Review of Atomic Energy Levels

LS-coupling scheme

for incomplete shells p^x, d^x, f^x.... we write out a complete list of microstates , each one corresponding to different combinations of m_s and m_ℓ. The number of microstates is

$$\frac{[2(2\ell+1)]!}{x![2(2\ell+1)-x]!}$$

Each microstate can be described by a value of M_L ($=\sum m_\ell$) and M_S ($=\sum m_s$).

Sets of microstates "belong" to terms defined by values of L and S.

Example of C with configuration p^2 ($\ell=1$)

6!/2!4! = 15 microstates

	+2	+1	0	-1	-2
+1		$\{+1^{+}0^{+}\}$	$\{+1^{+}\text{-}1^{+}\}$	$\{-1^{+}0^{+}\}$	
0	$\{+1^{+}+1^{-}\}$	$\{+1^{+}0^{-}\}\{+1^{-}0^{+}\}$	$\{+1^{+}\text{-}1^{-}\}\{+1^{-}1^{+}\}$ $\{0^{+}0^{-}\}$	$\{-1^{+}0^{-}\}\{-1^{-}0^{+}\}$	$\{-1^{+}\text{-}1^{-}\}$
-1		$\{+1^{-}0^{-}\}$	$\{-1^{-}+1^{-}\}$	$\{-1^{-}0^{-}\}$	

These can be condensed into three terms with
L=0, S=1 (^{3}P) 9 microstates,
L=0, S=0 (^{1}S) 1 microstate, and
L=2, S=0 (^{1}D) 6 microstate

Similarly we can show

d^2 (and d^8) gives rise to ^{3}F, ^{3}P, ^{1}D, ^{1}G, ^{1}S
etc.

The relative energies of the terms must be determined experimentally, although the ground states prove to be given by Hund's Rules, applied sequentially
#1 Maximum S
#2 Maximum L

so for p^2 atoms the ground state is ^{3}P
and for d^2 the ground state is ^{3}F

Spin-orbit coupling splits the terms into levels defined by values of the quantum number J. J = L+S, L+S-1,..... |L-S|

Hund's 3rd Rule determines that ground state level is one with the minimum value of J if the shell is less than half full, and is the one with the maximum value of J if the shell is more than half full.

So for p^2 ground state is $^3P_0$ (L = 1, S = 1)
for d^8 ground state is $^3F_4$ (L = 3, S = 1)

The energy differences between the J-levels are determined by the magnitude of the spin-orbit coupling parameter.

There are two spin-orbit parameters in use
ζ_{nl} for a single electron (these are tabulated) a positive quantity that varies with atomic number (~ Z^4) and oxidation state of the atom.

λ for a multi-electron term

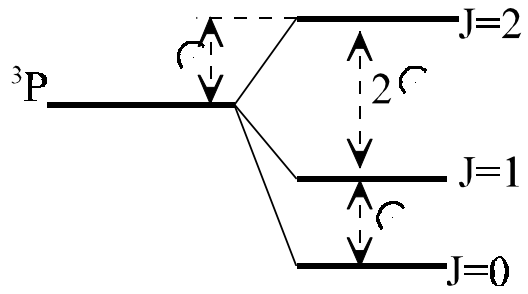
$$\lambda = \pm\zeta/2S$$

+ sign if shell is < half full
– sign if shell is > half full

The relative energies of the spin-orbit levels are given by two rules

1. $E(J_{max}) = LS\lambda$
2. $\Delta E[J_i - (J_i\text{-}1)] = J_i\lambda$ (Landé interval rule)

Example for p^2 case (λ positive)



The energy differences between the terms are expressed in terms of interelectronic repulsion parameters.

Two sets

Slater-Condon-Shortly F_2, F_4, ...

Racah B, C (defined as $B = F_2 - 5F_4$ and $C = 35F_4$)

Example for d^2 terms (energies above the Ground State ^3F)

^1S	$22F_2 + 135F_4$	or	22B + 7C
^1G	$12F_2 + 10F_4$		12B + 2C
^1D	$5F_2 + 45F_4$		5B + 2C
^3P	$15F_2 - 75F_4$		15B

Notice that the B and C parameters are defined in such a way that excited states with the same number of unpaired electrons as the ground state have energies that depend only upon one parameter, B.

Values of B, C, and ζ (or λ) can be estimated from atomic spectra.

Effects of ligand fields upon atomic energy levels

case 1
interelectronic repulsions > spin-orbit coupling > ligand field

examples: most complexes of lanthanides and actinides (f^x)

case 2
interelectronic repulsions > ligand field > spin-orbit coupling

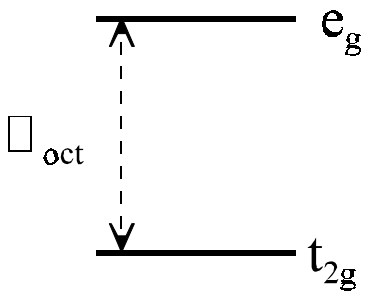
examples: most complexes of transition metals (d^x)

Term	L	Levels in an octahedral ligand field
S	0	A_1
P	1	T_1
D	2	$E + T_2$
F	3	$A_2 + T_1 + T_2$
G	4	$A_1 + E + T_1 + T_2$
H	5	$E + 2T_1 + T_2$
I	6	$A_1 + A_2 + E + T_1 + 2T_2$

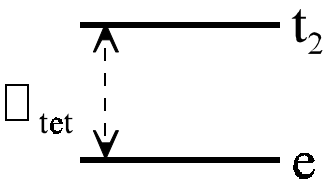
The representations bear “g” or “u” subscripts depending upon whether they are derived from d^x (g) or f^x (u) configurations.

Use of Orgel diagrams for the qualitative interpretation of spectra of weak-field cubic (octahedral, tetrahedral) complexes of d^x metal ions.

Relationship to orbital splitting patterns



O_h



T_d

For octahedral complexes

$d^1 = t_{2g}^1$	$^2T_{2g}$
$d^2 = t_{2g}^2$	$^3T_{1g}$
$d^3 = t_{2g}^3$	$^4A_{2g}$
$d^4 = t_{2g}^3 e_g^1$	^5E_g
$d^5 = t_{2g}^3 e_g^2$	$^6A_{1g}$
$d^6 = t_{2g}^4 e_g^2$	$^5T_{2g}$

etc.....

tetrahedral complexes

e^1	^2E
e^2	$^3A_2$
$e^2 t_2^1$	$^4T_1$

etc....

Diagrams show spin-allowed transitions...

For d^1 or d^6 one transition at Δ

for d^2 or d^7 three transitions

$^3T_{1g}(F) \rightarrow {}^3T_{2g}$ at 4/5 Δ

$^3A_{2g}$ at 9/5 Δ

$^3T_{1g}$ (P) at some function of Δ and B

Analysis of spectra of many octahedral complexes leads to parameterization of Δ and B, see Table.

$\Delta = fg\ (cm^{-1} \times 10^{-3})$

$B' = B_0(1 - hk)$

where B_0 is the value of B for the free ion, and B' is the value found for the complex,

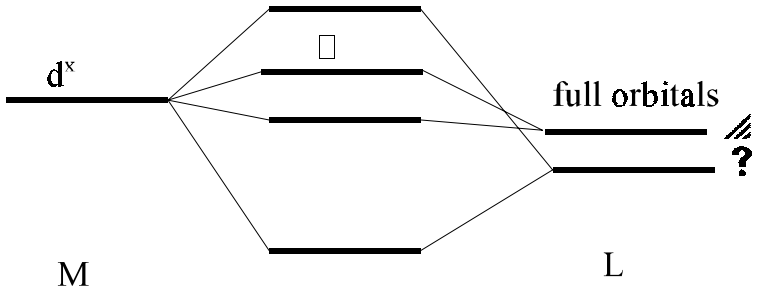
f and **h** are characteristic of the ligand, and **g** and **k** are characteristic of the metal ion.

The value of **f** determines the ligand's position in the Spectrochemical Series and the value of **h** determines the position of the ligand in the Nephelauxetic Series.

Lower symmetry complexes are classified as "axial" (E, T_1 and T_2 states are split into two levels each) or "rhombic" (all degeneracy is removed).

Interpretation of the Spectrochemical Series

weak-field ligands



strong-field ligands