Level scheme of two-electron atoms

Caveat:

* Radiative transition between singlet and triplet spin states are forbidden in the electric dipole approximation ($\Delta S = 0$).

* Spin-orbit interactions are neglected ($Z \lesssim 40$).

* Energy spectrum of 2-$\bar{e}$ (two-electrons) atoms/ions with low Z ($Z \lesssim 40$) 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.

$$\boxed{{}^{2S+1}L_J}$$

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
	↕	↕	↕	↕	↕	↕
	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: $np^1n'p^1$.

"L"

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

Clebsch Gordan series

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

l_1+l_2 ⇒ two orbital angular momenta are in same direction (L max).

$|l_1-l_2|$ ⇒ two orbital angular momenta are in opposite direction (L min)

"L" → integer. Thus, intermediate values will be obtained by successive subtraction of "1"

$np^1n'p^1$:

$l_1 = 1 \quad l_2 = 1$.

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

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

$L =$ 2 ↕ D, 1 ↕ P, 0 ↕ S.

"S"

Total spin angular momenta:

$S = s_1 + s_2, s_1 + s_2 - 1, s_1 + s_2 - 2, \ldots, |s_1 - s_2|$.

$s_1 + s_2$ → S_{max}; $|s_1 - s_2|$ → S_{min}

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

$n p^1 \; n' p^1$

$s_1 = \frac{1}{2}$ $\quad$ $s_1 = \frac{1}{2}$

$S_{max} = 1$ and $S_{min} = 0$.

$2S+1 = 3$ → multiplicity

$2S+1 = 1$ → spin multiplicity

Spin multiplicity: 3, 1.

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

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

P-4 "J"

For ^3D terms

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

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

$J_{max} \rightarrow (L+S) \qquad J_{min} \rightarrow |L-S|.$

J values: $3, (L+S-1), 1$

$\Rightarrow 3, 2, 1.$

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

For each J value:

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

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

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

No. of micro states:

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

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

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

Total 15 states ↓ defined by M_J values.

For ^3P term.

$L = 1, \quad S = 1.$

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

J values: 2, 1, 0.

Levels are: $^3P_2, \ ^3P_1, \ ^3P_0.$

Micro states:

$^3P_2$: $J = 2, \ 2J+1 = 5$

$^3P_1$: $J = 1, \ 2J+1 = 3,$

$^3P_0$: $J = 0, \ 2J+1 = 1.$

} Total 9 states → defined by M_J values.

For ^3S term.

$L = 0$ and $S = 1.$

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

Level: $^3S_1$ (Micro states : $2J+1 = 3$).

For ^1D term.

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

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

Micro states: $2J+1 = 5.$ | Level: $\boxed{^1D_2}$

^1P term

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

$J = 1$ (only). | Level: $^1P_1$.

Micro states: $2J+1 = 3$.

^1S term

$L = 0, \quad S = 0.$

$J = 0$ (only).

Level: $^1S_0$.

Micro states: $2J+1 = 1$.

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

$^3D \rightarrow 15$
$^3P \rightarrow 9.$
$^3S \rightarrow 3.$
$^1D \rightarrow 5$
$^1P \rightarrow 3.$
$^1S \rightarrow 1$

(36).

Grand elatic term: Hunds rule

* First we'll look into the spin multiplicity. Grand elatic 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.

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.

$^3D_1 < {}^3D_2 < {}^3D_3$.

$np^1 n'p^1$

$L=0, S=0$ — ^1S

$L=1, S=0$ — ^1P

$L=2, S=0$ — ^1D

$L=0, S=1$ — ^3S

$L=1, S=1$ — ^3P

$L=2, S=1$. — ^3D

E ↑

$J=0$ $^1S_0$.

$J=1$ $^1P_1$

$J=2$ $^1D_2$

$J=1$ $^3S_1$.

$J=2$ $^3P_2$

$J=1$ $^3P_1$

$J=0$ $^3P_0$

$J=3$ $^3D_3$

$J=2$ $^3D_2$

$J=1$ $^3D_1$

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