6.2 schroedinger in 3D spherical polars (cont)

we had that for any radially symmtectic potential $V(\underline{r}) = V(r, \theta.\phi) = V(r)$ then the wavefunction solution of the time independent Schroedinger equation $H\psi = E\psi$ separates into $\phi(\underline{r}) = R(r)\Theta(\theta)\Phi(\phi) = R(r)Y(\theta, \phi)$ where

$$\frac{1}{R}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R}{\partial r}\Big) - \frac{2mr^2}{\hbar^2}(V(r) - E) = -\Big(\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial Y}{\partial\theta}\Big) + \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\Big)$$

the rhs is a function only of r, the lhs is a function only of θ, ϕ. the only way these two can be equal to each other is if NEITHER has any r, θ, ϕ dependance i.e. its a constant.
and for ANY radial potential, the angular dependencies are the same! these functions are then very general and just tell us something about the spherical symmetry thats imposed by a radial potential. These functions Y are called spherical harmonics.
we can actually see what they are really all about by thinking of the special case of a rigid rotator. A particle of mass μ is attached to a rod of length a fixed at the origin but which can freely rotate about all axes. if there is no potential then $V = 0$. But there is no radial motion so all the radial derivatives vanish too. so the Schroedinger equation becomes

$$\frac{2ma^2}{\hbar^2}E = -\Big(\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial Y}{\partial\theta}\Big) + \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\Big)$$

but we can now see what all these angle terms are about - because this is fixed in radius, the kinetic energy can only be talking about angular motion - so we are really talking about angular momentum!!

7 Orbital angular momentum

7.1 cartesian coordinates

in 3D we can think about concepts involving angular momentum (in 1D by definition we can only do linear momentum!). We know from classical mechanics that the orbital angular momentum vector is $\underline{L} = \underline{r} \times \underline{p}$ where $\underline{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ is the posistion vector (in cartesian coordinates) and $\underline{p} = p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k}$ is linear momentum (also in cartesian coordinates).

$$\underline{L} = \underline{r} \times \underline{p} = (x\mathbf{i} + y\mathbf{j} + z\mathbf{k}) \times (p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k})$$
$$= xp_y\mathbf{k} + xp_z - \mathbf{j} + yp_x - \mathbf{k} + yp_z\mathbf{i} + zp_x\mathbf{j} + zp_y - \mathbf{i}$$
$$= (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k} = L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}$$

where

$$L_x = (yp_z - zp_y) \quad L_y = (zp_x - xp_z) \quad L_z = (xp_y - yp_x)$$

remembering back to operators, we replace x with $\hat{x} = x$ and p with $\hat{p_x} = -i\hbar\frac{\partial}{\partial x}$ so

$$\hat{L_x} = -i\hbar\Big(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\Big)$$
$$\hat{L_y} = -i\hbar\Big(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\Big)$$
$$\hat{L_z} = -i\hbar\Big(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\Big)$$

so $\underline{L} = -i\hbar(\underline{r} \times \underline{\nabla}) = \hat{L}_x\mathbf{i} + \hat{L}_y\mathbf{j} + \hat{L}_z\mathbf{k}$
All the operators $\hat{L_x}, \hat{L_y}, \hat{L_z}$ are Hermitian. We are not actually constraining both position and momentum along the same direction - we are constraining position along one axis, with the momentum along another axis!! and we can measure both of these together. Lets prove this eg for x and p_y

$$[x, p_y]\psi = (xp_y - p_yx)\psi = x. - i\hbar\frac{\partial\psi}{\partial y} - -i\hbar\frac{\partial}{\partial y}(x\psi) = -i\hbar(x\frac{\partial\psi}{\partial y} - x\frac{\partial\psi}{\partial y}) = 0$$

Heisenburg undertainty principle applies position and momentum along the SAME direction. any other orthoganoal direction is independent.
since these are Hermitian, their expectation values are real and their normalised eigenvectors are orthonormal.

7.2 combinations of Lx,Ly,Lz

As soon as we start trying to constrain combinations of these, then we run into trouble - its not hard, just keep your head and keep going!

$$[L_x, L_y] = [(yp_z - zp_y)(zp_x - xp_z)]$$

$$= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]$$

only position and momentum along the same coordinate have commutator $\neq 0$ e.g. $[x, p_x] = i\hbar$.

$$= [yp_z, zp_x] + [zp_y, xp_z] = yp_x[p_z, z] + xp_y[z, p_z] = -i\hbar yp_x + i\hbar xp_y = i\hbar L_z$$

likewise $[L_y, L_z] = i\hbar L_x$ and $[L_y, L_z] = i\hbar L_x$. These cannot be measured together.
so this all means that we cannot simultaneously measure all the components of L. we can't simultaneously know any pair of L_x, L_y, L_z. so is there any more information we can know about angular momentum together with one of its components?

7.3 Total angular momentum L^2

turns out that the thing we can measure alongside with one of the components is total angular momentum $L^2 = L_x^2 + L_y^2 + L_z^2$. This commutes with each of the components so $[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$. so we can measure any single component of angular momentum simultaneously with the total orbital angular momentum. We choose L_z as the one to measure along with L^2 because it has a relatively simple form compared to L_x and L_y in spherical polar coordinates. However, by choosing L_z and L^2 we know these commute, so they have a common set of eigenfunctions. so now we need to find them!!

7.4 Transformation to spherical polar coordinates

while we worked these out in cartesian coordinates, the real use of this will be in spherical polar coordinates. so we do the transformations with a lot of chain rule and get:

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$L^2 = -\hbar^2 \Big(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \Big)$$

AHA!!!! look at that!! L^2 is pretty much what we had in the spherical polar 3D Schroedinger equation!!!

$$\frac{1}{R}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R}{\partial r}\Big)-\frac{2mr^2}{\hbar^2}(V(\underline{r})-E)=-\Big(\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial Y}{\partial\theta}\Big)+\frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\Big)=\frac{L^2 Y}{\hbar^2 Y}$$

so now we can really see why we want to know about angular momentum!!!

7.5 Eigenfunctions of L_z

we were looking at the combination of $Y_{lm} = \Theta(\theta)\Phi(\phi)$. But since L_z only depends on ϕ we can solve this.
These must be of the form $L_z\Phi_m = m\hbar\Phi_m$ where we have put an $\hbar$ in for convienience

$$-i\hbar\frac{\partial\Phi_m}{\partial\phi} = m\hbar\Phi_m$$

$$\frac{\partial\Phi_m}{\partial\phi} = im\Phi_m$$

so $\Phi_m \propto e^{im\phi}$. When we normalise this we get $\Phi_m = (2\pi)^{-1/2}e^{im\phi}$
This equation is satisfied for any value of m, but in order for the solution to be single valued we require $\Phi_m(0) = \Phi_m(2\pi)$ i.e.

$$(2\pi)^{-1/2}e^{im0} = (2\pi)^{-1/2}e^{im2\pi}$$

$$1 = e^{im2\pi} = cosm2\pi + i\sin m2\pi$$

and this relation is satisfied only if $m = 0, \pm1, \pm2, \ldots$
Hence the eigenvalues of L_z are $0, \pm\hbar, \pm2\hbar\ldots$. Becasue the z-axis could be chosen to be along an arbitrary direction then the component of orbital angular momentum about ANY axis is quantised. m is called the magnetic quantum number, due to the role it plays in the response to a magnetic field.
since these are eigenfunctions, they are orthonormal.

$$\int_0^{2\pi}\Phi_n^*\Phi_m d\phi = \delta_{nm}$$

and we could write any function $f(\phi) = \sum c_m\Phi_m$