$ when $x = 0$. This yields $\Psi = d_1\cos kx$. The wave function is a simple sine wave.
This places no restrictions on the value of k, which means E can take any positive value. Thus for a free particle energy is unquantised.

Some practice with eigenvalue equations

Which of the following three is an acceptable eigenfunction of the operator d/dx? What is the eigenvalue?
(a) sin$x$ (b) kx^2 (c) e^{kx}

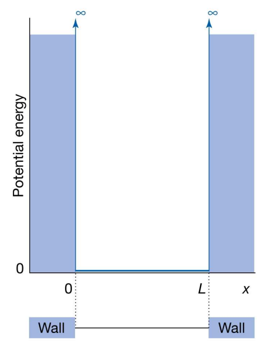
Show that f = a.exp(-bx) is an eigenfunction of the operator d^2/dx^2

Normalise the
above wavefunction.

A Recipe for Quantum Mechanical Calculations

- Write down the total (kinetic plus potential) energy in terms of momentum and position
- Place it in the operator form to yield the Hamiltonian operator.
- Solve the resultant Schroedinger for the wavefunction, (using any relevant boundary conditions)
- Check that the result is normalised

Application – A Particle in a 1-Dimensional Box



A particle is trapped between infinitely high potential energy barriers at $x = 0$ and $x = L$ (i.e in a box of length L). Between 0 and L the potential energy is zero.

The kinetic energy is $p^2/2m$, and the potential energy is zero or infinite depending on location

Between $-\infty$ and 0 and L and ∞ $V = \infty$, which requires the operator $V = \infty$. That requires the solution either $E = \infty$ (impossible) or $\Psi = 0$ in that region (possible).

Between 0 and L we need only consider the kinetic energy ($V = 0$). Thus the Schroedinger equation is the same as for the free particle problem

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = E\Psi$$

Which we know solves as

$$\boxed{\begin{aligned}\Psi &= d_1 \cos kx + d_2 \sin kx \\ k &= \left(\frac{2mE}{\hbar^2}\right)^{1/2}\end{aligned}}$$

The constants d_1 and d_2

We can specify the wavefunction a little more precisely, using some boundary conditions.

We know that Ψ must be continuous, so that (a) $\Psi = 0$ at $x = 0$ and (b) $\Psi = 0$ at $x = L$ What does this imply for our wavefunction?

(a)

$$\Psi = d_1 \cos kx + d_2 \sin kx = 0 \text{ when } \quad x = 0$$
$$d_1 \cos k0 + d_2 \sin k0 = d_1 + 0 = 0$$
$$d_1 = 0$$

(b)

$$\Psi = d_2 \sin kx = 0 \text{ when } \quad x = L$$
$$d_2 \sin kL = 0 \text{ when } \quad kL = n\pi$$
and n is an integer

The Solutions

We have obtained an expression for the energy from $kL = n\pi$, sub for k, rearrange

$$\boxed{E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}}$$

The energy is quantized (n dependence, n = 1,2,…) and the energy depends on the size of the box

We also have a (nearly) complete wavefunction (which is pure real)

$$\boxed{\Psi = d_2 \sin\left(\frac{2mE}{\hbar^2}\right)^{1/2} x}$$

Which can be completed by substituting for E and using the normalisation condition

$$d_2^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = 1$$

integrating and rearranging, using some trig.

$$d_2 = \left(\frac{2}{L}\right)^{1/2} \text{ so finally } \Psi = \left(\frac{2}{L}\right)^{1/2} \sin \frac{n\pi x}{L}$$

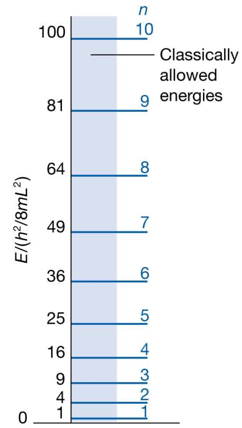
Properties of the solutions: Energies

The particle in a box can only occupy certain discrete energy levels, n = 1,2,3…

This is a quite different result to that for a classical particle (where any energy is allowed) and for a free particle (which is unquantised).

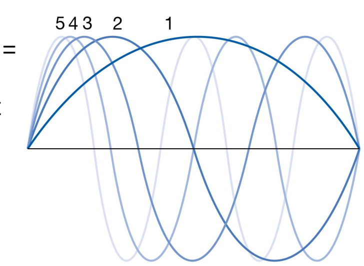
The energy increases for increasing n

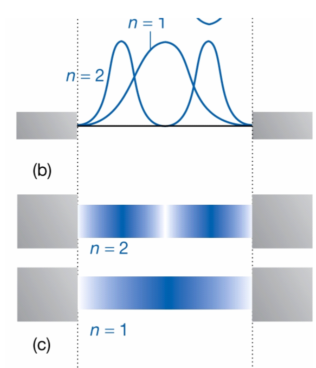
The separations between the energy levels is larger for larger n.



Properties of the solutions: Wavefunctions

For n = 1 the wavefunction has a maximum at x = L/2
For n = 2 the wavefunction goes through zero at L/2
Which is referred to a a node.
Again very different to the classical result





Consequently, for n = 1 the probability of finding the particle at L/2 is large, but for n = 2 it is zero.

For very large n the probability of finding the particle is the same throughout L, as it is for a classical particle. This is an example of the Bohr correspondence principle – for large quantum numbers QM recovers the classical result.