Production of Courseware

- Contents For Post Graduate Courses

Paper No. : Lasers, Atomic and Molecular Spectroscopy

Module: Coupling Schemes -2

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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. **Atoms with Two or More Equivalent Electrons**
2. **Orders of terms and fine structure levels**
3. **Vector Modeel for Two valence electron atom under L-S Coupling Scheme.**
4. **Selection Rules for Multi-electron atoms in L-S Coupling**
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8. **Electrons in different orbitals(non-equivalent)**
9. **Electrons in the same orbital (equivalent electrons)**

The students will be able to learn about the various coupling schemes.
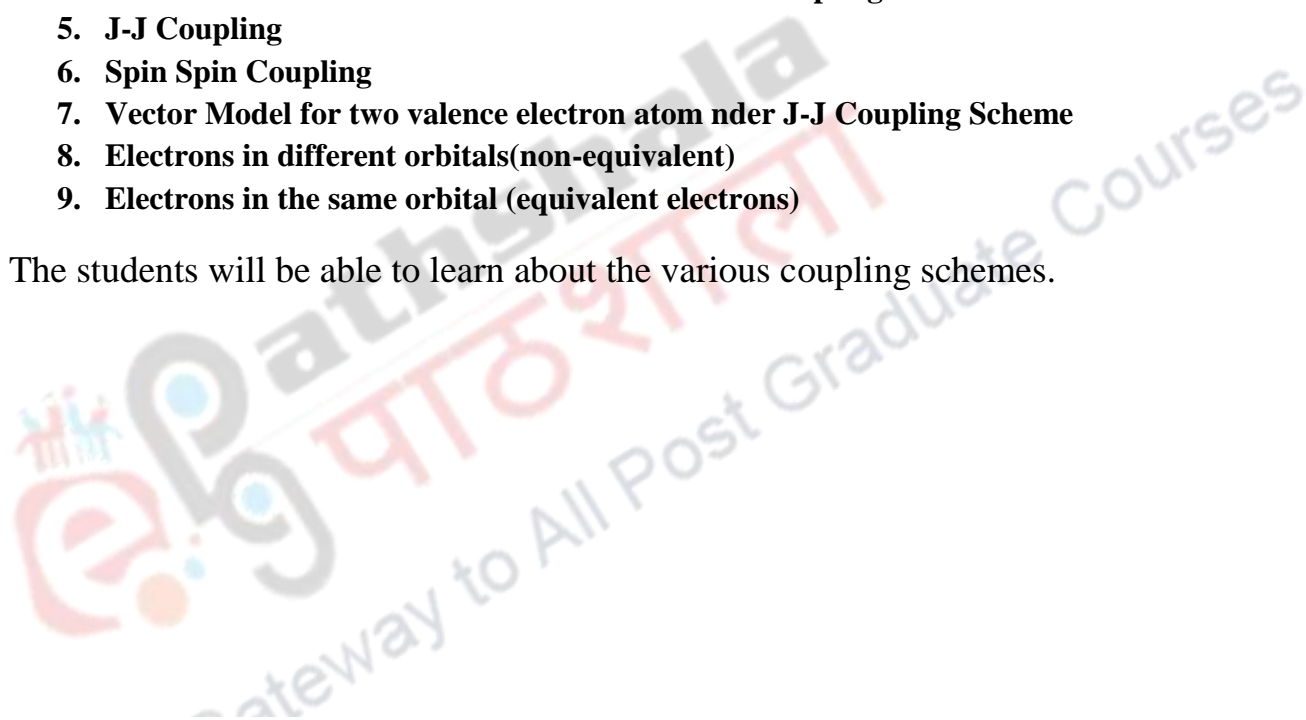
❖ Atoms with Two or More Equivalent Electrons:

For two equivalent electrons (same n and l values) the values of at least one of the remaining quantum numbers (m_l or m_s) must differ to satisfy Pauli's exclusion principle. Hence terms which were possible for two non-equivalent electrons are now not allowed. Let us now see how to obtain terms from a configuration involving equivalent electrons. Before we do so we must mention two important facts:

A closed sub-shell, such as s^2, p^6, d^{10},......…………. always forms a $^1s_0$ term only. The closed sub-shell consists of maximum number, $2(2l+1)$, of equivalent electrons in antiparallel pairs so that

$$\sum m_l = 0$$

$$\sum m_s = 0$$

And this means that

$$M_l = 0, M_s = 0$$

And so $L = 0$ (S- State),

$S = 0, 2S+1 = 1$ (Singlet)

And $J = 0$.

That is, the only possible term is $^1S_0$. Hence, we conclude that when a subshell is completely filled, the only allowed state is one in which the total spin angular momentum, total orbital angular momentum and total angular momentum are all zero. This means that the subshell has no net magnetic dipole moment.

b.) The terms of a configuration $(nl)^q$ are the same as the terms of the configuration $(nl)^{r-q}$, where is the maximum number of electrons, that is $2(2l+1)$. For example, the

terms of p^5 are the same as those of p^1, the terms of p^4 are the same as those of p^2, the terms of d8 are the same as those of d^2, and so on.

This simplification is based on the fact that a completed subshell like p^6 gives only a $^1s_0$ term (zero angular momentum). This means that the vector addition of the angular momenta of the terms of p^2 to the corresponding quantities for p^4 must give zero. From this it follow that the quantum numbers S and L must be same for p^2 and p^4, that is, the terms of p^2 are the same as those of p^4.

Calculate the spectral terms arising from two equivalent p-electrons (p^2). Let us imagine the atom to be placed in a very strong magnetic field where all the internal coupling are broken down. The individual l and s vectors then precess independently around the magnetic field with quantized components $m_l h/2\pi$ and $m_s h/2\pi$ respectively. The value of l for a p-electron is 1 and hence the values of m_l are 1, 0, -1; while those of m_s are +1/2 and -1/2. Now, all the possible combinations of m_l and m_s for a single p-electron are:

$m_l =$	1	0	-1	1	0	-1
$m_s =$	½	½	½	-1/2	-1/2	-1/2
	(a)	(b)	(c)	(d)	(e)	(f)

Thus, there are six possible states (a),(b),(c), (d), (e), (f) in which a single p-electron can exit in an atom. The possible states for two (equivalent) electrons can be obtained by taking all possible combinations of the above six states taken two at a time, with no two alike. There will be 15 such combinations.

ab, ac,ad,ae,af;

bc,bd,be,bf;

cd,ce,cf;

de,df;

ef.

For each of these 15 combinations of very strong field quantum numbers, we add two values of m_l to obtain the strong field values of M_L, and two values of ms to form Ms $[\sum m_l = M_L$ and $\sum m_s = M_S]$.

	Ab	ac	Ad	ae	Af	bc	Bd	Be	bf	cd	ce	cf	De	df	Ef
M_L	1	0	2	1	0	-1	1	0	-1	0	-1	-2	1	0	-1
M_S	1	1	0	0	0	1	0	0	0	0	0	0	-1	-1	-1

The highest value of M_L is 2 which indicates a D term (L = 2). Since this value of M_L occurs only with $M_S = 0$, the term is $^1D(S = 0)$.

$$
\begin{array}{cccccc}
 & ad & ae & af & bf & cf \\
M_L = & 2 & 1 & 0 & -1 & -2 \\
M_S = & 0 & 0 & 0 & 0 & 0
\end{array} \left.\rule{0pt}{3em}\right\} \; ^1D.
$$

Of the remaining M_L and M_S values, the highest M_L is 1 and the highest M_S is 1. These values must belong to a ^3p term (L=1, S=1).

$$
\begin{array}{ccccccccc}
ab & ac & bc & bd & cd & ce & de & df & ef
\end{array} \left.\rule{0pt}{2em}\right\}
$$

$$M_L = \quad 1 \qquad 0 \qquad -1 \qquad 1 \qquad 0 \qquad -1 \qquad 1 \qquad 0 \qquad -1 \qquad {}^3P$$

$$M_S = \quad 1 \qquad 1 \qquad 1 \qquad 0 \qquad 0 \qquad 0 \qquad -1 \qquad -1 \qquad -1$$

Only one combination be is left for which $M_L = 0$ and $M_S = 0$. It give only ${}^1S$ term ($L = 0, S = 0$).

$$\left.\begin{array}{l} \text{be} \\ M_L = 0 \\ M_S = 0 \end{array}\right\} \; {}^1S$$

Thus, two equivalent p-electrons give rise to ${}^1D$, ${}^3P$ and ${}^1S$ terms; and no others. The fine-structure levels are ${}^1D_2$, ${}^3P_{0,1,2}$ and ${}^1S_0$.

❖ ORDERS OF TERMS AND FINE-STRUCTURE LEVELS

The relative energies of the various terms and levels which rise from a given electron configuration may be deduced from a set of rules given by Hund. These rules are:

1) Of the terms arising from equivalent electrons, those with largest multiplicity lie lowest.

2) Of the terms with given multiplicity, and arising from equivalent electrons, that with largest L value lies lowest.

3) In the multiplets formed from equivalent electrons in a less half filled sub-shell, the level with lowest J lies lowest ("normal order").

4) In the multiplets formed from equivalent electrons in a more than half-filled sub-shell, the level with highest J lies lowest ("inverted order").

5) Terms arising from half-filled sub-shell show only very slight fine-structure splitting.

6) The lowest terms arising from the half-filled sub-shells are the S-terms and are specially stable. These terms are ${}^2s_{1/2}$ for half-filled s sub-shell, ${}^4S_{3/2}$ for a half–

filled p sub-shell, $^6S_{5/2}$ for a half-filled d sub-shell, and $^8f_{7/2}$ for a half-filled f sub-shell.

❖ VECTOR MODEL FOR TWO-VALENCE ELECTRON ATOM UNDER L-S COUPLING SCHEME

This is a common type of coupling which occurs in most of the lighter atoms. In the vector model for L-S coupling, the individual orbital angular momentum vectors l1 and l2 of the two electrons are strongly coupled to each other to form a resultant orbital angular momentum vector L about which both l_1 and l_2 precess rapidly. The corresponding quantum number L can take the values

$$L = |l_1-l_2|, | l_1-l_2|+1, …………………………(l_1+l_2).$$

This gives the various terms of the atom. These terms are designated as S, P, D, …………..terms accordingly as L = 0, 1, 2,……………………… .

Similarly, the individual spin angular momentum vectors s_1 , s_2 of the two electrons are strongly coupled to each other to form a resultant angular momentum vector S about which both s_1 and s_2 precess rapidly. The quantum number S can take the values

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, …………………………...(s_1+s_2) .$$

Since $s_1 = s_2 = 1/2$, we have

$$S = 0, 1.$$

Thus, the multiplicity (2S+1) has values 1 and 3; that is, the two (valence) electrons lead to singlet and triplet terms.

As a result of spin-orbit interaction, L and S are rather less strongly coupled with each other to form a total angular momentum vector J of the atom, that is

$$J = L + S.$$

Both L and S precess slowly around J. The quantum number J can take the values

$$J = |L-S|, |L-S|+1, \ldots\ldots\ldots\ldots\ldots\ldots(L+S).$$

Thus, the spin-orbit interaction breaks each level characterized by an L-value in a number of fine-structure levels, each characterized by a j-value. The collection of fine-structure levels is known as a 'multiplet'.

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This gives the various terms of the atom. These terms are designated as S, P, D, …………..terms accordingly as L = 0, 1, 2,………………………… .

Similarly, the individual spin angular momentum vectors s1 s2 of the two electrons are strongly coupled to each other to form a resultant angular momentum vector S about which both s1 and s2 precess rapidly. The quantum number S can take the values

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(s_1+s_2) .$$

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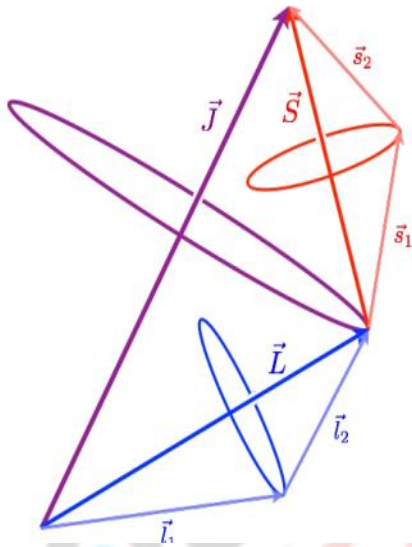

Fig.

Selection Rules for Multi-electron atoms in L-S Coupling

In the electric-dipole transitions in multi-electron atoms, the selection rules are -

1. For one valence electron system:-

    $$\Delta l = \pm 1$$
    $$\Delta S = 0$$
    $$\Delta J = 0, \pm 1 \quad \text{but } J = 0 \xleftarrow{\quad\diagup\quad} J = 0.$$

2. For multi-valence electron system:-

    $$\Delta l = 0, \pm 1$$
    $$\Delta S = 0$$

$$\Delta J = 0, \pm 1 \quad \text{but } J = 0 \longleftrightarrow J = 0.$$

3. There is no restriction on the total quantum number n of either electron.

4. Only transition between even and odd terms are allowed for dipole transition.

❖ J-J Coupling

TheJ-J coupling is an opposite extreme to the ideal L-S coupling and is approached by heavier atoms, for which the spin-orbit (magnetic) interaction term in the Hamiltonian predominates over the residual electrostatic interaction and the spin-spin correlation. This means that the interaction between the orbital and the spin momenta of a single electron is much greater than the interaction between the spin momenta of different electrons. Therefore, in this case the splitting of unperturbed energy level due to the introduction of the various perturbation takes place in the order: (a) spin-orbit interaction, (b) residual electrostatic interaction and spin-spin correlation.

(a)Due to strong spin-orbit interaction, the orbital and spin angular momentum vectors of each individual electrons are strongly coupled together to form a resultant angular momentum vector **J** of magnitude **√J(J+1)h/2π,** where **J= l-1/2** and **l+1/2**, that is, **J** takes half-integral values only. This mean that due to spin-orbit interaction, the unpeturbed energy level is splitted into a number of well-spaced levels, each corresponding to a different combination of the possible **J**-values for the individual optical electrons; the level corresponding to all the electrons having their smaller **J**-value**(J= l-1/2)** being lowest.

(b)As a result of the residual electrostatic interaction and spin-spin correlation, the resultant angular momentum vectors **J** of the individual electrons are less strongly coupled with one another to form the total angular momentum vector J vector of the atom, of magnitude **√J(J+1)h/2π.** The total angular momentum quantum number takes the values:

J= |J₁+J₂+………..|min, | J₁+J₂+………..|min+1, …………….(J₁+J₂+……….)

This means that each of the above levels is further splitted into a number of levels characterized by different values of **J**.

To understand this coupling let us take some examples

For the p-electron: $l_1=1$, $s_1=1/2$; and so $j_1=1/2, 3/2$.

For the d-electron: $l_2=2$, $s_2=1/2$; and so $j_2=3/2, 5/2$.

This gives four (j_1, j_2) combinations of possible j_1 and j_2 values. These are

(1/2, 3/2); (1/2, 5/2); (3/2, 3/2) and (3/2, 5/2).

Thus, the spin-orbit interaction splits the unperturbed energy level into four levels, of which (1/2, 3/2) lies lowest and (3/2, 5/2) lies highest.

Each of the above four levels is further spiltted by residual electrostatic interaction and spin-spin correlation into a number of J- levels, equal to the number of integrally spaced values of J that can be formed out of the two J-values. The above four (j_1, j_2) combination give J values as under:

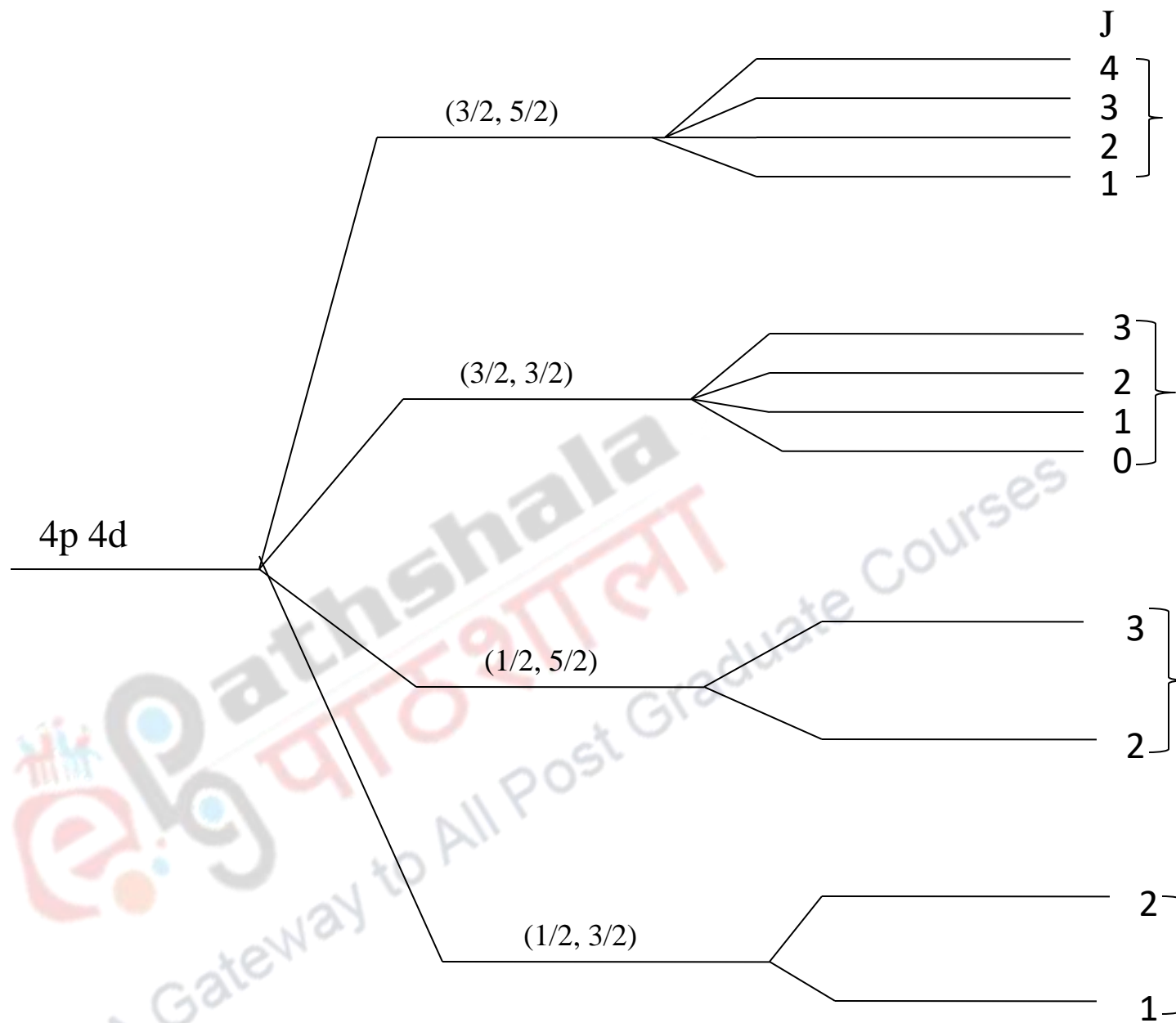(1/2, 3/2)   gives J = 1, 2.

(1/2, 5/2)   gives J = 2, 3.

(3/2, 3/2)   gives J = 0, 1, 2, 3.

 (3/2, 5/2)   gives J = 1, 2, 3, 4.

The complete splitting is shown in the following fig.

Unperturbed level + spin-orbit energy + electrostatic and spin-spin energy

❖ Spin-spin coupling

Spin-spin coupling is the coupling of the intrinsic angular momentum (spin) of different particles. Such coupling between pairs of nuclear spins is an important feature of nuclear magnetic resonance (NMR) spectroscopy as it can provide detailed information about the structure and conformation of molecules. Spin-spin coupling between nuclear spin and electronic spin is responsible for hyperfine structure in atomic spectra.

Term symbols are used to represent the states and spectral transitions of atoms, they are found from coupling of angular momenta mentioned above. When the state of an atom has been specified with a term symbol, the allowed transitions can be found through selection rules by considering which transitions would conserve angular momentum. A photon has spin 1, and when there is a transition with emission or absorption of a photon the atom will need to change state to conserve angular momentum. The term symbol selection rules are $\Delta S = 0$, $\Delta L = 0, \pm 1$, $\Delta l = \pm 1$, $\Delta J = 0, \pm 1$

The expression "term symbol" is derived from the "term series" associated with the Rydberg states of an atom and their energy levels. In the Rydberg formula the frequency or wave number of the light emitted by a hydrogen-like atom is proportional to the difference between the two terms of a transition. The series known to early spectroscopy were designated *sharp*, *principal*, *diffuse* and *fundamental* and consequently the letters S, P, D, and F were used to represent the orbital angular momentum states of an atom.

In atomic nuclei, the spin-orbit interaction is much stronger than for atomic electrons, and is incorporated directly into the nuclear shell model. In addition, unlike atomic-electron term symbols, the lowest energy state is not $L - S$, but rather, $\ell + s$. All nuclear levels whose ℓ value (orbital angular momentum) is greater than zero are thus split in the shell model to create states designated by $\ell + s$ and $\ell - s$. Due to the nature of the shell model, which assumes an average potential rather than a central Coulombic potential, the nucleons that go into the $\ell + s$ and $\ell - s$ nuclear states are considered degenerate within each orbital (e.g. The $2p3/2$ contains four nucleons, all of the same energy. Higher in energy is the $2p1/2$ which contains two equal-energy nucleons).

Selection Rules in J-J coupling

(1)   The parity of the configuration must change in an electric-dipole transition (Laporte rule).This means that if only one electron can jumps in the transition then for this electron we must have $\Delta l = \pm 1$. If two electrons jump then $\Delta l_1 = \pm 1$ and $\Delta l_2 = 0, \pm 2$.

(2) $\Delta j = 0, \pm 1$ for the jumping electron, and $\Delta j = 0$ for all the other electrons.

(3)   For the atom as a whole, $\Delta j = 0, \pm 1$ but $J = 0$ $J = 0$.

❖   **VECTOR MODEL FOR TWO-VALENCE ELECTRON ATOM UNDER J-J COUPLING SCHEME**

In the vector model of a two-electron atom under j-j coupling scheme, the orbital and the spin vectors l_1 and s_1 of one electron are strongly coupled to each other to form a resultant j_1 about which l_1 and s_1 precess rapidly. Similarly, l_2 and s_2 of the other electron form j_2. The vectors j_1 and j_2 are less strongly coupled to each other and form the total angular momentum vector J of the atom. The vectors j_1 and j_2 precess rather slowly about J shown in fig.
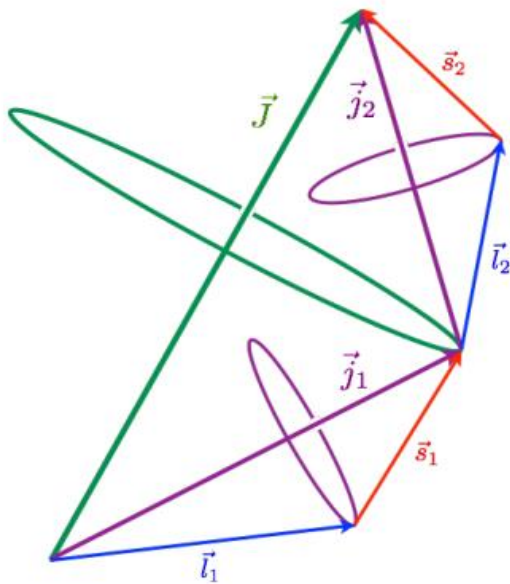

Fig.

❖ LS-Coupling

$$H = H_1 + H_{SO}$$

Where

$$H_1 = H_{CF} + H_{res}$$

- **Begin with:**
  $$H_{CF}\varphi_{CF} = E_{CF}\varphi_{CF}$$
  $$|\varphi_{CF}> = |n_1 l_1, n_2 l_2, \dots \dots \dots n_N l_N>$$

  This gives the electronicconfiguration

- **Then, calculate the first perturbation:**
  $$<\varphi_{CF}|H_{res}|\varphi_{CF}>$$
  - **(For the moment, we wait with the spin orbit Hamiltonian)**
  - $[H_{res}, L] = [H_{res}, S] = 0$
  - **This atomic term can characterized by the quantum numbers L and S**
  - ^{2S+1}L
  - $Eigenvector: |\varphi_{CF}> = |\gamma L S M_L M_S>$
  - $(\gamma: the electronicconfiguration)$
  - **Degenerescence in $M_L and M_S$**
  - **(2L+1)(2S+1) degenerate**

❖ How to find L and S

- **Take into account :**
  - **Rules for addition of angular momenta**
  - **The Pauli principle**
  - **For a filled shell:**
    $$M_S = \Sigma m_{s_i} and M_L = \Sigma m_{l_i}$$

$$\Rightarrow L = S = 0$$

  - **No contribution from the inner shells to the global L and S**
  - **It is enough to consider the valence electrons**

Electrons in different orbitals(non-equivalent)

- **The Pauli principle is already taken into account**
- **As an example,take a 2-electron atom:**
  - $nl_1, n'l_2\ (n \neq n')$
  - $L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots\ldots, |l_1 + l_2|$

    $S = |s_1 - s_2|, |s_1 - s_2| + 1, \ldots\ldots |s_1 + s_2|$

    $(s_1 = s_2 = \frac{1}{2}) \Rightarrow S = 0$ or $S = 1$

    (singlets and triplets)

  - **Example 1:**
    - $l_1 = l_2 = 1 \Rightarrow$ **configuration : np,n'p**
    - $L = 0\ or\ L = 1\ or\ L = 2$
    - $\Rightarrow$**possible terms are:**
    - ^1S , ^1P , ^1D , ^3S , ^3P , ^3D
  - **Example 2:**
    - $l_1 = 1, l_2 = 2 \Rightarrow$ **configuration : np , n'd**
    - $L = 1\ or\ L = 2\ or\ L = 3$
    - $\Rightarrow$ **possible terms are:**
    - ^1P , ^1D , ^1F , ^3P , ^3D , ^3F
  - **More than 2 electrons**
    - **A bit more complicated**

❖ Electrons in the same orbital (equivalent electrons)

- **This will normally be the case for ground state configurations**
- **More complicated , due to the Pauli principle**
- **Many states become forbidden**
  - **We will not cover this in detail**
    - **Example 1:**
  - $n_1 = n_2, l_1 = l_2 = 1 \Rightarrow configuration: np^2$
  - $(the case for, for example: C, Si, Ge ....)$
  - $\Rightarrow$ **possible terms : ^1S , ^1D , ^3P**
  - **(other terms possible for npnp' are forbidden due to the Pauli principle)**
    - **Example 2:**
      - $n_1 = n_2 = n_3, l_1 = l_2 = l_3 = 1$
        $\Rightarrow$configuration : np^3
      - $(the case for, for example : N, P, As ....)$
      - $\Rightarrow$possible terms : $^2P, ^2D, ^4S$

Electron Configuration	Terms
ns	^2S
ns^2	^1S
np, np^5	^2P
$np^2 np^4$	$^1S, ^1D$ ^3P
np^3	$^2P, ^2D$
np^6	^1S
nd, nd^9	^2D
nd^2, nd^8	$^1S, ^1D, ^1G$ $^3P, ^3F$
nd^3, nd^7	$^2P, ^2D, ^2F, ^2G, ^2H$ $^4P, ^4F$ (2)
nd^4, nd^6	$^1S, ^1D, ^1F, ^1G, ^1I$ $^3P, ^3D, ^3F, ^3G, ^3H$ ^5D (2) (2) (2) (4) (2)
nd^5	$^2S, ^2P, ^2D, ^2F, ^2G, ^2H, ^2I$ $^4P, ^4D, ^4F, ^4G$ ^6S (3) (2) (2)
nd^{10}	^1S