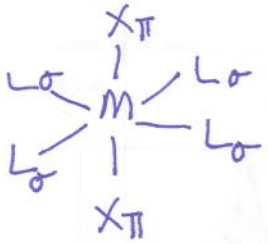


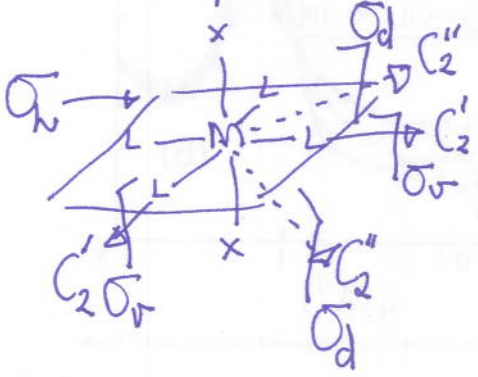
shape: octahedral

point group: D_{4h}

axial system and symmetry elements

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$

$C_4, C_2, S_4 (z)$ center of i on M



identify chemical fragments:

form ligand FOs → do in 2 stages $L_4 + X_2$.

take TM FOs

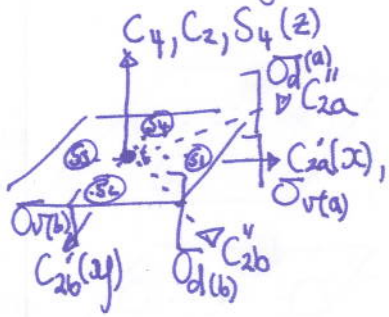
what are the FOs for L_4?

3 ways to approach this → symmetry adapted orbitals

→ $H_2 + H_2$ molecular fragments

→ "octahedral like" FOs

Generate Sym Adapted Orbitals for H_4 under O_{4h}



10 operations = 16

O_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{4Hs}	4	0	0	2	0	0	0	4	2	0
A_{1g}	1	1	1	1	1	1	1	1	1	1

- no of orbitals in basis set that do not move center
- sAOs so try totally symmetric a_{1g}.

$$\Gamma_{A_{1g}} = \frac{1}{16}\left[(1\cdot4\cdot1)+0+0+(2\cdot2\cdot1)+0+0+0+(1\cdot4\cdot1)+(2\cdot2\cdot1)+0\right]$$
$$= \frac{1}{16}\left[4+4+4+4\right] = 16/16 = 1$$

O_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{4s}-A_{1g}$ =	3	-1	-1	1	-1	-1	-1	3	1	-1
try E_u =	2	0	-2	0	0	-2	0	2	0	0
$\Gamma_{4s}-A_{1g}-E_u$ =	1	-1	1	1	-1	1	-1	1	1	-1

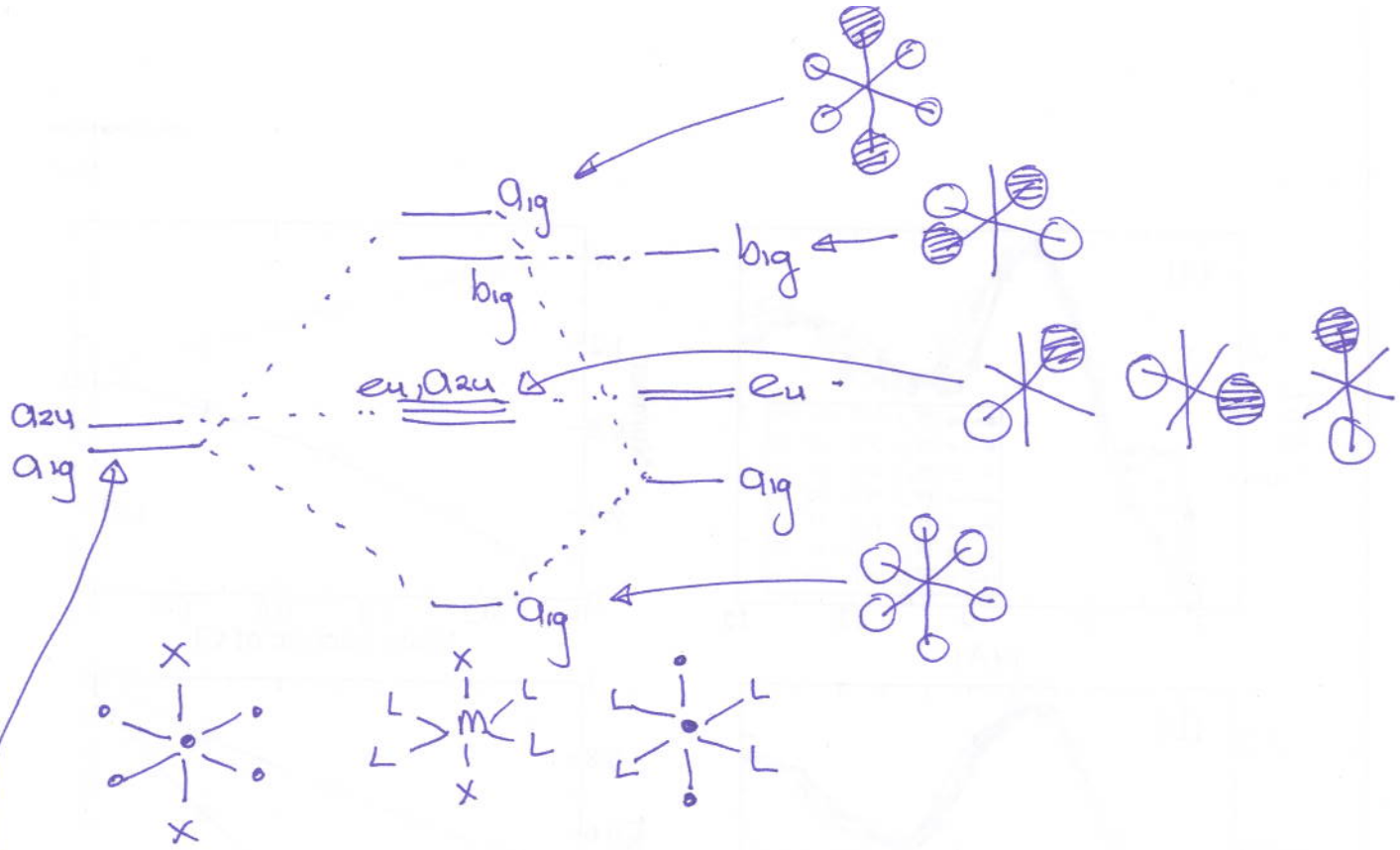
$= B_{1g}$

$$\Gamma_{4s} = a_{1g} + e_u + b_{1g}.$$

need to find 4 orbitals, use projection operator

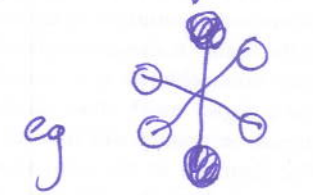
	E	C_4^1	C_4^3	C_2	$C_{2(a)}'$	$C_{2(b)}'$	$C_{2(a)}''$	$C_{2(b)}''$	i	S_4^1	S_4^3	σ_h	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{d(a)}$	$\sigma_{d(b)}$
$Q[S_1]$	S_1	S_2	S_4	S_3	S_1	S_3	S_4	S_2	S_3	S_2	S_4	S_1	S_1	S_3	S_4	S_2
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

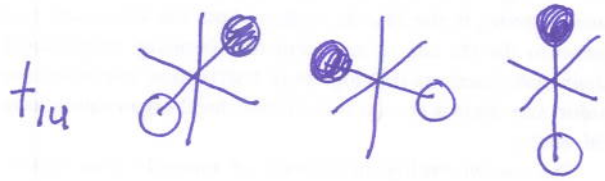
$$\psi_{a_{1g}} = \frac{1}{16}\left[S_1+S_2+S_4+S_3+S_1+S_3+S_4+S_2+S_3+S_2+S_4+S_1+S_1+S_3+S_4+S_2\right]$$
$$= \frac{1}{16}\left[4S_1+4S_2+4S_3+4S_4\right] = 4/16\left[S_1+S_2+S_3+S_4\right] = \frac{1}{4}\left[S_1+S_2+S_3+S_4\right]$$

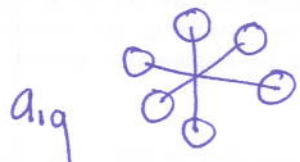


X more electronegative than L, slightly deeper and AOs are distant, only small stabilization destabilization.

This should look familar! the D_{4h} is only a slight distortion from O_h and L_6 orbitals form:

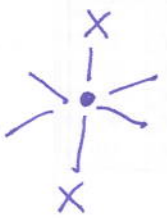


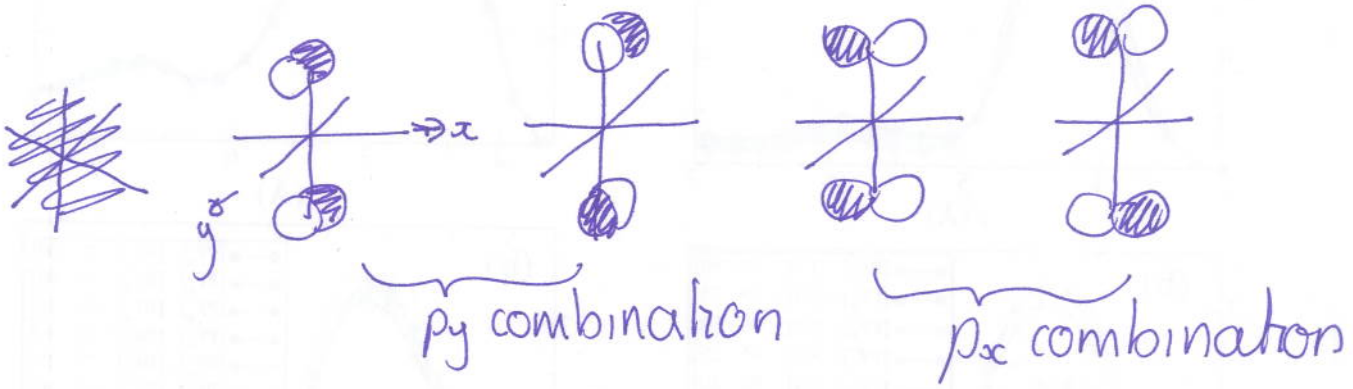




} so our orbitals do look like these ... we are on the right track!

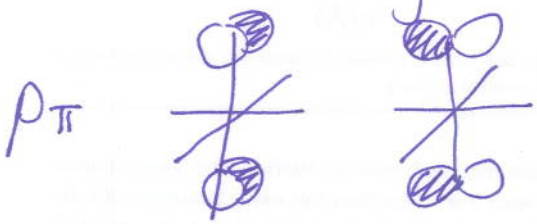
what about the symmetry of the p_π fragment orbitals? the "p_z" is already part of the σ-framework, we need to consider the p_x and p_y orbitals:



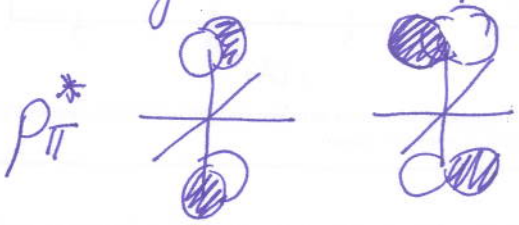


bonding set form degenerate p_π

antibonding set form degenerate p_π^*



same as p_x / p_y phase
$\Rightarrow e_u$.



$\Rightarrow e_g$

so.... putting all of this together....

also how much will these orbitals be split?
→ not by much, they are "π" and 2 bonds apart, interactions will be weak!

Now put our fragments together:

M and L_4X_2 then "add in" FOs for π-compone

the metal orbitals will be:

4p ≡ $p_x, p_y \rightarrow e_u$
$p_z \rightarrow a_{2u}$

4s — $s \rightarrow a_{1g}$

3d ≡ $d_{z^2} \rightarrow a_{1g}$
$d_{x^2-y^2} \rightarrow b_{1g}$
$d_{xy} \rightarrow b_{2g}$
$d_{xz} \rightarrow e_g$
$d_{yz} \rightarrow e_g$

relative energy of the ligand FOs?

this is a π donor system, the ligand orbitals will lie below the metal

π-donors tend to be quite electronegative and the π orbitals lie below the metal dAOs

↙ rough positioning.

p e_u, a_{2u} ≡

s a_{1g} —

d a_{1g}, b_{1g}, b_{2g}, e_g ≡ . . . . . — ← slightly below d AOs.

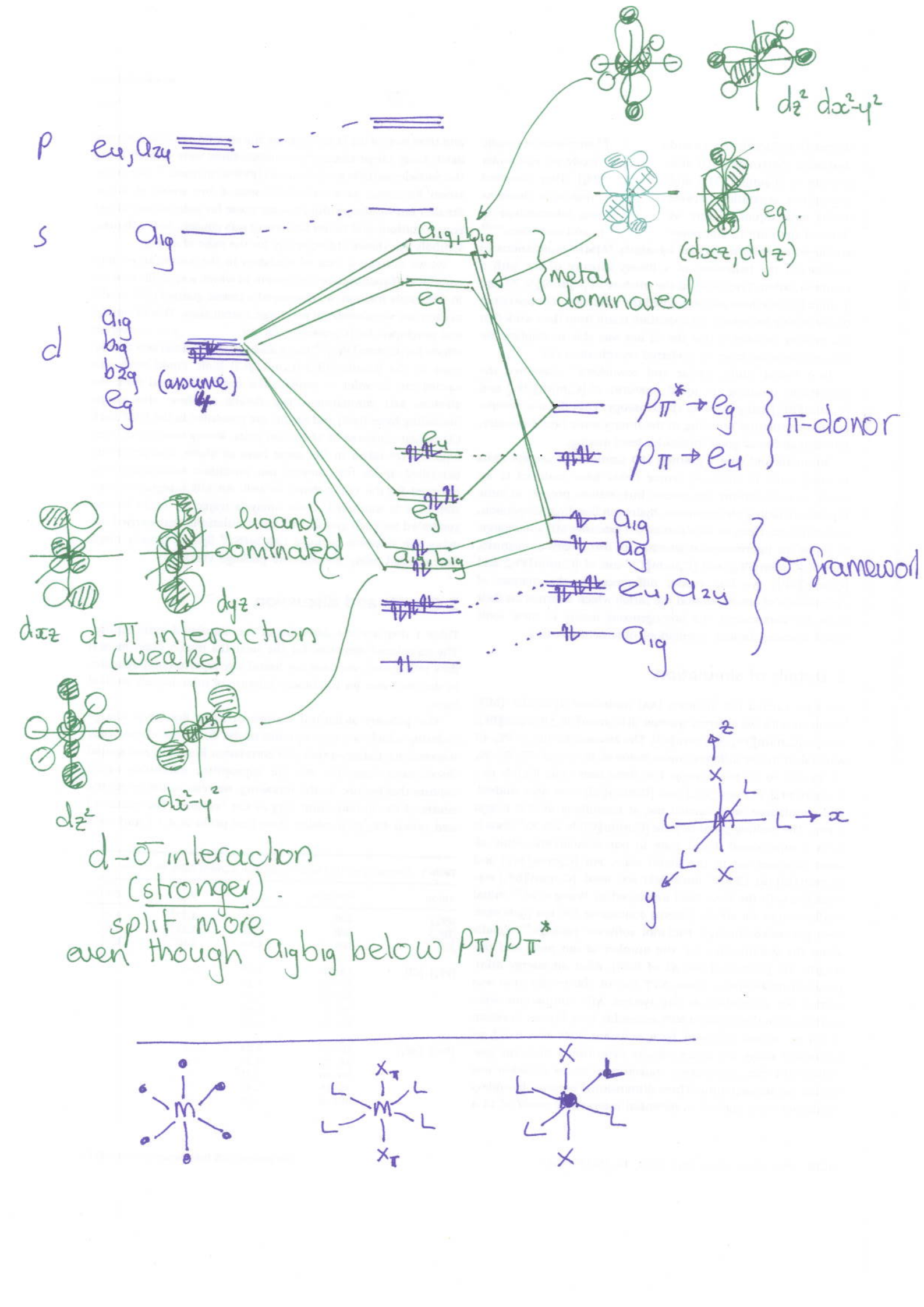
≡ π*

≡ π

— a_{1g}
— b_{1g}

≡ e_u, a_{2u}

— a_{1a}


p
s
d
e_u, a_{2u}
a_{1g}
a_{1g}, b_{1g}
e_g
a_{1g}
b_{2g}
b_{2g}
e_g
(assume)
d_{z^2} $d_{x^2-y^2}$
eg.
(d_{xz}, d_{yz})
metal dominated
$p_\pi^* \to e_g$
$p_\pi \to e_u$
π-donor
e_u
e_g
a_{1g}, b_{1g}
a_{1g}
b_g
e_u, a_{2u}
a_{1g}
σ framework
ligand dominated
d_{xz}
d_{yz}
d-π interaction
(weaker)
d_{z^2}
$d_{x^2-y^2}$
d-σ interaction
(stronger).
split more
even though $a_{1g}b_{1g}$ below p_π / p_π^*
z
x
y
L
X
M
X_T