



Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

PROBLEM 1 Determine the form of function R for the values of $n = 2$ and $l = 0$.

Substituting the given values of n and l in Eq. (29), we get

$$R_{2,0} = - \left\{ \left(\frac{2Z}{2a_0} \right)^3 \frac{(2 - 0 - 1)!}{2 \times 2 [(2 + 0)!]^3} \right\}^{1/2} \rho^0 e^{-\rho/2} L_2^1$$

where L_2^1 as given by Eq. (24) is

$$L_2^1 = \frac{d}{d\rho} L_2$$

where L_2 as given by Eq. (25) is

$$L_2 = e^\rho \frac{d^2}{d\rho^2} (\rho^2 e^{-\rho})$$

Now working in the reverse direction, we have

$$\begin{aligned} L_2 &= e^\rho \frac{d}{d\rho} \left\{ \frac{d}{d\rho} (\rho^2 e^{-\rho}) \right\} \\ &= e^\rho \frac{d}{d\rho} (2\rho e^{-\rho} - \rho^2 e^{-\rho}) \\ &= e^\rho (2 e^{-\rho} - 2\rho e^{-\rho} - 2\rho e^{-\rho} + \rho^2 e^{-\rho}) \\ &= (2 - 4\rho + \rho^2) \end{aligned}$$

$$L_2^1 = \frac{d}{d\rho} L_2 = \frac{d}{d\rho} (2 - 4\rho + \rho^2) = -4 + 2\rho,$$

Finally, since $\rho = \left(\frac{2Z}{n a_0} \right) r = \left(\frac{Z r}{a_0} \right)$, we have

$$\begin{aligned} R_{2,0} &= - \left\{ \left(\frac{Z}{a_0} \right)^3 \frac{1}{4 \times 8} \right\}^{1/2} e^{-\rho/2} (-4 + 2\rho) \\ &= \left(\frac{Z}{2a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \end{aligned}$$

Following the method given in Problem 1 , other functions with different values of n and l can be determined. Table 1 includes some such functions.



Quantization of Electronic Energies: The Hydrogen atom problem

Table 1 A FEW NORMALIZED $R_{n,l}$ FUNCTIONS

| n | l | $R_{n,l}$ |
|-----|-----|---|
| 1 | 0 | $2\left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)$ |
| 2 | 0 | $\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) \exp(-Zr/2a_0)$ |
| 2 | 1 | $\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) \exp(-Zr/2a_0)$ |
| 3 | 0 | $\frac{2}{3}\left(\frac{Z}{3a_0}\right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2 r^2}{9a_0^2}\right) \exp(-Zr/3a_0)$ |
| 3 | 1 | $\frac{2\sqrt{2}}{9}\left(\frac{Z}{3a_0}\right)^{3/2} \left(\frac{2Zr}{a_0} - \frac{Z^2 r^2}{3a_0^2}\right) \exp(-Zr/3a_0)$ |
| 3 | 2 | $\frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2} \left(\frac{Z^2 r^2}{a_0^2}\right) \exp(-Zr/3a_0)$ |

where $a_0 = \frac{h^2}{4\pi^2\mu e'^2}$

Energy of the Electron :

The allowed values of energy of the electron can be obtained from Eq. 22 and Eq.23. From Eq.23, we get

$$\alpha = \frac{4\pi^2\mu Ze'^2}{nh^2}, \quad (\text{since } \lambda = n)$$

Substituting this in Eq.22, we get

$$\left(\frac{4\pi^2\mu Ze'^2}{nh^2}\right)^2 = -\frac{8\pi^2\mu E}{h^2}$$

Cancelling the common terms, we get

$$E = -\frac{1}{n^2} \left(\frac{2\pi^2\mu Z^2 e'^4}{h^2}\right) \dots\dots\dots(35)$$

Eq.35 is identical with that derived earlier from the Bohr's theory. Thus, the energy of the electron depends on the value of the principal quantum number n and is independent of the values of l and m . Since the quantum number n appears only in the function $R(r)$, we conclude



Quantization of Electronic Energies: The Hydrogen atom problem

that the energy depends only on the distance of the electron from the nucleus and not on its angular dependence.

A Summary of the Quantum Mechanical Treatment of the Hydrogen –like systems

1. To describe the mechanical state of the hydrogen –like system, we need a function ψ which depends on the six independent variables, viz, three co-ordinates of the nucleus and three for the electron.

2. If the function ψ is written as

$$\Psi = \psi_M \psi_e$$

where ψ_M depends on the coordinates of the centre of mass and ψ_e on the internal coordinates, the Schrodinger equation separates into two independent equations; one for the motion of the atom as a whole and the other involving the internal coordinates of the atom. The latter one is of interest to us as it would give us the wave functions of the electron and the associated energies.

3. The Schrodinger equation involving the internal coordinates is then transformed into the Spherical polar coordinates.

4. The Schrodinger equation splits into three equations if we write ψ_e as

$$\psi_e = R\Theta\phi$$

The function R involves only r, Θ involves only θ and ϕ involves only ϕ . The three resultant equations can be solved for the functions R, Θ and ϕ by suitable transformations. In order that these functions are finite, well- behaved and consistent with the boundary conditions, certain quantum restrictions are introduced. These restrictions appear in the form of quantum numbers.

5a. The function R depends only on r, therefore, they describe the radial distributions of the electron. These functions depend upon two quantum numbers, n and l. The permitted values of these numbers are:

Principal quantum number: $n = 1, 2, 3, 4, \dots$

Azimuthal quantum number: $l = 0, 1, 2, \dots, (n-1)$

We have different R functions for different values of n and l.

(b) The function Θ depends only on the angle θ , therefore they describe the distribution as a function of angle θ . These functions again depend upon two quantum numbers, viz., l and m. Though the permitted values of m are $0, \pm 1, \pm 2, \dots, \pm l$, the Θ functions depend only on the magnitude of m, i.e., $|m|$.



Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

(c) The functions ϕ depend only on angle φ ; therefore, they describe the distribution as a function of angle φ . These functions depend only on the value of m .

The two functions Θ and ϕ taken together give the angular distribution of the electron. Thus the total wave function ψ_e which constitutes what is known as an orbital, depends on the quantum number n, l and m , i.e., we have different ψ_e functions (or orbitals) for different values of n, l and m and hence different behavior of the electron in the atom.

6a. The principal quantum number describes the energy of the electron in the hydrogen-like systems and is given by the relation

$$E = -\frac{1}{n^2} \left(\frac{2\pi^2\mu Z^2 e^4}{h^2} \right) = -\frac{1}{n^2} \left(\frac{Z^2 e^4}{2a_0} \right)$$

$$\text{where } a_0 = h^2/4\pi^2\mu e'^2$$

(b) The azimuthal quantum number describes the total angular momentum of the electron through the expression *

$$L^2 = l(l+1)(h/2\pi)^2$$

It is customary to design the values of l by letter as given below:

| Value of l : | 0 | 1 | 2 | 3 |
|-----------------------|-------|-----------|---------|-------------|
| designation: | s | p | d | f |
| spectroscopic terms : | sharp | principal | diffuse | fundamental |

The letter s, p, d and f are derived from the spectroscopic terms; sharp principal, diffuse and fundamental, respectively.

(c) The magnetic quantum number describes the z-component of the angular momentum of the electron through the equation

$$L_z = m \left(\frac{h}{2\pi} \right)$$

(7) The energy of the electron depends only on the value of n and not at all on l and m . Thus, all ψ_e functions (or orbitals) with the same value of n but different values of l and m are degenerate, i.e., they have the same energy.

*** It can be noted that for all states in which $l=0$ i.e., for all s orbitals, the orbital angular momentum has a zero value (this is not possible in the Bohr's theory). The orbital motion of the electron in s orbitals without angular momentum is difficult to visualize in classical terms**



Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

| Sl no | n | l | m | E |
|-------|-----|-----|-------|---|
| i | n=1 | l=0 | m =0 | $E = - \left(\frac{2\pi^2\mu Z^2 e^4}{h^2} \right)$ |
| ii | n=2 | l=0 | m =0 | $E = - \frac{1}{4} \left(\frac{2\pi^2\mu Z^2 e^4}{h^2} \right)$ (Four- fold degenerate) |
| | | | m =+1 | |
| | | l=1 | m =0 | |
| | | | m =-1 | |
| iii | n=3 | l=0 | m =0 | $E = - \frac{1}{9} \left(\frac{2\pi^2\mu Z^2 e^4}{h^2} \right)$ (Nine- fold degenerate) |
| | | | m =+1 | |
| | | l=1 | m =0 | |
| | | | m =-1 | |
| | | | m =+2 | |
| | | l=2 | m =0 | |
| | | | m =+1 | |
| | | | m =-2 | |

Thus, the degeneracy of orbitals for given value of n is equal to n^2 .

Spectra of Hydrogen -Like Atoms:

The spectra of atoms are obtained when the electron is transferred from one wave function (or the orbital) to another wave function. A more rigorous quantum -mechanical study of transition between quantum states (states with different values of n , l , and m) indicates that certain restrictions in the change in the values of l and m must be satisfied. The transitions which do not follow these restrictions are forbidden, i.e., they are not observed. These restrictions are referred to as the selection rules. For hydrogen-like atoms, we have the following rules

n may change by any integer. i.e.,

$$\Delta n = \text{any value}$$

l must change by ± 1 , i.e.,

$$\Delta l = \pm 1 \text{ and}$$

m may change by ± 1 or not at all i.e.,

$$\Delta m = 0, \pm 1$$

For example, if an electron changes its principal quantum number from $n=2$ to $n=1$, it must go from a state of $l=1$ to $l=0$, i.e., the transition $1s \leftarrow 2p$ is allowed. The transition $1s \leftarrow 2s$ where $l=0$ is forbidden.

A few other possible transitions in the hydrogen atom are shown in the Fig 2

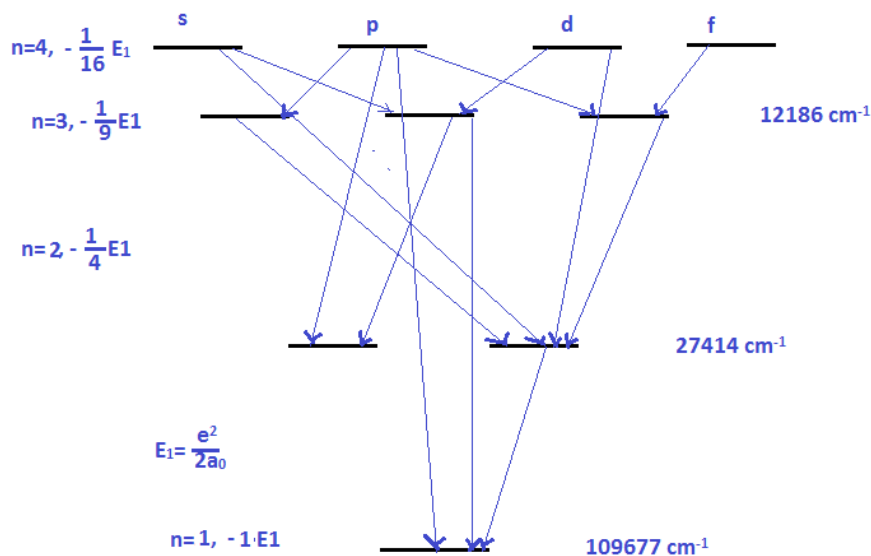


Fig2: The allowed transitions of the hydrogen atom. The diagram is known as Grotrian diagram.