

Level scheme of two-electron atoms

Caution:

- * Radiative transition between singlet and triplet spin states are forbidden in the electric dipole approximation ($\Delta S = 0$).
- * Spin-orbit interactions are neglected ($Z \leq 40$).
- * Energy spectrum of $2-\bar{e}$ (two-electron) atoms/ions with low Z ($Z \leq 40$) consists of two nearly independent systems of levels: — i) Singlet (para), ii) triplet (ortho)

Term - symbol

Atomic energy levels are called terms in spectroscopy and are designated by symbols.

$$\boxed{2S+1 \quad L \quad J}$$

A code letter is associated to the value of the total electronic orbital angular momentum quantum no. L .

$L =$	0	1	2	3	4	5
	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
	S	P	D	F	G	H

P-2.

To obtain the terms, we need to calculate:

i) "L"

ii) "S" and hence $(2S+1)$

iii) "J"

Example: $np^1 n'p^1$.

"L"

Task: to determine the possible values of
"L" \Rightarrow total orbital angular momentum quantum no.

Clebsch Gordon series

$$L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \dots, |l_1 - l_2|.$$

$l_1 + l_2 \Rightarrow$ two orbital angular momenta are in same direction (L_{\max}).

$|l_1 - l_2| \Rightarrow$ two orbital angular momenta are in opposite direction (L_{\min})

"L" \rightarrow integers. Thus, intermediate values will be obtained by successive subtraction of "1"

$np^1 n'p^1 :$

$$\begin{array}{cc} \downarrow & \downarrow \\ l_1 = 1 & l_2 = 1. \end{array}$$

$$L_{\max} = 2, \quad L_{\min} = 0.$$

$$L(\text{values}) = 2, 1(l_1 + l_2 - 1), 0(|l_1 - l_2|).$$

$$L = \begin{array}{ccc} 2 & 1 & 0 \\ \downarrow & \downarrow & \downarrow \\ D & P & S. \end{array}$$

"S"

Total spin angular momenta:

$$S = s_1 + s_2, \downarrow S_{\max}, s_1 + s_2 - 1, s_1 + s_2 - 2, \dots, |s_1 - s_2| \downarrow S_{\min}$$

Each electron has $s = \frac{1}{2}$.

$$\begin{array}{cc} n p^1 & n' p^1 \\ \downarrow & \downarrow \\ s_1 = \frac{1}{2} & s_2 = \frac{1}{2} \end{array}$$

$$\begin{array}{lcl} S_{\max} = 1. & \text{and} & S_{\min} = 0. \\ \downarrow & & \downarrow \\ 2S+1 = 3 & & 2S+1 = 1 \\ \downarrow & & \downarrow \\ \text{multiplicity} & & \text{spin multiplicity} \end{array}$$

Spin multiplicity: 3, 1.

Triplet terms: $3D, 3P, 3S.$

Singlet terms: $1D, 1P, 1S.$

P-4 "J"

For $3D$ terms

$$L = 2, S = 1.$$

$$J_{\max} = 3, \quad J_{\min} = 1.$$

$$\downarrow \\ (L+S)$$

$$\downarrow \\ |L-S|$$

$$J \text{ values: } 3, (L+S-1), 1$$

$$\Rightarrow 3, 2, 1.$$

Levels are: $3D_3, 3D_2, 3D_1$.

For each J value:

$$\text{Total angular momentum } \sqrt{J(J+1)} \hbar.$$



This can have $(2J+1)$ orientation defined by M_J values.

$$J, J-1, J-2, \dots, 0, \dots, -J.$$

No. of micro states:

$$3D_3 \rightarrow J=3, 2J+1=7.$$

$$3D_2 \rightarrow J=2, 2J+1=5$$

$$3D_1 \rightarrow J=1, 2J+1=3$$

Total
15 states
 \downarrow
defined by
 M_J values.

For 3p term

$$L = 1, S = 1.$$

$$J_{\max} = 2, J_{\min} = 0$$

$$J \text{ values: } 2, 1, 0.$$

Levels are: $3p_2, 3p_1, 3p_0.$

Micro states:

$$\left. \begin{array}{l} 3p_2 : J = 2, 2J + 1 = 5 \\ 3p_1 : J = 1, 2J + 1 = 3 \\ 3p_0 : J = 0, 2J + 1 = 1. \end{array} \right\} \begin{array}{l} \text{Total} \\ 9 \text{ states} \\ \downarrow \\ \text{defined by } MJ \\ \text{values.} \end{array}$$

For 3s term

$$L = 0 \text{ and } S = 1.$$

$$J_{\max} = 1 \text{ (only value for } J, \text{ as } J_{\min} = 1).$$

Level: $3s_1$ (Micro states: $2J + 1 = 3$).

For 1D term

$$L = 2, S = 0.$$

$$J_{\max} = 2 \text{ (only value, as } J_{\min} \text{ is also 2).}$$

$$\text{Micro states: } 2J + 1 = 5. \quad \left| \text{Level: } \boxed{1D_2} \right.$$

P-6

1P term

$$L = 1, S = 0.$$

$$J = 1 \text{ (only)}. \quad | \text{ Level: } 1P_1.$$

$$\text{Micro states: } 2J+1 = 3.$$

1S term

$$L = 0, S = 0.$$

$$J = 0 \text{ (only)}.$$

$$\text{Level: } 1S_0.$$

$$\text{Micro states: } 2J+1 = 1.$$

Total no. of energy states/micro states for
 $np^1 n'p^1$ configuration:

$$\left. \begin{array}{l} 3D \rightarrow 15 \\ 3P \rightarrow 9 \\ 3S \rightarrow 3 \\ 1D \rightarrow 5 \\ 1P \rightarrow 3 \\ 1S \rightarrow 1 \end{array} \right\} (36).$$

Ground state term: Hund's rule

* First we'll look into the spin multiplicity.
Ground state term will have greatest multiplicity.

3D, 3P, 3S will be lower in energy compared to 1D, 1P, 1S.

* Term with greatest orbital angular momentum will be of lowest energy.

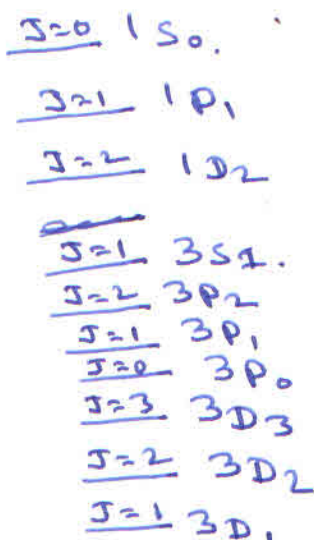
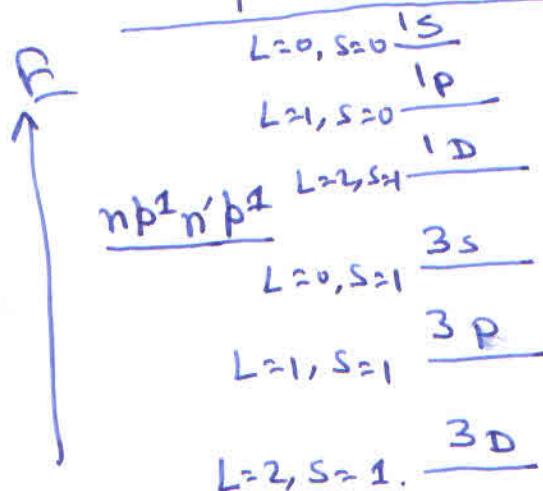
~~3D~~

Triplet: $3D < 3P < 3S$.

Singlet: $1D < 1P < 1S$.

* $np^1 n'p^1 \rightarrow$ p subshell is less than half-filled
For subshell, less than half filled: level with lowest J lies lowest in energy.

$$3D_1 < 3D_2 < 3D_3$$



Look into
Slide No 26
of L-10 (extra
class).