Quantum Chemistry

Corrections 5

1. *A particle in a spherically symmetric potential is in a state described by the wavefunction:*

$$\psi(x,y,z) = C(xy + yz + zx)e^{-\alpha r^2}$$

a. *What is the probability that a measurement of the square of the angular momentum ($\hat{L}^2$) yields zero?*

b. *What is the probability that it yields $6\hbar^2$?*

c. *If the value of l is found to be 2, what are the relative probabilities for m=-2,-1,0,1,2?*

Hint: write the wavefunction in terms of the spherical harmonics

The potential term of the Hamiltonian of this particle is spherically symmetric. Hence, the wavefunction can be separated into two parts, the radial (r) part and the angular (θ,ϕ) part. The part that depends only on (θ,ϕ) is simply the eigenvalue equation of the operator that we saw for the rigid rotator problem. Therefore, we know that the angular (θ,ϕ) part will be the eigenfunctions of the $\hat{L}^2$ operator (the spherical harmonics, $Y_l^m(\theta,\phi)$.).

To determine the probabilities required, we need to express our wavefunction $\psi(x,y,z) = C(xy + yz + zx)e^{-\alpha r^2}$ in polar coordinates using the following relation :

$$x = r\sin\theta\cos\varphi$$

$$y = r\sin\theta\sin\varphi$$

$$z = r\cos\theta$$

Which is :

$$\psi(r,\theta,\varphi) = Ce^{-\alpha r^2} r^2 (\tfrac{1}{2}\sin^2\theta\sin 2\varphi + \cos\theta\sin\theta\sin\varphi + \cos\theta\sin\theta\cos\varphi)$$

Note : The radial and the angular parts are separated because the potential is spherically symmetric.

Now we express the above wavefunction using the spherical harmonics :

$$\psi(r,\theta,\varphi) = Ce^{-\alpha r^2} r^2 . \left(i\sqrt{\frac{2\pi}{15}} Y_2^{-2} - i\sqrt{\frac{2\pi}{15}} Y_2^{2} + (1-i)\sqrt{\frac{2\pi}{15}} Y_2^{1} + (1+i)\sqrt{\frac{2\pi}{15}} Y_2^{-1} \right)$$

The wavefunction describing the state of our particle is therefore a linear combination of spherical harmonics describing the states (l=2, m=-2), (l=2, m=-1), (l=2, m=1), (l=2, m=2), in the eigenfunctions of $\hat{L}^2$.

Measurements obtained from the square of the angular momentum operator gives value according to the state (l,m) of the system : $L^2 = \hbar^2 l(l+1)$

a. We get L^2 =0 if l=0, thus $\mathrm{P}(l=0)=0$ because ψ is described only by spherical harmonics with l=2.

b. We get $L^2 = 6\hbar^2$ if l=2, thus $\mathrm{P}(l=2)=1$ because ψ is described only by spherical harmonics with l=2.

c. If $\psi(r,\theta,\phi) = f(r).\sum a_n Y$ is normalised, $\sum a_n Y$ is not ($\sum a_n^* a_n \neq 1$) so the probability of finding a certain m when we measure l=2 will be : $\dfrac{a_x^* a_x}{\sum a_n^* a_n}$

$$\mathrm{P}(m=-2/l=2) = \frac{2\pi/_{15} * 1}{2\pi/_{15}(2+2+1+1)} = 1/6 ,$$

$$\mathrm{P}(m=-1/l=2) = 1/3 ,$$

$$P(m=0/l=2) = 0 ,$$

$$\mathrm{P}(m=1/l=2) = 1/3 ,$$

$$\mathrm{P}(m=2/l=2) = 1/6$$