

## The Hydrogen Atom problem

The Hamiltonian for hydrogen atom, where electron of mass  $m_e$  is in the Coulomb field of the proton of mass  $m_p$ , is given by,

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_p} \nabla_p^2 + V(|\vec{r}_p - \vec{r}_e|), \quad V(|\vec{r}_p - \vec{r}_e|) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_p - \vec{r}_e|} \quad (27)$$

Hence the Schrödinger equation for hydrogen atom is

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_p} \nabla_p^2 + V(|\vec{r}_p - \vec{r}_e|) \right] \Psi(r_e, r_p) = E \Psi(r_e, r_p), \quad (28)$$

which cannot be solved by separation of variables  $\Psi(r_e, r_p) = \psi_e(r_e)\psi_p(r_p)$  because of the form of the potential. To get around this problem, the usual practice is to change over to relative and center-of-mass (cm) coordinates,  $(x_e, y_e, z_e)$  and  $(x_p, y_p, z_p) \rightarrow \vec{r} \equiv (x, y, z)$  and  $\vec{R} \equiv (X, Y, Z)$ ,

$$\vec{r} = \vec{r}_p - \vec{r}_e, \quad \vec{R} = \frac{m_e \vec{r}_e + m_p \vec{r}_p}{m_e + m_p} \quad (29)$$

In order to rewrite the hydrogen atom Schrödinger equation in terms of relative and cm coordinates we find that,

$$\begin{aligned} \frac{\partial \Psi}{\partial x_p} &= \frac{\partial \Psi}{\partial x} \frac{\partial x}{\partial x_p} + \dots + \frac{\partial \Psi}{\partial X} \frac{\partial X}{\partial x_p} + \dots = \frac{\partial \Psi}{\partial x} + \frac{m_p}{m_p + m_e} \frac{\partial \Psi}{\partial X} \\ \frac{\partial \Psi}{\partial x_e} &= -\frac{\partial \Psi}{\partial x} + \frac{m_e}{m_p + m_e} \frac{\partial \Psi}{\partial X} \\ \frac{\partial^2 \Psi}{\partial x_p^2} &= \frac{\partial^2 \Psi}{\partial x^2} + \left( \frac{m_p}{m_p + m_e} \right)^2 \frac{\partial^2 \Psi}{\partial X^2} \text{ etc.} \end{aligned} \quad (30)$$

The hydrogen atom Schrödinger equation now looks lot cleaner in terms of relative and cm variables and on top of that it can now be solved by separation of relative and cm coordinate variables,

$$\left[ -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 \right] \Psi(r, R) + V(r) \Psi(r, R) = E \Psi(r, R) \quad (31)$$

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}, \quad (32)$$

$$M = m_e + m_p, \quad \mu = \frac{m_e m_p}{m_e + m_p},$$

$$\nabla_r^2 \equiv \frac{\partial^2}{\partial x^2} + \dots, \quad \nabla_R^2 \equiv \frac{\partial^2}{\partial X^2} + \dots \quad (33)$$

$$\Psi(\vec{r}, \vec{R}) = \Phi(\vec{R}) \psi(\vec{r}) \quad \text{and} \quad E = E_r + E_{\text{cm}} \quad (34)$$

The Schrödinger equations for center-of-mass and reduced mass are,

$$-\frac{\hbar^2}{2M} \nabla_R^2 \Phi(\vec{R}) = E_{\text{cm}} \Phi(\vec{R}) \quad (35)$$

$$-\frac{\hbar^2}{2\mu} \nabla_r^2 \psi(\vec{r}) + V(r) \psi(\vec{r}) = E_r \psi(\vec{r}). \quad (36)$$

The center-of-mass equation (35) is just an equation for free particle and hence the center-of-mass of hydrogen atom is basically a free particle. The solution for relative coordinate equation (36) is the same as (13), *i.e.*

$$\psi(\vec{r}) \equiv \psi(r, \theta, \phi) = R(r) Y(\theta, \phi) = \frac{u(r)}{r} Y(\theta, \phi) \quad (37)$$

The angular and radial equations for hydrogen atom are,

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + l(l+1) Y = 0 \quad (38)$$

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + \left[ -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \right] u = E u \quad (39)$$

The angular equation (38) can be solved by further separation of variables  $Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$  and the two separated equations are,

$$\frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0 \quad (40)$$

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + [l(l+1) \sin^2 \theta - m^2] \Theta = 0 \quad (41)$$

Solving the  $\Phi$  equation is trivial,

$$\frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0 \Rightarrow \Phi(\phi) = A e^{im\phi} \quad (42)$$

$\exp(-im\phi)$  is not included in the solution of (42) because by making  $m$  both positive and negative can take care of that. Now, since the potential is symmetric in azimuthal angle  $\phi$ , we require,

$$\begin{aligned} \Phi(\phi + 2\pi) &= \Phi(\phi) \\ \rightarrow e^{im(\phi+2\pi)} &= e^{im\phi} \\ \text{or, } e^{i2m\pi} &= 1 \\ \Rightarrow m &= 0, \pm 1, \pm 2, \dots \end{aligned} \quad (43)$$

where  $m$  is known as *magnetic quantum number*. The normalization of  $\Phi$  determines the constant  $A$ ,

$$\int_0^{2\pi} d\phi |\Phi|^2 = 1 \rightarrow A^2 \int_0^{2\pi} d\phi = 1 \rightarrow A = \frac{1}{\sqrt{2\pi}} \Rightarrow \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (44)$$

Following residue theorem of complex integration, one can show orthogonality of  $\Phi(\phi)$ ,

$$\int_0^{2\pi} d\phi \Phi_m^*(\phi) \Phi_n(\phi) = \delta_{mn}.$$

The  $\Theta$  equation (41) can be solved using Frobenius method, and the solution is,

$$\Theta_l^m(\theta) = A P_l^m(\cos \theta), \quad (45)$$

where  $P_l^m(\cos\theta)$  is the associated Legendre polynomial of  $l$  degree and  $m$  order, and is generated by,

$$P_l^m(x) = (1-x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_l(x) \quad (46)$$

$$P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l (x^2-1)^l \quad (47)$$

where  $l$  is integer and known as *orbital angular momentum* quantum number and the magnetic quantum number  $m$  is restricted over  $-l \leq m \leq +l$ . Hence, the complete solution for the angular equation (38) is,

$$Y_{lm}(\theta, \phi) = N_{lm} e^{im\phi} P_l^m(\cos\theta), \quad (48)$$

where the normalized angular wave function  $Y_{lm}$  is called *spherical harmonics* and  $N_{lm}$  is the normalization constant. The orthogonality of angular wave function is stated as,

$$\int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}$$

An interesting consequence of the angular solution follows from the allowed values of  $m$  – the  $l$ -th eigenstate is degenerate and, because of  $-l \leq m \leq l$ , is  $2l + 1$ -fold degenerate. A few examples,

$$\begin{aligned} l = 0 \quad m = 0, \quad Y_{00} &= \sqrt{\frac{1}{4\pi}} \\ l = 1 \quad m = 0, \quad Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos\theta \\ m = \pm 1, \quad Y_{1\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} e^{\pm i\phi} \sin\theta \\ l = 2 \quad m = 0, \quad Y_{20} &= \sqrt{\frac{5}{16\pi}} (3 \cos^2\theta - 1) \\ m = \pm 1, \quad Y_{2\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \sin\theta \cos\theta \\ m = \pm 2, \quad Y_{2\pm 2} &= \sqrt{\frac{15}{32\pi}} e^{\pm i2\phi} \sin^2\theta \quad \text{etc.} \end{aligned}$$

The solution of the radial part (39) is rather illustrative since it leads to the quantization of energy in hydrogen atom, the thing that Bohr attempted using semi-classical treatment,

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2} \left[ E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] u = 0. \quad (49)$$

As is done in SHO, to cast the equation (49) in some standard form in terms of dimensionless variable, we attempt a change of variable,

$$\rho = \alpha r \quad \rightarrow \quad \frac{d}{dr} = \alpha \frac{d}{d\rho} \quad \text{and} \quad \frac{d^2}{dr^2} = \alpha^2 \frac{d^2}{d\rho^2}$$

The radial equation (49) now becomes,

$$\begin{aligned} \alpha^2 \frac{d^2u}{d\rho^2} + \left[ \frac{2\mu E}{\hbar^2} + \frac{\mu Z e^2 \alpha}{2\pi\epsilon_0 \hbar^2} \frac{1}{\rho} - \frac{l(l+1)\alpha^2}{\rho^2} \right] u &= 0 \\ \text{or, } \frac{d^2u}{d\rho^2} + \left[ \frac{2\mu E}{\alpha^2 \hbar^2} + \frac{\mu Z e^2}{2\pi\epsilon_0 \hbar^2 \alpha} \frac{1}{\rho} - \frac{l(l+1)}{\rho^2} \right] u &= 0. \end{aligned} \quad (50)$$

To simplify (50) let,

$$\alpha^2 = -\frac{8\mu E}{\hbar^2} \quad \text{and} \quad \lambda = \frac{\mu Z e^2}{2\pi\epsilon_0\alpha\hbar^2} = \frac{Z e^2}{4\pi\epsilon_0\hbar} \sqrt{\frac{-\mu}{2E}} \quad (51)$$

and the radial Schrödinger equation for hydrogen atom now in terms of dimensionless variable is,

$$\frac{d^2 u}{d\rho^2} + \left[ \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] u = 0 \quad (52)$$

At large  $\rho$ , the asymptotic form of the solution is obtained from (52) as  $\rho \rightarrow \infty$ ,

$$\frac{d^2}{d\rho^2} \approx \frac{u}{4} \quad \Rightarrow \quad u(\rho) \sim e^{-\rho/2}. \quad (53)$$

The next obvious thing is to determine the behavior at  $\rho$  small, because singularity here is at  $\rho = 0$ . But since such problem can still be dealt with Frobenius method, we assume the general form of the solution to be,

$$u(\rho) = f(\rho) e^{-\rho/2} \quad (54)$$

and consequently the radial differential equation in  $f(\rho)$  becomes,

$$\frac{d^2 f}{d\rho^2} - \frac{df}{d\rho} + \left[ \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right] f = 0 \quad (55)$$

The Frobenius method can be applied to solve the above equation (55), where  $f(\rho)$  can be expressed as,

$$f(\rho) = \rho^{s+1} \sum_{m=0}^{\infty} b_m \rho^m. \quad (56)$$

The reason behind additional power in  $\rho^{s+1}$  is the actual solution to radial Schrödinger equation is  $r R(r) = u(r)$ . Putting the power series solution (56) in equation (55), we find,

$$\begin{aligned} \sum_m [(m+s+1)(m+s)b_m \rho^{m+s-1} - (m+s+1)b_m \rho^{m+s} + \lambda b_m \rho^{m+s} - l(l+1)b_m \rho^{m+s-1}] &= 0 \\ \sum_m [\{(m+s+1)(m+s) - l(l+1)\} b_m \rho^{m+s-1} + \{\lambda - (m+s+1)\} b_m \rho^{m+s}] &= 0 \end{aligned} \quad (57)$$

Since the above (57) is valid for all powers of  $\rho$ , coefficients of each power of  $\rho$  can be equated to zero. The indicial equation is,

$$m = 0, \quad \text{and} \quad b_0 \neq 0: \quad s(s+1) = l(l+1) \quad \Rightarrow \quad s = l, \quad \text{or} \quad -l-1 \quad (58)$$

The  $s = -l-1$  is not acceptable since that would make the solution diverge at  $\rho = 0$ . In general for  $\rho^{m+s}$ ,

$$\begin{aligned} [(m+s+2)(m+s+1) - l(l+1)] b_{m+1} + [\lambda - m - s - 1] b_m &= 0 \\ \frac{b_{m+1}}{b_m} &= \frac{m+s+1-\lambda}{(m+s+2)(m+s+1) - l(l+1)} \end{aligned} \quad (59)$$

From the recursion relation (59) it follows that for  $s = l$  starting with  $b_0$  generates all the coefficients of the power series. However, just as in SHO, not all the solution so obtained are normalizable! For at very large  $m$ , the recursion formula (59) behaves as,

$$\frac{b_{m+1}}{b_m} \xrightarrow{m \rightarrow \infty} \frac{1}{m}. \quad (60)$$

If we compare the adjacent coefficients of the series  $e^\rho$ , it is exactly  $1/m$ , the one we got in (60) and therefore, asymptotically  $f(\rho)$  is behaving as  $e^\rho$  and in turn,  $u(\rho)$  in (54) as  $e^{\rho/2}$ , which diverges at large  $\rho$ . Hence our requirement of normalizable solution can be met if the series (56) is made to terminate at some highest  $m$ , say  $m = n_r$ , beyond which all coefficient  $b_{n_r+1}$  are zero. This results in,

$$\lambda = n = n_r + l + 1, \quad n_r = 0, 1, 2, \dots, \quad n = 1, 2, 3, \dots \quad (61)$$

The integers  $n_r$  and  $n$  are known as *radial quantum number* and *principle quantum number*. The *angular momentum quantum number*  $l$  can take values

$$l = 0, 1, \dots, n - 1 \quad (62)$$

The  $\lambda$  determines the energy of hydrogen atom (51) with  $Z = 1$  and is,

$$E = - \left( \frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{\mu}{2\hbar^2\lambda^2} \Rightarrow E_n = - \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{\mu}{2\hbar^2} \frac{1}{n^2}. \quad (63)$$

This is same as the Bohr's famous expression for hydrogen atom energy levels obtained semi-classically. Before deriving the wave functions of hydrogen atom, let us discuss the degeneracy in the energy of hydrogen atom. We know that the *azimuthal quantum number*  $m$  can take values in  $[-l, +l]$ , a total of  $2l + 1$ . The *orbital angular momentum quantum number*  $l$  can take values  $0, 1, \dots, n - 1$ , as total of  $n$ . Therefore, the total degeneracy of the energy level  $E_n$  is,

$$E_n \text{ degeneracy} : \sum_{l=0}^{n-1} (2l + 1) = 2 \cdot \frac{n(n-1)}{2} + n = n^2 \quad (64)$$

The ground state  $n = 1$  is obviously non-degenerate. Here we have neglected the spin of the electron, but if we include it by neglecting its all possible effects, the degeneracy is  $2n^2$ .

The hydrogen atom wave function, for the state with quantum numbers  $(n, l, m)$  is,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad (65)$$

The Bohr's radius is defined as

$$a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = 0.53 \times 10^{-10} \text{ m} \quad (66)$$

and in terms of Bohr's radius,

$$\alpha = \frac{2}{a_0 n} \rightarrow \rho = \frac{2r}{a_0 n}.$$

Let us construct a few wave functions for hydrogen atom before we generalize the solution.

**$R_{10}(r)$ :** This implies  $n = 1, l = 0$  and the series (56) terminates at  $\max(m) = n_r = n - l - 1 = 0$ . Hence,

$$u_{10}(r) = b_0 \rho e^{-\rho/2} = b_0 \frac{2r}{a_0} e^{-r/a_0} \Rightarrow R_{10}(r) = \frac{u_{10}(r)}{r} = \frac{2b_0}{a_0} e^{-r/a_0}. \quad (67)$$

Normalizing the wave function  $R_{10}$ ,

$$1 = \int_0^\infty |R_{10}|^2 r^2 dr = \frac{4|b_0|^2}{a_0^2} \int_0^\infty e^{-2r/a_0} r^2 dr = \frac{4|b_0|^2}{a_0^2} \frac{a_0^3}{4} \Rightarrow b_0 = \frac{1}{\sqrt{a_0}}$$

therefore, the ground state radial wave function of hydrogen atom is,

$$R_{10}(r) = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}. \quad (68)$$

The full ground state wave function of hydrogen atom is,

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_{00}(\theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}. \quad (69)$$

**R<sub>20</sub>(r):** This implies  $n = 2, l = 0$  and the series (56) terminates at  $\max(m) = n_r = n - l - 1 = 1$ . Hence we need to know  $b_1$  from (59),

$$\frac{b_1}{b_0} = \frac{0 + 0 + 1 - 2}{2 \cdot 1 - 0} = -1$$

$$u_{20}(r) = (b_0 \rho + b_1 \rho^2) e^{-\rho/2} = b_0 \rho (1 - \rho) e^{-\rho/2} = \frac{b_0 r}{a_0} \left(1 - \frac{r}{a_0}\right) e^{-r/2a_0} \quad (70)$$

Therefore the radial wave function of first excited state  $R_{20}$  is,

$$R_{20}(r) = \frac{b_0}{a_0} \left(1 - \frac{r}{a_0}\right) e^{-r/2a_0} \quad \text{normalization} \rightarrow R_{20}(r) = \frac{1}{\sqrt{2a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \quad (71)$$

The full first excited state wave function of hydrogen atom is,

$$\psi_{200}(r, \theta, \phi) = R_{20}(r) Y_{00}(\theta, \phi) = \frac{1}{4\sqrt{2\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \quad (72)$$

**R<sub>21</sub>(r):** This implies  $n = 2, l = 1$  and the series (56) terminates at  $\max(m) = n_r = n - l - 1 = 0$ . Hence,

$$u_{21}(r) = b_0 \rho^2 e^{-\rho/2} = \frac{b_0}{a_0^2} r^2 e^{-r/2a_0} \Rightarrow R_{21}(r) = \frac{u_{21}(r)}{r} = \frac{b_0}{a_0^2} r e^{-r/2a_0} \quad (73)$$

Normalizing the wave function  $R_{21}$  in (73),

$$1 = \int_0^\infty |R_{21}|^2 r^2 dr = \frac{|b_0|^2}{a_0^4} \int_0^\infty r^4 e^{-r/2a_0} dr = \frac{|b_0|^2}{a_0^4} 24a_0^5 \Rightarrow b_0 = \frac{1}{\sqrt{24a_0}},$$

therefore the radial wave function  $R_{21}$  is,

$$R_{21}(r) = \frac{1}{\sqrt{24a_0^3}} \frac{r}{a_0} e^{-r/2a_0}. \quad (74)$$

Hence the full  $n = 2, l = 1$  and  $m = 0, \pm 1$  wave functions of hydrogen atom are,

$$\psi_{210}(r, \theta, \phi) = R_{21}(r) Y_{10}(\theta, \phi) = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta \quad (75)$$

$$\psi_{21\pm 1}(r, \theta, \phi) = R_{21}(r) Y_{1\pm 1}(\theta, \phi) = \mp \frac{1}{8\sqrt{\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi} \quad (76)$$

The normalized general solution for  $R_{nl}(r)$  follows from combining (54) and (56), which is,

$$R_{nl}(r) = N_{nl} \frac{f(\rho)}{r} e^{-\rho/2} = N_{nl} \rho^l e^{-\rho/2} L_{n+l}^{2l+1}(\rho) \quad (77)$$

where  $L_q^p(x)$  is an *associated Laguerre polynomial*, generated by

$$L_q^p(x) = \frac{d^p}{dx^p} L_q(x) \quad \text{and} \quad L_q(x) = e^x \frac{d^q}{dx^q} (e^{-x} x^q). \quad (78)$$

With all the normalizations thrown in, the general hydrogen atom wave function is rather intimidating,

$$Y_{lm}(\theta, \phi) = (-1)^m \left[ \frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi} \quad (79)$$

$$R_{nl}(r) = - \left[ \left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3} \right]^{1/2} \left( \frac{2r}{na_0} \right)^l e^{-r/na_0} L_{n+l}^{2l+1}(2r/na_0) \quad (80)$$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi). \quad (81)$$

Probability density of finding an electron in hydrogen atom in the  $n, l, m$  quantum state is

$$|\psi_{nlm}|^2 = \psi_{nlm}^*(r, \theta, \phi) \psi_{nlm}(r, \theta, \phi),$$

and probability of finding electron in  $n, l, m$  state in volume element  $d\tau = r^2 dr \sin \theta d\theta d\phi$  is

$$|\psi_{nlm}|^2 d\tau. \quad (82)$$

The above probability density (82) is not very illuminating since such multi-dimensional object cannot be plotted. To visualize the angular dependence of  $|\psi_{nlm}|^2$ , density or *orbital* plot of  $Y_{lm}$  is employed. To visualize the radial dependence, the radial probability density is defined as, regardless of direction  $(\theta, \phi)$ , the probability of finding electron between  $r$  and  $r + dr$ ,

$$\begin{aligned} D_{nl}(r) dr &= |R_{nl}(r)|^2 r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi |Y_{lm}|^2 \\ &= r^2 |R_{nl}(r)|^2 dr \end{aligned} \quad (83)$$

A few visualization frames for hydrogen atom wave functions follow.







