Notes For Lectures on Quantum Mechanics *

Hydrogen Atom Energy Levels

A. K. Kapoor
http://0space.org/users/kapoor
akkapoor@cmi.ac.in; akkhcu@gmail.com

Contents

---

1 Radial equation

The classical Hamiltonian for an electron and a nucleus of charge Ze is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{Ze^2}{|\vec{r}_1 - \vec{r}_2|} \tag{1}$$

where m_1, m_2 are the masses of the electron and the nucleus and $\vec{r}_1, \vec{r}_2$ denote their respective positions.The case $Z = 1$ corresponds to H atom, $Z = 2$ singly ionized He atom and $Z = 3$ doubly ionized Li atom and so on. The Schrödinger equation for the electron nucleus system takes the form

$$-\frac{\hbar^2}{2m_1}\Big(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\Big)\Psi - \frac{\hbar^2}{2m_2}\Big(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\Big)\Psi - \frac{Ze^2}{|\vec{r}_1 - \vec{r}_2|}\Psi = \mathcal{E}\Psi. \tag{2}$$

Since the potential depends on relative position only, the two body problem can be reduced to an equivalent one body problem with reduced mass by changing the frame of reference to the centre of mass frame. We introduce the centre of mass and relative coordinates defined by

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}, \qquad \vec{r} = \vec{r}_1 - \vec{r}_2. \tag{3}$$

The centre of mass will move like a free particle, and the relative motion reduces to that of a particle of reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$. Therefore, it is not surprising that the separation of variables in the Schrödinger equation can be achieved by changing

* qm-lec-16005 Updated:; Ver 0.x

to these new variables $\vec{r}$ and $\vec{R}$. In terms of these variables the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2M}\Big(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\Big)\Psi(\vec{R},\vec{r}) \tag{4}$$

$$-\frac{\hbar^2}{2\mu}\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\Big)\Psi(\vec{R},\vec{r})-\frac{Ze^2}{r}\Psi(\vec{R},\vec{r})=\mathcal{E}\Psi(\vec{R},\vec{r}). \tag{5}$$

Here $M=m_1+m_2$ is the total mass, μ is the reduced mass. If we now write the full wave function $\Psi(\vec{R},\vec{r})$ as

$$\Psi(\vec{r},\vec{r})=U(\vec{R})u(\vec{r}) \tag{6}$$

and substitute it in Eq.(5), the variables $\vec{R}$ and $\vec{r}$ get separated and we would get the following differential equations for $U(\vec{R})$ and $u(\vec{r})$

$$-\frac{\hbar^2}{2M}\Big(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\Big)U(\vec{R})=E_{\rm cm}U(\vec{R}) \tag{7}$$

$$-\frac{\hbar^2}{2\mu}\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\Big)u(\vec{r})-\frac{Ze^2}{r}u(\vec{r})=Eu(\vec{r}). \tag{8}$$

$E_{\rm cm}, E$ are constants appearing from the process of separation of variables so that $E+E_{\rm cm}=\mathcal{E}$. The equation (7) is a free particle equation for the centre of mass and Eq.(8) describes the relative motion of the electron and the nucleus.

The Schrödinger equation (8) can now be solved by separation of variables in spherical polar coordinates r,θ,ϕ. The angular part of the wave function is given by the spherical harmonics $Y_{\ell 2m}(\theta,\phi)$ and therefore we write

$$u(\vec{r})=R(r)Y_{\ell m}(\theta,\phi). \tag{9}$$

The radial equation for $R(r)$ takes the form

$$\frac{1}{r^2}\frac{d}{dr}\Big(r^2\frac{dR}{dr}\Big)+\frac{2\mu E}{\hbar^2}\Big(E+\frac{Ze^2}{r}-\frac{\ell(\ell+1)}{\hbar^2}\Big)R(r) = 0, \tag{10}$$

$$\frac{d^2R(r)}{dr^2}+\frac{2}{r}\frac{dR(r)}{dr}+\frac{2\mu E}{\hbar^2}\Big(E+\frac{Ze^2}{r}-\frac{\ell(\ell+1)}{\hbar^2}\Big)R(r) = 0. \tag{11}$$

The radial equation involves effective potential

$$V_{\rm eff}(r)=-\frac{Ze^2}{r}+\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}. \tag{12}$$

Remembering that $\ell(\ell+1)\hbar^2$ is the eigenvalue of the square of orbital angular momentum, L^2, the second term is seen to be the centrifugal barrier term that appears in classical mechanics. The effective potentail goes to zero for large r. Hence for $E>0$ the energy eigenvalues will be continuous and the bound states exist only for negative E, so we write $E=-|E|$. It is convenient to work with dimensionless variables ρ and λ defined by

$$\rho=\alpha r, \qquad \alpha^2=\frac{8\mu|E|}{\hbar^2} \tag{13}$$

$$\lambda=\frac{2\mu Ze^2}{\alpha\hbar^2} = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}. \tag{14}$$

The equation for radial wave function written in terms of ρ takes the form

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \Big(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\Big)R = 0. \tag{15}$$

The above equation (15) can be transformed into a form similar to one dimensional Schrödinger equation by introducing $\chi(\rho) = \rho R(\rho)$ which gives the following equation for $\chi(\rho)$

$$\frac{d^2\chi}{d\rho^2} + \Big(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\Big)\chi(\rho) = 0. \tag{16}$$

2 Large ρ behaviour

The behaviour of the radial wave function for large ρ can be easily found by taking large ρ limit of Eq.(16). Neglecting the terms $\frac{\lambda}{\rho}$ and $\frac{\ell(\ell+1)}{\rho^2}$ compared to 1/4 we get

$$\frac{d^2\chi(\rho)}{d\rho^2} - \frac{1}{4}\chi(\rho) = 0. \tag{17}$$

showing that the wave function behaves like $\exp(\pm\rho/2)$ for large ρ. The wave function must be bounded everywhere including at infinity, so we must have $\chi(\rho) \approx e^{-\rho/2}$. This suggests that we write $R = e^{-\rho/2}F(\rho)$, and solve for $F(\rho)$. The equation for $F(\rho)$ turns out to be

$$\frac{d^2F(\rho)}{d\rho^2} + \left(\frac{2}{\rho} - 1\right) + \left[\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1}{\rho^2}\right] \tag{18}$$

3 Solution by Frobenius method

We now find solution of the differential equation for $F(\rho)$ by the method of series solution. Assuming the form

$$F(\rho) = \sum_{m=0} a_m \rho^{c+m},, \tag{19}$$

substituting in Eq.(18), and equating coefficients of lowest power of ρ to zero we get

$$c(c+1) - \ell(\ell+1) = 0 \Longrightarrow c = -\ell - 1, \ell \tag{20}$$

Since $\ell > 0$, the value $c = -\ell(\ell+1)$ give solution diverging at $\rho = 0$. Therefore we choose $c = \ell =$ and the recurrence relation for the coefficients a_m turns out to be

$$a_{m+1} = \frac{(m + \ell + 1 - \lambda)}{(m+1)(m+2\ell+2)} a_m. \tag{21}$$

The ratio of coefficients for large m

$$\frac{a_{m+1}}{a_m} \sim \frac{1}{m} \tag{22}$$

coincides with the corresponding value for the series $\rho^k \exp(\rho)$. Hence if the series does not terminate, the solution $F(\rho)$ gives the radial wave function diverging like $\rho^k \exp(\rho/2)$ for large ρ. This is unacceptable and hence the series must terminate.

This happens if all terms vanish after some n' *i.e.* $a_m = 0$ for all $m > n'$. For this to happen we must have $a_{n'+1} = 0$. Hence from Eq.(21) we get

$$\lambda = n' + \ell + 1. \tag{23}$$

The energy is then given by

$$\boxed{E_n = -|E_n| = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2} = \frac{Z\alpha^2}{2n^2}(\mu c^2)}. \tag{24}$$

where c is velocity of light and $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$ is the fine structure constant.

4 Properties of H atom wave functions

The final expressions for wave functions for hydrogen like problems is given by

$$u_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r) Y_{\ell m}(\theta,\phi) \tag{25}$$

$$R_{n\ell}(r) = N_{n\ell}\, \rho^\ell\, L^{2\ell+1}_{n+\ell}(\rho) e^{-\rho/2} \tag{26}$$

$$N_{n\ell} = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\big((n+\ell)!\big)}} \tag{27}$$

with

$$\rho = \Big(\frac{2Z}{na_0}\Big) r, \qquad a_0 = \frac{\hbar^2}{\mu e^2}. \tag{28}$$

and n is the principle quantum number. Here $L^p_q(\rho)$ are associated Laguerre polynomials and a_0 is the radius of first Bohr orbit of the the electron in hydrogen atom. The energy levels are given by

$$E_n = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2}. \tag{29}$$

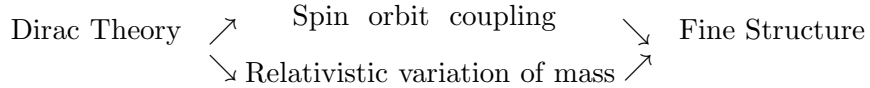
The first few radial wave functions are

$$R_{10} = (Z/2a_0)^{\frac{3}{2}} 2 \exp(-Zr/2a_0)) \tag{30}$$

$$R_{20}(r) = (Z/2a_0)^{\frac{3}{2}} (2 - Zr/a_0) \exp(-Zr/2a_0)) \tag{31}$$

$$R_{20}(r) = (Z/2a_0)^{\frac{3}{2}} (Zr/\sqrt{3}\, a_0) \exp(-Zr/2a_0)) \tag{32}$$

A comment on hydrogen atom energy levels Finally we wish to remind you that the non-relativistic result $-R/n^2$ for the energy levels of H-atom is not the end of story for H-atom levels. Precision experiments show that each level is not a single level. To understand the experimental facts we must take into account of relativistic effects using Dirac theory of electron



Also a hyperfine structure, seen in the energy levels, requires a treatment of the spin-spin interaction of electron with the nucleus and an explanation of a tiny 'Lamb shift' requires use of quantum field theory.

Hyperfine structure	→ Effect of Nuclear Spin
Lamb shift	→ Quantum field Theory, Vacuum Polarization Effect