Production of Courseware

- Contents For Post Graduate Courses

Paper No. : Lasers, Atomic and Molecular Spectroscopy

Module: Coupling Schemes-I

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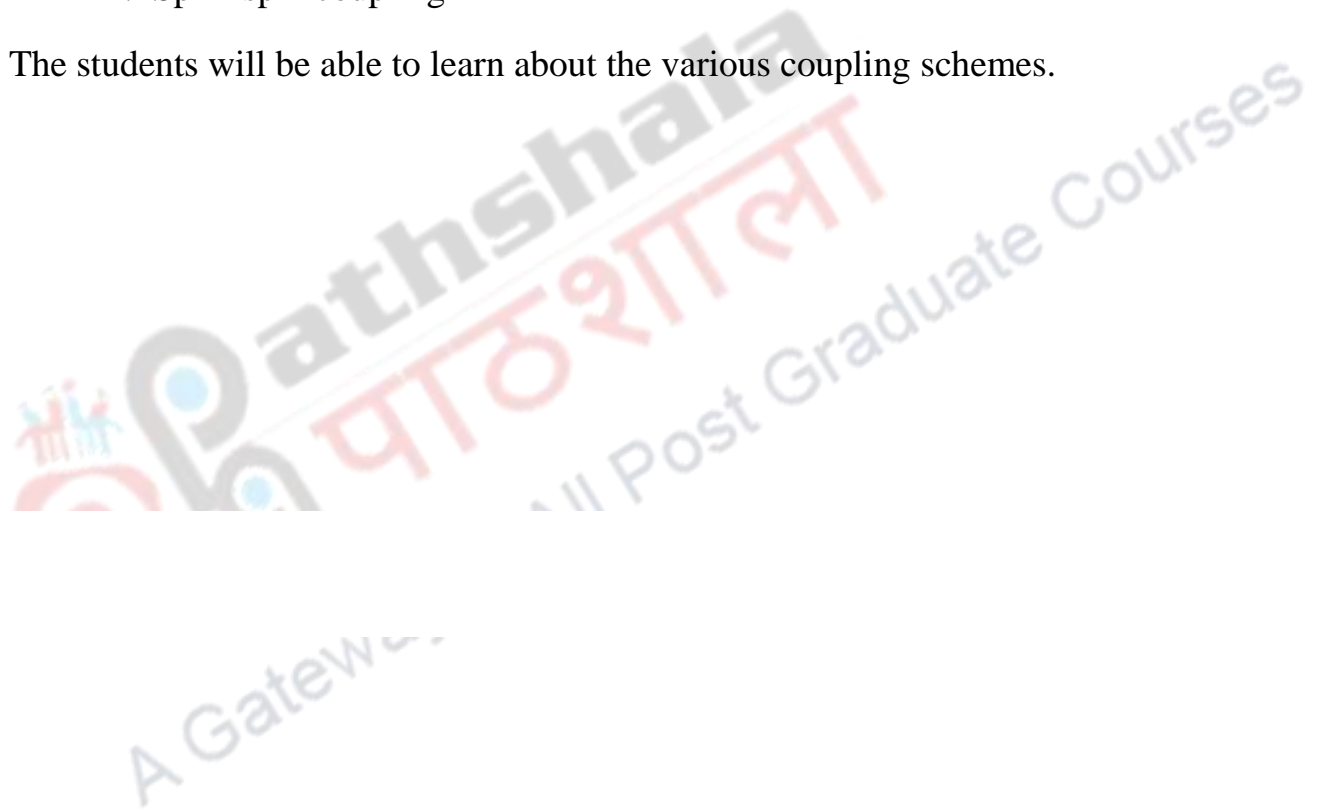| Description of Module	
Subject Name	Physics
Paper Name	Lasers, Atomic and Molecular Spectroscopy
Module Name/Title	Coupling schemes
Module Id	

Contents:

1. Angular coupling momentum
2. LS coupling
3. JJ coupling
4. Spin -spin coupling

The students will be able to learn about the various coupling schemes.

I. Angular momentum coupling

As the name suggests, constructing eigen states of total angular momentum out of eigen-states of separate angular momenta is called angular momentum coupling. The orbit and spin of a single particle can interact through spin–orbit interaction, where the complete physical picture includes spin-orbit coupling.

Or

Two charged particles, each with a well-defined angular momentum, may interact by Coulomb forces, where coupling of the two one-particle angular momenta to a total angular momentum is a useful step in the solution of the two-particle Schrödinger Equation.

In both the cases the separate angular momenta are no longer constants of motion, but the sum of the two angular momenta usually is still.

Angular momentum coupling in atoms is of importance in **atomic spectroscopy** while angular momentum coupling of electron spins is of importance in **quantum chemistry**. Likewise, angular momentum coupling in the nuclear shell model is ubiquitous.

In astronomy, spin-orbit coupling reflects the general law of conservation of angular momentum that also holds for celestial systems.

The direction of the angular momentum vector is neglected in simple cases. The spin-orbit coupling is the ratio between the frequency with which a planet or other celestial body spins about its own axis to that with which it orbits another body. This is commonly known as orbital resonance.

1. Angular momentum conservation

The total angular momentum of a system has a constant magnitude and direction if the system is subjected to no external **torque**. **Angular momentum** is considered as a property of a physical system:

- The system experiences a spherically symmetric potential field
- The system moves in isotropic space

In both the cases the angular momentum operator commutes with the Hamiltonian of the system. Thus the angular momentum and the energy (eigenvalue of the Hamiltonian) can be measured at the same time by using Heisenberg's Uncertainty principle.

An example of the <u>first situation</u> is :

an atom whose electrons only experience the Coulomb force of its atomic nucleus. If the electron-electron interaction (and other small interactions such as spin orbit coupling) is ignored, the *orbital angular momentum* **l** of each electron commutes with the total Hamiltonian. In this model the atomic Hamiltonian is a sum of kinetic energies of the electrons and the spherically symmetric electron-nucleus interactions. The individual electron angular momenta l_i commute with this Hamiltonian. That is, they are conserved properties of this approximate model of the atom.

An example of the <u>second situation</u> is a rigid rotator moving in field-free space. A rigid rotor has a well-defined, time-independent, angular momentum.

These two situations originate in classical mechanics. The third kind of conserved angular momentum, associated with spin, does not have a classical counterpart. However, all rules of angular momentum coupling apply to spin as well.

In general the conservation of angular momentum implies full rotational symmetry and, conversely, spherical symmetry implies conservation of angular momentum. If two or more physical systems have conserved angular momenta, it can be useful to

combine these momenta to a total angular momentum of the combined system—a conserved property of the total system. The building of eigen-states of the total conserved angular momentum from the angular momentum eigen-states of the individual subsystems is referred to as *angular momentum coupling*.

Application of angular momentum coupling is useful when there is an interaction between subsystems that, without interaction, would have conserved angular momentum. By the very interaction the spherical symmetry of the subsystems is broken, but the angular momentum of the total system remains a constant of motion. Use of the latter fact is helpful in the solution of the Schrödinger equation.

Examples

As an example we consider two electrons, 1 and 2, in an atom (Helium atom). If there is no electron-electron interaction, but only electron-nucleus interaction, the two electrons can be rotated around the nucleus independently of each other; nothing happens to their energy. Both operators, $\mathbf{l}_1$ and $\mathbf{l}_2$, are conserved. However, if we switch on the electron-electron interaction that depends on the distance d (1,2) between the electrons, then only a simultaneous and equal rotation of the two electrons will leave $d(1,2)$ invariant. In such a case neither $\mathbf{l}_1$ nor $\mathbf{l}_2$ is a constant of motion in general, but the total orbital angular momentum is $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$. Given the eigenstates of $\mathbf{l}_1$ and $\mathbf{l}_2$, the construction of eigenstates of $\mathbf{L}$ (that still is conserved) is the *coupling of the angular momenta of electrons 1 and 2*.

The total orbital angular momentum quantum number $\mathbf{L}$ is restricted to integer values.

In quantum mechanics, coupling also exists between angular momenta belonging to different Hilbert spaces of a single object, e.g. its spin and its orbital angular momentum. If the spin has half-integer values, such as 1/2 for an electron, then the total (orbital plus spin) angular momentum will also be restricted to half-integer values.

Further, the quantum states of composed systems (i.e. like two Hydrogen atoms or two electrons) in basis sets which are made of tensor products of quantum states that in turn describe the subsystems individually, can be extended. We assume that the states of the subsystems can be chosen as eigenstates of their angular momentum operators (and of their component along any arbitrary z axis).

The subsystems are therefore correctly described by a set of ℓ, m quantum numbers, then there is interaction among the subsystems, the total Hamiltonian contains terms that do not commute with the angular operators acting on the subsystems only. However, these terms *do* commute with the *total* angular momentum operator. Sometimes one refers to the non-commuting interaction terms in the Hamiltonian as *angular momentum coupling terms*, because they necessitate the angular momentum coupling.
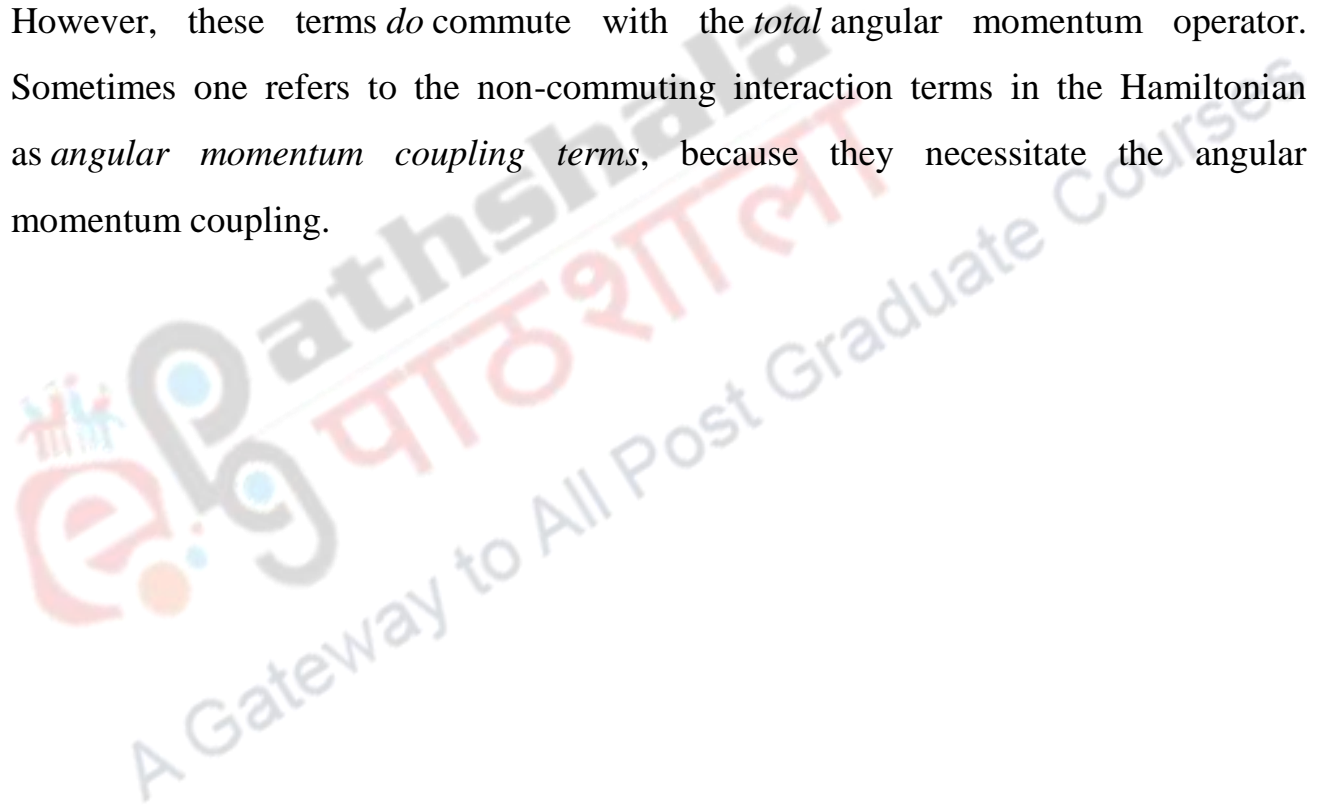
Spin-orbit coupling

The behavior of atoms and smaller particles is well described by the theory of quantum mechanics, in which each particle has an intrinsic angular momentum called spin and specific configurations e.g. electrons in an atom are described by a set of quantum numbers. Collections of particles also have angular momenta and corresponding quantum numbers, and under different circumstances the angular momenta of the parts couple in different ways to form the angular momentum of the whole. Angular momentum coupling is a category including some of the ways that subatomic particles can interact with each other.

In atomic physics, spin-orbit coupling, also known as **spin-pairing**, describes a weak magnetic interaction, or coupling, of the particle spin and the orbital motion of this particle, e.g. the electron spin and its motion around an atomic nucleus . One of its effects is to separate the energy of internal states of the atom, e.g. spin-aligned and spin-antialigned that would otherwise be identical in energy.

L-S coupling and J-J coupling

Hamiltonian of the system depends on

1. Kinetic energy of the electrons
2. Potential energy of the electrons due to the interaction between the nucleus and the electrons
   For these two factors Hamiltonian act as unperturbed Hamiltonian
3. Energy due to interaction between the electrons
4. Spin-spin correlation energy
5. Spin-orbit interaction
   For these three factors Hamiltonian act as perturbed Hamiltonian

For **lighter elements** the spin orbit interaction energy is much less as compared to the interaction energy between electrons and spin-spin correlation energy and there will be L-S coupling for lighter element.

For **heavier elements** the spin orbit interaction energy is much greater than interaction energy between electrons and spin- spin correlation energy and there will be j-j coupling for heavier elements.

L-S coupling

In L-S coupling it is assumed that, when several electrons are present in an atom, each with a definite value of orbital angular momentum l_i^* and spin angular momentum s_i^* such that $li^* = l_i(l_i+1)h/2\pi$ and $si^* = s_i(s_i+1) h/2\pi$.

Due to the domination of interaction energy between electrons the orbital angular momentum of indivisible electrons will intract with each other and the total orbital angular momentum is given by $L = L(L+1) h/2\pi$, where L varies from | $l_1+l_2+l_3$……..|minimum to | $l_1+l_2+l_3$…….|maximum the states with different values of L have fairly large energy difference, the state of largest L of being lowest energy. The different levels are designated as S, P, D, F, G……..according as L=0,1,2,3,4,5……. Thus:

For 3p 4d electrons: l1=1, l2=2.

$$\therefore L = |l1-l2|, | l1-l2|+1, ……(l1+l2)$$

$$= 1, 2, 3 \text{ (P, D, F states)}.$$

For 3p, 4d, 5f electrons: l1=1, l2=2, l3=3. The electrons which are tightly bound to the nucleus will interact first.

$$\therefore L = |l1-l2|, | l1-l2|+1, ……(l1+l2)$$

$$= 1, 2, 3 \text{ (P, D, F states)}.$$

Now L combining with l3=3

$$\therefore L = 0, 1, 2, 3, 4, 5, 6(S, P, D, F, G, H, I \text{ states})$$

2. Due to the domination of spin-spin correlation energy the spin angular momentum of individual electron will interact with each other and the total spin angular momentum is given by $S=\sqrt{S(S+1)}\dfrac{h}{2\pi}$

The quantum number S can take the values :

$S = |s1+s2+s3+\ldots\ldots|$min to $| s1+s2+s3+\ldots\ldots|$max. . The states with different

values of S have considerable energy difference, the state of highest S being of lowest energy. The different levels are designated by their multiplicity, (2S+1). Thus:

For one electron: $S= s = ½$.

$$\therefore (2S+1) = 2 \text{ (doublet level)}.$$

For two electrons: $s1 = ½$, $s2 = ½$.

$$\therefore S = |s1 - s2|, |s1 - s2| + 1, \ldots\ldots(s1+s2) = 0, 1.$$

$$\therefore (2S+1) = 2 \text{ (singlet and triplet levels)}$$

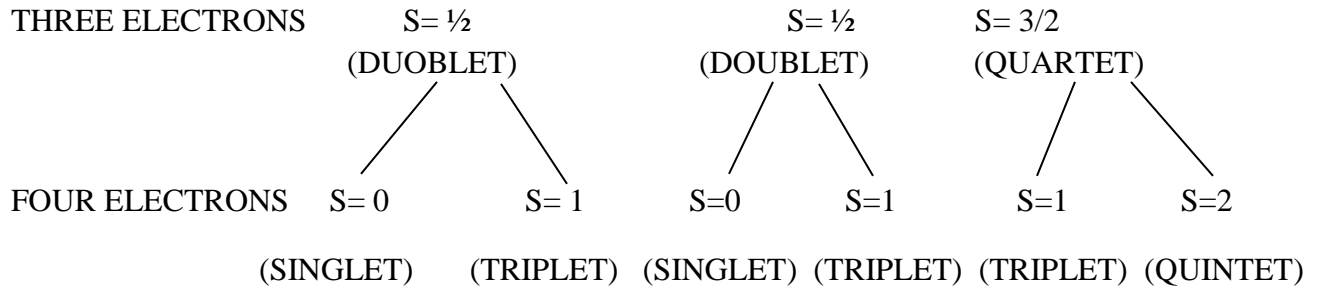For three electrons: $s1 = ½$, $s2 = ½$, $s3 = ½$.

To combine three spins, we first combine two of them to obtain S' = 0, 1, and then combine the third S3= ½ to each of them. Thus, if we couple s3 = ½ to s' =0; we get s= ½; and if we couple s3 = ½ to s' =1, we get s= 1/2, 3/2. Thus for three electrons, we get

S =1/2, 1/2, 3/2 (two sets of doublets, and one set of quartets).

The followings branching diagram illustrates the possible total spin quantum numbers which can be obtained by combining several independent electron spins.

ONE ELECTRON   S= ½

                                (DOUBLET)

TWO ELECTRONS   S= 0   S=1

            (SINGLET)   (TRIPLET)

THREE ELECTRONS	S= ½ (DUOBLET)		S= ½ (DOUBLET)		S= 3/2 (QUARTET)	
FOUR ELECTRONS	S= 0	S= 1	S=0	S=1	S=1	S=2
	(SINGLET)	(TRIPLET)	(SINGLET)	(TRIPLET)	(TRIPLET)	(QUINTET)
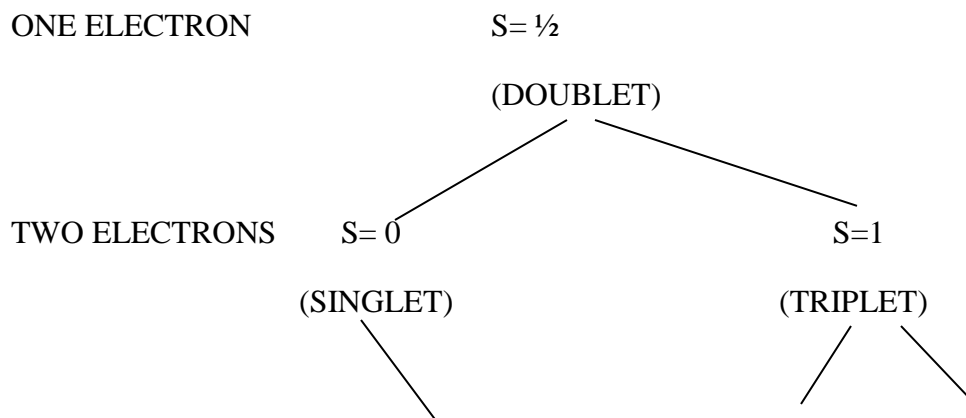
In the general case of N electrons, the possible values of S are

$$S=0,1,2,………..N/2 \text{ for even } N.$$
$$S= 1/2, 3/2, 5/2…….N/2 \text{ for odd } N.$$

The dominant spin-spin correlation and the residual electrostatic interaction having been taken into accounts as a first peturbation, the smaller spin- orbit interaction is included in L-S coupling as an additional perturbation.

As a result of smaller spin – orbit magnetic interaction, the resultant orbital angular momentum vector L and the resultant spin angular momentum vector S are less strongly coupled with each other to form a total angular momentum vector J of the atom:

$$J = L + S$$

the magnitude of J, L and S remaining constant. The magnitude of J is $\sqrt{J(J+1)}\, h/2\pi$, where the quantum number J takes the value:

$$J= |L-S|, |L-S|+1, ………..(L-S).$$

J is integral or half – integral according as S is integral or half integral. The number of J values is (2S+1) when L > S, or (2L+1) when S > L. This mean that due to spin orbit magnet interaction; a level characterized by given values of L and S is further broken up into comparative closer (2S+1) or (2L+1) levels, each characterized by a different J value. The group of these J-levels forms a fine structure multiplet'. The relative spacing of the fine structure levels with in a multiplet is governed by Lande interval rule.

Lande Interval Rule

Under L-S coupling, the spin-orbit interaction energy is of the form

$$\Delta E_{s,l} = a(L.S),$$

Where a is an interaction constant. Let us write

$$J = L+S.$$

Taking the scalar self product we have

$$J.J = L.L + S.S + 2L.S.$$

$$|J|^2 = |L|^2 + |S|^2 + 2L.S.$$

$$L.S = \tfrac{1}{2}[|J|^2 - |L|^2 - |S|^2].$$

$$\therefore \Delta E_{s,l} = a/2[J(J+1) - L(L+1) - S(S+1)]h^2/4\pi^2,$$

Because $J = J(J+1) h/2\pi$, and so on. We can write it as

$$\Delta E_{s,l} = A[J(J+1) - L(L+1) - S(S+1)],$$

Where A is another constant.

The various fine-structure levels of a Russell-Saunders multiplet have the same values of L and S, and differ only in the value of J. Hence, the energy difference between two fine-structure levels corresponding to J and J+1 is

$$E_{j+1} - E_j = A[(J+1)(J+2) - J(J+1)]$$

$$= 2A(J+1).$$

Thus, the energy interval (spacing) between consecutive levels J and J+1 of a fine-structure multiplet is proportional to J+1, that is, to the larger of the two J-values involved. This is 'Lande interval rule'.

NORMAL AND INVERTED MULTIPLETS

Within a given multiplet, usually the level with smallest J value lies lowest. Such a multiplet is a 'Normal' multiplet. There are, however, multiplets in which the largest J level lies lowest. Such multiplets are 'inverted' multiplets.

It is easy to understand how smallest J level lies lowest. The magnet field B produced by the orbital motion of the electron in the electric field of the nucleus is in the same direction as the orbital angular momentum L. In this field the most stable state, that is, the state of the lowest energy must be one in which the spin magnetic moment μ_s of

the electron lies up in the direction of B. We know that μs is directed opposite to S because the electron is negatively charged.

$$J = L - S \qquad\qquad J = L + S$$
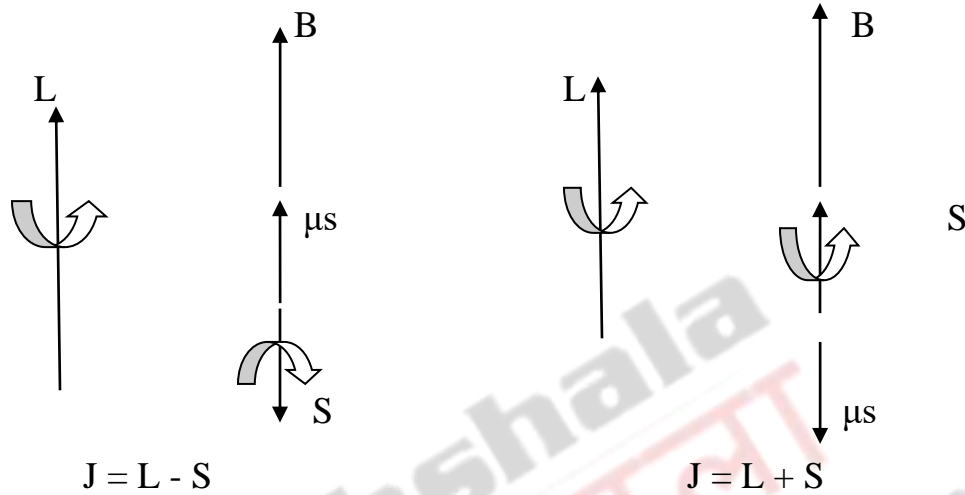
Thus, in the lowest energy state, L and S are in opposite directions and so the value of J is lowest. When L and S are in the same direction, which corresponds to highest J, then μs is opposite to B and the state is least stable.

The inverted multiplets arise due to some perturbing influences.

DETERMINATION OF SPECTRAL TERMS FOR L-S COUPLING

(1) **Atoms with one optical electron:** For hydrogen-like atom, the ground state configuration is
1s.

For this, we have $\qquad s = \frac{1}{2}; l = 0$,

So that $\qquad\qquad S = s = \frac{1}{2}$; multiplicity $2S+1 = 2$,

$\qquad\qquad L = l = 0$(S-state),

And $\qquad\qquad J = |L-S|, \dots\dots\dots\dots (L+S) = \frac{1}{2}$.

Thus, the ground state term of a hydrogen-like atom is

$\qquad\qquad ^{2}S_{1/2}$.

The excited state configuration and the corresponding terms for a hydrogen-like atom would be

$\qquad\qquad$ 2s, 3s, 4s, $\dots\dots\dots\dots\dots\dots ^{2}S_{1/2}$

2p, 3p, 4p, …………………………...$^2p_{1/2}$, $^2p_{3/2}$.

The ground state configuration for all alkali atoms is $^2S_{1/2}$.

(2) Atoms with two or more Non-equivalent optical electrons: 4p 4d

For this, we have

$s_1 = ½$, $s_2 = ½$, $l_1 = 1$, $l_2 = 2$.

The possible values of S and L are :

S = |s₁ - s₂|, |s₁ - s₂| + 1, …………………….....(s₁+s₂)

= 0, 1; multiplicity (2S+1) = 1,3

And **L = |l₁-l₂|, | l₁-l₂|+1, ……………………………(l₁+l₂).**

= 1, 2, 3, (P, D, F, state).

Thus, we have in all six terms, three singlet terms and three triplet terms. These terms can be written as

^1P, ^1D, ^1F, ^3P, ^3D, ^3F.

To take into account spin-orbit interaction, let us combine L and S to form J.

J= |L-S|, |L-S|+1, …………………..(L+S).

For singlet terms, we have

S = 0; L = 1; J = 1; $^1P_1$.

S = 0; L = 2; J = 2; $^1D_2$.

S = 0; L = 3; J = 3; $^1F_3$.

For triplet terms, we have

S = 1; L = 1; J = 0, 1, 2; $^3P_0$, $^3P_1$, $^3P_2$.

S = 1; L = 2; J = 1, 2, 3; $^3D_1$, $^3D_2$, $^3D_3$.

S = 1; L = 3; J = 2, 3, 4; $^3F_2$, $^3F_3$, $^3F_4$.

Thus, a single degenerate level of configuration 4p 4d is splitted into 12 levels as shown in fig.
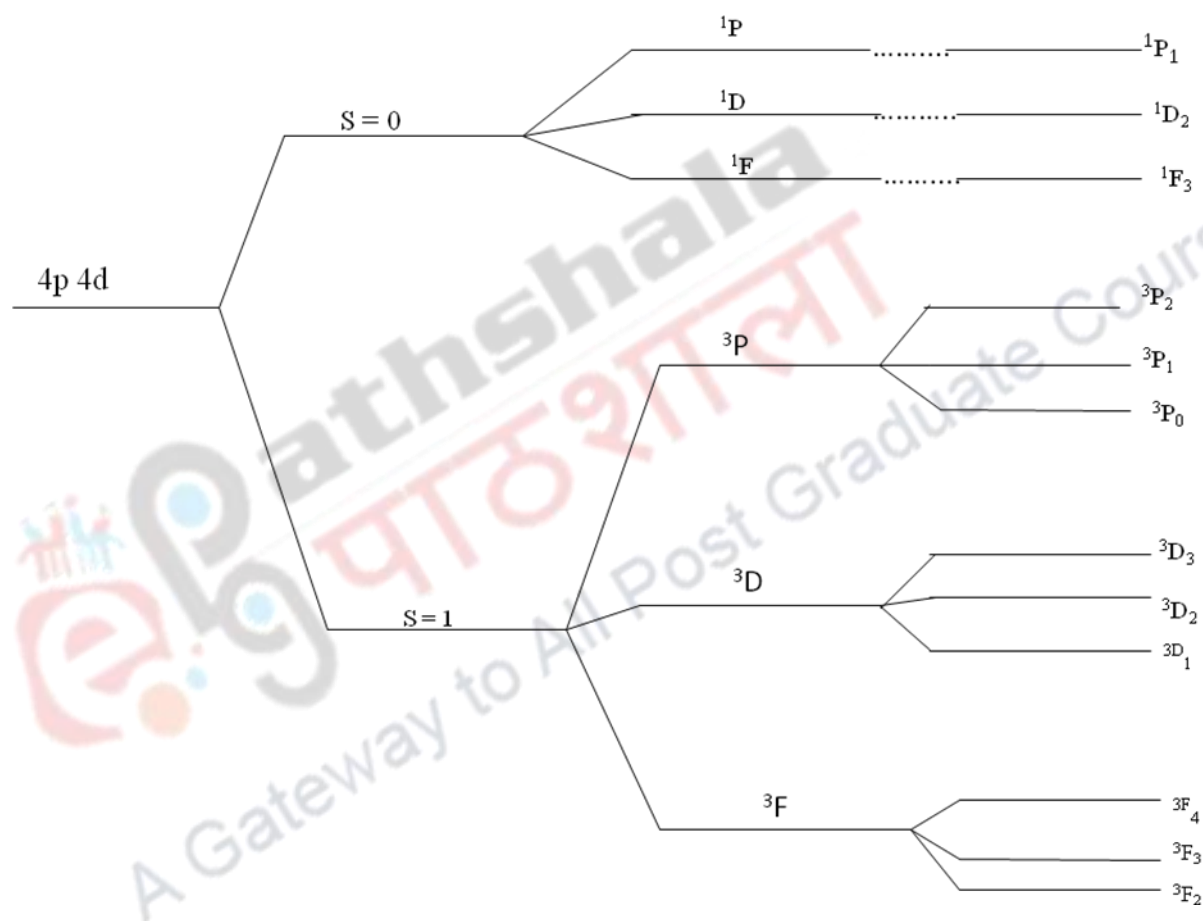
unperturbed level   spin-spin correlation energy + residual electrostatic energy + spin-orbit   magnetic energy