Lecture 7: Angular Momentum, Hydrogen Atom

1 Vector Quantization of Angular Momentum and Normalization of 3D Rigid Rotor wavefunctions

Consider $l = 1$, so $L^2 = 2\hbar^2$. Thus, we have $|L| = \hbar\sqrt{2}$. There are three possibilities for L_z depending on the value of m_l. We have $L_z = 0$, or $L_z = \hbar$ or $L_z = -\hbar$. For all of these, the length of angular momentum vector is $\hbar\sqrt{2}$. Thus, we have a vector whose length is $\sqrt{2}\hbar$ and whose projection on the Z-axis can take only 3 possible values. Thus, the angular momentum vector can either be in the X-Y plane or, anywhere on cones at angles of ± 45 degrees to the Z-axis. This is referred to as vector quantization of angular momentum. Similarly, we can work out for the $l = 2$ states.

In order to normalize the eigenfunctions of the rigid rotor Hamiltonian, we need to do an integral over the angles θ and ϕ. The conversion of the volume integral in 3D from Cartesian to spherical polar coordinates involves a Jacobian of transformation so that we have

$$dxdydz = r^2 \sin(\theta) dr d\theta d\phi$$

Thus the normalization condition for $\psi(\theta, \phi)$ is given as

$$\int_0^{2\pi} \int_0^{\pi} \psi^*(\theta, \phi) \psi(\theta, \phi) \sin(\theta) d\theta d\phi = 1$$

2 The Hydrogen Atom

Explaining the stability of the Hydrogen atom is one of the triumphs of the quantum theory. Treating the H-atom as a proton of mass m_p at $\vec{R}$ and an electron of mass m_e at $\vec{r}$, we can write the Hamiltonian as

$$\hat{H}(\vec{R}, \vec{r}) = -\frac{\hbar^2}{2m_p}\nabla_R^2 - \frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{1}{4\pi\epsilon}\frac{e^2}{|\vec{R} - \vec{r}|}$$

Using a change of coordinates to center of mass and relative coordinates, we can write for the relative motion

$$\hat{H}(\vec{r}) = -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{4\pi\epsilon}\frac{e^2}{r}$$

where the Laplacian is with respect to the relative coordinate and r is the distance between the electron and the nucleus. The reduced mass μ is given by

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \approx \frac{1}{m_e}$$

. In other words, we can approximate this system as a fixed nucleus and an electron orbiting about it.

The Laplacian can be written in spherical polar coordinates and now the potential depends only on r and not the angles. Thus we can write the Hamiltonian operator as

$$\hat{H}(r, \theta, \phi) = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\right) - \frac{1}{4\pi\epsilon}\frac{e^2}{r}$$

The Schrödinger equation

$$\hat{H}(r, \theta, \phi)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

is solved by separation of variables

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

. The angular part is exactly the spherical harmonics discussed in the rigid rotor problem. The radial part is denoted by $R(r)$ and is dependent on two quantumnumbers, the principal quantum number n and the azimuthal

quantum number l, which also appears in the spherical harmonics. Thus we have

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$$

We mention here the form of $R_{n,l}(r)$. You are not expected to remember this but it helps to understand the key parts of the wavefunction. For convenience we define $\rho = 2r/na_0$ where

$$a_0 = \frac{h^2\epsilon_0}{\pi m_e e^2}$$

is referred to as the Bohr radius and is equal to 0.529 Å. The radial part of the wavefunction can now be written as

$$R_{n,l}(r) = N_{n,l}\rho^l L_{n,l}(\rho)e^{-\rho/2}$$

where $L_{n,l}(\rho)$ is referred to as the associated Laguerre polynomial, a polynomial whose degree is $n-1$ and $N_{n,l}$ is the normalization constant. The first few wavefunctions are given below:

$$\begin{aligned}
n = 1, l &= 0, \ 1s \text{ orbital} \quad \psi_{1,0,0} = \text{R}_{1,0}(\text{r})\text{Y}_{0,0}(\theta,\phi)\\
&= 2\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}\left(\frac{1}{4\pi}\right)^{1/2}
\end{aligned}$$

$$\begin{aligned}
n = 2, l &= 0, \ 2s \text{ orbital} \quad \psi_{2,0,0} = \text{R}_{2,0}(\text{r})\text{Y}_{0,0}(\theta,\phi)\\
&= \frac{1}{8^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}\left(\frac{1}{4\pi}\right)^{1/2}
\end{aligned}$$

$$\begin{aligned}
n = 2, l &= 1, m_l = 0, \ 2p_z \text{ orbital} \quad \psi_{2,1,0} = \text{R}_{2,1}(\text{r})\text{Y}_{1,0}(\theta,\phi)\\
&= \frac{1}{24^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta
\end{aligned}$$

$$\begin{aligned}
n = 2, l &= 1, m_l = 1, \ 2p_1 \text{ orbital} \quad \psi_{2,1,0} = \text{R}_{2,1}(\text{r})\text{Y}_{1,0}(\theta,\phi)\\
&= \frac{1}{24^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta e^{i\phi}
\end{aligned}$$

$$n = 2, l = 1, m_l = -1, \ 2p_{-1} \text{ orbital} \quad \psi_{2,1,0} = R_{2,1}(r)Y_{1,0}(\theta, \phi)$$

$$= \frac{1}{24^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta e^{-i\phi}$$

The last two are combined to give the real $2p_x$ and $2p_y$ orbitals.

The energy of a state, however, depends only on the principal quantum number n and is given by

$$E_n = -\frac{m_e e^4}{8h^2 \epsilon_0^2 n^2}$$

The restrictions on the quantum numbers are as follows:

$$n = 1, 2, 3, \ldots \quad l = 0, 1, 2 \ldots n-1 \quad m_l = 0, \pm 1 \ldots \pm l$$

and they are referred to as principal, azimuthal and magnetic quantum numbers. The wavefunction $\psi_{n,l,m}$ is the wavefunction of a single electron and is referred to as an *orbital* or a *spatial orbital*.

Plotting of wavefunctions is a very powerful tool. Since the wavefunction depends on a 3D position of the electron, we prefer to plot the angular and radial parts separately. Since the angular parts have already been plotted before when we looked at rotational states, we plot the first few radial parts below.

Notice that for 1s and 2s, the wavefunction is maximum at the nucleus, but for 2p the wavefunction is zero at the nucleus. The corresponding plots of the square of the radial part can easily be plotted.

1s

2s

2p

3s

r

r

r

r