Multi electron Atoms – Constructing a Term

ASTR 3013

Electrons with orbital angular momentum $\vec{\ell}_i$ have $(2\ell_i + 1)$ degenerate (unless there is a BIE-field present) energy levels.

Each electron also has a spin m_s. Pauli's exclusion principle forbids 2 electrons from having identical wavefunctions in the same orbital.

ONLY $2 \cdot (2\ell + 1)$ e^- allowed in each orbital

(2: due to m_s; $(2\ell+1)$: due to m_ℓ)

$\ell = 0$ s orbital $\quad 2 \cdot (2 \cdot 0 + 1) = 2$ e^-

$\uparrow\downarrow$ $= m_s = \pm 1/2$

$m_\ell = 0$

$\ell = 1$ p orbital $\quad 2 \cdot (2 \cdot 1 + 1) = 6$ e^-

$m_\ell =$	-1	0	$+1$	$\leftarrow m_s = \pm 1/2$
	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	

$\ell = 2$ d orbital $\quad 2 \cdot (2 \cdot 2 + 1) = 10$ e^-

$m_\ell =$	-2	-1	0	$+1$	$+2$	$\leftarrow m_s = \pm 1/2$
	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	

The periodic table is organized by the energy of the orbitals $(n\ell)$

(n: principle quantum number: i.e. 1s, 2s, 2p, etc.)

Due to electromagnetic interactions, the e^- orbital angular momenta and spin couple. We use the rules of vector addition of quantized angular momenta.

For elements in the $\approx 1^{st}$ half of the periodic table, the "L-S Coupling" or Russell-Saunders Coupling best describes these interactions:

Each individual e^- has $\vec{l}_i$ and $\vec{s}_i$

$$\vec{L} = \sum_i \vec{l}_i \qquad M_L = \sum_i m_{l_i} \leftarrow \text{scalar values}$$

$$\vec{S} = \sum_i \vec{s}_i \qquad M_S = \sum_i m_{s_i} \leftarrow \text{scalar values}$$

$$\vec{J} = \vec{L} + \vec{S} \qquad \vec{J} \text{ is total angular momentum}$$

$$J = L+S,\ L+S-1,\ \ldots,\ |L-S| \qquad \text{Scalar values given by Clebsch-Gordon Series}$$

NOTE: We only have to really consider "valence electrons" in <u>unfilled</u> orbitals to construct the "term".

Spectroscopy: Atomic Terms Examples

H I $1s^1 \Rightarrow \ell_1 = 0 \Rightarrow L = 0 \Rightarrow$ S term

$s_1 = 1/2 \Rightarrow S = 1/2 \Rightarrow 2S+1 = 2$

$\Rightarrow J = 0 + \frac{1}{2} = \frac{1}{2}$

Ground State TERM: $^2S_{1/2}$

Note: this is the same answer for all Alkaki Metals in the 1st column of periodic table since they all have valence electrons in a ns^1 configuration.

C II $(1s^2 2s^2)2p^1 \Rightarrow \ell_1 = 1 \Rightarrow L = 1 \Rightarrow$ P term

$s_1 = 1/2 \Rightarrow S = 1/2 \Rightarrow 2S+1 = 2$

$\Rightarrow J = 1+1/2, |1-1/2| = 3/2, 1/2$

$\Rightarrow$ 2 energy levels!

Ground State TERMS: $^2P_{1/2}$ $^2P_{3/2}$ ("Fine structure" Splitting)

The transition between these levels is @ 158 μm!

He I $1s^2 \Rightarrow \ell_1 = 0 \quad \ell_2 = 0 \Rightarrow L = 0 \Rightarrow$ S term

$s_1 = 1/2 \quad s_2 = 1/2 \Rightarrow S = \frac{1}{2}+\frac{1}{2}, |\frac{1}{2}-\frac{1}{2}| = 1, 0$

So $2S+1 = 3, 1$

$\Rightarrow J = 1+0, 0+0$

$= 1, 0$

Terms: $^1S_0$ $^3S_1$ ← Note that helium energy level diagram is usually organized into "singlet" terms & "triplet" terms.

NOTE: For $1s^2$ config, Pauli Exclusion will eliminate this term, but it exists for $1s^1 2s^1$ etc.