Physical Chemistry

Particle in a box

The particle in a box theory is heavily related to the Schrödinger equation and this should be heavily referenced when this theory is being assessed. The particle in a box can be used practically when the electron movements through a conjugated system is being calculated. Also "building up the wave equation" should be considered at all times.

The basics

The particle in a box theory is based on the idea that a particle (quantum or otherwise) can be held in a box with an infinite potential on either side of it. This stops any possibility of the molecule leaving.

This also imposes certain boundary conditions on the molecule. Assuming that one side of the box is labelled 0 and the other side of the box is a distance of L across. The molecule must have a node at either side of these. This means that a node must be present at 0 and a node present at L. This means that the length of the box has an effect; this is useful as it gives another potential variable. This is important otherwise there would be a **discontinuity** in the wave function, this cannot occur.

It is also useful to know that it is impossible for the molecule to be found outside of the box. This means that there is a 100% chance of the molecule being found at one point.

The equation

$$\Psi = Ae^{ikx} \pm Ae^{-ikx}$$

This equation is explained in a large amount of detail in "building a wave function".

The substitution of the expondential term, puts the equation into a easier to understand:

$$\Psi = A[(\cos kx + i\sin kx) \pm (\cos(-kx) + i\sin -kx)]$$

$$A[(\cos kx + i\sin kx) \pm (\cos kx - i\sin kx)]$$

$$2A\cos kx \ OR \ 2Ai\sin kx$$

The boundary conditions of this equation are only satisfied when:

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

Where L is the length of the box.

This still leaves 2 possible equations for the wavefunction. As explained above a parameter is set of x=0.

This gives:

$$At\ x = 0\ or\ x = L$$

$$2A\cos\frac{n\pi}{L}(0) = 0 \ or \ 2A\cos\frac{n\pi L}{L} = -1$$

This means that the wavefunction cannot be mapped using the cos function.

$$2iA\sin\frac{n\pi}{L}(0) = 0 \ or \ 2iA\sin\frac{n\pi L}{L} = 0$$

This means that the wavefunction for a particle in a box is:

$$\Psi = N\sin\left(\frac{n\pi x}{L}\right)$$

This is where:

$$N = 2iA$$

Applications of this equation

When this equation is taken the formula for finding the observable needs to be taken and then applied to the wavefunction equation. Keeping the constants the same.

A particle can have a kinetic energy E of:

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

It has been shown above that:

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

This means that:

$$E = \frac{\hbar^2 n^2 \pi^2}{L^2 2m} = \frac{n^2 h^2}{8mL^2}$$

Normalisation

This leaves an interesting point to what N represents.

It is known as the normalisation constant and its value is determined with the knowledge that the particle must occur in the box. This is represented by the integration of the probability of finding an electron in the box:

$$\int_{x=0}^{x=L} \Psi^* \Psi \, dx = 1$$

We also know what the wavefunction is:

$$\int_{x=0}^{x=L} \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

This needs to be integrated so:

$$\sin^2 x = \frac{1}{2}(1 - \cos 2x)$$

$$N^2 \int_{x=0}^{x=L} \frac{1}{2}\left[1 - \cos\frac{2n\pi x}{L}\right] dx = 1$$

Which after integration becomes:

$$\frac{1}{2}N^2\left[L - \left(\frac{L}{2n\pi}\right)[\sin(2n\pi) - \sin 0]\right] = 1$$

$$\frac{1}{2}N^2\left[L - \left(\frac{L}{2n\pi}\right)[0 - 0]\right] = 1$$

$$\frac{1}{2}N^2 L = 1$$

$$N = \sqrt{\frac{2}{L}}$$

Therefore the wavefunction has been normalised!!!

$$\Psi = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

Mean values

The mean value of the wavefunction for it being found at any point along the length of the box is represented by the equation:

$$\int \Psi^* G \Psi \, d\tau$$

$$\int_0^L \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\frac{\pi x}{L} x \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\frac{\pi x}{L}$$

$$\left(\frac{2}{L}\right)\int_0^L x \sin^2\frac{\pi x}{L}$$

Now it is known that the integral of this by parts:

$$x = \frac{L}{2}$$

No surprise there then.

Probabilities

In normalising the wave function we used some interesting methods for finding some real values when the rest of the wavefunction was being compared.

If a probability of a wavefunction between two points needs to be found then the following equations have to be used:

$$\int \sin^2 ax = \frac{x}{2} - \frac{1}{4a}\sin 2ax$$

This is a really important equation to remember and I don't really know where ti came from JUST REMEMBER!

<u>The use of particle in a box for π conjugated molecules</u>

Using some assumptions from a particle in a box to a conjugated polymer:

- The polymer moves in 1D (it doesn't there is no-linearality to the motion.
- Electrons move independently from one another (they don't but very close to)
- Electrons fill orbitals according to Pauli principle.

Assuming that an electron can travel from one side of the molecule to another with little hinderance the molecule can be treated as a box.

To do this a molecule needs to be found: retinal has 12 conjugated carbon atoms and therefore 6 double bonds. It can be assumed that all of the central atoms donate 1 whole length and the end atoms ½. Using the equation for energy the following equation can be made:

$$E = \frac{n^2h^2}{8mL^2}$$

Now we have established that L=11 but what about n? It is known that 12 atoms have donated electrons so the HOMO is 6 and the LUMO is 7. This means the equation is:

$$\frac{h^2}{8mL^2}(7^2 - 6^2) = E$$