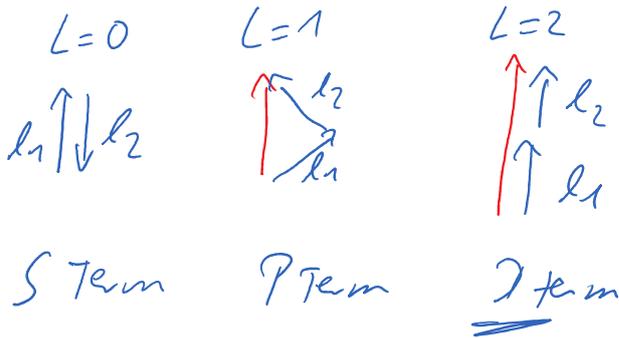


multi-electron cont'd

Mittwoch, 24. November 2021 16:26



C atom: p^2

$$\vec{L} = \vec{l}_1 + \vec{l}_2$$

$$|\vec{L}| = \sqrt{L(L+1)} \hbar$$

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

\uparrow largest \uparrow smallest L

quantum number determines term character

$$L = 0, 1, 2, 3, \dots$$

$\downarrow \downarrow \downarrow \downarrow$
 S P D F, G, ...

3rd Hund's rule
 min energy with largest L
 ground state of atom

in our example C p^2 $l_1 = 1$
 $l_2 = 1$

$$\Rightarrow L = 2 \rightarrow D \text{ state}$$

This does **NOT** mean that the individual e^- are in n of states!

Optical selection rules (electric dipole radiation)

$$\boxed{\Delta l = \pm 1} \text{ for the } \underline{\text{electron}}$$

and

$$\boxed{\Delta L = 0, \pm 1} \text{ for the } \underline{\text{atom}}$$

$\Delta L = 0$ only possible for heavy atoms (large Z)

because $\Delta L = 0$ means that Z electrons "jumped"

→ needs strong coupling

example con'd:

$$\text{total spin } s_i = \pm \frac{1}{2}$$

$$\hookrightarrow S = \frac{1}{2} \pm \frac{1}{2} = 0, 1$$

optical selection rules (electric dipole radiation):

$$\boxed{\Delta S = 0}$$

$\hat{=}$ no spin flip of e^- with electric dipole transition

now we couple L and S

$$\vec{J} = \vec{L} + \vec{S} \quad |\vec{J}| = \sqrt{J(J+1)} \hbar$$

$$j = L \dots$$

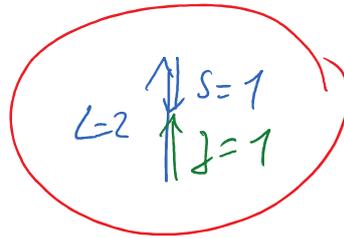
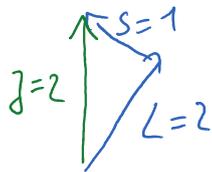
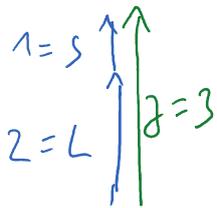
$$|s| - |l| \leq j \leq |s| + |l|$$

$$j \text{ for } S=0 \Rightarrow j=L$$

$$S=1 \Rightarrow j = \underbrace{L+1, L, L-1}$$

} terms

schematically $L=2, S=1 \quad j=3, 2, 1$



4th Hund's rule

lowest Energy state \equiv ground state of atom.

if last shell \leq half-filled

then g.s. is for lowest j

last shell $>$ half-filled

then highest j

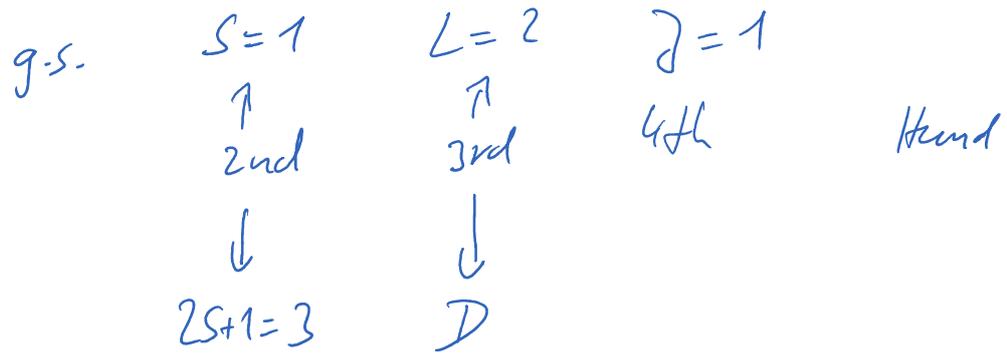
Carbon : 2 p electrons out of 6

$\hookrightarrow \leq$ half-filled \Rightarrow lowest $j=1$

term symbol

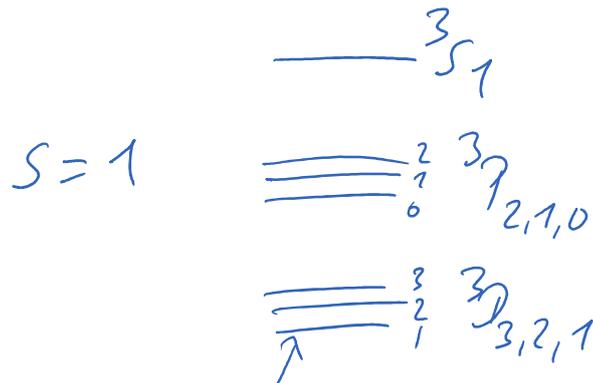
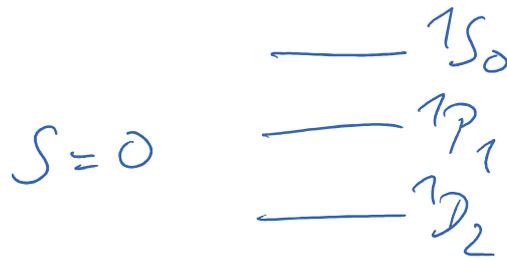
$$2S+1 \quad L_j$$

our example $2e^-$ in p state ($l=1$)



$$\boxed{3D_1} = g.s.$$

$2e^-$ in p state



$\boxed{3}$

j-j-coupling

heavy atoms (Large Z)