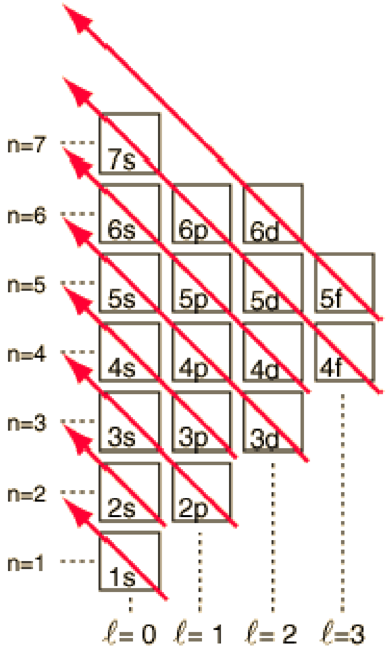
Hund's rules

Mittwoch, 30. November 2022 16:07



Z electrons all spin $\vec{s_i}$ and angular momentum $\vec{l_i}$

all coupled to all

↳ complicated

Easier : Ground state $\hat{=}$ minimum energy

How to couple $\vec{s_i}$, $\vec{l_i}$ to get $E = \min$

$\Rightarrow$ Hund's rules

Z		e^- config	1s	2s	2p	total spin
1	H	$1s^1$	↑			$1/2$
2	He	$1s^2$	↑↓			0
3	Li	$1s^2 2s^1$	↑↓	↑		$1/2$
4	Be	$1s^2 2s^2$	↑↓	↑↓		0
5	B	$1s^2 2s^2 2p^1$	↑↓	↑↓	↑	$1/2$

					p_x p_y p_z	
5	B	$1s^2\,2s^2\,2p^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$1/2$
6	C	$1s^2\,2s^2\,2p^2$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow \mid \uparrow \mid \;}$	1
7	N	$1s^2\,2s^2\,2p^3$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\ \uparrow\ \uparrow$	$3/2$
8	O	-"- $2p^4$	-"-		$\underbrace{\uparrow\downarrow}_{0}\ \underset{1/2}{\uparrow}\ \underset{1/2}{\uparrow}$	1
9	F				$\uparrow\downarrow\ \uparrow\downarrow\ \uparrow$	$1/2$
10	Ne				$\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow$	0

1) Full subshells s^2, p^6, d^{10}

have $\left.\begin{aligned} \vec{S} &= \sum_i \vec{s}_i = 0 \\ \vec{L} &= \sum_i \vec{l}_i = 0 \end{aligned}\right\} \quad \vec{J} = \vec{L} + \vec{S}$

Nomenclature

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

Spectroscopic symbol

n: principal quantum number of last (un)filled shell (last added e^-)

$2S+1$: multiplicity

L: Total orbital ang. mom.

J: total angular momentum

$\Rightarrow$ only look @ unfilled shells

Coupling is in 2 ways

- LS-coupling light atoms

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  "usual way"
- jj-coupling Hg, Pb

LS-coupling : $\vec{L} = \sum_i \vec{l}_i$

$$\vec{S} = \sum_i \vec{s}_i$$

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

j-j coupling : each e^- $\vec{j}_i = \vec{l}_i + \vec{s}_i$

$$\vec{J} = \sum_i \vec{j}_i$$

2nd Hund rule

$\vec{S} = \sum_i \vec{s}_i$

$$\boxed{\text{lowest energy (g.s.) is achieved with maximal multiplicity } 2S+1 \quad (S = \max)}$$

ground state

ex. C : $2p^2$ $\uparrow \; \uparrow$ $S = 1$ $2S+1 = 3$

not $\uparrow\downarrow$ $S = 0$ $2S+1 = 1$

$\vec{L} = \sum_i \vec{l}_i$

3rd Hund

lowest energy state is the one with maximal L

considering that the total w.f. must be antisymmetric (e^- = Fermions)

p_x p_y

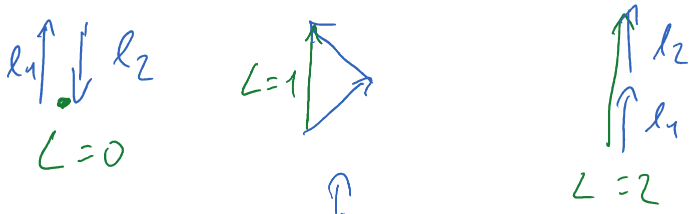
C : $2p^2$ $\uparrow \; \uparrow$ $\rightarrow$ $S = 1$

$\hat{=}$ spin wave function = symmetric if you relabel the electrons

$\Rightarrow$ spatial w.f. must be antisymmetric

$l_1 = 1$
$l_2 = 1$ $\quad$ 2× p state

$L=0$ $\qquad$ $L=1$ $\qquad$ $L=2$



symmetric $\qquad$ antisymmetric $\qquad$ symmetric

Clebsch-Gordan $\quad C^{LM}_{lm_1,lm_2} = (-1)^L \, C^{LM}_{lm_2,lm_1}$

$\Rightarrow$ C ground state has $L=1$

in the term: $\quad L = 0, 1, 2, 3, \ldots$
$\Rightarrow \quad S, P, D, F, \ldots$

C gr.s. $\qquad S = 1 \Rightarrow 2S+1 = 3$ triplett
$\qquad L = 1 \Rightarrow$ "P" state

$n\,{}^3P_{\bigcirc}$ $\quad$ J total ?

2p shell
is being
filled

4th Hund rule:

if last shell $\leq$ half-filled
then lowest energy = lowest J
else highest J

Carbon 2 out of 6 p electrons

$\Rightarrow$ $\leq$ half filled $\rightarrow$ lowest J

$L=1, \; S=1$

$J=2$

$J=1$

$\boxed{J=0}$

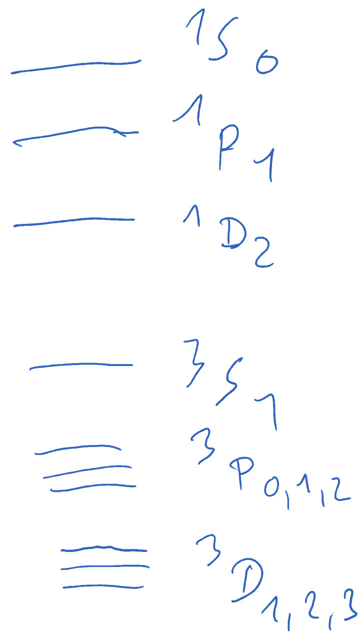
Carbon $\boxed{2\,{}^3P_0}$

Si $\hat{=}$ C $\underline{2e^- \text{ in}}$ $\underline{p \text{ state}}$

Ground state $2\,{}^3P_0$ C

$3\,{}^3P_0$ Si

$S = 0$



$S = 0$
$L = 2$

$S = 1$

$\boxed{\text{B}}$ j-j coupling

heavy atoms $\rightarrow$ <u>large Z</u>

$\rightarrow$ spin-orbit coupling of each electron is large

$\boxed{\text{spin-orbit of } 1e} > \boxed{\text{Coulomb energy between } 2e^-}$

$L, S \neq$ good quantum numbers

$$\vec{j}_i = \vec{l}_i + \vec{s}_i$$

$$\vec{J} = \sum_{i=1}^{Z} \vec{j}_i$$

Selection rules for electric dipole transition (E1)

$\Delta J = 0, \pm 1$ but NOT $J = 0 \leftrightarrow 0$

$\Delta m_J = 0, \pm 1$ but NOT $m_J = 0 \leftrightarrow 0$ for $\Delta J = 0$

$\left.\begin{array}{l}\Delta S = 0 \\ \Delta L = 0, \pm 1\end{array}\right\}$ for the atom

$\left.\begin{array}{l} \\ \Delta l = \pm 1 \text{ for the electron}\end{array}\right\}$ LS coupling

$\Delta j = 0, \pm 1$ for the electron jj - coupling

$2S+1$

$2e^-$: $S = 0$ singlett $\uparrow\downarrow$

$S = 1$ triplett $\uparrow\uparrow$

$3e^-$: $S = \frac{1}{2}$ doublett $\uparrow\downarrow\uparrow$

$S = \frac{3}{2}$ quartett $\uparrow\uparrow\uparrow$

$4e^-$: $S = 0, 1$

$S = 2$ quintett

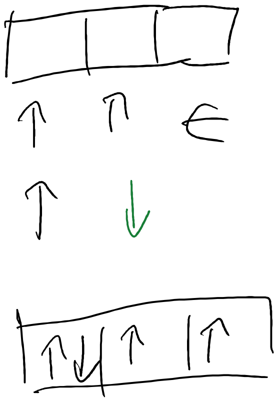
$5e^-$: $S = \frac{1}{2}, \frac{3}{2}$

$S = \frac{5}{2}$ sextett

1

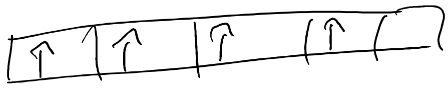
s

p

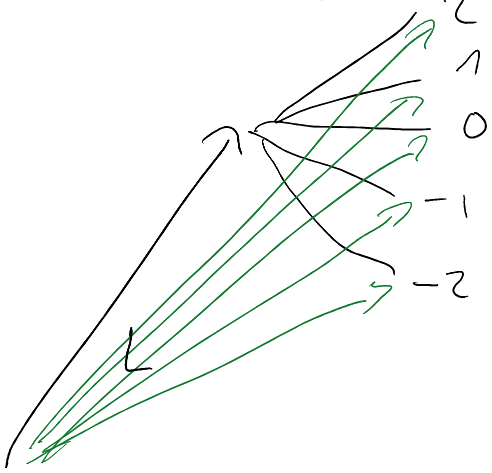


$S = 1$

d



$S = 2$



$S = 2$

$m_s = -2, -1, 0, 1, 2$