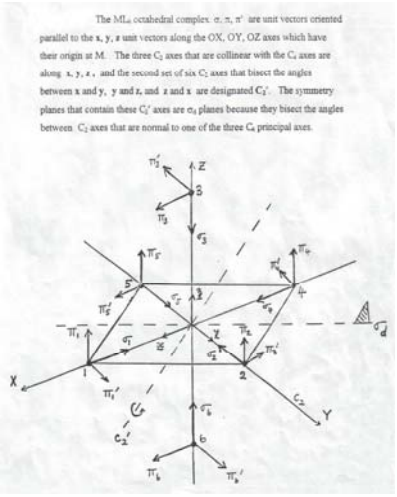
Applications: Transition Metal Complexes

C734b

Example:

ML_6 O_h complex using coordinate system designated below:



Metal Orbitals

nd	(5)
(n+1)s	(1)
(n+1)	(3)

9 orbitals total

Ligand Orbitals

6 p-orbitals pointing to M (σ-orbitals)
12 p-orbitals perpendicular to σ
≡ π (6 in total), π' (6 in total)

18 orbitals total

Overall orbital count = 27. This means in principle we need a 27 x 27 matrix representation!

Step 1

Examine the character table for O_h. (for the metal)
Find (although not stated) that s transforms as A_{1g}
The p-orbitals transform as T_{1u}
The d-orbitals transform as $E_g \oplus T_{2g}$

Note: the largest degeneracy is 3-fold in cubic symmetry. Therefore d-orbital set split.

The T_{2g} set (d_{xy}, d_{yz}, d_{xz}) "point" between the ligands.
The E_g set (d_{z2}, d_{x2-y2}) "point at the ligands.

Therefore $E(T_{2g}) < E(E_g)$

These are crystal field arguments based on electrostatic repulsion between central atom electrons and ligand electrons

Step 2

Write down the characters of the representations based on ligand p-orbitals labelled σ

No need to construct matrix representations. Use "quick" method of noting how contours of the basis functions transform under symmetry operator (T)

Assign +1 to χ(T) if is there is no change, -1 is the contour changes sign, and 0 if the orbital transforms to another orbital (implying an off diagonal matrix element in the matrix representation).

Characters for the irreducible representations of the point group $O_h = O \otimes C_i$.

O_h	E	$8C_3$	$6C_2'$	$6C_4$	$3C_2$	I	$8IC_3$ $8S_6$	$6IC_2'$ $6\sigma_d$	$6IC_4$ $6S_4$	$3IC_2$ $3\sigma_h$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	1	-1	-1	1
E_g	2	-1	0	0	2	2	-1	0	0	2
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1
T_{2g}	3	0	1	-1	-1	3	0	1	-1	-1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	-1	1	1	-1
E_u	2	-1	0	0	2	-2	1	0	0	-2
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1
T_{2u}	3	0	1	-1	-1	-3	0	-1	1	1

σ-orbitals

O_h	E	$8C_3$	$6C_2^{'}$	$6C_4$	$3C_2$	i	$8S_6$	$6\sigma_d$	$6S_4$	$3\sigma_h$
Γ_σ	6	0	0	2	2	0	0	2	0	4

Reduction yields: $\Gamma_\sigma = A_{1g} \oplus Eg \oplus T_{1u}$

Step 3

σ-bonding. Need to use projection operators to find linear combination of ligand σ-orbitals having A_{1g}, E_g and T_{1u} symmetry

Hard work!!

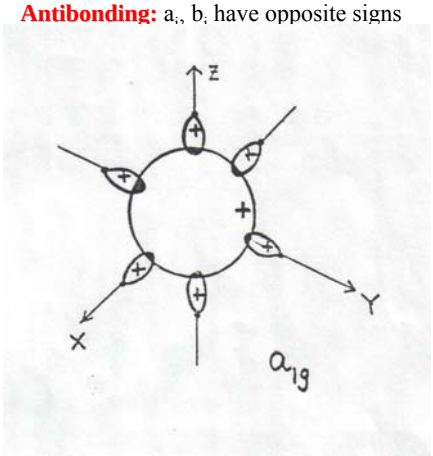
Omitting normalization factors, they are:

$$\psi(A_{1g}) = \underset{E}{1(\sigma_1)} + \underset{8C_3}{1(\sigma_2+\sigma_3+\sigma_5+\sigma_6+\sigma_3+\sigma_5+\sigma_2+\sigma_6)}$$
$$+\underset{6C_2'}{1(\sigma_2+\sigma_5+\sigma_4+\sigma_4+\sigma_3+\sigma_6)} + \underset{6C_4}{1(\sigma_2+\sigma_5+\sigma_6+\sigma_3+\sigma_1+\sigma_1)}$$
$$+\underset{3C_2}{1(\sigma_4+\sigma_4+\sigma_1)} + \underset{i}{1(\sigma_4)} + \underset{8S_6}{1(\sigma_5+\sigma_6+\sigma_2+\sigma_3+\sigma_6+\sigma_2+\sigma_3+\sigma_5)}$$
$$+\underset{6\sigma_d}{1(\sigma_5+\sigma_2+\sigma_1+\sigma_1+\sigma_6+\sigma_3)} + \underset{6S_4}{1(\sigma_2+\sigma_5+\sigma_6+\sigma_3+\sigma_4+\sigma_4)} + \underset{3\sigma_h}{1(\sigma_1+\sigma_1+\sigma_4)}$$

Therefore $\psi(A_{1g}) = \sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6$

$$\therefore a_{1g} = a_1[(n+1)s] + b_1(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$$

Bonding: a_i, b_i have the same sign
Antibonding: a_i, b_i have opposite signs



Similarly:

$$\psi_1(E_g) = 2\sigma_1 - 2(\sigma_2 + \sigma_3 + \sigma_5 + \sigma_6) + 2(\sigma_1 + 2\sigma_4)$$
$$+ 2\sigma_4 - 2(\sigma_2 + \sigma_3 + \sigma_5 + \sigma_6) + 2(2\sigma_1 + \sigma 4)$$

$$\Rightarrow \psi_1(E_g) = 2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6$$

Starting with σ_2 and then σ_3 gives cyclic permutations:

$$\psi_2(E_g) = 2\sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_5 - \sigma_6 - \sigma_1$$

$$\psi_3(E_g) = 2\sigma_3 - \sigma_4 - \sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2$$

Can't have 3 linearly independent basis functions for E_g

Want 2 combinations that are orthogonal (in the ZOA) and which overlap M-atom orbitals of E_g symmetry: dz2, dx2-y2

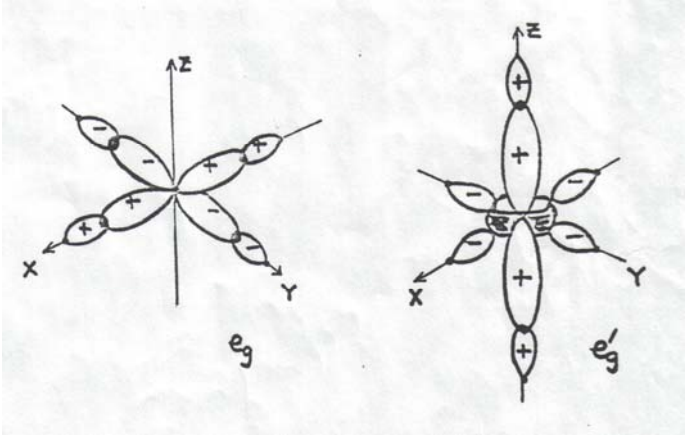
A suitable choice is:

$$\psi_1(E_g) - \psi_2(E_g) = \sigma_1 - \sigma_2 + \sigma_4 - \sigma_5 \quad (\text{xy plane})$$

$$\psi_3(E_g) = 2\sigma_3 - \sigma_4 - \sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 \quad (\text{z-direction})$$

$$\therefore e_g = a_2\left[nd_{x^2-y^2}\right] + b_2\left(\sigma_1 - \sigma_2 + \sigma_4 - \sigma_5\right)$$

$$e_g' = a_3\left[nd_{3z^2-r^2}\right] + b_3\left(2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5\right)$$



Similarly for the T_{1u} representation

$$\psi_1(T_{1u}) = 3\sigma_1 - 1(\sigma_2 + \sigma_5 + \sigma_3 + \sigma_6 + 2\sigma_4) + 1(\sigma_2 + \sigma_5 + \sigma_6 + \sigma_3 + 2\sigma_1)$$
$$-1(2\sigma_4 + \sigma_1) - 3\sigma_4 + 1(\sigma_5 + \sigma_2 + 2\sigma_1 + \sigma_6 + \sigma_3) - 1(\sigma_2 + \sigma_5 + \sigma_6 + \sigma_3 + 2\sigma_4)$$
$$+1(2\sigma_1 + \sigma_4)$$

$$\Rightarrow \boxed{\psi_1(T_{1u}) = \sigma_1 - \sigma_4} \qquad \text{(x-direction)}$$

By cyclic permutation

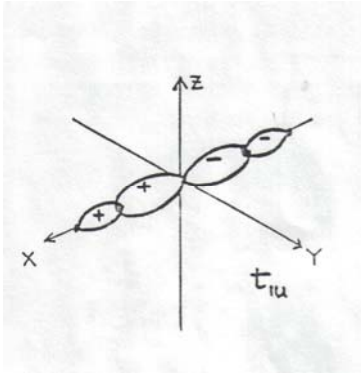
$$\psi_2(T_{1u}) = \sigma_2 - \sigma_5 \qquad \text{(y-direction)}$$

$$\psi_3(T_{1u}) = \sigma_3 - \sigma_6 \qquad \text{(z-direction)}$$

$$\therefore t_{1u} = a_4\left[(n+1)p_x\right] + b_4(\sigma_1 - \sigma_4)$$

$$t'_{1u} = a_5\left[(n+1)p_y\right] + b_5(\sigma_2 - \sigma_5)$$

$$t''_{1u} = a_6\left[(n+1)p_z\right] + b_6(\sigma_3 - \sigma_6)$$



Repeat procedure for the π, π' orbitals

π, π'-orbitals

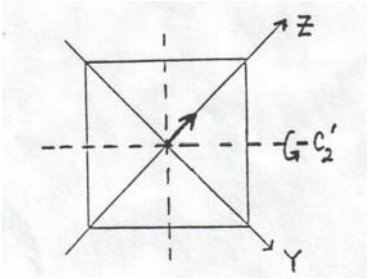
O_h	E	$8C_3$	$6C_2'$	$6C_4$	$3C_2$	i	$8S_6$	$6\sigma_d$	$6S_4$	$3\sigma_h$
Γ_π	12	0	0	0	−4	0	0	0	0	$(-4+4)=0$
										$\pi \quad \pi'$

Reduction yields: $\Gamma_\pi = T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$

Next, use projection operators to find linear combinations of ligand π and π' orbitals that form bases for the T_{1u}, T_{2g} , T_{2u}, and T_{1g} IRs

Start with π_1 as our arbitrary function (**hard work!!**).

Sometimes hard to visualize.
Diagram showing for example how π_1 transforms under the C_2' operator in the yz plane



T_{1u}

$$\psi_1(T_{1u}) = 3(\pi_1) - 1(-\pi_2 - \pi_5 + \pi_4' - \pi_4' + \pi_3 - \pi_6)$$
$$+1(\pi_2 + \pi_5 + \pi_1' - \pi_1' + \pi_6 - \pi_5) - 1(\pi_4 - \pi_1 - \pi_4)$$
$$-3(-\pi_4) + 1(\pi_5 + \pi_2 - \pi_1' + \pi_1' - \pi_6 + \pi_3)$$
$$-1(-\pi_5 - \pi_2 - \pi_4' + \pi_4' - \pi_3 + \pi_6) + 1(-\pi_1 + \pi_4 + \pi_1)$$

$$\Rightarrow \boxed{\psi_1(T_{1u}) = \pi_1 + \pi_2 + \pi_4 + \pi_5 = \pi_z}$$

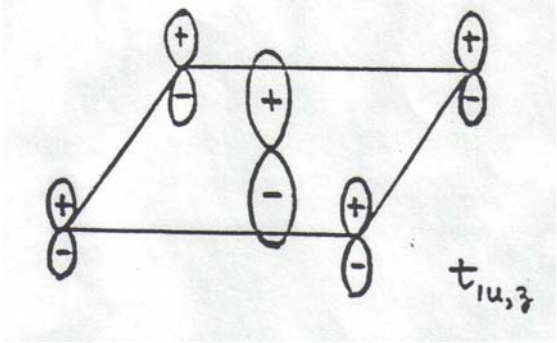
Since Ox and Oy are equivalent in O_h symmetry

$$\psi_2(T_{1u}) = -\pi_2' + \pi_3 + \pi_5' + \pi_6 = \pi_x$$

$$\psi_3(T_{1u}) = \pi_1' + \pi_6' - \pi_4' + \pi_3' = \pi_y$$

MOs which form bases for T_{1u} are:

$$t_{1u,x} = a_7\left[(n+1)p_x\right] + b_7\pi_x$$
$$t_{1u,y} = a_8\left[(n+1)p_y\right] + b_8\pi_y$$
$$t_{1u,z} = a_9\left[(n+1)p_z\right] + b_7\pi_z$$



T_{2g}

$$\psi_1(T_{2g}) = 3(\pi_1) + 1(-\pi_2 - \pi_5 + \pi_3 - \pi_6) - 1(\pi_2 + \pi_5 + \pi_6 - \pi_3)$$
$$-1(-\pi_1) + 3(-\pi_4) + 1(\pi_5 + \pi_2 - \pi_6 + \pi_3)$$
$$-1(-\pi_5 - \pi_2 - \pi_3 + \pi_6) - 1(\pi_4)$$

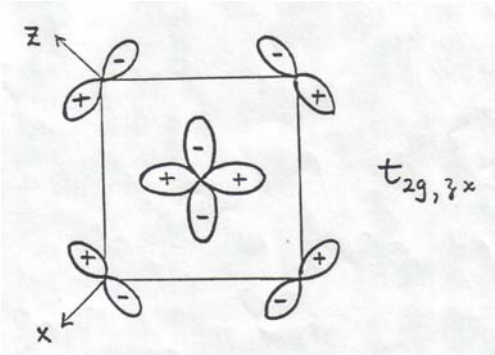
$$\Rightarrow \psi_1(T_{2g}) = \pi_1 - \pi_4 + \pi_3 - \pi_6 = \pi_{zx}$$

Similarly

$$\psi_2(T_{2g}) = \pi_2 - \pi_3' - \pi_5 - \pi_6' = \pi_{yx}$$
$$\psi_3(T_{2g}) = \pi_1' - \pi_2' + \pi_4' - \pi_5' = \pi_{xy}$$

Therefore MOs of T_{2g} symmetry are:

$$t_{2g,xy} = a_{10}\left[nd_{xy}\right] + b_{10}\pi_{xy}$$
$$t_{2g,yz} = a_{11}\left[nd_{yz}\right] + b_{11}\pi_{yz}$$
$$t_{2g,zx} = a_{12}\left[nd_{zx}\right] + b_{12}\pi_{zx}$$



T_{1g}

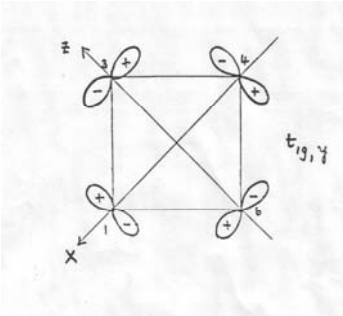
$$\psi_1(T_{1g}) = 3(\pi_1) - 1(-\pi_2 - \pi_5 + \pi_3 - \pi_6) + 1(\pi_2 + \pi_5 + \pi_6 - \pi_3)$$
$$-1(-\pi_1) + 3(-\pi_4) - 1(\pi_5 + \pi_2 - \pi_6 + \pi_3)$$
$$+1(-\pi_5 - \pi_2 - \pi_3 + \pi_6) - 1(\pi_4)$$

$$\Rightarrow \boxed{\psi_1(T_{1g}) = \pi_1 - \pi_3 - \pi_4 + \pi_6}$$

Since there is no M T_{1g} orbital means $\psi_1(T_{1g})$ is a non-bonding orbital $\equiv t_{1g,y}$

The 3 degenerate MO's are:

$$t_{1g,x} = b_{13}\left(\pi_2 + \pi_3' - \pi_5 + \pi_6'\right)$$
$$t_{1g,y} = b_{14}\left(\pi_1 + \pi_3 - \pi_4 + \pi_6\right)$$
$$t_{1g,z} = b_{15}\left(\pi_1' + \pi_2' - \pi_4' + \pi_5'\right)$$



T_{2u}

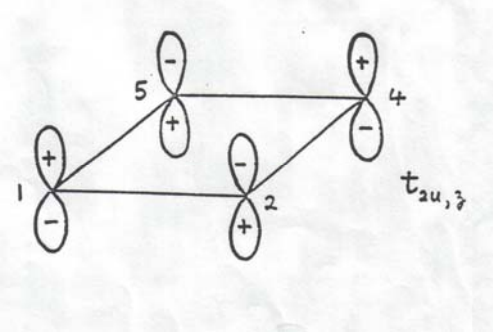
$$\psi_1\left(T_{1g}\right) = 3\left(\pi_1\right) + 1\left(-\pi_2 - \pi_5 + \pi_3 - \pi_6\right) - 1\left(\pi_2 + \pi_5 + \pi_6 - \pi_3\right)$$
$$-1\left(-\pi_1\right) + 3\left(-\pi_4\right) - 1\left(\pi_5 + \pi_2 - \pi_6 + \pi_3\right)$$
$$+1\left(-\pi_5 - \pi_2 - \pi_3 + \pi_6\right) + 1\left(\pi_4\right)$$

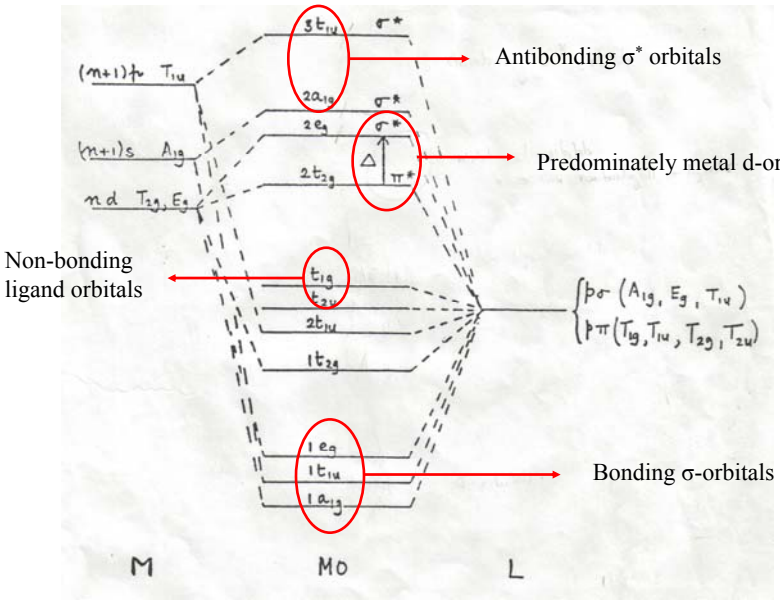
$$\Rightarrow \boxed{\psi_1\left(T_{2u}\right) = \pi_1 - \pi_2 + \pi_4 - \pi_5}$$

Since there is no M T_{2u} orbital means $\psi_1(T_{2u})$ is a non-bonding orbital $\equiv t_{2u,z}$

By symmetry the 3 degenerate MOs are:

$$t_{2u,x} = b_{16}\left(\pi_2' + \pi_3 - \pi_5' + \pi_6\right)$$
$$t_{2u,y} = b_{17}\left(\pi_1' - \pi_6' - \pi_4' + \pi_3'\right)$$
$$t_{2u,z} = b_{18}\left(\pi_1 - \pi_2 + \pi_4 - \pi_5\right)$$





Crystal Field Theory picture

(t_{2g})^3 configuration appropriate for a $[MoCl_6]^{3-}$ complex