Schrödinger's equation and the wave function

Wave functions

The wavefunction contains all the vital information about a particle. The wavefunction is given as the symbol Ψ. The wavefunction has a highly specialised value. This is due to the fact that it must stay as a constant and also any operators need to remain the same.

Schrödinger's time independent equation is one the most recognised quantum mechanical equations.

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

The differential equation

All wave functions are solutions to a single differential equation:

$$\frac{d^2\Psi}{dx^2} = -k^2\Psi$$

It is easy to see how this gives a continuous wave as it measures the direction of the gradient. This means that when one value is positive the double differential becomes negative bringing the value back down. This forms a constant wave.

As we know from past experience the energy of a wave is given as:

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

This can be substituted to:

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

Therefore:

$$\frac{d^2\Psi}{dx^2} = -\frac{2Em\Psi}{\hbar^2}$$

Which then becomes:

$$\frac{d^2\Psi}{dx^2}\left(\frac{\hbar^2}{2m}\right) = E\Psi$$

Now that's fucking sexy.

Now the total energy of the system may be made from a potential and a kinetic amount this equation above shows a perfect system where all energy is kinetic so all energy below must be:

$$\frac{d^2\Psi}{dx^2}\left(\frac{\hbar^2}{2m}\right) = (E - V)\Psi$$

It is important to remember that only energy that the particle has as kinetic energy effects how it forms a wave.

<u>Quantum mechanical operators</u>

Quantum mechanical operators act on the wave function to give back the original wave function multiplied by a scalar value λ. This is called an eigenvalue equation. The eigenvalue λ is always a real value as it corresponds to a real observable (e.g. energy).

This then leaves work to be carried out with operators and as the wavefunction is a vector this normally involves: translation, rotation, stretching or some form of derivative. This helps to describe how a specific operator can be used to the wavefunction to give a specific property of the system such as energy, position, angular momentum.

The wavefunction describes how the state of the system changes with space and time, the remaining enigenvalue are then considered together giving the number that corresponds to a value of energy, poisiton, momentum etc.

Depending on the value wanted a different operator is used. These operators all extract a different observable function and are therefore highly important in quantum mechanical operations.

When the wavefunction is plotted on a graph it must be a smooth curve and must not tend to infinity in the range specified. If the equation tends to infinity then it is considered undefined and cannot therefore be used for physical calculations.

The two wavefunctions shown below are examples of where there is a discontinuous point and a multiply valued area. The discontinuous point would have either a infinite or zero gradient and therefore the dervitive of the wave function would be un-resolved.

The graph that crosses back on itself has two Y values for the same value of x. When this is made to equal probability there are two values of probability for the particle showing up in the same space. This is impossible and is therefore not allowed by quantum mechanics.

(c)

Multiply valued

(b)
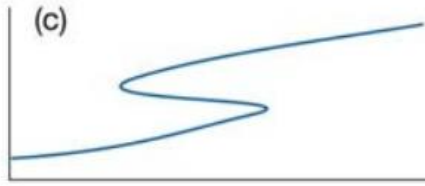
Discontinuous

This doesn't leave many possibilities for a quantum mechanical operator.

<u>Wave functions explained in molecules and Schrödinger's equation</u>

Due to the diffraction patterns caused by molecules during the young's slit experiments performed on molecules it was decided that the energy was quantized. The explanation of this though was hard to come across until Bohr proposed that the electrons acted like waves.

Now for the "huhh durr" stuff…

If a wave is travelling round in a circle the end of the wave and the beginning of the wave need to start and end in the same place. This means that only certain radii are actually "allowed" mathematically otherwise the wave would not link up causing the wave to not form. Simple. This was then explained by Bohr and represented in many equations after as being the integer n so often seen in wave equations.

This can be represented in Rydberg's equation:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1} - \frac{1}{n_2} \right)$$

This is where R_H is a constant for a hydrogenic atom and n1 and n2 are integers.

This can also be explained using Schrödinger's equation, this can be summarised with the "particle in a box" thought experiment:

The box represents a container that has ∞ potential outside of it and zero potential inside of it. This means that the electron cannot leave the container. The mathematical function for the electrons is represented as a continuous function (strings do not have kinks in). This means that the wave-function must be zero at the boundaries; due to this there are only a certain number of waves that can actually occur in between the two boundaries. This means that only certain frequencies (therefore energies) are allowed.

So in the region:

$$0 \leq x \leq L$$

$$U(x) = 0$$

This means that the wave function must satisfy:

$$-\frac{\bar{h}^2}{2m}\frac{d^2\psi(x)}{dx^2}$$

This then leaves the possible wavelengths equal to:

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

$$\lambda = \frac{2\pi}{k} = \frac{2L}{n}$$

This is where n is an integer.

The possible energy levels that can then be formed correspond to the integer squared multiplied by the energy of the ground state.

$$n^2 E_1 = E_n$$

Setting up the Schrödinger equation

The equation can only be set up by finding out the Hamiltonian operator.

As the Hamiltonian operator represents the observable energy of a system the operator must represent both potential and kinetic energy. This means that the operator can be represented as $H = T + V$. This is where T is the kinetic energy of the system and V is the potential energy of the system.

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\delta^2}{\delta x^2} + V(x)$$

This then leaves the operator as:

$$-\frac{\hbar^2}{2m}\frac{\delta^2\Psi}{\delta x^2} + V(x)\Psi = E\Psi$$

Schrödinger then assumed that the particle was free in space and therefore there was no potential energy in the system.

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

The differential equation is solved for Ψ.

This equation can be manipulated and shown as a constant.

$$\frac{\delta^2\Psi}{\delta x^2} + k^2\Psi = 0$$
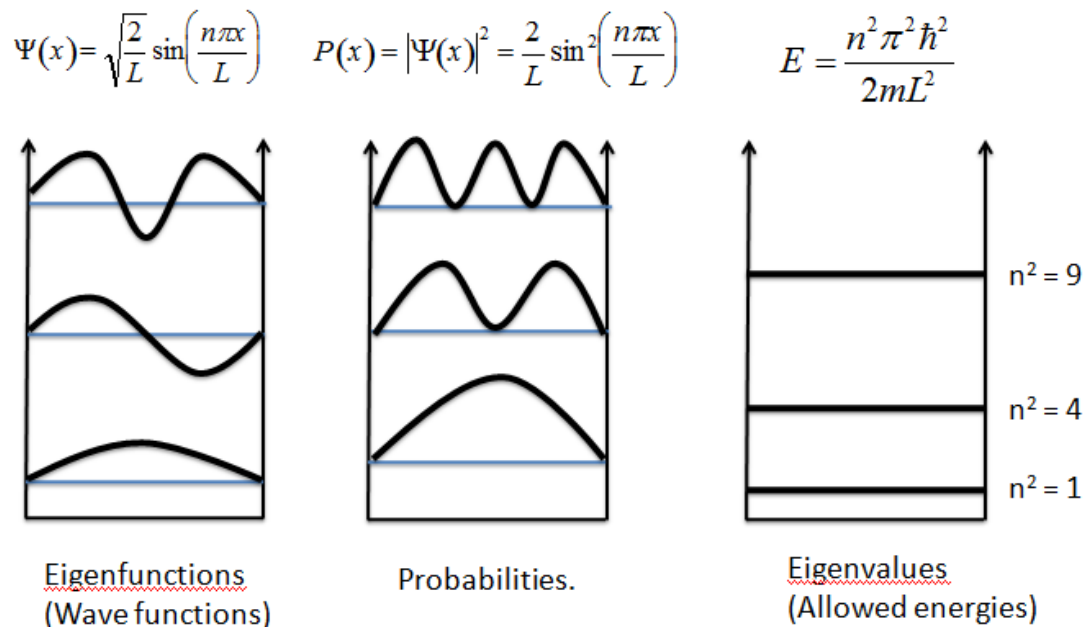
$$k^2 = \frac{2mE}{\hbar^2}$$

With these constants in place the Schrödinger equation can be mapped as a wave function.

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

Every equation has a real and imaginary part of the wavefunction. This is represented as:

$$\psi\psi^*$$

When these are multiplied together the answer is always real. This means that the observable of a wavefunction can always be found.

$$\Psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \qquad P(x) = |\Psi(x)|^2 = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right) \qquad E = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Eigenfunctions
(Wave functions)

Probabilities.

Eigenvalues
(Allowed energies)

$n^2 = 9$

$n^2 = 4$

$n^2 = 1$

The waves above show where the molecule can or can't be. For the wave at $n^2=1$ the electron will be predominantly found in the middle of the box and will not be seen at the sides. This continues with the electron being found at the peaks of the waves and not at the nodes.

As each Eigenvalue represents a higher energy level as particles gain more energy the positions in which they can be found across the box become more spaced and better distributed. This then

allows normal sized molecules, which have a comparatively massive energy to be positioned at almost any point along the box. This is because the frequency will be so high that there will be many peaks occurring in one phase meaning the molecule can be everywhere (basically).

<u>Differential forms of the Schrödinger equation</u>

This form of the Schroedinger equation is known as the homogeoneous equation with the solution:

$$y = e^{\lambda x}$$

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

The solution to the equation:

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

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

This leaves the following solutions:

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

When there are two solutions to a wavefunction it is assumed that the wavefunction takes a mixture of the two.

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

A special form of this equation is where:

$$a = 0 \text{ and } b = \omega^2$$

Which has the solution (where the constants are given from the solutions of 0 and ω^2)

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

This according to Euler's relation is:

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

When this is related to the free particle version of the Schrödinger equation it is found that the cosine function is equal to 0 when a boundary condition is imposed. This gives the wavefunction being a simple sin wave.

$$\Psi = d_1 sinkx$$

As the wavefunction is now a simple sine wave there is no restriction placed on k meaning that this wavefunction can take any form. As this is a free particle that can take any form this process makes sense.

It is recommended that the particle in a box document is referred to. This contains important calculations that derive some of the properties of the particles in a box.

<u>Other manipulations of wavefunctions</u>

It is important that where two eigenfunctions of the same operator are associated the net product must be orthogonal.

This means that when two valid wavefunctions are placed together the net overlap of the particle needs to be zero. This does not mean they have to form a straight line but that the total integration of the wavefunctions is equal to 0.

<u>Mean values</u>

It is also important to remember how a mean value can tell the observer a lot about the wave function. This can be found when the