# PHYS-505/551

## The hydrogen atom

*Lecture-1*

# *Introduction-a*

- The study of the hydrogen atom is important in quantum mechanics because it is the only atom where the Scrhoedinger equation can be exactly solved in the limit where all the interactions, except the electrostatic, between the proton and the electron can be ignored.

# *Introduction-b*

- The Scrhoedinger equation takes the form:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi \qquad (1.1)$$

$$\nabla^2\psi + \left(\varepsilon - U\left(r\right)\right)\psi = 0 \qquad (1.2)$$

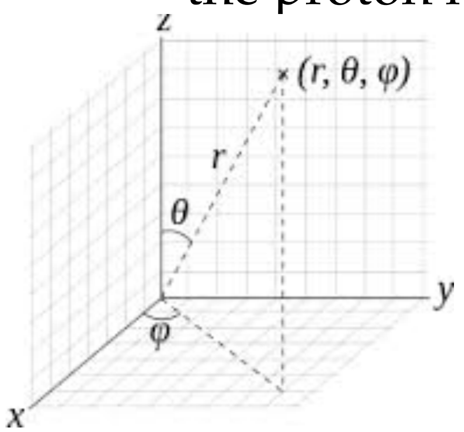
$$\varepsilon = \frac{2mE}{\hbar^2} \qquad U\left(r\right) = \frac{2mV(r)}{\hbar^2} \qquad V\left(r\right) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

# *Introduction-c*

- Since the interaction Hamiltonian depends only on *r*, the proper coordinate system for the study of this problem is the system of spherical coordinates, where:

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} \qquad (1.3)$$

- Since the mass of the proton is much larger than the electron's, the proton has been considered as a heavy motionless particle.



# *Solution of Shroedinger equation-a*

- In solving the Schroedinger equation for the hydrogen atom we must take into account two important conservation principles:
- The conservation of energy
- The conservation of angular momentum since the Coulomb force between proton and electron is a central force.
- The Schroedinger equation is solved with the method of separating variables

# *Solution of Shroedinger equation-b*

- The wavefunctions for the hydrogen electron are given by:

$$\psi_{nlm}\left(r,\ \theta,\ \phi\right) = \underbrace{R_{nl}(r)}_{\text{radial part}}\underbrace{Y_l^m\left(\theta,\ \phi\right)}_{\text{angular part}} \qquad (1.4)$$

- As you may see they consist of a radial and an angular part

## *The angular part-a*

- The angular part of the wavefunction is given by the so-called **spherical harmonics**:

$$Y_l^m(\theta,\ \phi) = \varepsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^m(\cos\theta)e^{im\phi} \qquad (1.5)$$

$$\varepsilon = \begin{cases} (-1)^m, & m \geq 0 \\ 1 & m < 0 \end{cases}$$

$P_l^m(\cos\theta)$ associated Legendre function

## *The angular part-b*

- The associated Legendre functions polynomials are generated from the Legendre polynomials from the following relations:

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

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

# *The angular part-c*
# *some associated Legendre polynomials*

$$P_0^0 = 1 \qquad P_2^0 = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$P_1^1 = \sin\theta \qquad P_3^3 = 15\sin\theta\left(1 - \cos^2\theta\right)$$

$$P_1^0 = \cos\theta \qquad P_3^2 = 15\sin^2\theta\cos\theta$$

$$P_2^2 = 3\sin^2\theta \qquad P_3^1 = \frac{3}{2}\sin\theta\left(5\cos^2\theta - 1\right)$$

$$P_2^1 = 3\sin\theta\cos\theta \qquad P_3^0 = \frac{1}{2}\sin\theta\left(5\cos^3\theta - 3\cos\theta\right)$$

# *The angular part-d*

- The **spherical harmonics** are normalized and orthogonal to each other:

$$\int_0^{2\pi}\int_0^{\pi}\left[Y_l^m(\theta,\ \phi)\right]^*\left[Y_{l'}^{m'}(\theta,\ \phi)\right]\sin\theta d\theta d\phi = \delta_{ll'}\delta_{mm'} \qquad (1.6)$$

- The spherical harmonics are eigenfunctions of the square angular momentum operator and of the angular momentum operator along the *z*-direction

$$\mathbf{l}^2 Y_l^m = \hbar^2 l(l+1) Y_l^m, \quad l_z Y_l^m = \hbar m Y_l^m \qquad (1.7)$$

# The angular part-e
# the first few spherical harmonics

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

$$Y_2^0 = 3\left(\frac{5}{16\pi}\right)^{1/2} \left(3\cos^2\theta - 1\right)$$

$$Y_2^{\pm1} = \mp3\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_2^{\pm2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm2i\phi}$$

$$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} \left(5\cos^3\theta - 3\cos\theta\right)$$

$$Y_3^{\pm1} = \mp\left(\frac{21}{16\pi}\right)^{1/2} \sin\theta\left(5\cos^2\theta - 1\right)e^{\pm i\phi}$$

$$Y_3^{\pm2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm2i\phi}$$

$$Y_3^{\pm3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm3i\phi}$$

## *The angular part-e*

- The **integer** number ***l*** is known as **azimuthal quantum number** and gets the values

$$l = 0,\ 1,\ 2,\ \ldots,\ \infty$$

- The **integer** number ***m*** is known as **magnetic quantum number** and gets the values

$$m = -l, \ldots\ldots\ldots\ldots, +l$$

# The radial part-a

- The radial part of the solution is given by:

$$R_{nl}(r) = Ne^{-r/na_0}\left(\frac{2r}{na_0}\right)^l \left[L_{n-l-1}^{2l+1}\left(2r/na_0\right)\right] \qquad (1.8)$$

$$N = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}} \qquad a_0 \equiv \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.529\times 10^{-10}\,m$$

Bohr radius

$L_{n-l-1}^{2l+1}\left(2r/na_0\right)$ associated Laguerre polynomial

# The radial part-b

- The associated Laguerre polynomials are generated from the Laguerre polynomials from the following relations:

$$L_{q-p}^{p}(x) \equiv (-1)^{p}\left(\frac{d}{dx}\right)^{p} L_{q}(x)$$

$$L_{q}(x) \equiv e^{x}\left(\frac{d}{dx}\right)^{q}\left(e^{-x}x^{q}\right)$$

# The radial part-c

## Some associated Laguerre polynomials

$$L_0^0 = 1 \qquad L_0^2 = 2$$

$$L_1^0 = -x + 1 \qquad L_1^2 = -6x + 18$$

$$L_2^0 = x^2 - 4x + 2 \qquad L_2^2 = 12x^2 - 96x + 144$$

$$L_0^1 = 1 \qquad L_0^3 = 6$$

$$L_1^1 = -2x + 4 \qquad L_1^3 = -24x + 96$$

$$L_2^1 = 3x^2 - 18x + 18 \qquad L_2^3 = 60x^2 - 600x + 1200$$

# *The radial part-c*
## *Discussion*

- It can be shown that the radial part of the electrons wavefunction defines a function

$$u \equiv rR_{nl}(r) \qquad (1.9)$$

which satisfies the so-called ***radial equation***

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]}_{\text{effective potential}} u = Eu \qquad (1.10)$$

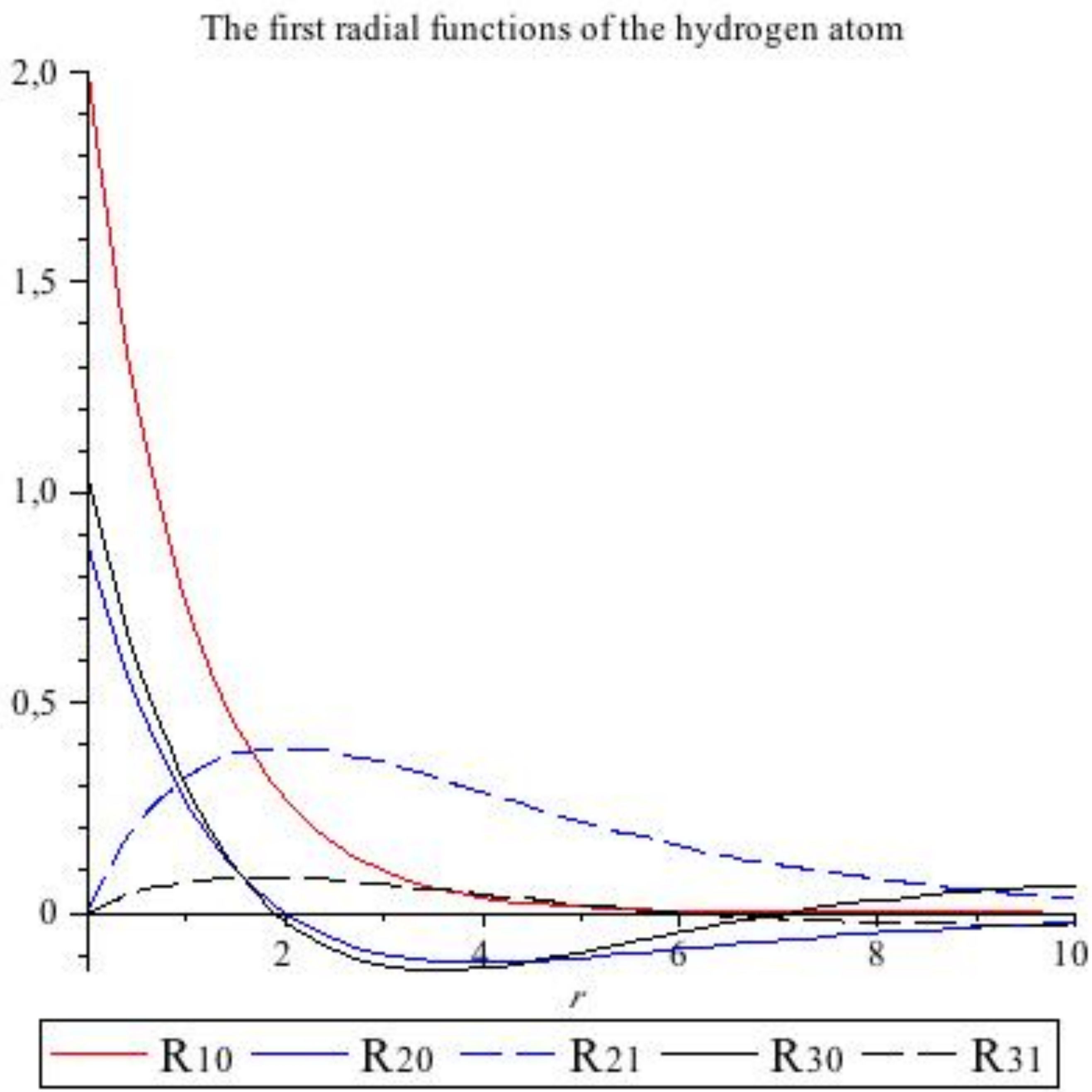
# *The radial part-c*
## *Discussion*

- The functions *u* satisfy the following boundary conditions:

$$u(0) = 0, \qquad u(\infty) = 0, \quad \text{while} \quad 0 < r < \infty$$

- Thus the radial equation describes an one-dimensional motion where at 0 we have a "wall" and at infinity the wavefunction becomes zero.
- The radial equation contains the term $\hbar^2 l(l+1)/(2mr^2)$

which is the so called **centrifugal term**.


The first radial functions of the hydrogen atom
2,0
1,5
1,0
0,5
0
2
4
6
8
10
r
R10
R20
R21
R30
R31

# The total wavefunctions

- The total wavefunctions for the hydrogen atom are given by:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l \left[L_{n-l-1}^{2l+1}(2r/na_0)\right] Y_l^m(\theta,\phi) \quad (1.11)$$

$$\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} \psi_{nlm}^{*} \psi_{n'l'm'} r^2 \sin\theta \, dr\, d\theta\, d\phi = \delta_{nn'}\delta_{ll'}\delta_{mm'} \quad (1.12)$$

# The energy spectrum of the hydrogen atom-a

- The energies of the electron states are given by the following formula:

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \qquad n = 1,\ 2,\ 3,\ \ldots \qquad (1.13)$$

- Where *E*1 is the ground state energy given by

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right] = -13.6\ eV$$

- The number *n* is called the **principal quantum number**.

# *The energy spectrum of the hydrogen atom-b*

- One of the most impressive characteristic of the hydrogen atom energy spectrum is its ***degeneracy***.
- By degeneracy we mean that there can be more than one states with the same energy. This is obvious since the energy does not depend on the numbers *l* and *m*.
- The principal quantum number *n* imposes the following restriction on the values of the azimuthal quantum number:

$$l = 0,\ 1,\ 2,\ \ldots,\ n-1$$

- We can prove that the number of different states that have the same energy is given by

$$d_n = n^2$$