Production of Courseware

- Contents For Post Graduate Courses

Paper No. : Atomic, Molecular and Laser Spectroscopy

Module: 1.01

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Description of Module	
Subject Name	Physics
Paper Name	Atomic, Molecular and Laser Spectroscopy
Module Name/Title	Introduction
Module Id	

Contents:

The students will be able to learn about **electron spin** and **spectra of one electron atom** and **spin orbit interaction energy of orbits.**

1. Introduction

The interaction of photon of the electromagnetic radiation with matter has given birth to a very important field called spectroscopy. One can go back to the Newton's observation of the spectrum when sun light pass through a prism and light get dispersed in to colour components.

The spectrum is basically a series of radiant energy arranged in order of wavelength/frequency.

The spectra can be interpreted for obtaining fundamental information on energy levels, transtion probabilities for atoms and molecules. The information so obtained can be used in various kind of analysis like absorption and emission of light, line widths and profile of spectral line and finally came a device named as LASER which became a very important tool as spectroscopy light source. Now a days all types of spectroscopy is done with laser like non linear spectroscopy, laser

Raman spectroscopy, time resoled spectroscopy, coherent spectroscopy which further is being used for various application in chemistry, environmental , biology and medicine. To cite a few, isotope separation with lasers, single molecules detection, atmospheric measurement with LIDAR, spectroscopic detection of water pollution, energy transfer in complexes , cancer diagnostic and therapy and so on.

Neil’s Bohr has given an atomic model for hydrogen molecule for explaining the observed spectrum. The model incorporates the idea which was proposed by Rutherford and the concept of light photon given by Einstein (Photoelectric effect) the postulates of the Bohr Theory are:

- an electron in an atom moves in circular orbit around the nucleus under the influence of coulomb field of force
- electron in these orbit is in stable state and do not radiate in spite of constant acceleration
- Out of the infinity number of the orbits, electron exist in the orbit for which the orbital angular momentum L = n h /2π

The radiation is emitted or absorbed by a transition of the electron from one orbit to another and the frequency is equal to $E_i - E_f$

For hydrogen atom the total energy of electron is given by

$$E= -\frac{2\pi^2 m_e e^4 Z^2}{(4\pi\varepsilon_0)n^2 h^2}$$

That is

$$E= -\frac{13.6(eV)Z^2}{n^2}$$ for Hydrogen atom.

In this way from the expression

$$V = R\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

the spectral lines like Lyman, Balmer, Paschen, Bracket , Pfund are found.

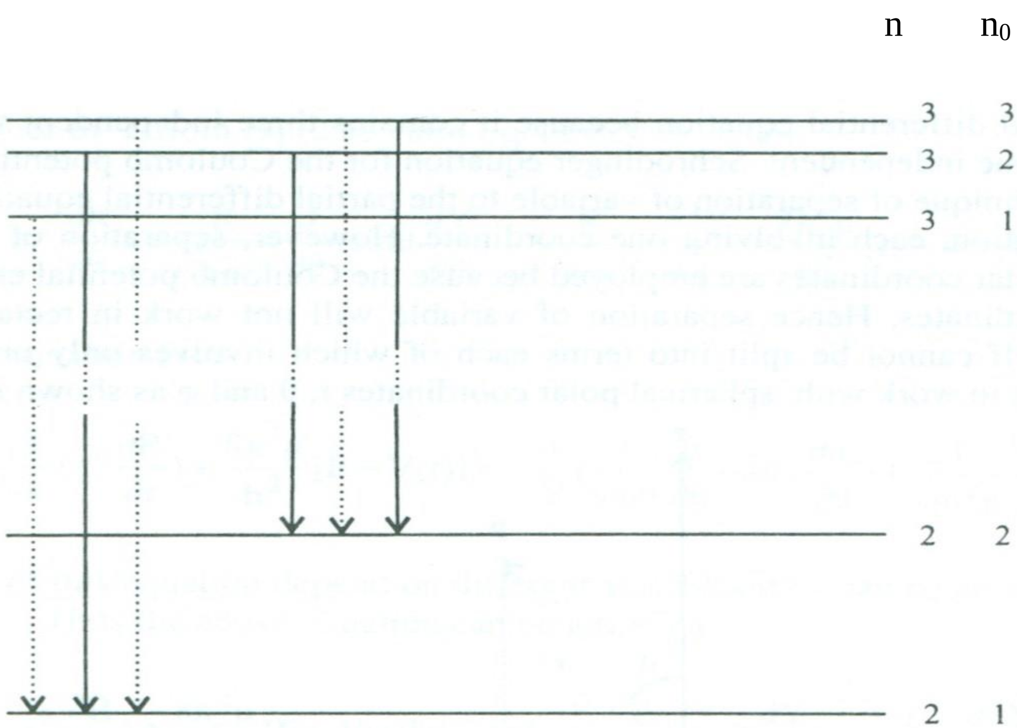
Bohr Theory has not taken in the account the fine structure (splitting of spectral lines into several component) of the spectra of hydrogen atom.

Summerfield extended the Bohr model and included elliptical orbit. In case of electron in a hydrogen atom , the total energy is negative and hence the path of electron is considered as an ellipse as it is clear from the figure that the radius vector R varies periodically .

The Summerfield postulated

- The electron in atoms move in elliptical path with nucleus at one of the foci
- Out of the infinite number of the elliptical orbits, only certain discrete orbit following certain conditions occur
- The radiation emitted and absorbed when electron undergoes a transition from an orbit of a energy E_i to another orbit of energy E_f and the total energy e is written as exactly the same as derived by Bohr's model of circular orbit.

An electron in an elliptical orbit has velocity that is different at different position, speeding up when the electron is near the nucleus and slow down when it is far away and also precession rate is different for different elliptical orbit so the fine structure splitting of energy levels of the hydrogen atom (n=2 and n=3) are shown in the figure where in the solid lines are observed while the dotted lines are not seen



Though the Bohr-Summerfeld theory has successfully explained the various aspects of atomic spectra of hydrogen like atoms but enable to explain the energy level of atoms with two or more electrons but the theory doesn't explain relative intensities of the spectral lines. These were explained by considering non- relativistic Schrödinger wave equation and the quantum theory of hydrogen atoms.

Remarks:

The atomic orbit differ from orbital as

1. The orbits are characterized by principle quantum number n. an orbital doesn't indicate the exact location of an electron. The square of wave function gives the probability finding the electron at a given point in space and hence is characterized by quantum number n, l and m.
2. The representation of orbit is two dimensional while that of the orbital is three dimensional and hence spherical Polar coordinates (r, θ and ϕ) are used.
3. An orbit having a principal quantum number n can accommodate $2n^2$ electrons (with spin taken into account). The size of the orbital part is determined by the radial part and their shape by angular part the wave-function.

Notation:

(a) The orbitals with l quantum numbers (l=0, 1, 2,3…..) are denoted by s,p,d,f,g….

(b) The principle quantum number n is placed before these letters

(c) The magnetic quantum number m is placed as subscript

For n=1,l=0 we have 1s orbital

n=3,l=2 we have 3d orbital

Further we have done with the solution of Schrodinger wave equation and finding $\psi_{nlm}(r,\theta,\phi)$ that contains radial as well as angular parts.

(a) The radial part means, the dependence on the radius only describing the values and distribution of electron density in atomic orbitals.

It depend s on n and l and not on m. this means for 2l+1 functions for a given value of l, there is same radial distribution of electron density.

(b) The angular part $\psi_{lm}(\theta,\phi)$ depend on l and m quantum numbers and not on n. Therefore all the orbital with same l have the same form.

(c) The quantum no. m determines the orbital orientation.

(d) 2l+1 gives the possible orientation as for (i) s orbital is one

(ii) p orbital is three

(iii) d orbital is five….

(e) All the possible orientations are equivalent and have the same energy value, so these orbitals are called degenerate

(f) s orbitals are spherically symmetric ; as these depend on radius and are independent of θ and ϕ

(g) The p orbitals exist with n=2

l=1, m can take values m= 1,0,-1

three p orbitals are p_1,p_0,p_{-1}

(h) The d orbitals exist beginning with n=3 and now for l=2, m =2,1,0,-1,-2

five d orbitals are d_2,d_1,d_0,d_{-1},d_2

Note: Where $\psi_{nlm}(r,\theta,\phi)=0$ i.e. either $\psi_{lm}(\theta,\phi)=0$ or $R_{nl}(r)=0$: there is some space called nodes or nodal surface

2. Electron Spin

Though many aspects could be understood by the introduction of the Schrodinger theory for hydrogen like atom but certain details in the spectrum of hydrogen and of similar atoms were to be understood as the quantum numbers n, l and m alone could not explain certain experimental observations

(1) Many spectral lines actually consist of two separate lines that are very close together. For example theory predicts a single line of wavelength 656.3 nm for the first line of Balmer series ($H_\alpha$line). However, two lines 0.14 nm apart were observed for H_α.

(2) The number of transitions observed when the atoms were placed in an external magnetic field could not be accounted for.

(3) In 1992, Stern and Gerlach measured the possible values of **<u>magnetic dipole moments</u>** of silver atoms. A beam of silver atoms was used in a region in which there are strong gradient of the magnetic field $\frac{\partial B}{\partial z}$ in z direction (transverse to the beam). If the atom has a magnetic moment μ the there is a force on the atom of magnetic $\mu_z\frac{\partial B}{\partial z}$ and transverse deflection of the beam may be observed. Stren and Gerlach found two traces symmetrically displaced on either side of the beam axis with no undeflected trace. The magnetic moment of the electron due to orbital motion is $-\beta_e g_1$ L $2\pi/h$

The z component of magnetic moment is proportional to m_1 (magnetic quantum no.) and can take 2l + 1 is odd. If the magnetic moment of an atom is associated only with the orbital motion, there would be an odd number of discrete traces including the undeflected one because of $m_1=0$.

This all suggest that there is requirement of another quantum number for which the number of projections on z axis (quantization axis) is even. To explain these observations Uhlenbeck and Goudsmit in 1925 assigned a new angular momentum to the electron. They suggested that the electron in any state spins about its own mechanical axis and therefore the electron has intrinsic angular momentum denoted by s. This spin angular momentum is in addition to the orbital angular momentum. The experimental observations were explained by assigning the electron, a spin angular momentum $\hbar/2$. For spin angular momentum, there are only two orientation of the angular momentum .The idea of electron spin s proved to be successful in explaining the various atomic effects.

The magnitude of s and z components s_z of the spin angular momentum are related to two quantum numbers s and m_s that are identical to those for orbital angular momentum.

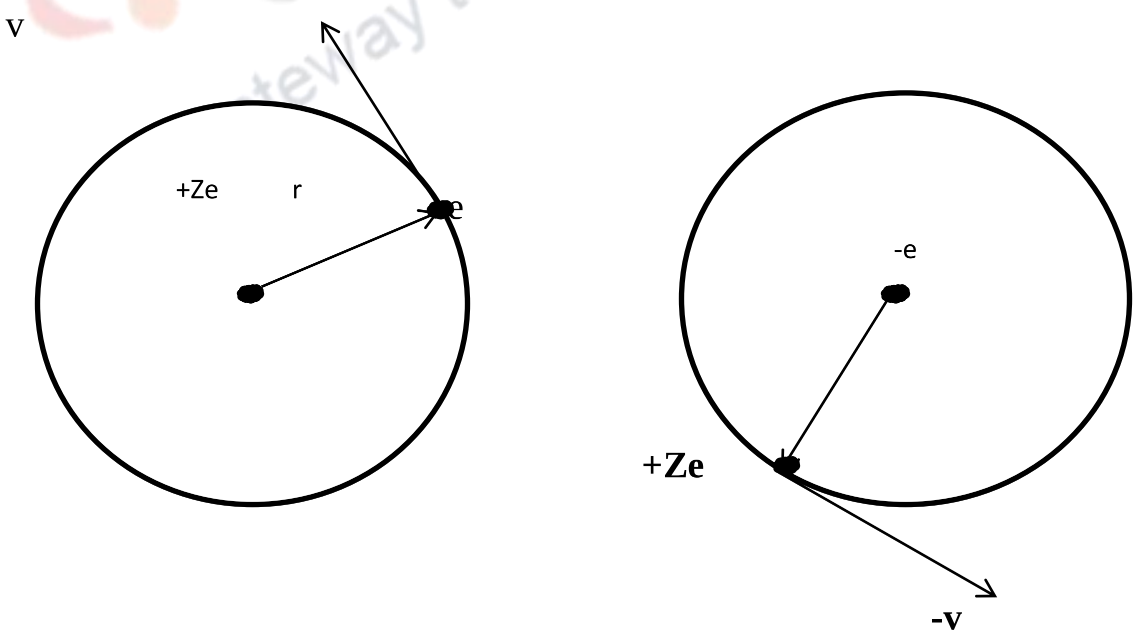
$$s = (h/2\pi)[s(s+1)]^{1/2} \qquad (3.1)$$

$$s = m_s(h/2\pi) \qquad (3.2)$$

Where $m_s = ½$ and is called spin magnetic quantum number. Now we have four quantum numbers n,l,m_l and m_s to describe each possible state of an atomic electron.

3. Spin orbit interaction

Consider an electron of charge –e moving in Bohr's orbit around the nucleus of charge +Ze. Considering the velocity of the electron relative to the nucleus be **v** and its position w.r.t. the nucleus is **r**. As the motion is relative therefore consider the electron to be at rest, while the nucleus is going round the electron in a circle of radius **r** and velocity **–v** (fig.)



(a) **(b)**

(a) An electron moves in Bohr's circular orbit, the motion is seen by the nucleus

(b) The same motion, but as seen by the electron. From the point view of the view of the electron, the nucleus moves around it

The motion of the nucleus constitutes a current loop, which produces a magnetic field, and electron is located inside this current loop. The current element j because of motion of nucleus is

$$j = -Zev$$

According to Ampere's law this produces a magnetic field B that at a distance r is

$$\mathbf{B} = \frac{\mu_0}{4\pi}\frac{j\times r}{r^3} = -\frac{Ze\mu_0}{4\pi}\frac{v\times r}{r^3}$$

According to Coulomb law the force between electron of charge –e and nucleus of charge + Ze, The electric field is

$$E=\frac{Zer}{4\pi\varepsilon_0 r^3}$$

$$B=-\varepsilon_0\mu_0\, v\times E = -\frac{v\times E}{c^2}$$

Here $c^2=1/\varepsilon_0\mu_0$.

The quantity **B** is magnetic field strength experienced by the electron when it is moving with velocity **v** w.r.t. the nucleus, and therefore through the electric field of strength **E** that the nucleus exert on it. The spin –orbit interaction energy ΔE results from the interaction between field **B** and spin magnetic moment

$$\mu_s= -\frac{g_s e s}{2m_e} = -\frac{2\pi g_s\beta_e s}{h}$$

The orientational potential energy of spin magnetic moment in this magnetic field is

$$\Delta E = - \mu_s .B \qquad = \quad g_s \beta_e \frac{2\pi s.B}{h}$$

But energy has been evaluated in a frame of reference in which the electron is at rest, but the interest is to find its value in the frame of reference in which the nucleus is at rest. Transforming back to frame of references in which nucleus is at rest results in a reduction of the orientational potential energy by a factor of two. Thus, spin- orbit interaction energy (As above) changes to

$$\Delta E = g_s \beta_e \frac{\pi s.B}{h}$$

Using F=-eE

$$B = \frac{v \times F}{ec^2}$$

And as **F**=$-\frac{dV}{dr}\frac{r}{r}$ **B**= $-\frac{v \times r}{ec^2 r}\frac{dV}{dr}$

Multiply and dividing by electron mass m_e,

$$\mathbf{B} = \frac{r \times p}{m_e e c^2 r}\frac{dV}{dr}$$

With L=r×p, the above equation reduces to

$$\mathbf{B} = \frac{L}{m_e e c^2 r}\frac{dV}{dr}$$

Magnetic field experienced by the electron because of its motion about the nucleus with orbital angular momentum **L**is proportional to the magnetic of **L** and also that **B** is in the same direction as **L**.

The spin orbit interaction energy now is

$$\Delta E = \frac{2\pi \beta_e}{m_e e h c^2 r}\frac{dV}{dr} \, L.s$$

Energy (wave numbers) is thus

$$\Gamma = \frac{\Delta E}{hc} = \frac{1}{2m_e hc^3 r}\frac{dV}{dr} \text{L.s} = a\, \mathbf{L}.s$$

Where a is constant (except for its dependence on r) given by

$$\frac{1}{2m_e hc^3 r}\frac{dV}{dr}$$

4. The vector model for atoms

Vector model describes the relationship between the angular momenta and their components in atoms.

In quantum mechanics we have the commutation relation among the components of angular momentum L as

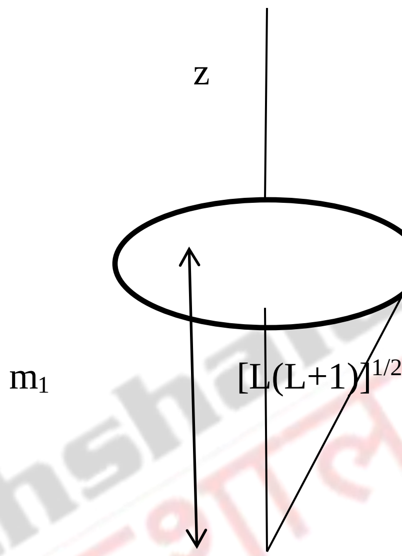
$[L_x,L_y]= i(h/2\pi)L_z;[L_y,L_z]=i(h/2\pi)L_x;[L_z,L_x]= i(h/2\pi)L_y$

So, L_x,LandL$_z$ do not commute. If the magnitude of L is considered

$$L^2= L_x^2+L_y^2+L_z^2$$

then L^2 commute with L_x, $L_y$and L_z. Thus L^2 and one of its components can be precisely measured simultaneously. In classical mechanics the angular momentum L is a vector that can have fixed components L_x, $L_y$and L_z. According to quantum mechanical commutation rules, only one of three components can be fixed. The other two components must vary with time so that L_x and L_y cannot be quantized if L_z is quantized.

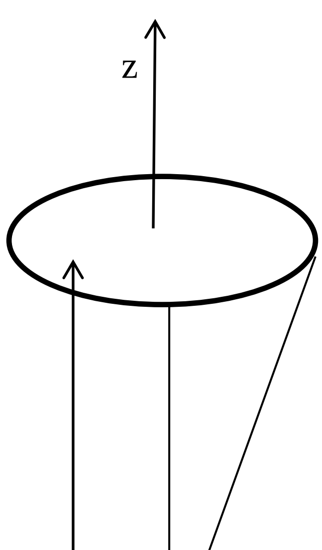
The vector model is the summary of the general result for angular momentum . The vector model diagram of a single angular momentum vector **L**is shown in fig. where L appears to precess around z-axis, if it did not precess L_x and are quantized and thus would violate commutation rules. The vector L has a length given by $h/2\pi[L(L+1)]^{1/2}$ where Lis an integer and the projection m_1 of L along the z-axis can never be perfectly aligned along z-axis.



The figure depicts the precession of orbital angular momentum L about the axis of quantization z

If the angular momentum is only due to spin, then s having a magnitude $h/2\pi[L(L+1)]^{1/2}$ will precess about the z-axis. The projection of s along the z-axis is given by m_s(fig).

Now considering the two angular momentum L and s that satisfy the commutation rules. If there is no coupling between L and s;



$m_s[s(s+1)]^{1/2}$

Precession of spin angular momentum s about the axis of quantization z

The vector corresponding to L and s precess independently about z-axis their projection m_l and m_s respectively on the z-axis shown in fig..

L and s could precess together and add to form a resultant angular momentum **j**. The only projection along z-axis in this case would be m_j as shown in fig..