Pauli's Exclusion Principle

In an atom two e^-s cannot have same (all 4) q.no.

i.e. n, l, m_l, m_s value of two e^-s cannot be same

$\Rightarrow$

(1) for $n = 1$

$l = 0,\ m_l = 0$

$m_s = \frac{1}{2}$ & $-\frac{1}{2}$

so the two quantum states are: $(1, 0, 0, \frac{1}{2})$ & $(1, 0, 0, -\frac{1}{2})$

Similarly for $n = 2$, 8 quantum states are possible

Hence; Maximum number of e^{-}s in a subshell

$$= 2(2l+1)$$

<u>or;</u>

Total no. of e^{-} in n^{th} shell

$$= \sum_{l=0}^{n-1} 2(2l+1)$$

$$= 2[1+3+5+7+\dots+(2n-1)]$$

$$= 2\left[\frac{n}{2}(1+(2n-1))\right]$$

$$= 2n^2.$$ (same as proposed by Bohr)

Q. No. for Many Electron

Many Electron system –

Atoms having more than one e^- in its valence orbit

⇒ Ang. Momentum is due to contribution of all these e^-s

⇒ Q. No of these system are L S J are vector sum of q. nos of valence e^-s.

⇒ possible values of M_L, M_J & m_J are $(2L+1)$, $(2S+1)$ & $(2J+1)$

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Hence ; A Multi e^- system has Q. Nos –

$n, L, S, J, m_L, m_S \& m_J$

(1) Total Orb. Q. No. L

$\vec{L} = \vec{l_1} + \vec{l_2} + \vec{l_3} + \ldots$

Total orb. ang. Momentum $\vec{L}$ is vector sum of individual $\vec{l}$

eg: $l_1 = 2$, $l_2 = 1$

$\vec{L} = \vec{l_1} + \vec{l_2}$ to $\vec{l_1} - \vec{l_2}$

$\vec{L} = 3, 2, 1$

[2] Total Spin Q. No. (S)

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(2) Total Spin Q. No. S

$$\vec{S} = \vec{s_1} + \vec{s_2} + \vec{s_3} + \dots$$

for each e^- $\vec{s} = \frac{s h}{2\pi}$

$$s = \frac{1}{2}$$

** Spin vectors can be either parallel or antiparallel,
They can not have any other orientation.

** Hence;

for odd no of e^-s

$\vec{S} - \frac{1}{2}$ odd integral Multiple.

for even no. of e^-s

$\vec{S} \rightarrow \frac{1}{2}$ Multiple of even integer

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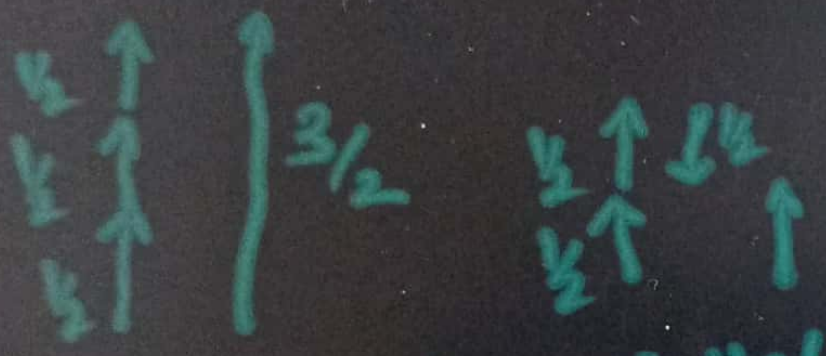
eg:

for 3 e^- system

S can be $\frac{1}{2}$ or $\frac{3}{2}$ only

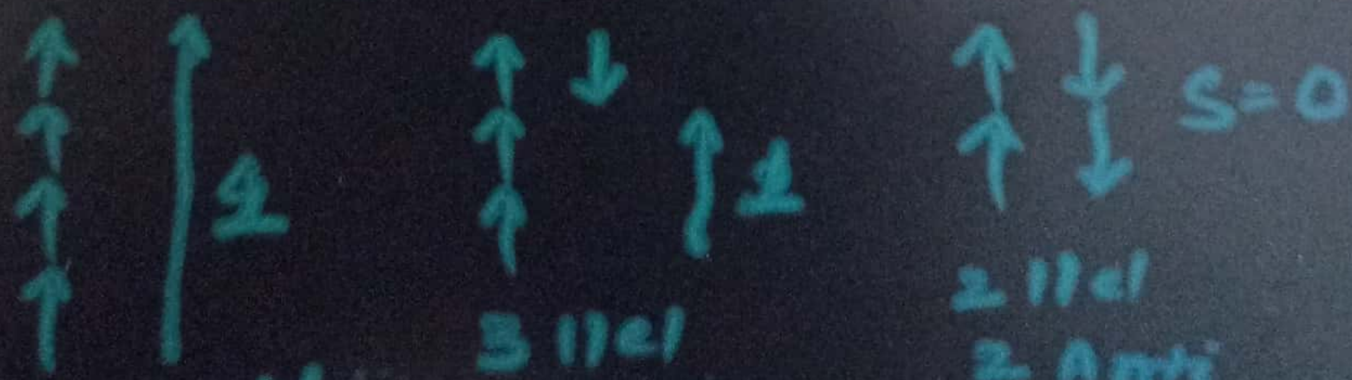


All Parallel

2 ||el
1 anti parallel

for 4 e^- system

$S = 0, 1, 2$



All parallel

3 ||el
1 Anti

2 ||el
2 Anti

(5) Total Quantum No J and coupling

Tot Ang Mom = Total orbital + spin

Coupling can occur in two ways

(i) L-S coupling

(ii) j-j coupling

(i) L-S coupling

Orbital Mom. of val. e^- gets added first then Add with Total spin Mom of all val e^-

i.e. $\vec{L} = l_1 + l_2 + l_3 + \ldots$

$\vec{S} = s_1 + s_2 + s_3 + \ldots$

$\vec{J} = \vec{L} + \vec{S}$

In this way —

(i) L, S, J all are quantized

(ii) $L = 0, 1, 2 \ldots$

(iii) $S = 0, 1, 2 \ldots$ for even no. of e^-s

$= \frac{1}{2}, \frac{3}{2}, \ldots$ for odd no. of e^-s

(iv) $J = 0, 1, 2, \ldots$ for even e^-s

$J = \frac{1}{2}, \frac{3}{2}, \ldots$ for odd e^-s

(v) $L > S$

J has $(2S+1)$ values

$L < S$

$J = (2L+1)$ values

$L = 0$ $J = S$ (only one value)

(vi) $\underline{J = +ve}$

Eg:

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

$J = (2+1) \text{ to } (2-1)$

$= 3, 2, 1$

$\because L > S; \quad J = 2\times1+1$ values

$= 3$ values

Eg; $L = 2 \quad , \quad S = \frac{1}{2}$

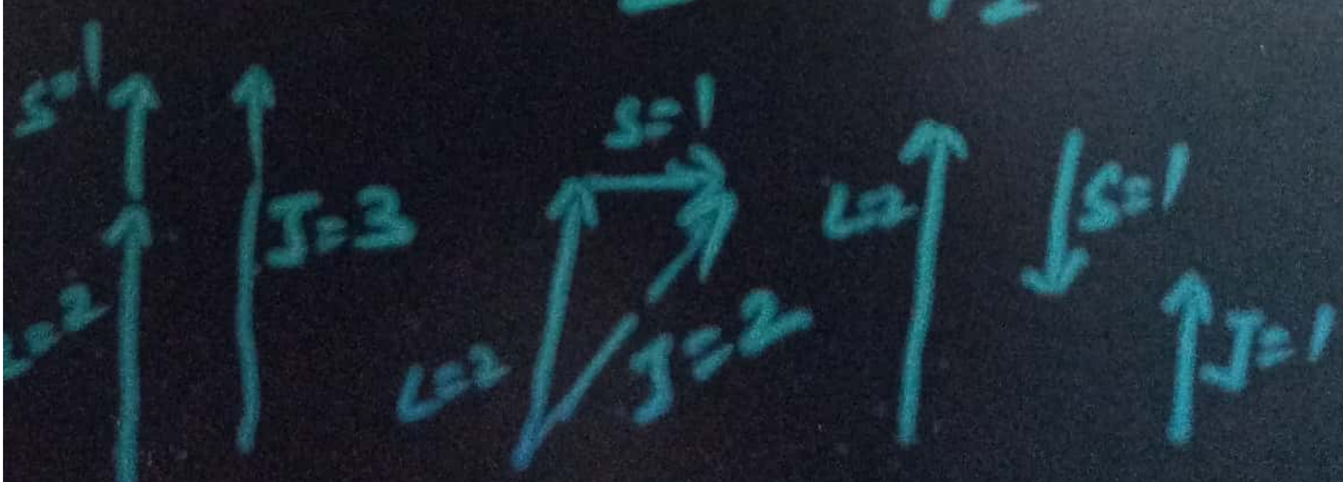
$L > S; \quad J = 2S+1$ values

$= 2\times\frac{1}{2}+1$

$= 2$ values.

$J = 2+\frac{1}{2} = 5/2$

$2-\frac{1}{2} = 3/2$



(ii) j-j coupling

→ Each e^-'s total ang. Mom → obtained by coupling of

$$\vec{l}_1 + \vec{s}_1 = \vec{J}_1$$

→ Then all $\vec{J}$'s couple to get new T. ang. Mom.

$$\vec{J} = \vec{J}_1 + \vec{J}_2 + \vec{J}_3 + \cdots$$

→ $(\vec{l}_1 + \vec{s}_1) + (\vec{l}_2 + \vec{s}_2) + \cdots = J$

→ Such coupling is Rare

Multiplicity of Energy level / state

Possible values of J for given 'L' & 'S' gives no. of energy state & called as Multiplicity (r)

Thus,

$$r = 2S+1 \quad L > S$$
$$= 2L+1 \quad L < S$$
$$= 1 \quad L = 0$$

⇒ for Ground State (L=0) Multiplicity is single

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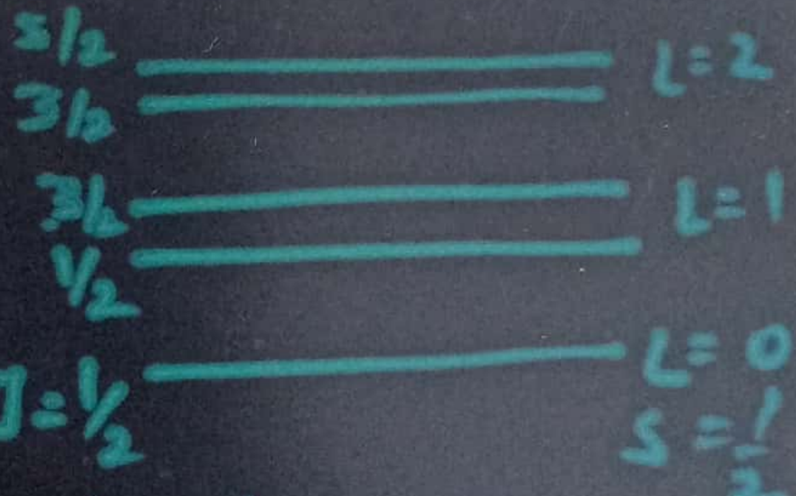
(i) for one e^- system

$S = s = \frac{1}{2}$

so; Except of ground state each state is a doublet



(ii) for Multi electron system

If $S = 0$, $r = 1 = 2S+1$

$S = \frac{1}{2}$ $r = 2S+1 = 2$

$S = 1$ $r = 3$

$S = 3/2$ $r = 4$ ....

Spectroscopic Notation of Energy State

Electronic configuration -
$1s^2 2s^2 2p^6 3s^1 \ldots$

$l = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \ldots$
sym = s p d f g h ...

Spectroscopic Notation
(L, J)

$L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \ldots$
sym = S P D F G ....

$\boxed{{}^{r}L_J}$ eg: ${}^{4}D_{3/2}$ ${}^{2}P_{3/2}$

Eg: ${}^{4}D_{3/2}$; 4 - multiplicity of state
D - L = 2
J = 3/2 ; 2S+1 = 4
S = 3/2

$^4D_{3/2} \Rightarrow L = 2$

& $2S+1 = 4$

$S = \frac{4-1}{2} = \frac{3}{2}$

$J = 2+\frac{3}{2} = \frac{7}{2}$ to $2-\frac{3}{2} = \frac{1}{2}$ || $J = L+S$ to $L-S$

$J = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$

$^4D_{3/2}$ — one of the four states

$^4D_{7/2}$ $^4D_{5/2}$ $^4D_{3/2}$ $^4D_{1/2}$

Solve for:

$$^{2}P_{3/2} \; ??$$

L =

S =

J =

Single e^- system

Ground state — Singlet
($L = 0$)

All other states — Doublet
$L > 0$

so;

$^2S_{1/2}$, $^2P_{1/2}$, $^2P_{3/2}$, $^2D_{3/2}$, $^2D_{5/2}$
. . . . .

Ground state Multiplicity is 1 but it is tradition to write '2' to Represent Multiplicity of the system

* Selection Rule & Intensities of Spectral Line

→ follows transition Rule

(i) $\Delta L = \pm 1$

(ii) $\Delta J = 0, \pm 1$

(iii) $m_L = 0, \pm 1$

(iv) $m_J = 0, \pm 1$

⇒ (i) $\Delta L = \Delta J$ – Highest Intensity

(ii) $\Delta L = \Delta J$ for 2 lines
Higher J – More intense

(iii) $\Delta L = -\Delta J$ Least Intense

Spectral Series

		ΔL	ΔJ
Principal	$^2P_{\frac{1}{2}} \rightarrow {}^2S_{1/2}$	1	0
	$^2P_{3/2} \rightarrow {}^2S_{1/2}$	1	1
Sharp	$^2S_{1/2} \rightarrow {}^2P_{1/2}$	-1	0
	$^2S_{1/2} \rightarrow {}^2P_{3/2}$	-1	-1
Diffuse	$^2D_{5/2} \rightarrow {}^2P_{3/2}$	1	1
	$^2D_{3/2} \rightarrow {}^2P_{3/2}$	1	0
	$^2D_{3/2} \rightarrow {}^2P_{1/2}$	1	1
Fundamental	$^2F_{7/2} \rightarrow {}^2D_{5/2}$	1	1
	$^2F_{5/2} \rightarrow {}^2D_{5/2}$	1	0
	$^2F_{5/2} \rightarrow {}^2D_{3/2}$	1	1