B.Sc. (Sem. - 4) Physics

Course: US04CPHY21

Electromagnetic Theory and Spectroscopy

UNIT-3 Lecture 3

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UNIT -III

Atomic Spectra

UNIT - III Atomic Spectra-Topics

- L-S Coupling
- J-J Coupling
- Fine structure of Hydrogen atom
- Spectral terms and their notations
- Positronium
- Mesonic atoms

Coupling Schemes:

L-S Coupling

j-j Coupling

Coupling Schemes: L-S Coupling

- $L = \sum l_i$ and $S = \sum s_i$
- $J = L + S$
- $J = (l_1 + l_2 + l_3 + \ldots.) + (s_1 + s_2 + s_3 + \ldots.)$
- *J follows certain quantum rules*

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Coupling Schemes: L-S Coupling

- $L = \sum l_i$ and $S = \sum s_i$
- $J = L + S$
- *J follows certain quantum rules*
- *(i) All the three vectors L, S and J must be quantized.*

Coupling Schemes: L-S Coupling

- $L = \sum l_i$ and $S = \sum s_i$
- $J = L + S$
- *J follows certain quantum rules*
- *(ii) L may have values 0, 1, 2, 3, … depending upon the number of electrons in the atom and the directions of their orbital vectors.*

Coupling Schemes: L-S Coupling

- *J follows certain quantum rules*
- *(iii) S may have values 0,* $\frac{1}{2}$*, 1,* $\frac{3}{2}$ *, 2,* $\frac{5}{2}$*, 3, … depending upon the number of electrons in the atom and the directions of their spin vectors.*
- *S may have* ***integral*** *value for* ***even*** *number of electrons in the atom.*

Coupling Schemes: L-S Coupling

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- *(iii) S may have values 0,* $\frac{1}{2}$*, 1,* $\frac{3}{2}$ *, 2,* $\frac{5}{2}$*, 3, … depending upon the number of electrons in the atom and the directions of their spin vectors.*
- *S may have **half-integral** for **odd** number of electrons in the atom.*

Coupling Schemes: L-S Coupling

- *J follows certain quantum rules:*

- *(iv) J may have values 0, 1, 2, 3, … when S is an integer*
- *i.e. for **even** number of electrons in the atom.*

Coupling Schemes: L-S Coupling

- *J follows certain quantum rules*
- *(iv) J may have values* $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ *when S is a half-integer*
- *i.e. for **odd** number of electrons in the atom.*

Coupling Schemes: L-S Coupling

- *For* ***an atom with only one electron*** *in normal state*
- $l = 0$
- $L = 0$ (Only one value)
- $S = \frac{1}{2}$
- $\therefore J = L + S = \frac{1}{2}$

Coupling Schemes: L-S Coupling

- *For an atom with* ***two electrons*** *in normal state*
- *Suppose $l = 0$ and $l = 1$*
- *$L = 0 + 1 = 1$ (Only one value)*
- *$S = \frac{1}{2} + \frac{1}{2} = 1$ or $\frac{1}{2} - \frac{1}{2} = 0$*
- *$\therefore J = L + S = 0, 1, 2$ designated by $^3P_0, {}^3P_1, {}^3P_2$*

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Splitting of P state into a Triplet and $J = 0$ and state ${}^1P_1$

Coupling Schemes: L-S Coupling

- *Suppose* $L = 2$ *and* $S = \frac{3}{2}$

Here $L > S$ *therefor there are* $(2S+1)$ *possible values of* J

- $\therefore J = L + S = (2 + \frac{3}{2} = \frac{7}{2}), \ldots, (2 - \frac{3}{2} = \frac{1}{2})$

- *Possible values of J are* $\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$

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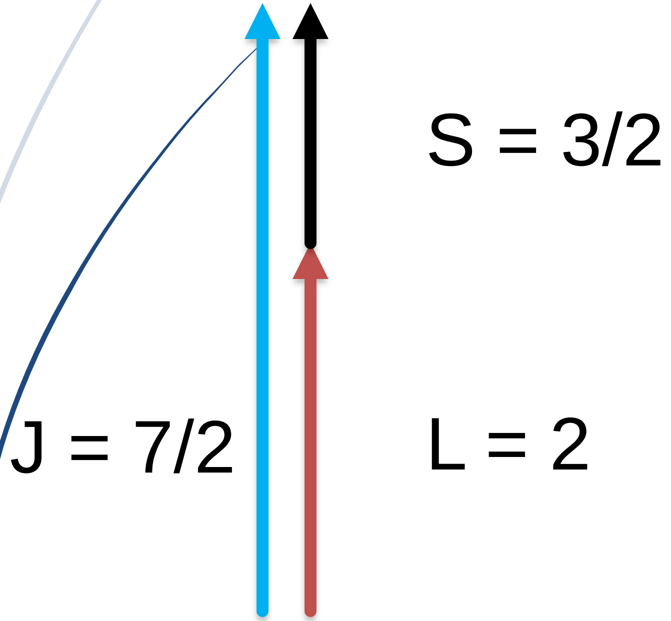
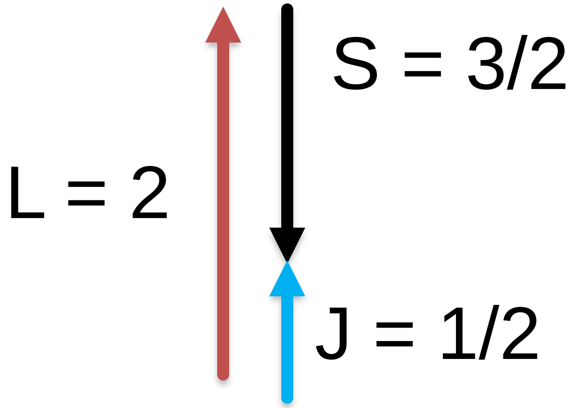
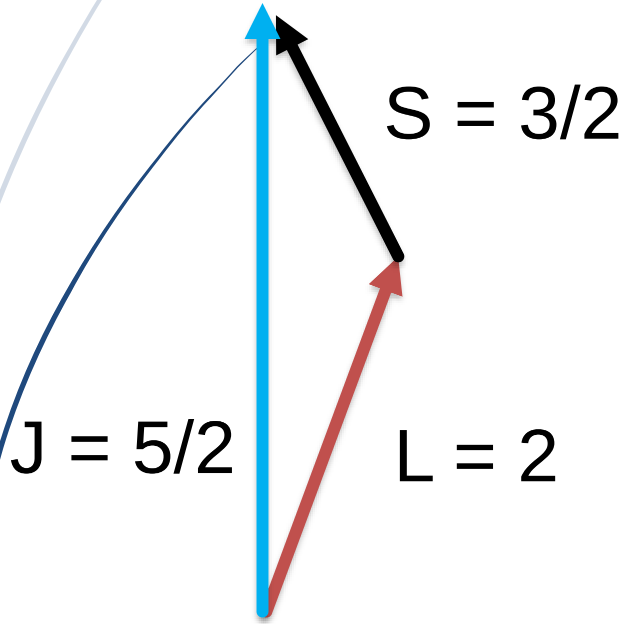
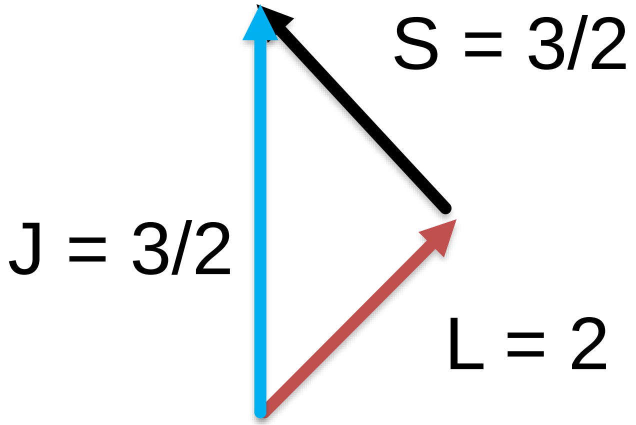




Coupling Schemes: L-S Coupling

- *Suppose $L = 2$ and $S = \frac{3}{2}$*
- *Possible values of J are $\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$*





Coupling Schemes: L-S Coupling

- *Suppose $L = 1$ and $S = 2$ [For practice]*

Here $L < S$ therefor there are $(2L+1)$ possible values of J

- *Possible values of J are ? ? ? ? ?*

Coupling Schemes: j-j Coupling

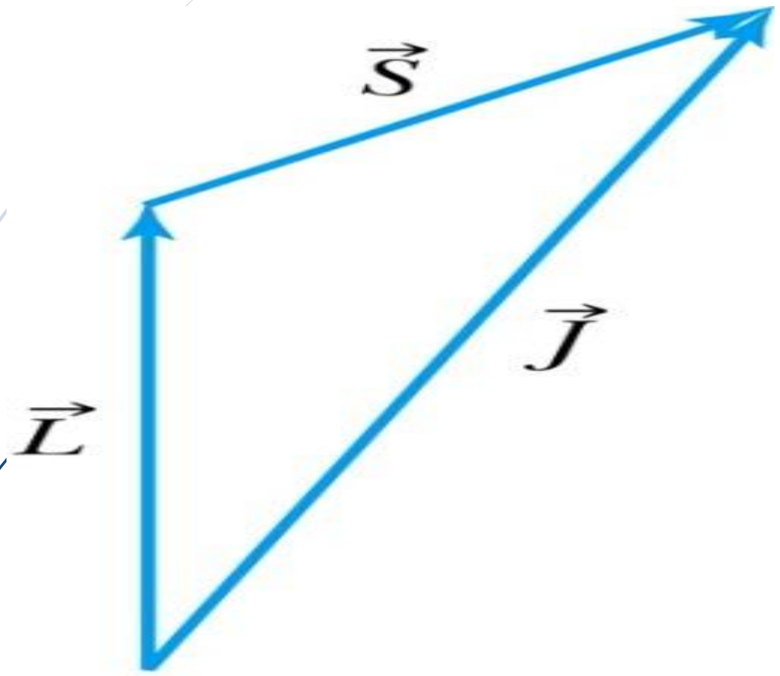
- In this type of coupling, each electron contributes to the total angular momentum of the atom by combing first its individual spin and orbit vectors by the relation

$$J = l + s$$

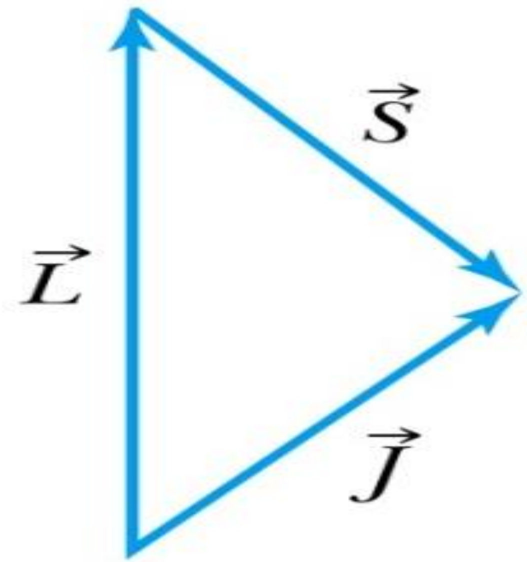
- Then the vector sum of each j corresponding to each electron gives the total angular momentum J to the atom

$$(l_1 + s_1) + (l_2 + s_2) + (l_3 + s_3) + \ldots = J$$

Coupling Schemes: j-j Coupling



$$j = \ell + s = 1 + \frac{1}{2} = \frac{3}{2}$$



$$j = \ell - s = 1 - \frac{1}{2} = \frac{1}{2}$$

3.7 FINE STRUCTURE OF HYDROGEN LINES

3.7 FINE STRUCTURE OF HYDROGEN LINES

- How to explain fine structure doubling of spectral lines?

- Having explained the action of magnetic field on **small atomic magnets** in Stern-Gerlach experiment, we may visualize the fine structure doubling of spectral lines on the basis of a **magnetic interaction** between the **spin and angular momenta of atomic electrons.**

3.7 FINE STRUCTURE OF HYDROGEN LINES

- **Magnetic Moment:**

- An electron revolving round a proton finds itself in a magnetic field because, in its own frame of reference, the proton is circling about it.

- This magnetic field then acts upon the electron's own magnetic moment to produce a kind of internal Zeeman effect.

3.7 FINE STRUCTURE OF HYDROGEN LINES

- The magnetic energy V_m of a magnetic dipole moment μ in a magnetic field of flux density **B** is

$$V_m = -\mu . \boldsymbol{B} \qquad (1)$$

$$V_m = \pm \frac{e\,\hbar}{2\,m} \boldsymbol{B} \qquad (2)$$

- where $\frac{e\,\hbar}{2\,m}$ is **spin magnetic moment** in the direction of B.

3.7 FINE STRUCTURE OF HYDROGEN LINES

- Depending upon the **orientation of its spin vector**, the energy of the electron in a given atomic state will be **higher** or **lower** by the $\frac{e\hbar}{2m}B$ than its value in the absence of spin orbit interaction.

3.7 FINE STRUCTURE OF HYDROGEN LINES

- The **result is the splitting of every quantum state** (except S state) into two separate sub-states and consequently, the **splitting of every spectral line into two component lines.**

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- The result is the splitting of every quantum state (except S state) into two separate sub-states and, consequently, the **splitting of every spectral line into two component lines.**

- The assignment of **s =** $\boldsymbol{\frac{1}{2}}$ is the only one that conforms to the **observed fine structure doubling**.

3.7 FINE STRUCTURE OF HYDROGEN LINES

- Let us now have the estimate of **magnetic flux density** and **magnetic energy** in fine structure doubling.
- The circular wire loop of radius *r* that carries the current *i* has a magnetic field of flux density at its centre

$$B = \frac{\mu_o \, i}{2\, r} \qquad (3)$$

- where μ_o is the permeability of the vacuum.

3.7 FINE STRUCTURE OF HYDROGEN LINES

- An orbital electron say in a hydrogen atoms 'sees' itself circled ***f*** times each second by a proton of charge **+e** for a resulting **flux density** of

$$B = \frac{\mu_o f e}{2 r} \qquad (4)$$

- In the **ground state of hydrogen atom** $f = 6.8 \times 10^{15}$ cps and $r = 5.3 \times 10^{-11}$ metre, so that

$$B = 13 \text{ Tesla (abbreviation T)} \qquad (5)$$

- which is a **very strong magnetic field**.

3.7 FINE STRUCTURE OF HYDROGEN LINES

- The value of **Bohr magneton** is

$$\frac{e\,\hbar}{2\,m} = 9.27 \times 10^{-24}\ \text{J/T} \qquad (5)$$

- Hence, **magnetic energy (V_m)** of one such electron is

$$V_m = \frac{e\,\hbar}{2\,m}\,B = (\,9.27 \times 10^{-24}\ \text{J/T}) \times 13\,T$$

$$V_m = 1.2 \times 10^{-22}\ \text{joules} \qquad (6)$$

3.7 FINE STRUCTURE OF HYDROGEN LINES

- The wavelength shift in such a change in energy is about **2 ^{0}A** for a spectral line of unperturbed wavelength **6563 ^{0}A**, somewhat more than the observed splitting of the line originating in the $n = 3 \rightarrow n = 2$ transition.

- However, the flux density of the magnetic field at the orbits of higher order is less than for ground state orbit, which accounts for the discrepancy.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

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- The optical spectrum of an element is the characteristic of the valence electron, i.e., optical spectrum particularly depends upon the electrons which are not interlocked in closed shells.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- The different atoms having different number of valence electrons in their outermost orbit show different types of spectra.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- For example, the alkali metals show one type of spectrum, while alkaline earth of another type, since they possess one and two valence electrons, respectively in their outermost shell.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- Further, the state of electron, is described in terms of the different values of *l, s and j*.

- The small letters *l, s and j* depict the state of an electron, while

- the capital letters, *L, S and J* depict the state of an atom as a whole

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- But when we are dealing with one valence electron system, the values of L, S and J are the same as those of l, s and j, respectively, since the interlocked electrons in closed shells and sub-shells contribute nothing to the total angular momentum.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- Dealing with many electron systems, the vectors L, S and J which define the **state of an atom** are vector sums of l, s and j, respectively for different free electrons.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- The electrons having 0, 1, 2, 3.. etc. values for l are represented by the small letters s, p, d, f, ... etc. respectively.

- Similarly, the capital letters, S, P, D, F depict the state of the atom for the value if L as 0, 1, 2, 3, ...,etc.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- In the case of one-electron system the value of S is $+\frac{1}{2}$ and hence the multiplicity of the state is 2.
- The multiplicity of a state is given by $r = 2S + 1$.
- Hence the single-electron system always gives rise to a **double state**, corresponding to the value $(L + \frac{1}{2})$ and $(L - \frac{1}{2})$ for J with the exception of ground state.

$$J = (L + \frac{1}{2}) \text{ and } J = (L - \frac{1}{2})$$

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- The multiplicity of a state is given by $r = 2S + 1$.
- In the case of many electron system, S may not necessarily have the value 1/2, but, it may have any value.
- For example, in two electron system S = 0 or 1. Therefore, the state is either singlet or triplet.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- The multiplicity of a state is given by r = 2S + 1.

- In three electron system S = $\frac{1}{2}$ or $\frac{3}{2}$ and hence state is doublet or quartet, and so on except the ground term.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- Now if we want to depict the state of an atom, we must mention the values of L, S, J and r.
- This is done by writing the state having L=1, S =1/2 and as J = 3/2 as $^{2}P_{3/2}$.
- The term $^{2}P_{3/2}$, clearly indicates that
- the value of L is given by the capital letter,
- the value of J by right subscript below the capital letter and
- the value of r by left superscript at the top of capital letter.
- Since r = 2S + 1, the S is obviously determined.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- L=1, S =1/2 and as J = 3/2 as $^2P_{3/2}$.
- Sometimes the value of principal quantum number is also mentioned before the capital letter as $2\ ^2P_{3/2}$
- Here the value of n is 2.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- In **one-electron system**, every state is **doublet** and may be depicted as below:

$$^2S_{1/2},\ ^2P^{1/2},\ ^2P_{3/2},\ ^2D_{3/2},\ ^2D_{5/2} \text{ and so on.}$$

- Here one point is important to note that **multiplicity symbol of the system is used always** whether all the terms are present or not.

- For example, the ground term is here written as $^2S_{1/2}$. But actually, the state is singlet and we should write $^1S_{1/2}$.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- To write the **ground state** as $^2S_{1/2}$ is preferable because it indicates to which system the ground term belongs, as in this case to the doublet system.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- **Why is the ground state always singlet?**
- We know that the value of J is given by L + S to L - S with a difference of one.
- Since in **one-electron system** $S = \pm 1/2$ (with respect to L) hence $J = L + ½$ and $J = L - ½$, i.e. J has only two values and the state is said to be **doublet**.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- For the ground state **L = 0**, J = ½ or J = - ½. But net angular momentum of the atom is always positive and the possibility of -1/2 is ruled out.

- Therefore, the ground state of single electron system is always singlet.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- In case of **many-electron system** for the ground state L = 0 and J = S, S can assume any value of 0, 1/2, 3/2 etc.

- When L < S, the multiplicity of the state is given by (2L + 1) which leads again to the possible value of J as **one** and the state is **singlet**.

3.8. SPECTRAL TERMS AND THEIR NOTATIONS

- The notation for a single-electron atom becomes $n^{2S+1}\,L_J$
- The letters and numbers are called **spectroscopic symbols**.
- There are **singlet** states ($S = 0$) and **triplet** states ($S = 1$) for two electrons.

3.9 POSITRONIUM

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- The combined structure, the **positronium**, as it is called, revolves round the common centre of gravity.

- Thus the system is very **much identical to the hydrogen atom** and so the formulae derived for hydrogen atom may be applied for this system.

3.9 POSITRONIUM

- Hence the **orbital radius** is given by

$$r_n = \frac{\hbar^2}{e^2}\,\frac{m+m}{m^2}\,\frac{n^2}{Z}\,(4\,\pi\,\varepsilon_0) \qquad (1)$$

- For ground state, $r_0 = \dfrac{2\,\hbar^2\,(4\,\pi\,\varepsilon_0)}{m\,e^2} \approx 1\,°A$

- Thus, the orbital radius increases by a factor **two**.

3.9 POSITRONIUM

- The **energy of dissociation** is given by

$$E = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{e^4}{2\hbar^2}\frac{m^2}{m+m} = -\frac{m e^4}{4\hbar^2}\frac{1}{(4\pi\varepsilon_0)^2} \qquad (2)$$

- This is **one half of the ionization potential of the hydrogen atom**.

3.9 POSITRONIUM

- The positronium exists in **two states** depending upon the state of spin orientation.
- These are **ortho-positronium** in which **the spins of the two particles are parallel** and **para-positronium** in which **spins are anti-parallel**.

3.9 POSITRONIUM

- In **para-positronium**, as two particles have their spin **anti-parallel**, the system is an **unstable** one with a life time 1.25 x 10^{-10} sec. The para-positronium decays into **two** photons.

- The **ortho-positronium** is **stable** enough and has a life time of the order of 1.4 x 10^{-7} sec.
- It decays into **three** γ-photons so as to maintain the conservation of spin.

3.9 POSITRONIUM

- The ground level of **ortho-positroniuro** lies above the ground state of para-positronium by only 0.84 x 10^{-2} eV.

- The difference between the life times of two photons accelerates the annihilation process.

- Thank you..