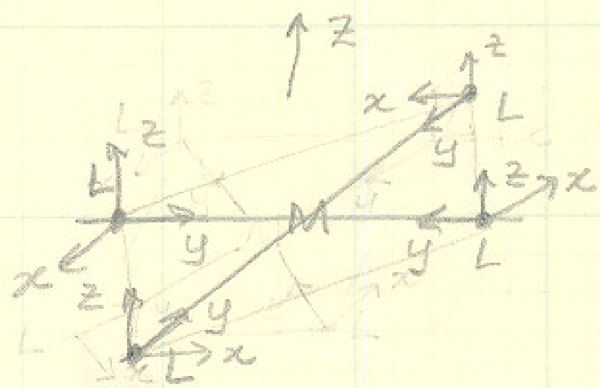
ATOMS, MOLECULES & RESEARCH

COORDINATION CHEMISTRY – SPRING – WEEK 7.

Determine the reducible representations for the basis set that represents the four ligands in the square planar complex ML_4. Then reduce them to their irreducible components.



Let the basis set for the $4L$ ligands be the four p_x } π-bonding four p_z } four p_y } σ-bonding orbitals on each of the ligands.

Generate Γ_{p_x}, Γ_{p_y}, Γ_{p_z} seperately.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{p_y}	4	0	0	2	0	0	0	4	2	0
Γ_{p_x}	4	0	0	−2	0	0	0	4	−2	0
Γ_{p_z}	4	0	0	−2	0	0	0	−4	2	0

# of times A_{2g} is in $\Gamma_{2p_x} = \frac{1}{16}\left[4\cdot1 + (-2)(2)(-1) + 4\cdot1 + (-2)(2)(-1)\right]$

$= 1$

# of times B_{2g} is in $\Gamma_{2p_x} = \frac{1}{16}\left[4\cdot1 + (-2)(2)(-1) + 4(1) + (-2)(2)(-1)\right]$

$= 1$

\# of times E_u is in $\Gamma_{2p_x} = \frac{1}{16}\left[4\cdot 2 + (-2)(2)\cdot 0 + (+4)(2) + (2)(0)(2)\right]$

$= 1$

$$\Gamma_{2p_x} = \underline{\underline{A_{2g} + B_{2g} + E_u}}$$

\# of times A_{1g} is in $\Gamma_{2p_y} = \frac{1}{16}\left[4\cdot 1 + (2)(+2)\cdot 1 + 4\cdot 1\cdot 1 + 2\cdot 2\cdot 1\right] = 1$

\# of times B_{1g} is in $\Gamma_{2p_y} = \frac{1}{16}\left[4\cdot 1 + (2)(2)1 + 4\cdot 1\cdot 1 + 2\cdot 2\cdot 1\right] = 1$

\# of times E_u is in $\Gamma_{2p_y} = \frac{1}{16}\left[4\cdot 2 + 2\cdot 2\cdot 0 + 4\cdot 2 + 2\cdot 2\cdot 0\right] = 1$

$$\Gamma_{2p_y} = \underline{\underline{A_{1g} + B_{1g} + E_u}}$$

\# of times A_{2u} is in $\Gamma_{2p_z} = \frac{1}{16}\left[4\cdot 1 + (-2)(2)(-1) + (-4)(-1) + (2\cdot)(2)1\right] = 1$

\# of times B_{2g} is in $\Gamma_{2p_z} = \frac{1}{16}\left[4\cdot 1 + (-2)(2)(-1) + (-4)\cdot 1 + (2)(2)(-1)\right]$

$= 0$

\# of times B_{2u} is in $\Gamma_{2p_z} = \frac{1}{16}\left[4\cdot 1 + (-2)(2)(-1) + (-4)\cdot 1\cdot(-1) + (2)(2)(1)\right]$

$= 1$

\# of times E_g is in $\Gamma_{2p_z} = \frac{1}{16}\left[4\cdot 2 + (-2)(2)0 + (-4)\cdot 1\cdot(-2) + (2)(2)(0)\right]$

$= 1$

$$\Gamma_{2p_z} = \underline{\underline{A_{2u} + B_{2u} + E_g}}$$

Chapter 11

③ (a) ^2D $\quad 2S+1 = 2 \Rightarrow \underline{S = 1/2}$

D term $\Rightarrow \underline{L = 2}$

$\underline{M_L = \pm 2, \pm 1, 0}$ $\quad \underline{M_S = \pm 1/2}$

(b) ^3G $\quad 2S+1 = 3 \Rightarrow \underline{S = 1} \Rightarrow M_S = \underline{\pm 1, 0}$

G term $\Rightarrow \underline{L = 4} \Rightarrow M_L = \underline{\pm 4, \pm 3, \pm 2, \pm 1, 0}$

(c) ^4F $\quad 2S+1 = 4 \Rightarrow \underline{S = 3/2} \Rightarrow M_S = \underline{\pm 3/2, \pm 1/2}$

$\underline{L = 3} \Rightarrow M_L = \underline{\pm 3, \pm 2, \pm 1, 0}$

④ $\underline{^2D}$ $\quad L = 2 \quad S = 1/2 \Rightarrow J = 5/2, 3/2$

d^3 config. $\therefore$ $\underline{^2D_{3/2}}$ is ground state

$\underline{^3G}$ $\quad L = 4, \quad S = 1 \Rightarrow J = 5, 4, 3$

d^4 config. $\therefore$ $\underline{^3G_3}$

$\underline{^4F}$ $\quad L = 3, \quad S = 3/2 \Rightarrow J = 9/2, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$

d^7 config. $\therefore$ $\underline{^4F_{9/2}}$