Some other manipulations with wavefunctions: orthogonality

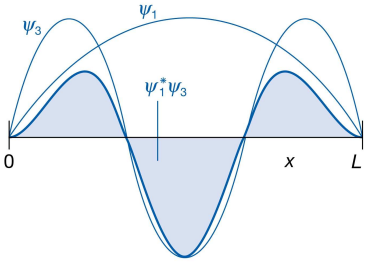
If two eigenfunctions of the same operator are associated with different eigenvalues then the two eigenfuntions must be orthogonal.

What does it mean?????

Two valid wavefunctions giving different energies have a net overlap of zero.

$$\int \Psi_1^* \Psi_2 d\tau = 0$$

This condition again severely limits the number of allowed wavefunctions.



Some other manipulations with wavefunctions: mean values

A further very useful piece of information we may extract from the wavefunction is the mean value of an observable.

To do this we evaluate the integral over all space of the complex conjugate of the wavefunction x the operation of the operator of the observable on that wavefunction, or, more succinctly

$$\int \Psi^* \hat{G} \Psi d\tau$$

Where it has been assumed the wavefunction is normalised

What is the average position of the particle in the n = 1 level of a particle in a box?

$$\int_0^L \frac{2}{L} \sin\frac{\pi x}{L} \bullet x \bullet \frac{2}{L} \sin\frac{\pi x}{L} dx = \frac{2}{L} \int_0^L x \bullet \sin^2 \frac{\pi x}{L} dx$$

$$\text{by parts} = \frac{L}{2} \text{(no surprise there then)}$$

Some other manipulations with wavefunctions: Probabilities

We interpret the integral over ΨΨ* as the probability. If we put limits on the integral we can find the likelihood that our particle is in a particular region.

What is the probability of finding the particle in the middle third of the box in the n = 1 state?

We need to integrate ΨΨ* between L/3 and 2L/3

$$\int_{x=\frac{L}{3}}^{x=\frac{2L}{3}}\left[\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\right]^2 dx=\left(\frac{2}{L}\right)\int_{x=\frac{L}{3}}^{x=\frac{2L}{3}}\sin^2\frac{\pi x}{L}\,dx$$

$$\text{use the standard integral } \int\sin^2 ax=\frac{x}{2}-\frac{1}{4a}\sin 2ax$$

$$\left(\frac{2}{L}\right)\left[\frac{x}{2}-\frac{L}{4\pi}\sin\frac{2\pi x}{L}\right]_{x=\frac{L}{3}}^{x=\frac{2L}{3}}=\left[\frac{2}{3}-\frac{1}{2\pi}\sin\frac{4\pi}{3}\right]-\left[\frac{1}{3}-\frac{1}{2\pi}\sin\frac{2\pi}{3}\right]$$

$$=0.33+1.732/\pi=0.88$$

What have we learned?

- We can set up the Schroedinger equation for a simple system, and solve it.
- We can determine the form of the wavefunctions.
- We can calculate the energy levels of that system.
- We find that the energy levels reveal a rich energy structure, compared to the uninteresting classical results.
- We can take the wavefunctions and use them to calculate the mean value of any observable and the probability of finding our particle within particular bounds.
- Can we apply it to any significant chemical system?
- Yes – the electronic spectroscopy of polyenes are quite well represented by this model.

Electronic Spectra of Polyenes

We can treat polyenes as electrons in 1D boxes, with some assumptions

- The electron moves in 1D (polyenes are slightly nonlinear)
- Electrons move independently (they don't but, as we see it's near enough).
- Electrons fill levels according to the Pauli principle (2 per level).

Consider the electronic spectra of butadiene ($CH_2CH_2CH_2CH_3$).

- Take the average carbon-carbon bond length as 0.14 nm.
- There are 4 π electrons, filling the n = 1 and 2 levels.
- What is the energy of the first transition (n = 2 → n = 3)?

The Calculation is Straightforward

We will need the mass of the electron (9.11 x 10^{-31} kg), the value of $\hbar$ (1.05 x 10^{-34} Js) and the length of the box (=4 x 0.14 nm = 0.56 nm).

$$\Delta E = \frac{\pi^2\hbar^2}{2mL^2}\left(n_u^2 - n_l^2\right) = \frac{\pi^2\hbar^2}{2mL^2}\left(3^2 - 2^2\right)$$

$$= \frac{(3.14)^2(1.05\bullet10^{-34}\,Js)^2(5)}{2\bullet9.11\bullet10^{-31}kg\bullet(0.56\bullet10^{-9}\,m)^2} = 9.5\bullet10^{-19}\,J$$

Using $E = h\nu$ we find ν = 1.43 x 10^{15} s^{-1} and $\nu = c/\lambda$ we find λ = 208 nm

The experimental value is 217 nm, excellent agreement!

One swallow does not a summer make – try retinal

retinal is involved in many important photobiological reactions. It has 12 conjugated carbon atoms (6 double bonds). Calculate the wavelength of the first absorption.

Other quantised systems

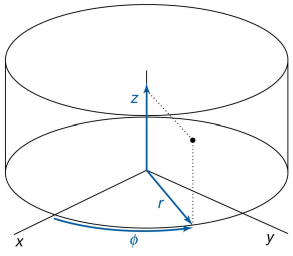
Motion in 2D and 3D boxes. The treatment is the same, but the results more complex, e.g. for a 3D box

$$E = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \frac{\hbar^2}{2m}$$

Rotational Motion – imagine a particle moving on a frictionless ring of radius *r* in the xy plane. Again we have $V = 0$, and kinetic energy $J^2/2I$, where J is the angular momentum and I the moment of inertia. To obtain the Hamiltonian we can work in 2 Cartesian coordinates of one polar coordinate

$$\hat{H} = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \text{ or } \frac{-\hbar^2}{2I} \frac{d^2}{d\phi^2}$$

Where the angles are defined in the fihure. The latter is clearly easier to deal with.



Other quantised systems

The Schroedinger equation becomes

$\frac{-\hbar^2}{2I}\frac{d^2\Psi}{d\phi^2} = E\Psi$ which rearranges as

$\frac{d^2\Psi}{d\phi^2} + k_l^2\Psi = 0$ with $k_l = \left(\frac{2IE}{\hbar^2}\right)^{1/2}$

which is a form well known to us, with solution

$\Psi = Ce^{im_l\phi}$ where $m_l = \pm k_l$

normalising yields $\Psi = \frac{1}{(2\pi)^{1/2}}e^{im_l\phi}$

the boundary condition is $\Psi(0) = \Psi(2\pi)$ for a continuous function

This requires $m_l = 0, \pm 1, \pm 2...$

Rotation is quantized

Other quantised systems

- Later we will see that vibrational motion is quantised.
- We will not show here that an extension of the particle in a ring argument to the Hydrogen atom (including a Coulombic *V* term) yields an exactly solvable Schroedinger equation, This is turn yields the wavefunctions of the H atom, the s, p, d… orbitals, and hence all of molecular structure.
- Next we consider the problem of quantum mechanical tunnelling.