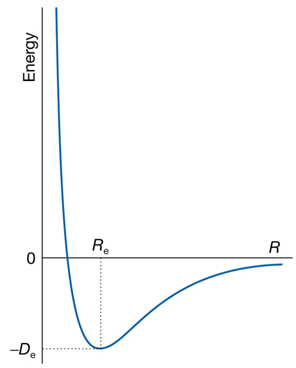
The Born Oppenheimer Approximation

- We have solved for a set of energies as a function of nuclear coordinates (the SHO).
- We have done the same for electron energy levels (e.g. the pi electrons in the polyene box).
- In general then we have to solve a Schrödinger equation for molecules where the wavefunction has both nuclear and electronic coordinates. This is very hard (terms in electron and nuclear KE!)
- Fortunately nuclei move much more slowly than electrons (ca 1000 times). This means that we can regard the nuclei as fixed while we calculate the electron energies (bond strength, electronic spectra, etc.) associated with that nuclear configuration.
- This is called the Born-Oppenheimer approximation – the separation of electronic and nuclear motion.
- If we calculate the electron energy for each (fixed) set of nuclear coordinates we end up with the potential energy surface.



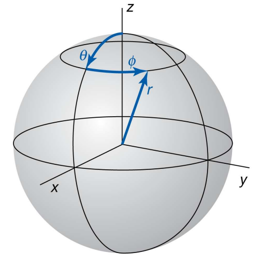
Schroedinger Equation For the Hydrogen Atom

Difficulties?

There are two particles (therefore 2 sets of coordinates) to deal with. We can show that this is not really a problem – locate the origin of the coordinate system on one particle (e.g. the proton) and only look at relative position of the electron.

The potential term is now distant dependent (it is a Coulomb potential). This makes the math hard.

We have to worry about motion in 3D (*x.y.z* coordinates). It turns out to be easier to think in terms of N-e distance *r* and TWO polar angles (Θ, Φ).



Leaving us to solve the Schroedinger equation…

$$\frac{\hbar^2}{2\mu}\left\{\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right]+\frac{1}{\sin^2\Theta}\frac{\partial}{\partial\Theta}\left[\sin\Theta\frac{\partial}{\partial\Theta}\right]+\frac{1}{\sin^2\Theta}\frac{\partial^2}{\partial\Phi^2}\right\}\Psi-r^2\left[E+\frac{Ze^2}{r}\right]\Psi=0$$

Where the Ze^2/r represents the coulombic attraction.

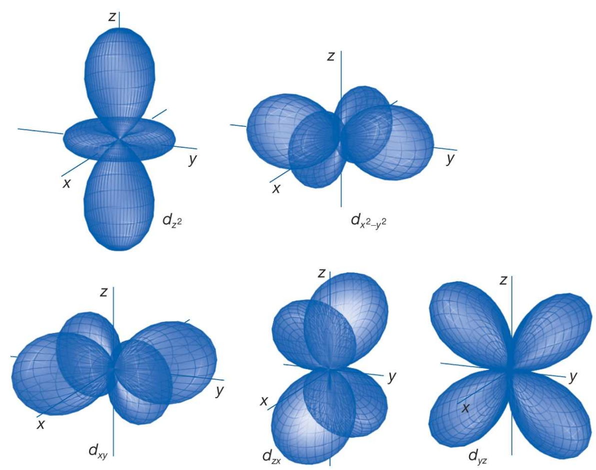
The equation has no less than three variables!

The solution is monumentally tedious, but involves breaking the equation down into three separate differential equations, each with only one variable, solving each, and then multiplying out the product.

The result is a keystone of chemistry, the atomic wavefunctions, whose form is well known.

Note that any more complex atomic problem is not **exactly** solvable – basically it is impossible to take into account the electron – electron terms. For the He atom and anything larger we rely on approximate methods (which are actually incredibly accurate, even for large molecules).

End of the line for exactly solvable Schrödinger equations…



The Heisenberg Uncertainty Principle revisited

Previousle (lecture 1) we stated the uncertainty principle in seemingly rather vague terms as

$$\Delta p.\Delta x \geq \hbar/2$$

In reality the 'uncertainty' is rather precisely defined as the standard deviation of the quantity, where the standard deviation, σ is the square root of the variance, which is the mean of the squares minus the square of the mean

$$(\Delta x)^2 = \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

Provided we know the wavefunction, we can easily calculate the mean or expectation, values. In general for the mean of an observable *g* we calculate

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

Mean Position

Restricting ourselves to the particle in a box, with n = 1 so $\Psi = \left(\frac{2}{L}\right)^{1/2} \sin\frac{\pi x}{L}$

We determined earlier that $\langle x \rangle = L/2$, as expected.

What about $\langle x^2 \rangle$? We need to evaluate the following

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

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

using the standard form $\int x^2 \sin^2 ax = \frac{x^3}{6} - \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right)\sin 2ax - \frac{x\cos 2ax}{4a^2}$

and making the definite integration

$$\langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2\pi^2}$$

Precise value of uncertainty in position is

$$(\Delta x)^2 = \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \left(\frac{L^2}{3} - \frac{L^2}{2\pi^2} \right) - \frac{L^2}{4}$$

$$= \frac{L^2}{12} - \frac{L^2}{2\pi^2}$$

$$\text{or } \Delta x = L \left(\frac{1}{12} - \frac{1}{2\pi^2} \right)^{1/2}$$

We can play the same game with **momentum**, e.g. if we wish to evaluate the mean momentum we need

$$\langle p_x \rangle = \int_0^L \left(\frac{2}{L} \right)^{1/2} \sin \frac{\pi x}{L} \cdot \frac{h}{i} \frac{d}{dx} \cdot \left(\frac{2}{L} \right)^{1/2} \sin \frac{\pi x}{L} \, dx$$

$$= \frac{2\hbar}{iL} \int_0^L \sin \frac{\pi x}{L} \frac{d}{dx} \sin \frac{\pi x}{L} \, dx = \frac{2\pi\hbar}{iL^2} \int_0^L \sin \frac{\pi x}{L} \cos \frac{\pi x}{L} \, dx$$

Which evaluates as zero!
No surprise, the particle has as much probability as going in the –*x* as the *x* direction, so the average must be zero.

Precise value of uncertainty in momentum is…

The relevant operator is $-\hbar^2(d^2/dx^2)$, so, using the same wavefunction the integral to be evaluated is of $\sin^2 ax$, which we have used before. Placing the proper limits yields

$$\langle p_x^2 \rangle = \frac{\pi^2 \hbar^2}{L^2} \quad \text{thus}$$

$$(\Delta p_x)^2 = \frac{\pi^2 \hbar^2}{L^2} - 0^2 = \frac{\pi^2 \hbar^2}{L^2}$$

$$\Delta p_x = \frac{\pi \hbar}{L}$$

So finally we can find

$$\Delta x \Delta p_x = L \left(\frac{1}{12} - \frac{1}{2\pi^2} \right)^{1/2} \frac{\pi \hbar}{L} = 0.57\hbar$$

In agreement with the uncertainty principle.

More Generally…

We can see that the uncertainty in position is a linear function of *L*, so for a longer box the uncertainty in position increases.

The converse is true for momentum, the uncertainty in momentum is largest for a small box. Thus there is a transfer of uncertainty as the box gets longer.

For the *n*th level of the 1D box we can find

$$\Delta x \Delta p_x = \hbar \left[\frac{n^2 \pi^2}{12} - \frac{1}{2} \right]^{1/2}$$

From which we conclude that the minimum uncertainty is for the lowest energy

Generalised uncertainty Principle

The uncertainty principle is even more general than we have implied. It does not only apply to position and momentum, but to any pair of complementary observables. A pair of observable are complementary if their operators do not commute. That is the order in which they are applied to the wavefunction makes a difference to the result. Mathematically

$$\hat{G}_1\left(\hat{G}_2 \Psi\right) \neq \hat{G}_2\left(\hat{G}_1 \Psi\right)$$

It is easy to see that this applies to position and momentum – which have multiplication and differentiate operators respectively. It makes a difference if you multiply by x before or after differentiation. In quantum mechanics we make use of the commutator

$$\left[\hat{G}_1, \hat{G}_2\right] = \hat{G}_1 \hat{G}_2 - \hat{G}_2 \hat{G}_1$$

and the most general uncertainty principle is

$$\Delta g_1 \Delta g_2 \geq \frac{1}{2} \left| \left\langle \left[\hat{G}_1, \hat{G}_2\right] \right\rangle \right|$$

Another important pair of complementary pairs is Energy and Time.

Conclusion

- The uncertainty principle is a rather precise tool.
- It does not make quantum mechanics, or spectroscopy, or molecular structure, or anything else ‘fuzzy’.
- On the contrary it puts precise limits on what we can know (and not know) about a system.