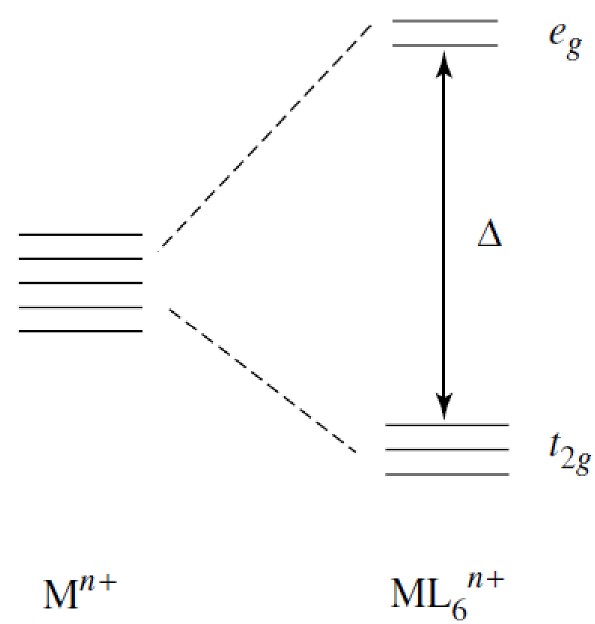
Crystal Field Theory

Describes how the *d orbitals of the transition metal are affected by the presence* of coordinating ligands.

- Imagine the metal ion surrounded by a uniform spherical electric field where the d orbitals are degenerate.
- As the ligands approach the metal from the six octahedral directions ±x, ±y, and ±z, the ***degeneracy is broken***
- The $dx^2{-}y^2$ and dz^2 orbitals point toward the L groups are destabilized by the negative charge of the ligands and move to higher energy.
- Those that point away from L (dxy, dyz, and dxz) are less destabilized.

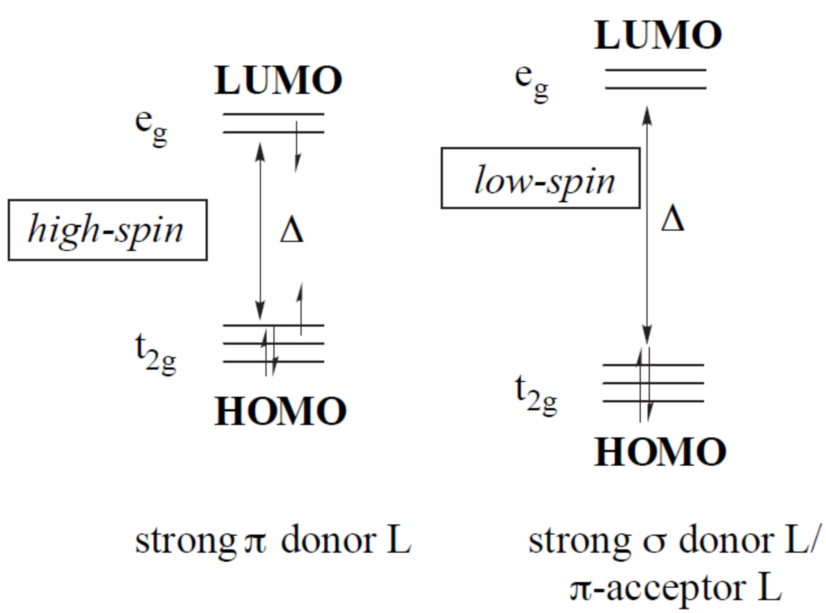


Octahedral

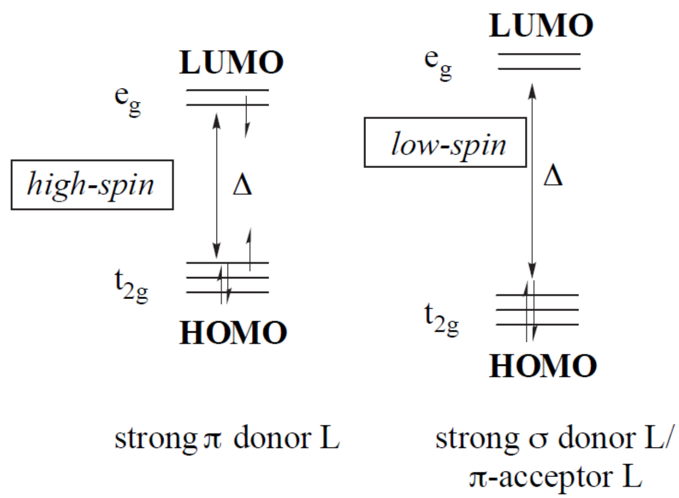
- The ***crystal field splitting energy*** (Δ - sometimes labeled 10Dq) depends on the value of the effective negative charge and therefore on the nature of the ligands.
- Higher Δ leads to stronger M−L bonds.

High spin *vs.* low spin electron configuration

- If **Δ** is low enough, electrons may arrange in a "high spin" configuration reducing electron- electron repulsion that occurs upon pairing up in the same orbital.
- In 1st row metals complexes, low-field ligands (strong π - donors) favor high spin configurations whereas high field ligands (π-acceptors/ strong σ donors) favor low spin.
- The majority of 2nd and 3rd row metal complexes are low-spin irrespective of their ligands.



- **Low-oxidation state complexes also tend to have lower Δ than high-oxidation state complexes.**
- **High oxidation state→ increased χ →increased Δ → low-spin configuration**



$$Mn^{2+} < V^{2+} < Co^{2+} < Fe^{2+} < Ni^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Rh^{3+} < Ir^{3+} < Pt^{4+}$$

← 1st row/low-valent low Δ

2nd,3rd row/high-valent high Δ →

Construction of MO diagrams for Transition Metal Complexes

σ bonding only scenario

General MO Approach for MX_n Molecules

- To construct delocalized MOs we define a *linear combination of atomic orbitals (LCAOs)* that combine central-atom AOs with combinations of pendant ligand orbitals called SALCs:

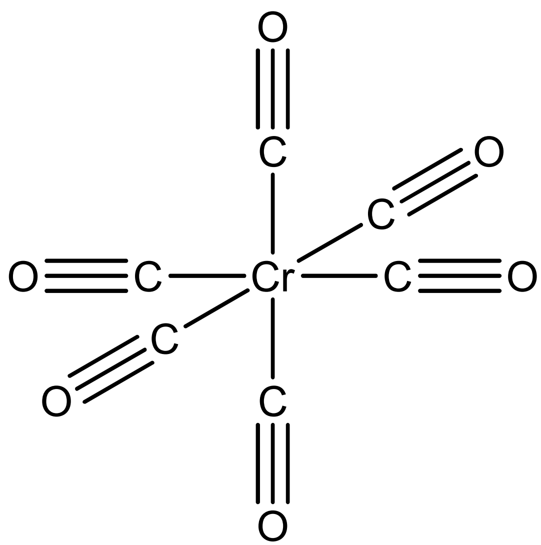
$$\Psi_{MO} = a\,\Psi\,(\text{Metal AO}) \pm b\,\Psi\,(\text{SALC } n\text{X})$$

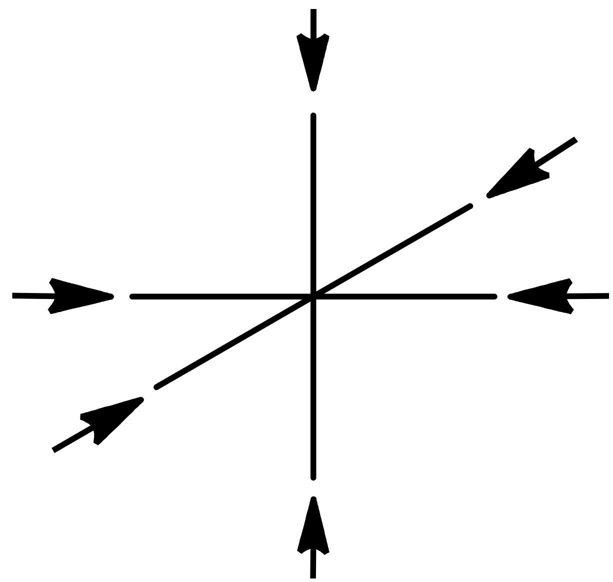
(SALC = Symmetry Adapted Linear Combination)

- SALCs are constructed with the aid of group theory, and those SALCs that belong to a particular species of the group are matched with central-atom AOs with the same symmetry to make bonding and antibonding MOs.

$$\Psi_{SALC} = c_1\,\Psi_1 \pm c_2\,\Psi_2 \pm c_3\,\Psi_3 \ldots. \pm c_n\,\Psi_n$$

1. **Use the directional properties of potentially bonding orbitals on the outer atoms (shown as vectors on a model) as a basis for a representation of the SALCs in the point group of the molecule.**

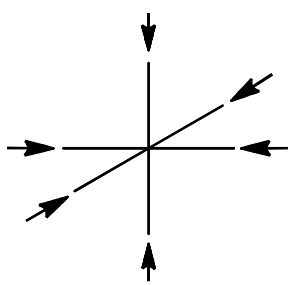




point group = O_h

2. **Generate a reducible representation for all possible SALCs by noting whether vectors are shifted or non-shifted by each class of operations of the group.**

   - **Each vector shifted through space contributes 0 to the character for the class. Each non-shifted vector contributes 1 to the character for the class.**



point group = O_h

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

3. Decompose the reducible representation into its component irreducible representations to determine the symmetry species of the SALCs.

- For complex molecules with a large dimension reducible representation, identification of the component irreducible representations and their quantitative contributions can be carried out systematically using the following equation

$$n_i = \frac{1}{h} \sum_c g_c \chi_i \chi_r$$

n_i : number of times the irreducible representation *i* occurs in the reducible representation

h : order of the group

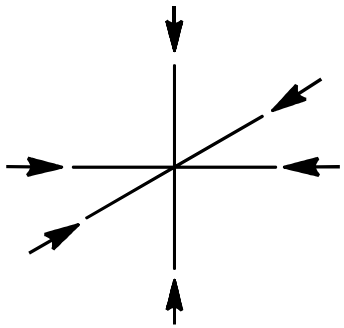
c : class of operations

g_c : number of operations in the class

χ_i : character of the irreducible representation for the operations of the class

χ_r : character of the reducible representation for the operations of the class

- The work of carrying out a *systematic reduction* is better organized by using the tabular method, rather than writing out the individual equations for each irreducible representation



point group = O_h

Character Table for O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h = 48$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2,\ x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
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	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Transformation Properties of Central AOs

- Transformation properties for the standard AOs in any point group can be deduced from listings of vector transformations in the character table for the group.

s – transforms as the totally symmetric representation in any group.

p – transform as x, y, and z, as listed in the second-to-last column of the character table.

d – transform as xy, xz, yz, x^2-y^2 , and z^2 (or $2z^2$-x^2-y^2)

e.g., in T_d and O_h , as listed in the last column of the character table.

Mulliken Symbols
- Irreducible Representation Symbols

- In non-linear groups:

A	:	non-degenerate;	symmetric to C_n where $\chi(C_n) > 0$.
B	:	non-degenerate;	anti-symmetric to C_n where $\chi(C_n) < 0$.
E	:	doubly-degenerate;	$\chi(E) = 2$.
T	:	triply-degenerate;	$\chi(T) = 3$.
G	:	four-fold degeneracy;	$\chi(G) = 4$, observed in I and I_h
H	:	five-fold degeneracy;	$\chi(H) = 5$, observed in I and I_h

- In linear groups $C_{\infty v}$ and $D_{\infty h}$:

$\Sigma \equiv A$	non-degenerate;	symmetric to C_∞ ; $\chi(C_\infty) = 1$.
$\Pi, \Delta, \Phi \equiv E$	doubly-degenerate;	$\chi(E) = 2$.

Mulliken Symbols - Modifying Symbols

- With any degeneracy in any centrosymmetric groups:

subscript *g* : *gerade* ; symmetric with respect to inversion ; $\chi_i > 0$.

subscript *u* : un*gerade* ; anti-symmetric with respect to inversion ; $\chi_i < 0$.

- With any degeneracy in non-centrosymmetric non-linear groups:

prime (‘) : symmetric with respect to σ_h ; $\chi(\sigma_h) > 0$.

double prime (“) : anti-symmetric with respect to σ_h ; $\chi(\sigma_h) < 0$.

- With non-degenerate representations in non-linear groups:

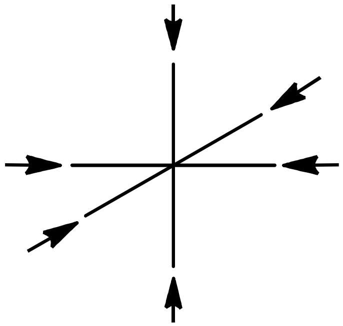
subscript *1* : symmetric with respect to C_m ($m < n$) or σ_v ;
$\chi(C_m) > 0$ or $\chi(\sigma_v) > 0$.

subscript *2* : anti-symmetric with respect to C_m ($m < n$) or σ_v ;
$\chi(C_m) < 0$ or $\chi(\sigma_v) < 0$.

- With non-degenerate representations in linear groups ($C_{\infty v}$ and $D_{\infty h}$):

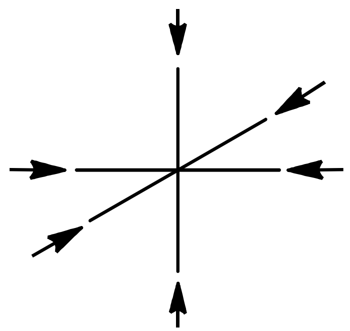
subscript + : symmetric with respect to ∞C_2 or $\infty\sigma_v$;
$\chi(\infty C_2) = 1$ or $\chi(\infty\sigma_h) = 1$.

subscript – : anti-symmetric with respect to ∞C_2 or $\infty\sigma_v$;
$\chi(\infty C_2) = -1$ or $\chi(\infty\sigma_h) = -1$.



Systematic Reduction for O_h

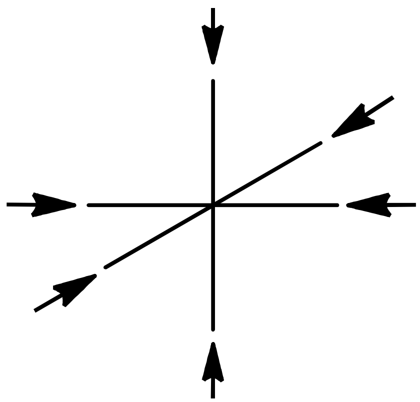
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Σ	$n_i = \Sigma/h$
Γ_σ	6	0	0	2	2	0	0	0	4	2		(h = 48)
A_{1g}												
A_{2g}												
E_g												
T_{1g}												
T_{2g}												
A_{1u}												
A_{2u}												
E_u												
T_{1u}												
T_{2u}												



Systematic Reduction for O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Σ	$n_i = \Sigma/h$
Γ_σ	6	0	0	2	2	0	0	0	4	2		(h = 48)
A_{1g}	6	0	0	12	6	0	0	0	12	12	48	1
A_{2g}	6	0	0	-12	6	0	0	0	12	-12	0	0
E_g	12	0	0	0	12	0	0	0	24	0	48	1
T_{1g}	18	0	0	12	-6	0	0	0	-12	-12	0	0
T_{2g}	18	0	0	-12	-6	0	0	0	-12	12	0	0
A_{1u}	6	0	0	12	6	0	0	0	-12	-12	0	0
A_{2u}	6	0	0	-12	6	0	0	0	-12	12	0	0
E_u	12	0	0	0	12	0	0	0	-24	0	0	0
T_{1u}	18	0	0	12	-6	0	0	0	12	12	48	1
T_{2u}	18	0	0	-12	-6	0	0	0	12	-12	0	0

4. The number of SALCs, including members of degenerate sets, must equal the number of ligand orbitals taken as the basis for the representation.

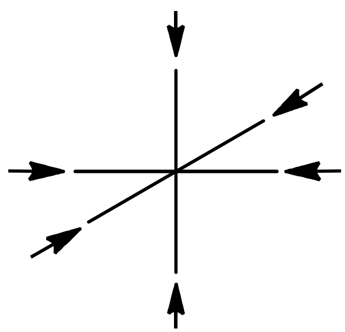


point group = O_h

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$

$$d_\Gamma = 1 + 2 + 3 = 6$$

5. **Determine the symmetries of potentially bonding central-atom AOs by inspecting unit vector and direct product transformations listed in the character table of the group.**



point group = O_h

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$

Cr bonding AOs

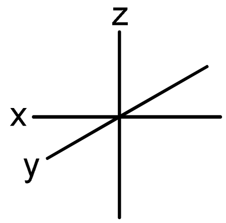
A_{1g} : 4*s*

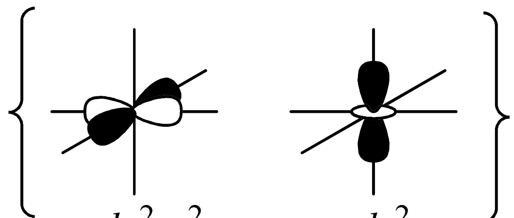
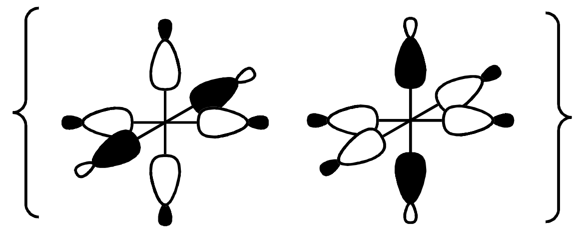
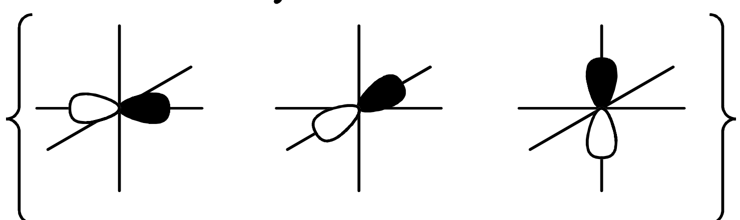
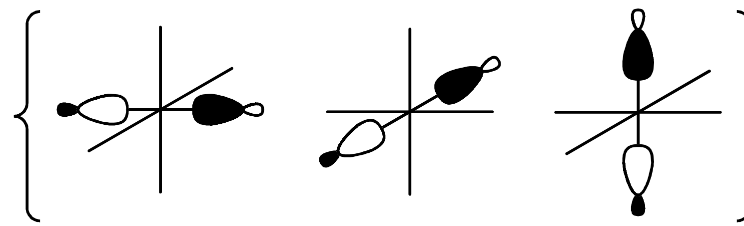
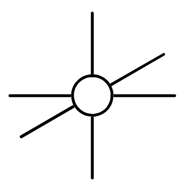
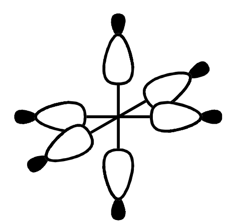
T_{1u} : ($4p_x$, $4p_y$, $4p_z$)

E_g : ($3dx^2\text{-}y^2$, $3dz^2$)

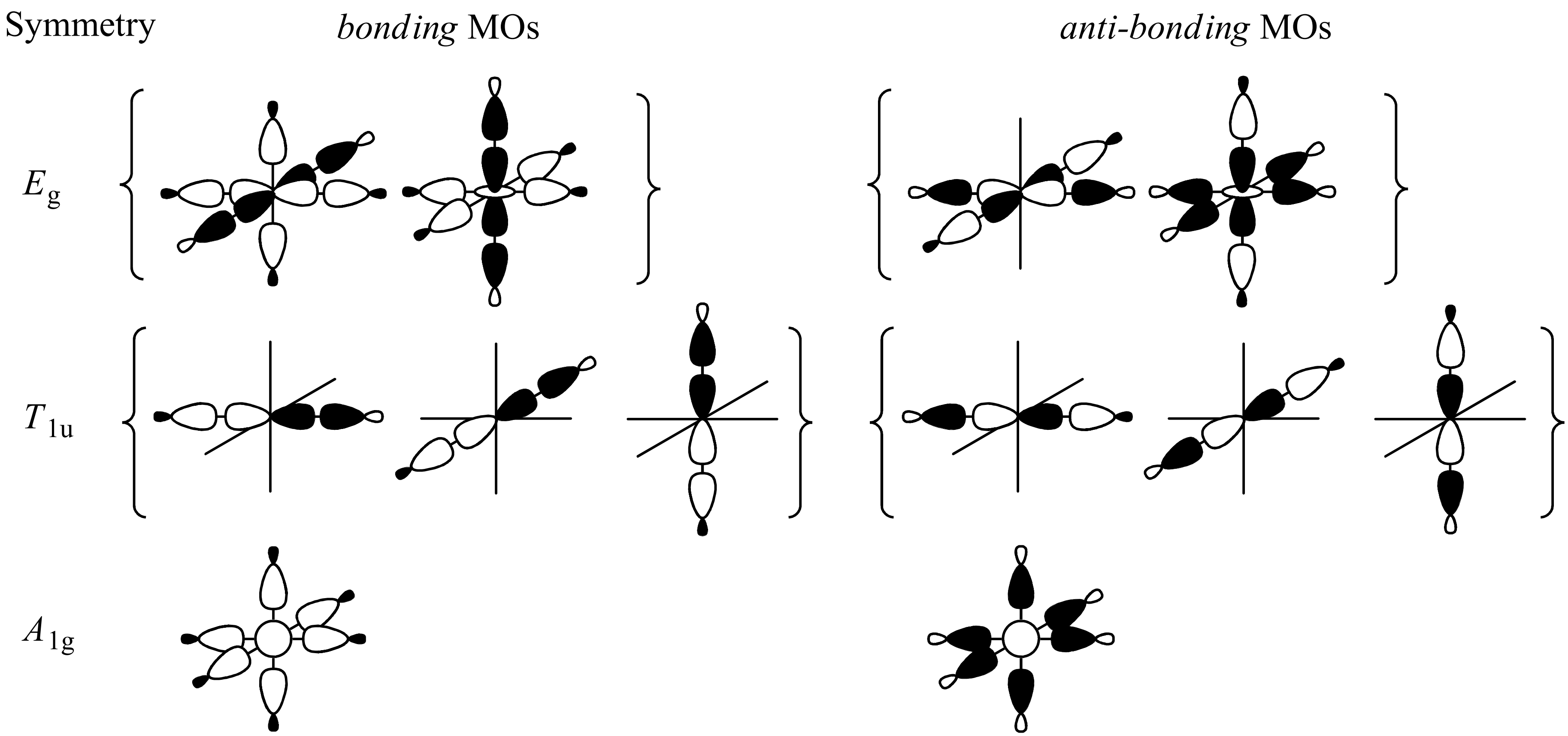
Cr non-bonding AOs

T_{2g} : (3*d*xy, 3*d*xz, 3*d*yz)

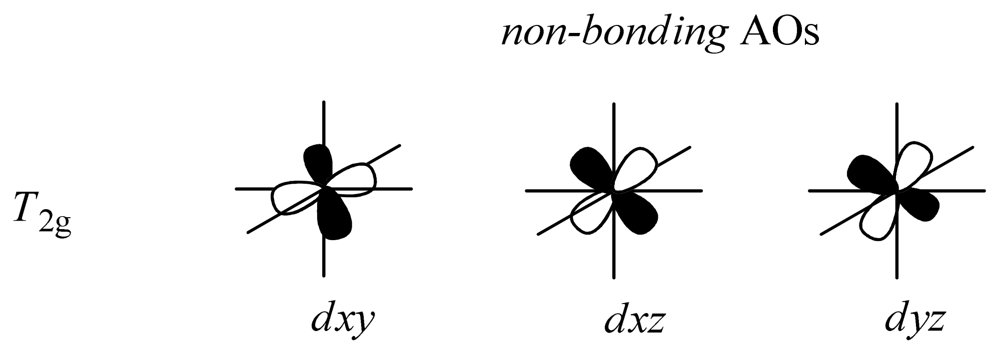
define Cartesian axis 

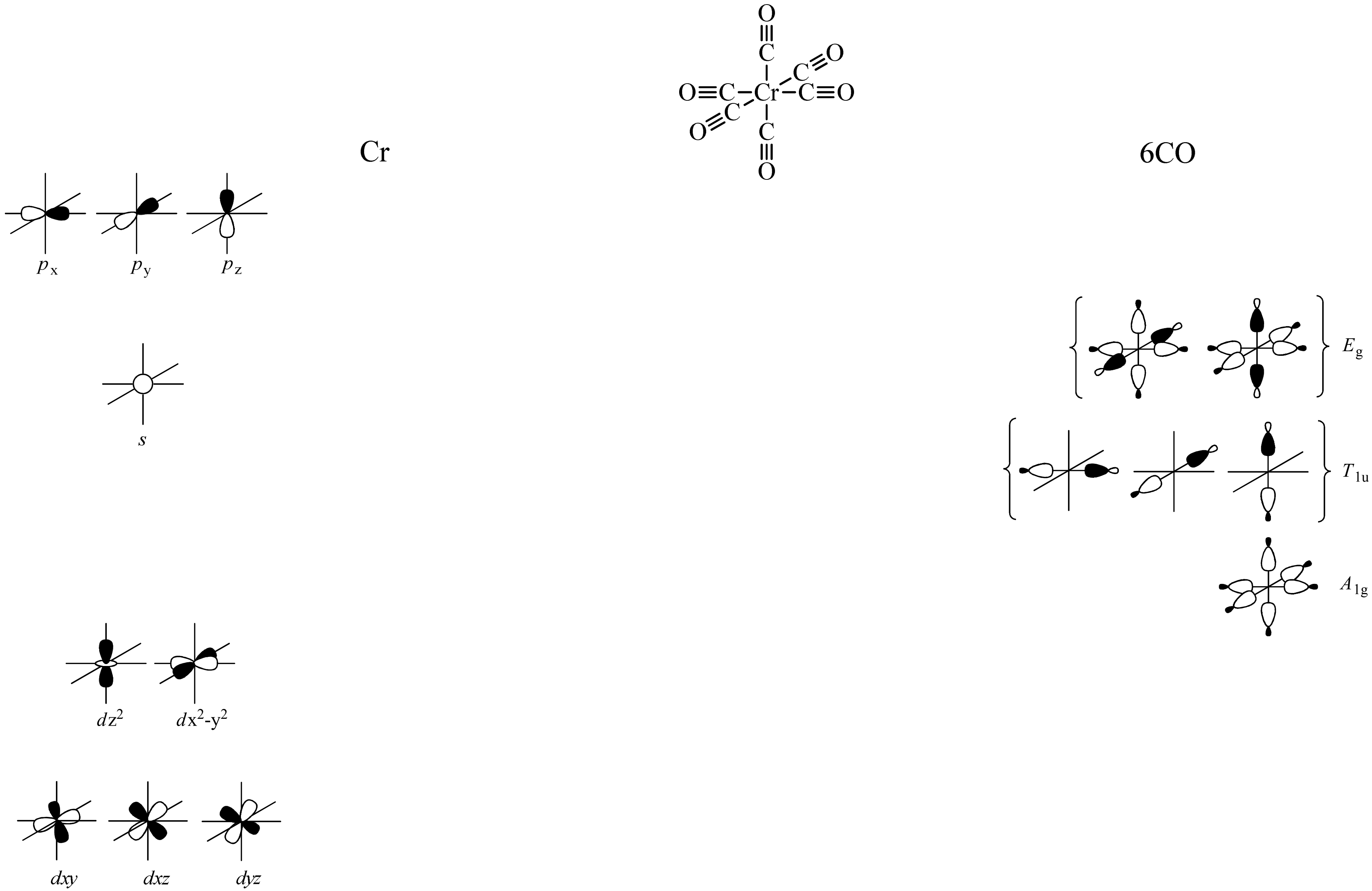
Symmetry	AOs	SALCs
E_g	 $d\text{x}^2\text{-y}^2$ $d\text{z}^2$	
T_{1u}	 p_x p_y p_z	
A_{1g}	 s	

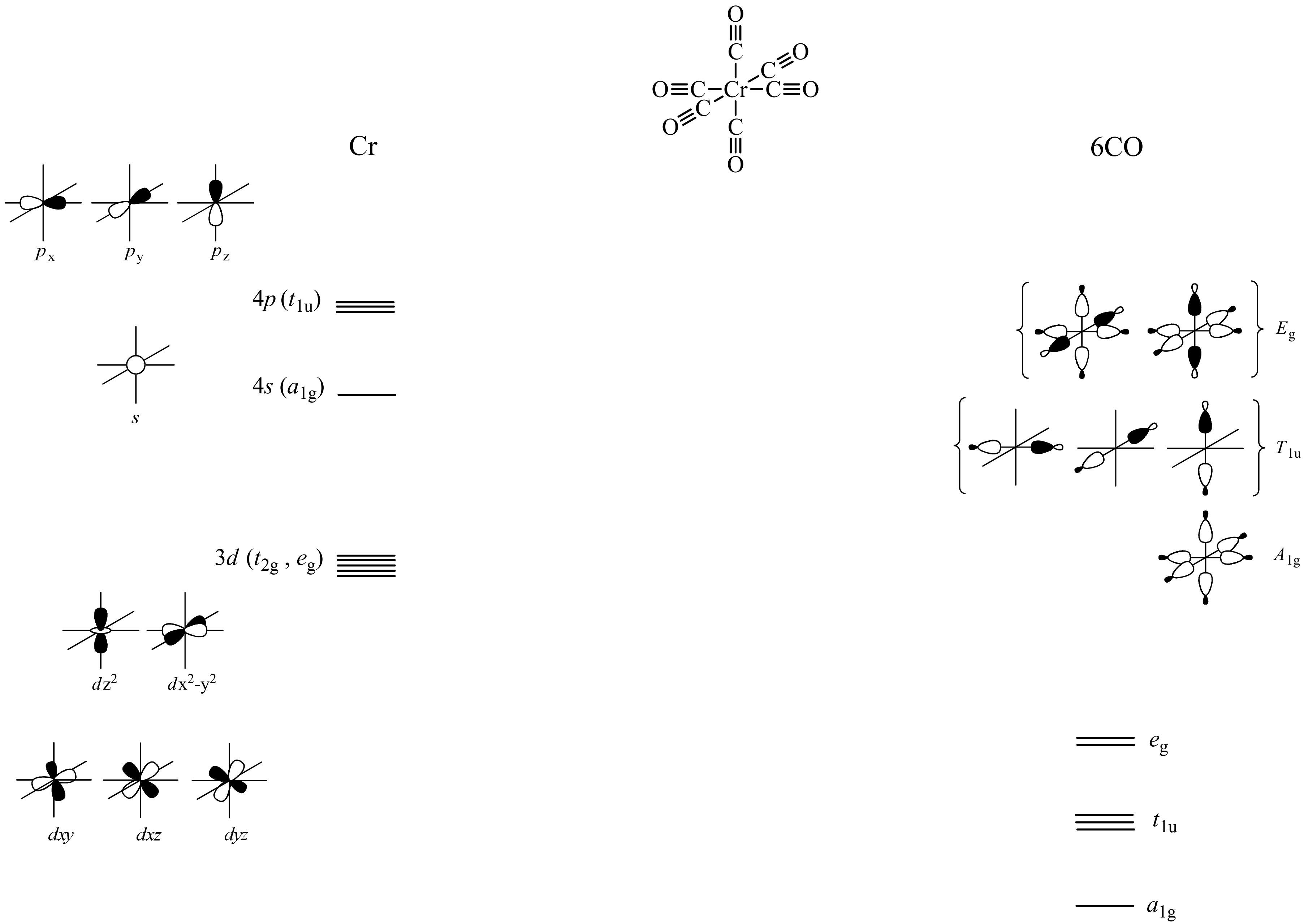
6. Central-atom AOs and pendant-atom SALCs with the same symmetry species will form both bonding and antibonding LCAO-MOs.



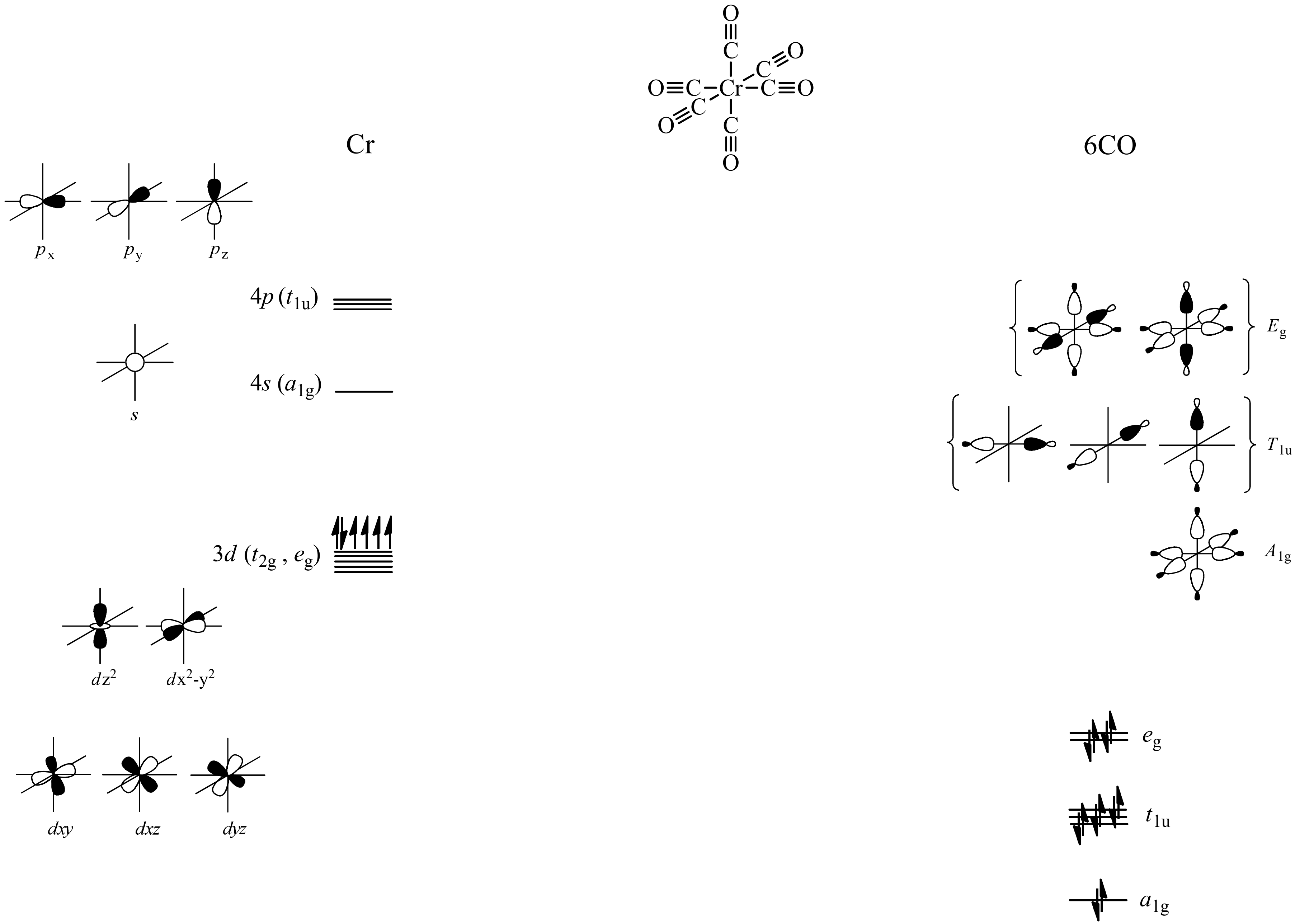
7. Central-atom AOs or pendant-atom SALCs with unique symmetry (no species match between AOs and SALCs) form nonbonding MOs.

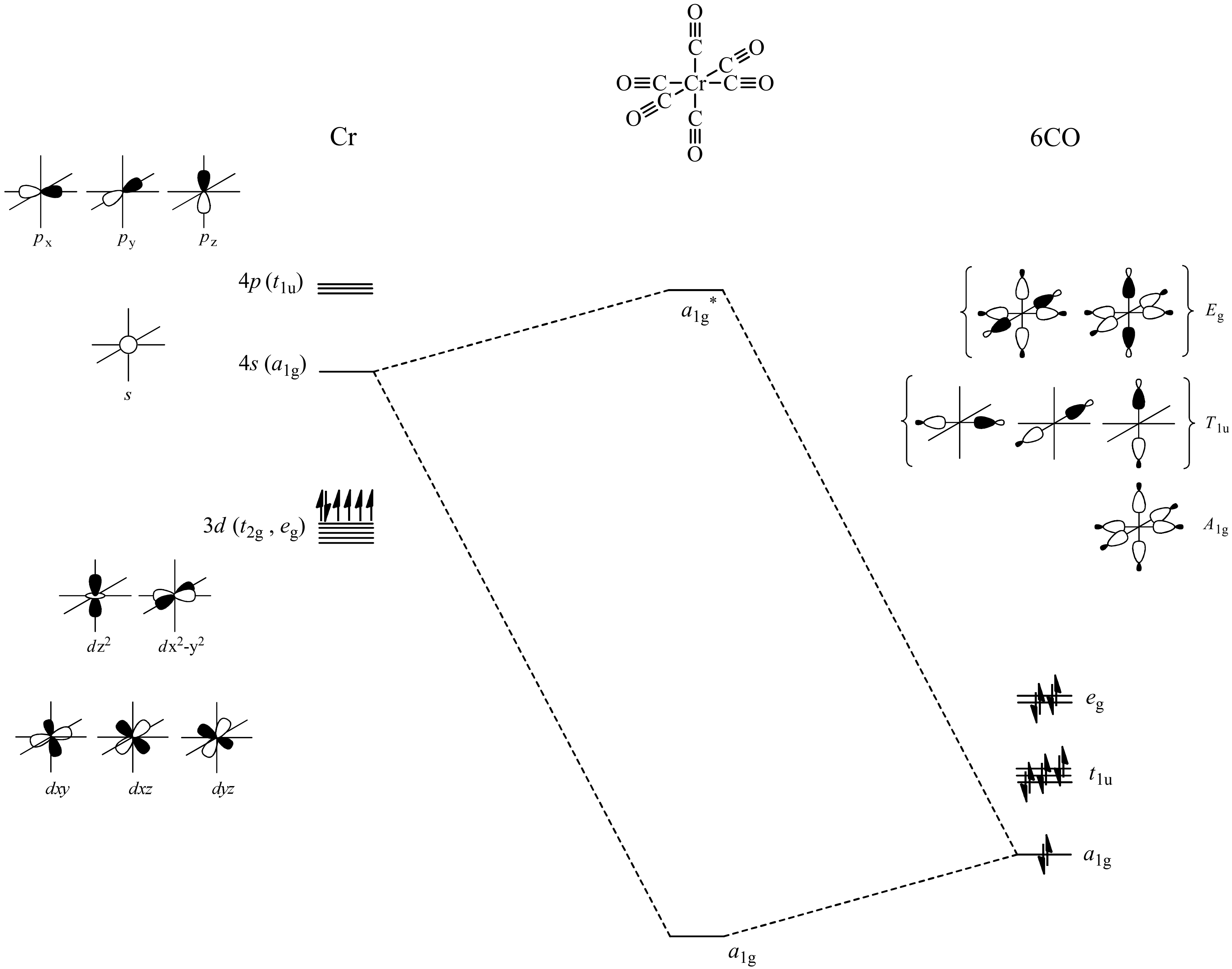



Cr
6CO
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
Eg
T1u
A1g

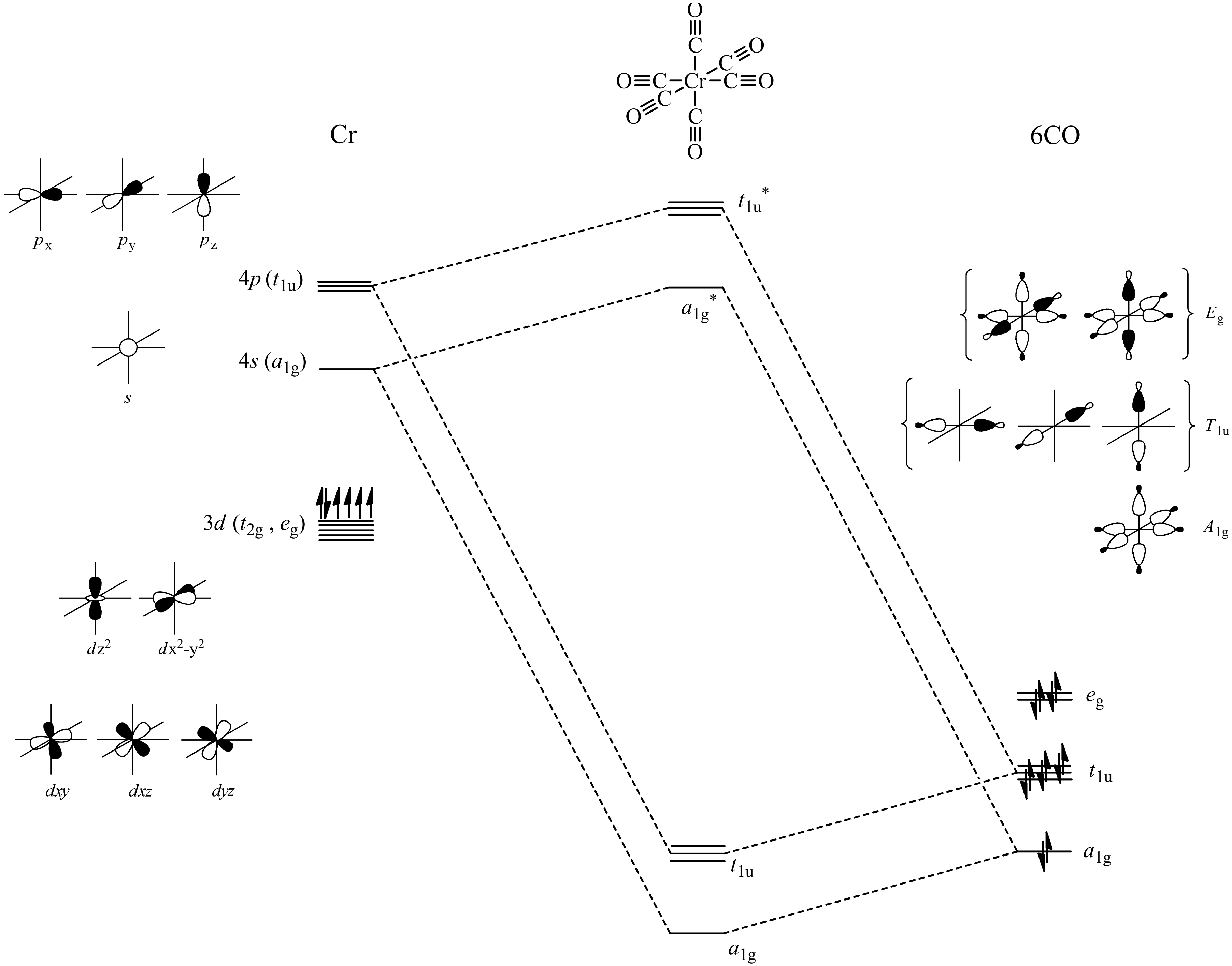


Cr
6CO
O≡C–Cr–C≡O
p_x p_y p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2 $dx^2\text{-}y^2$
dxy dxz dyz
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}

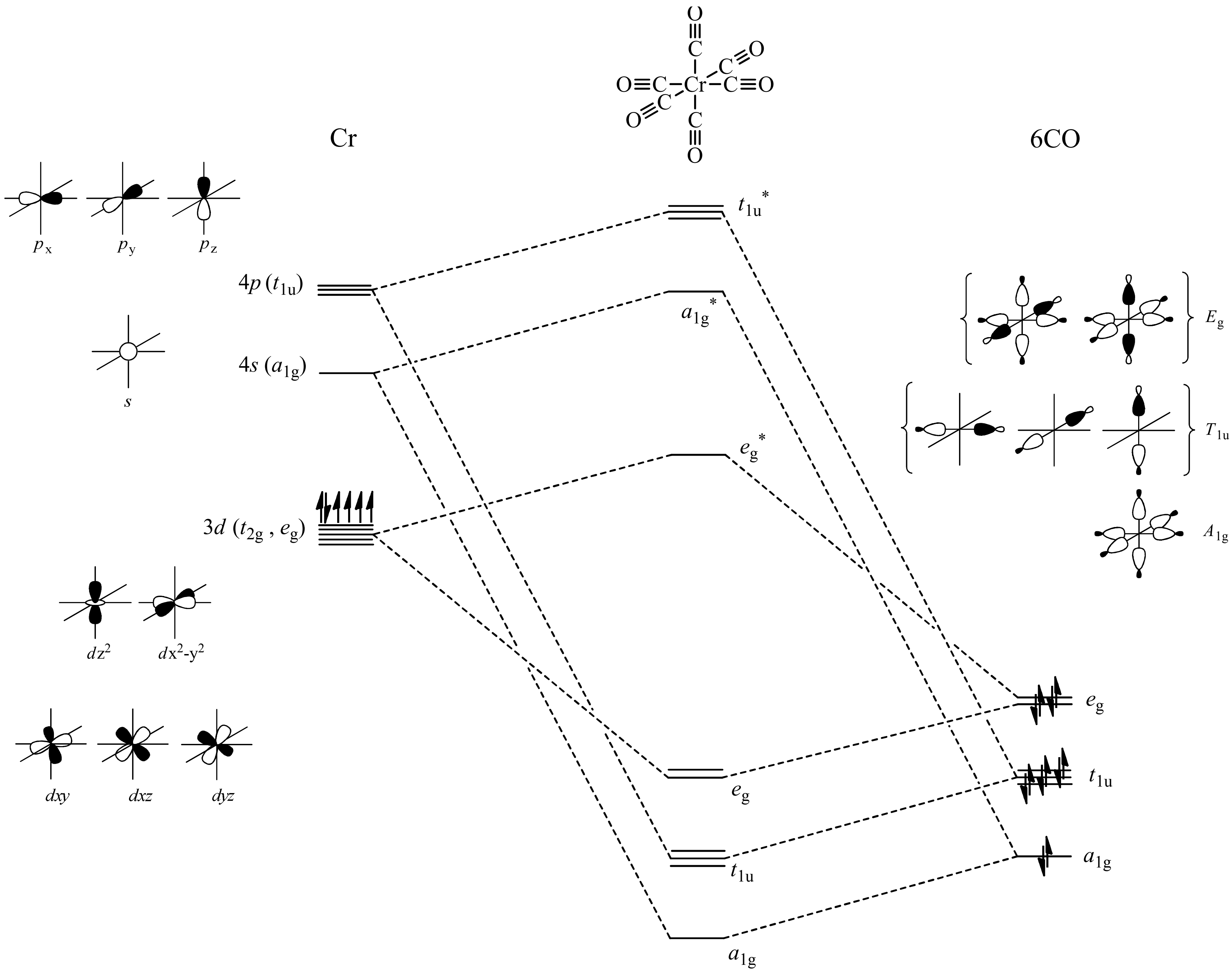

Cr
6CO
px
py
pz
4p (t1u)
s
4s (a1g)
3d (t2g , eg)
dz2
dx2-y2
dxy
dxz
dyz
Eg
T1u
A1g
eg
t1u
a1g



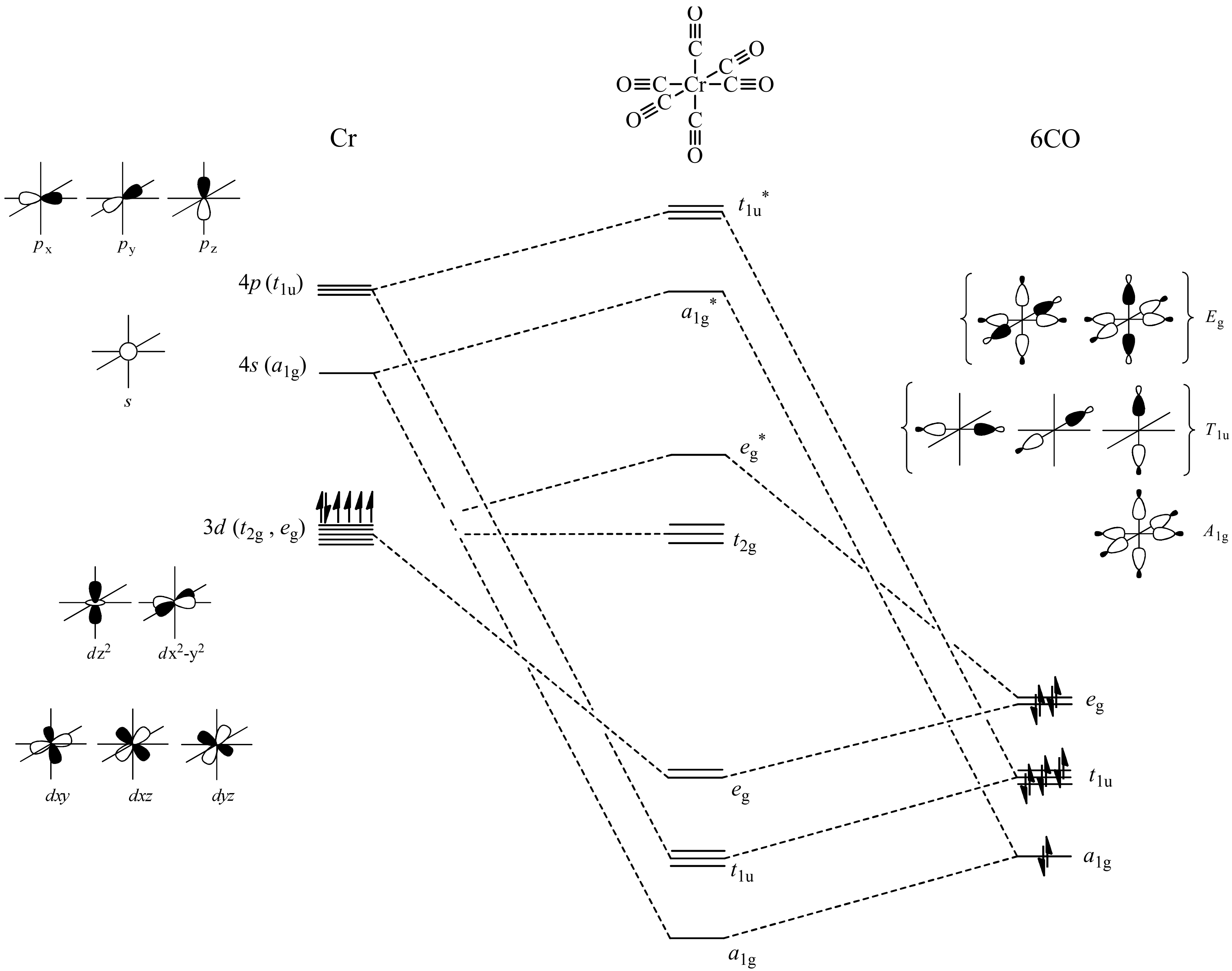
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2
dx^2-y^2
dxy
dxz
dyz
a_{1g}^*
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



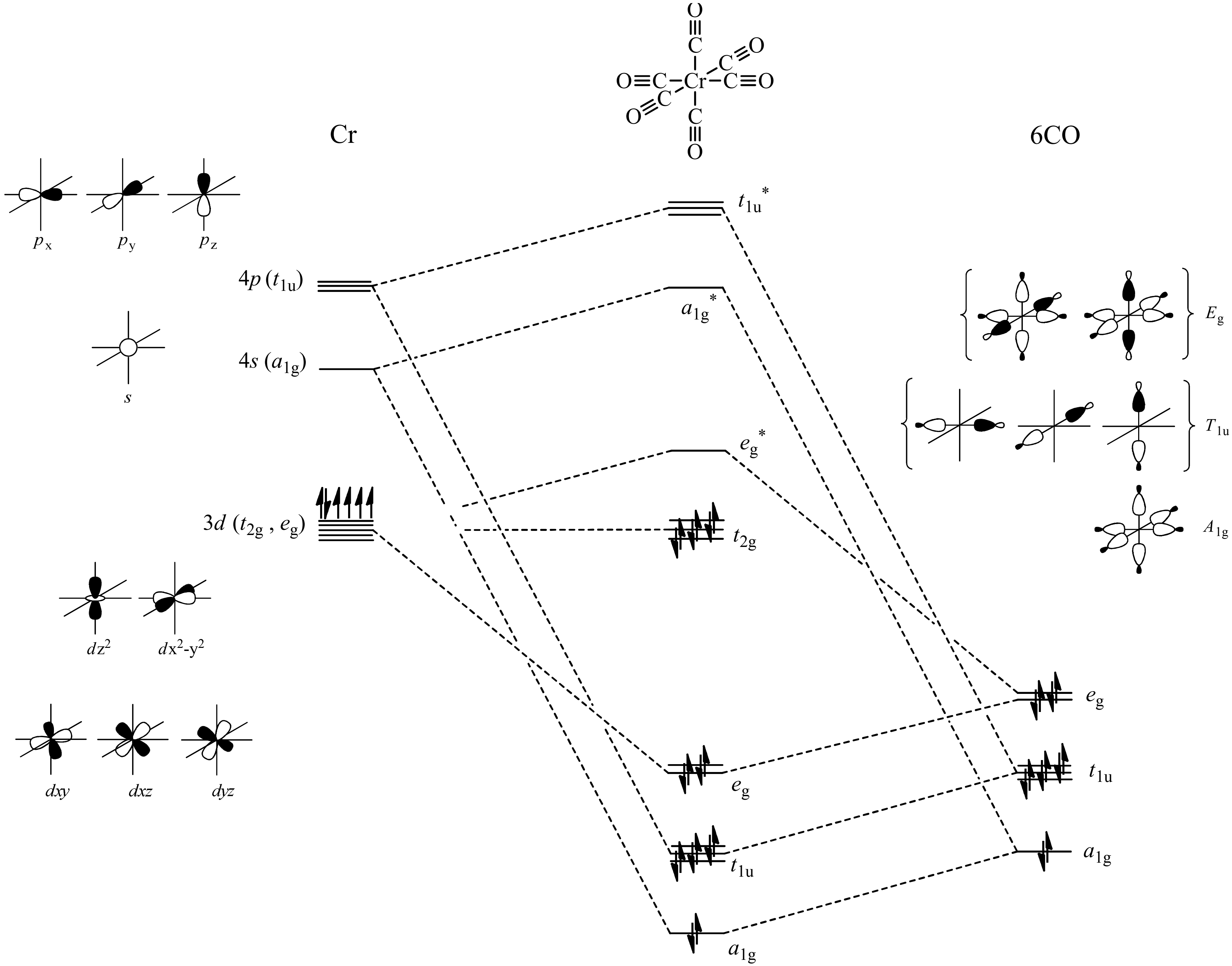
Cr
6CO
p_x
p_y
p_z
$4p$ (t_{1u})
s
$4s$ (a_{1g})
$3d$ (t_{2g} , e_g)
dz^2
dx^2-y^2
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



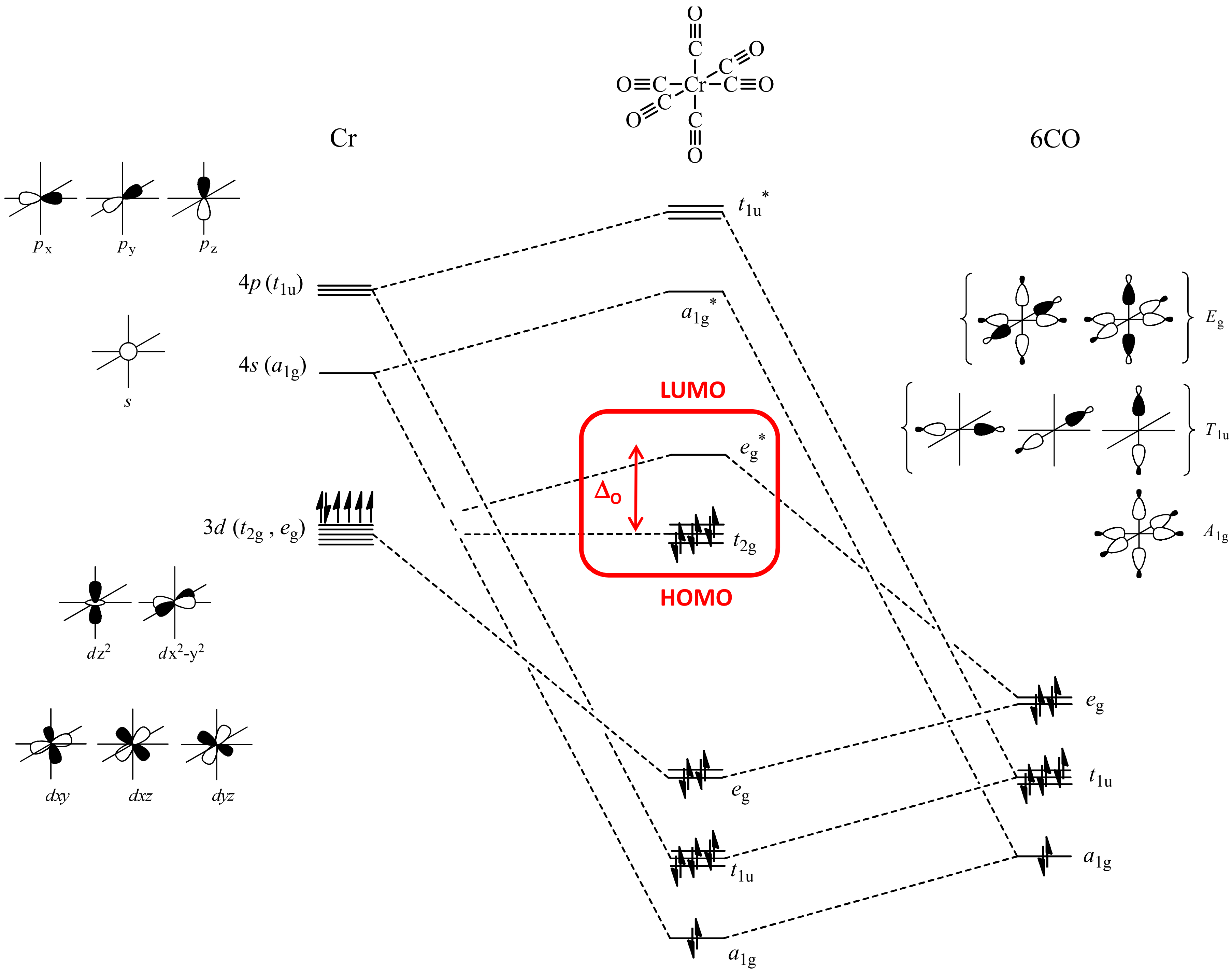
Cr
6CO
p_x
p_y
p_z
$4p$ (t_{1u})
s
$4s$ (a_{1g})
$3d$ (t_{2g} , e_g)
dz^2
dx^2-y^2
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
e_g^*
e_g
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



Cr
6CO
p_x p_y p_z
4p (t_{1u})
s
4s (a_{1g})
3d (t_{2g} , e_g)
dz^2 dx^2-y^2
dxy dxz dyz
t_{1u}^*
a_{1g}^*
e_g^*
t_{2g}
e_g
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



Cr
6CO
p_x
p_y
p_z
s
$4p\ (t_{1u})$
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
e_g^*
t_{2g}
e_g
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}

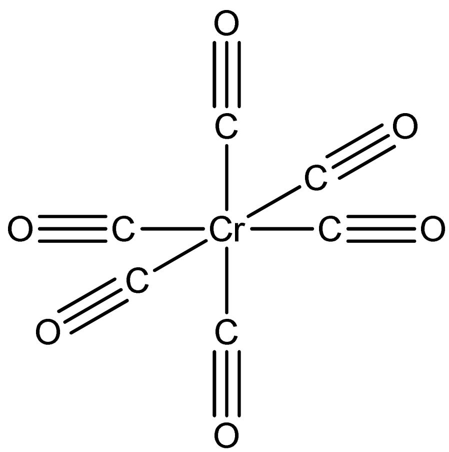


Cr
6CO
O≡C–Cr–C≡O
4p (t1u)
4s (a1g)
3d (t2g , eg)
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
t1u*
a1g*
LUMO
eg*
Δo
t2g
HOMO
eg
t1u
a1g
Eg
T1u
A1g

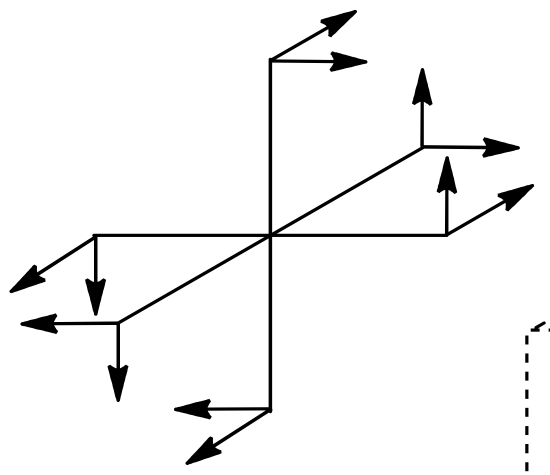
Construction of MO diagrams for Transition Metal Complexes

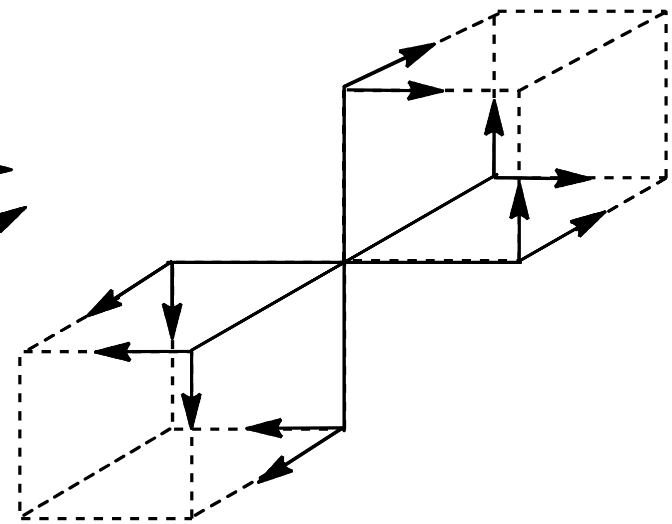
π bonding complexes

Example: Constructing a MO for Chromium Hexacarbonyl, $Cr(CO)_6$



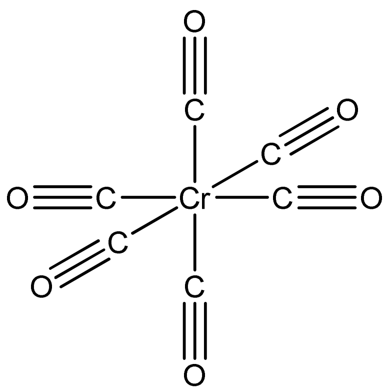
point group = O_h

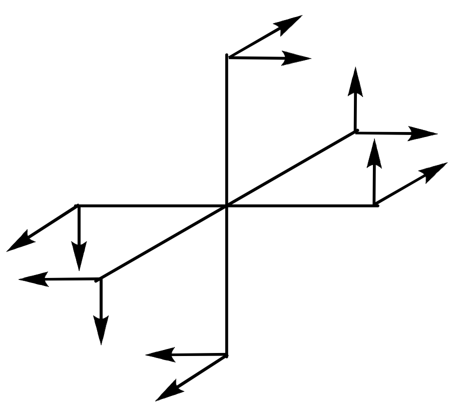




- Each vector shifted through space contributes 0 to the character for the class.
- Each non-shifted vector contributes 1 to the character for the class.
- ***Each vector shifted to the negative of itself (180°) contributes -1 to the character for the class.***

Example: Constructing a MO for Chromium Hexacarbonyl, $Cr(CO)_6$





point group = O_h

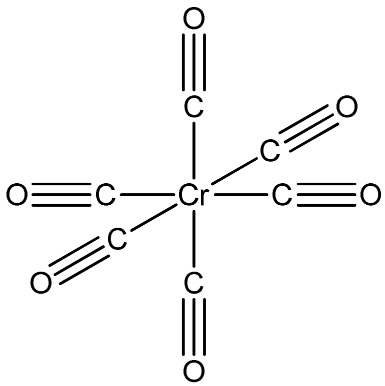
$h = 48$

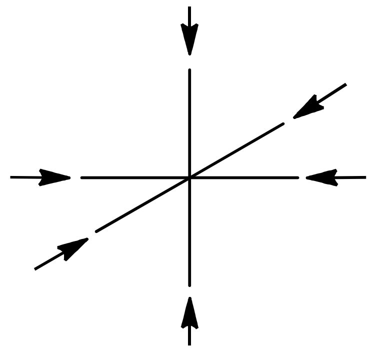
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Σ	Σ/h
Γ_π	12	0	0	0	-4	0	0	0	0	0		
A_{1g}	12	0	0	0	-12	0	0	0	0	0	0	0
A_{2g}	12	0	0	0	-12	0	0	0	0	0	0	0
E_g	24	0	0	0	-24	0	0	0	0	0	0	0
T_{1g}	36	0	0	0	12	0	0	0	0	0	48	1
T_{2g}	36	0	0	0	12	0	0	0	0	0	48	1
A_{1u}	12	0	0	0	-12	0	0	0	0	0	0	0
A_{2u}	12	0	0	0	-12	0	0	0	0	0	0	0
E_u	24	0	0	0	-24	0	0	0	0	0	0	0
T_{1u}	36	0	0	0	12	0	0	0	12	0	48	1
T_{2u}	36	0	0	0	12	0	0	0	12	0	48	1

$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

$$d_\Gamma = 3 + 3 + 3 + 3 = 12$$

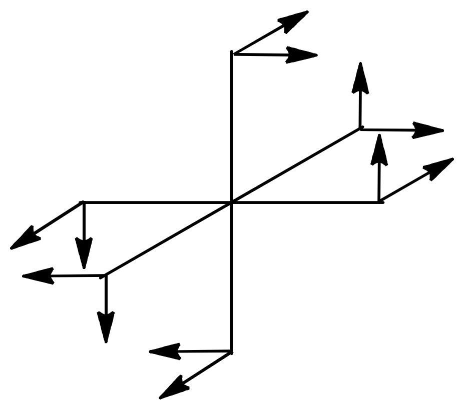
Example: Constructing a MO for Chromium Hexacarbonyl, $Cr(CO)_6$





point group = O_h

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$



point group = O_h

$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

Example: Constructing a MO for Chromium Hexacarbonyl, $Cr(CO)_6$

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$

Cr σ-bonding AOs

A_{1g} : $4s$

T_{1u} : $(4p_x, 4p_y, 4p_z)$

E_g : $(3dx^2\text{-}y^2, 3dz^2)$

Cr non-bonding AOs

T_{2g} : (3*d*xy, 3*d*xz, 3*d*yz)

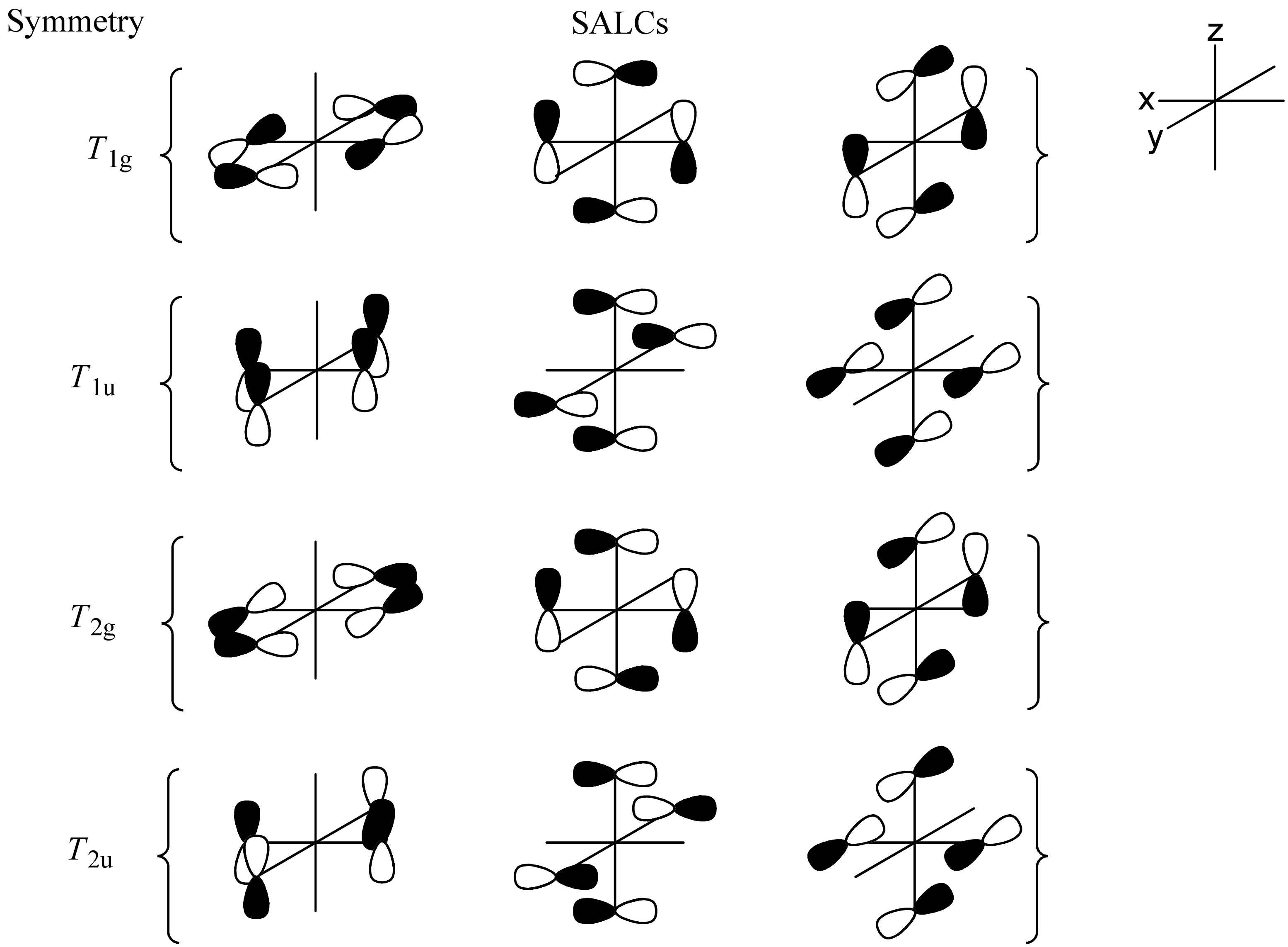
$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

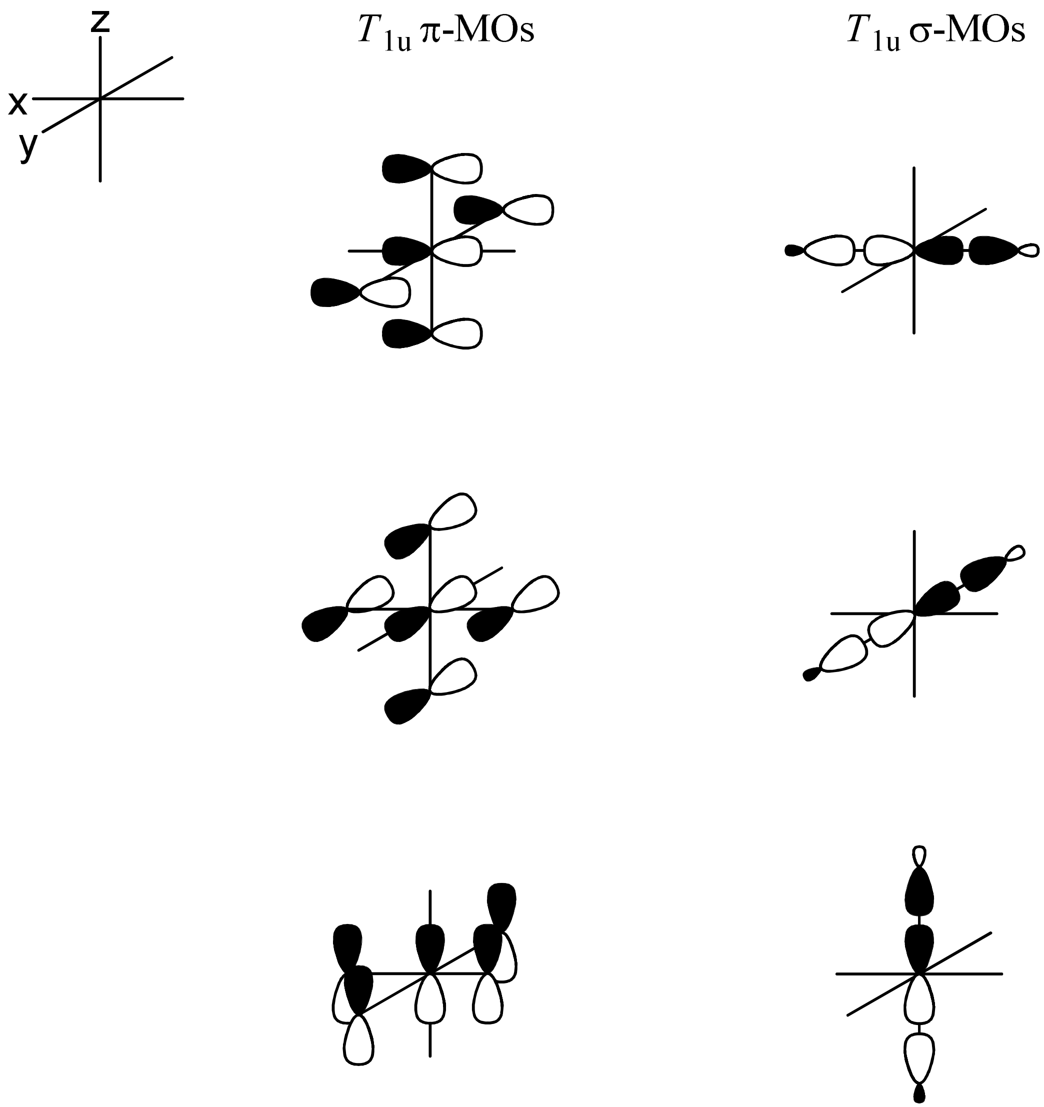
Cr π-bonding AOs

T_{2g} : (3*d*xy, 3*d*xz, 3*d*yz)

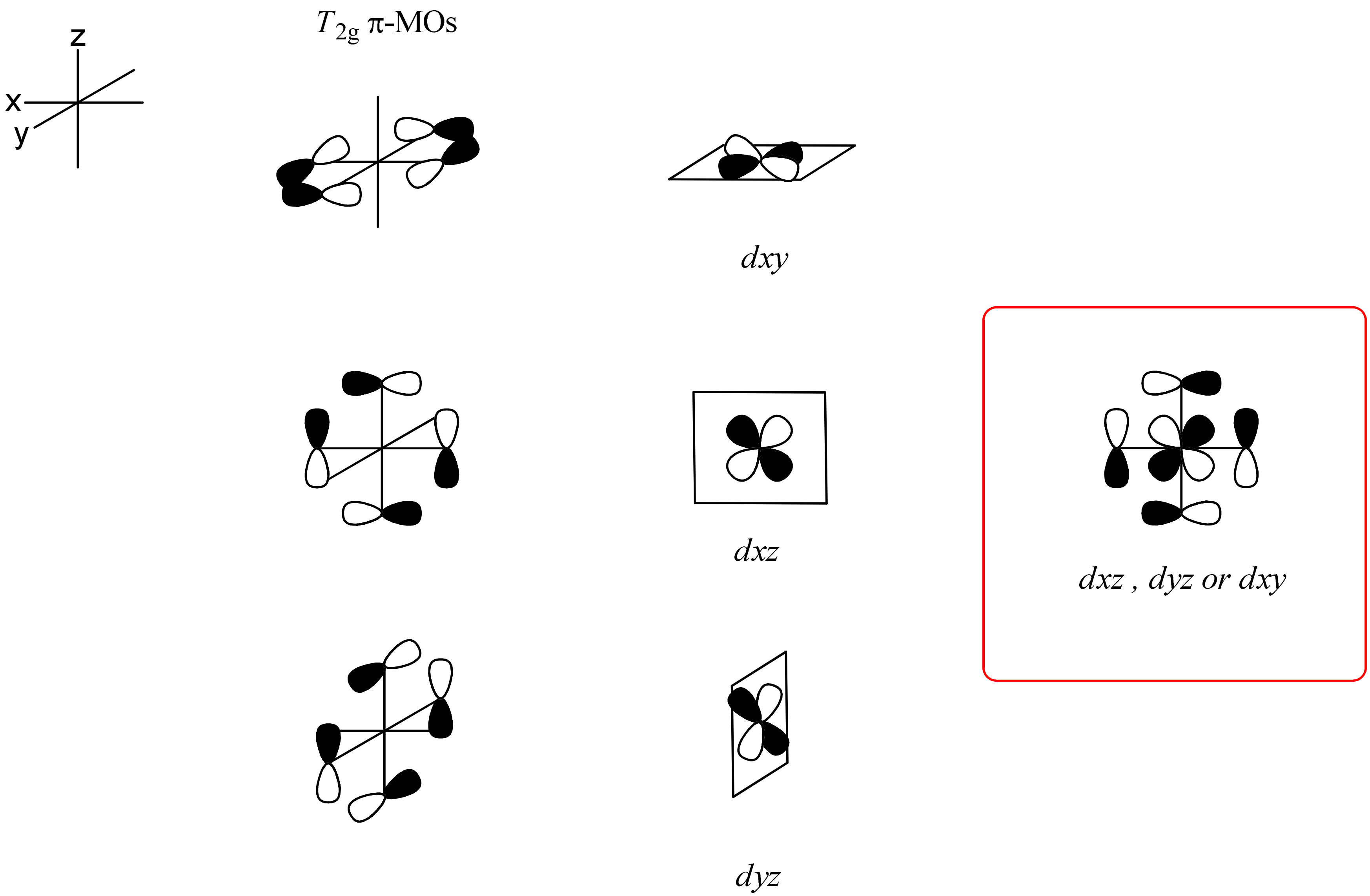
T_{1u} : $(4p_x, 4p_y, 4p_z)$

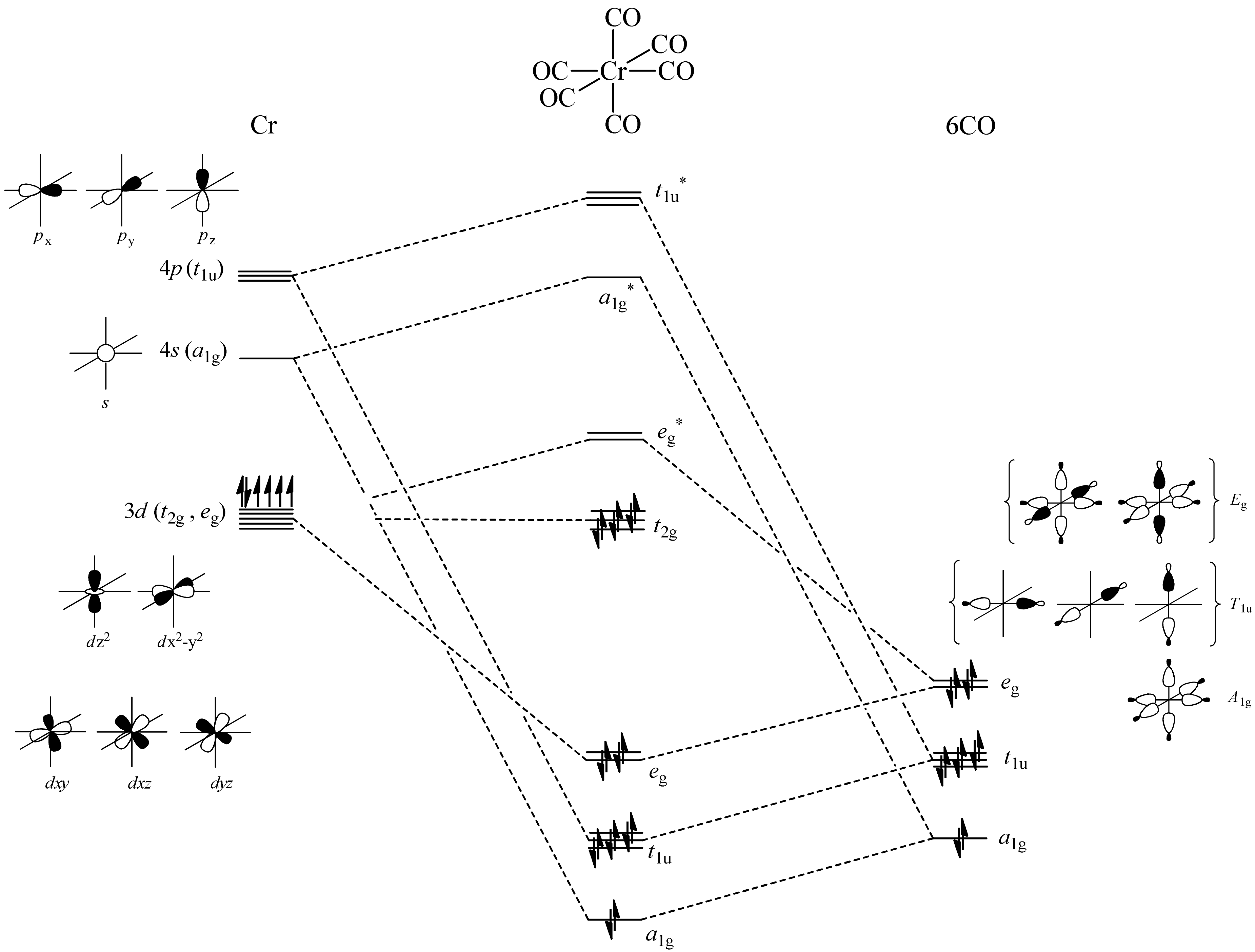
- T_{2g} previously considered non-bonding in σ-bonding scheme
- T_{1u} combines with T_{1u} SALC in in σ-bonding scheme
- T_{1g} , T_{2u} π-SALCs are non-bonding


Symmetry
SALCs
z
x
y
T_{1g}
T_{1u}
T_{2g}
T_{2u}

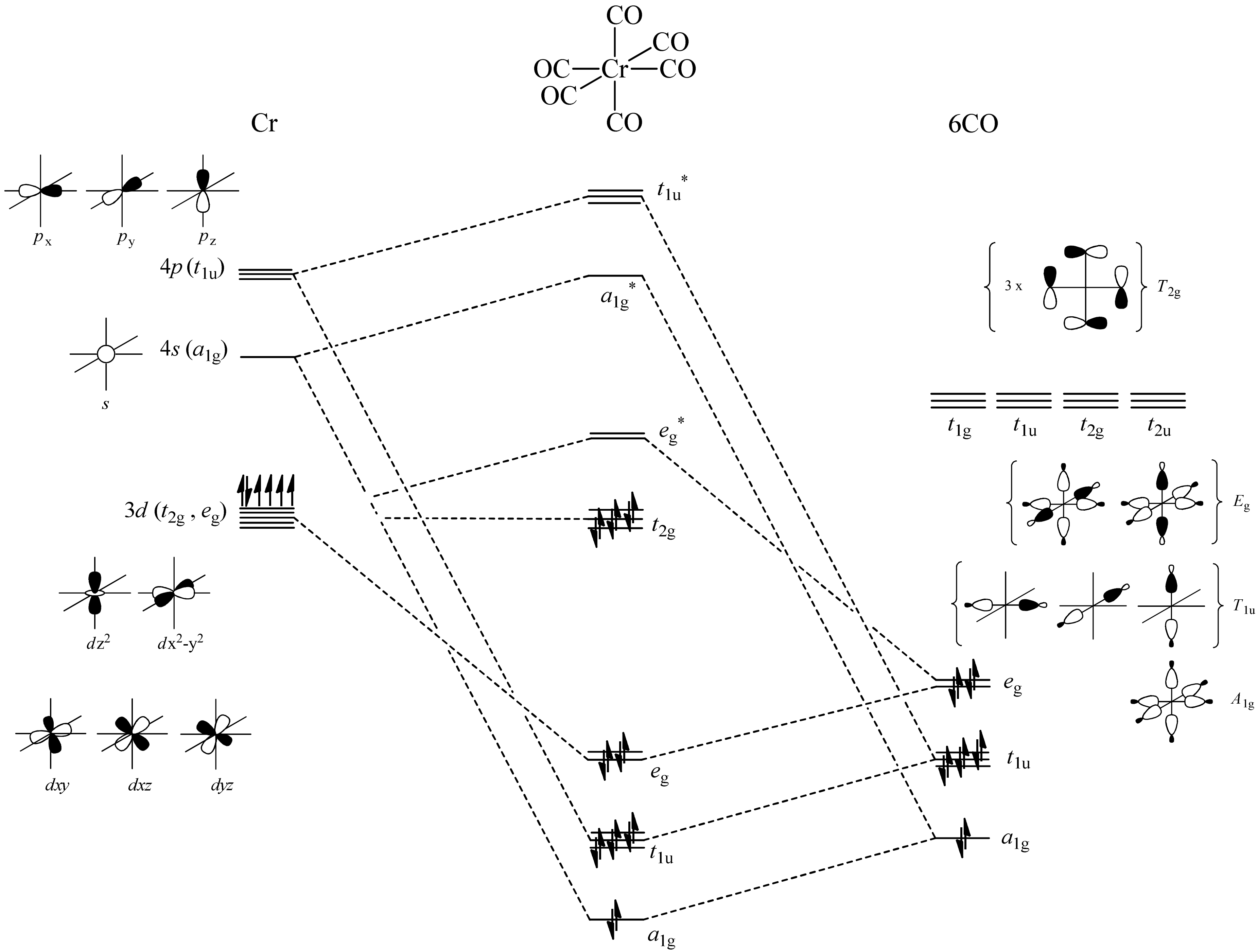


- T_{1u} AOs overlap more effectively with T_{1u} σ-SALC thus the π-bonding interaction is considered negligible or at most only weakly-bonding.

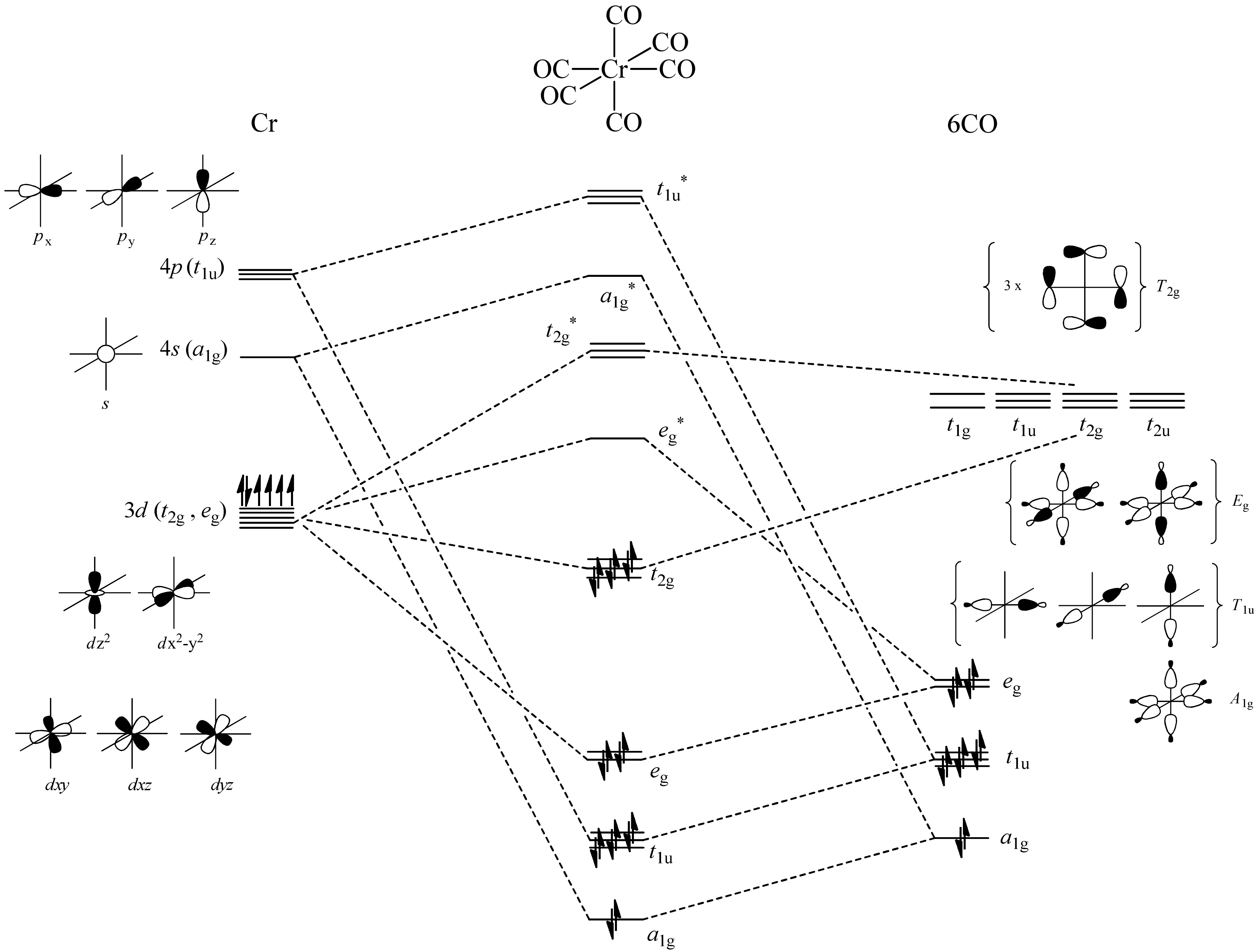

z
x
y
T_{2g} π-MOs
dxy
dxz
dxz , dyz or dxy
dyz



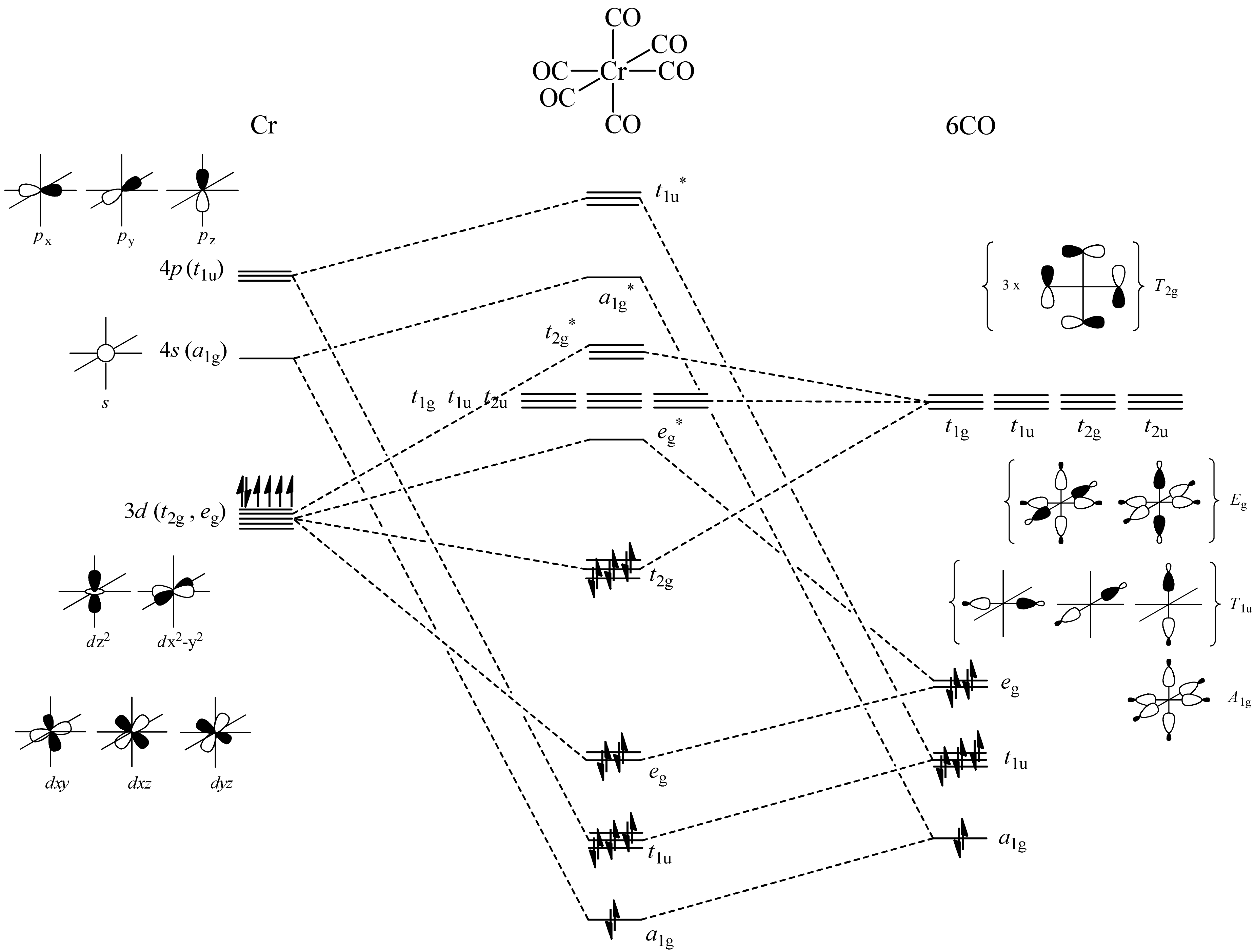
CO
CO
OC
Cr
CO
OC
CO
Cr
6CO
t1u*
4p (t1u)
a1g*
4s (a1g)
s
px
py
pz
e_g*
3d (t2g , eg)
t2g
dz2
dx2-y2
dxy
dxz
dyz
eg
t1u
a1g
Eg
T1u
A1g
eg
t1u
a1g

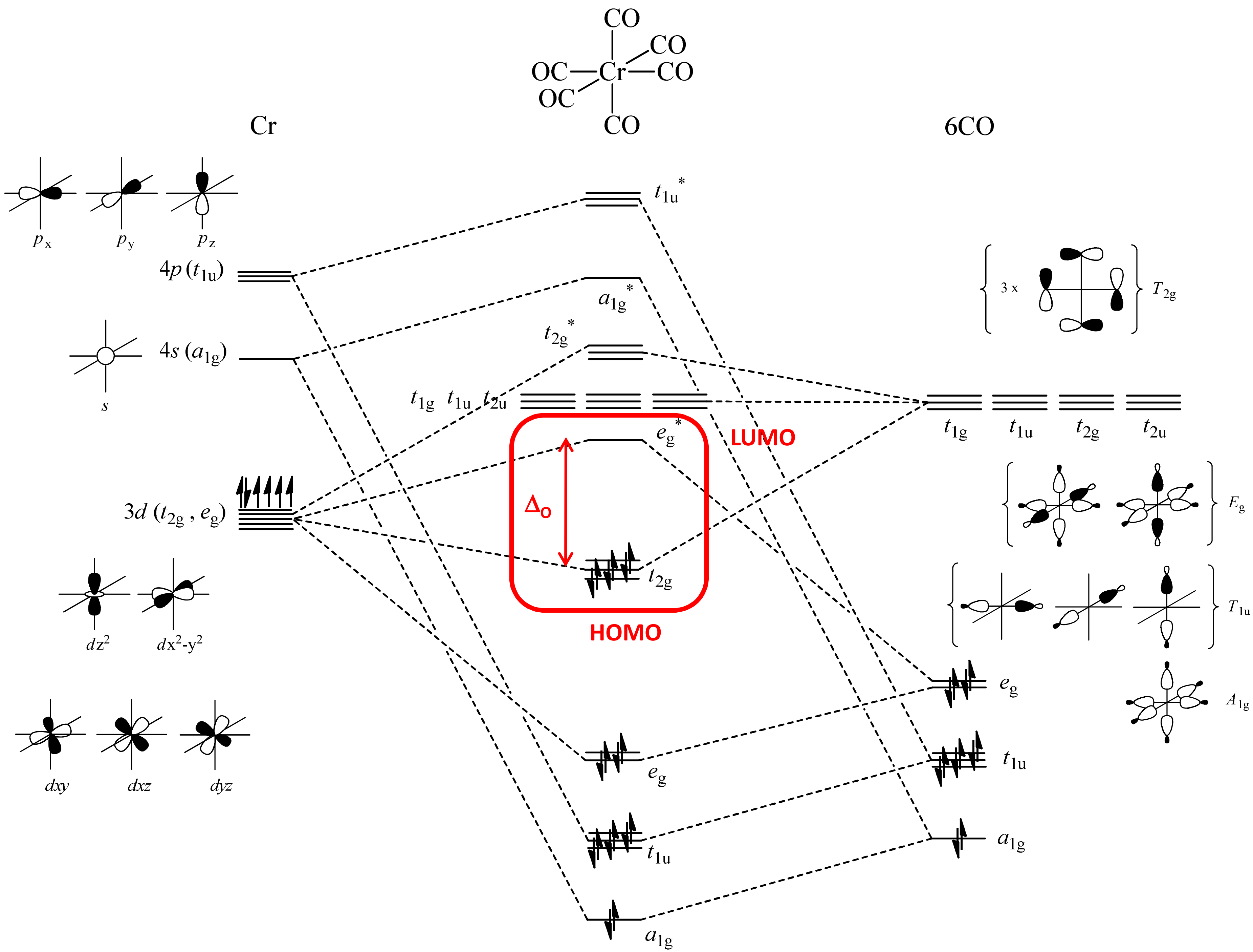


CO
CO
OC—Cr—CO
OC
CO
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
$4s\ (a_{1g})$
s
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
e_g^*
t_{2g}
e_g
t_{1u}
a_{1g}
3 x
T_{2g}
t_{1g}
t_{1u}
t_{2g}
t_{2u}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}

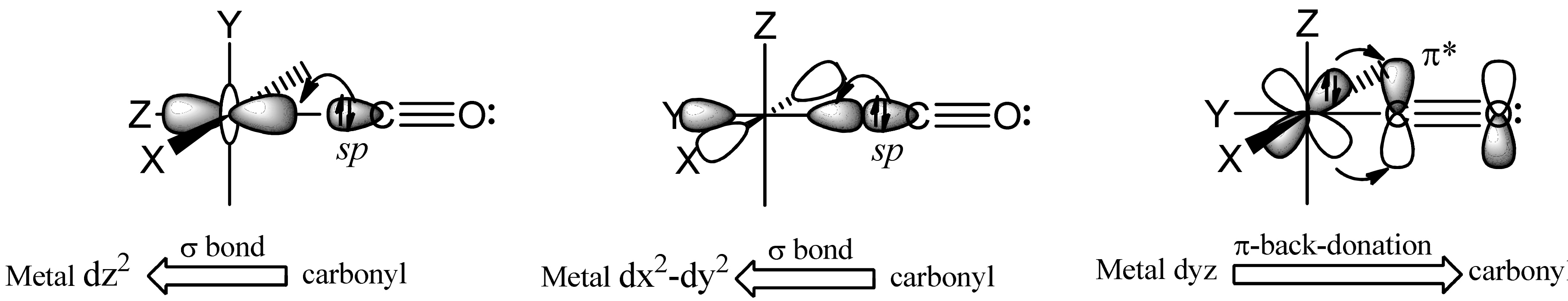


CO
CO
OC
Cr
CO
OC
CO
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
$4s\ (a_{1g})$
s
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
t_{2g}^*
e_g^*
t_{2g}
e_g
t_{1u}
a_{1g}
3 x
T_{2g}
t_{1g}
t_{1u}
t_{2g}
t_{2u}
E_g
T_{1u}
e_g
A_{1g}
t_{1u}
a_{1g}


CO
CO
OC
Cr
CO
OC
CO
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
t_{1u}^*
a_{1g}^*
3 x
T_{2g}
$4s\ (a_{1g})$
s
t_{2g}^*
t_{1g} t_{1u} t_{2u}
t_{1g} t_{1u} t_{2g} t_{2u}
e_g^*
E_g
$3d\ (t_{2g}, e_g)$
t_{2g}
dz^2
$dx^2\text{-}y^2$
T_{1u}
e_g
A_{1g}
dxy
dxz
dyz
e_g
t_{1u}
t_{1u}
a_{1g}
a_{1g}


CO
CO
OC
Cr
CO
OC
CO
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
$4s\ (a_{1g})$
s
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
t_{2g}^*
t_{1g} t_{1u} t_{2u}
e_g^*
LUMO
Δ_o
t_{2g}
HOMO
e_g
t_{1u}
a_{1g}
3 x
T_{2g}
t_{1g} t_{1u} t_{2g} t_{2u}
E_g
T_{1u}
e_g
A_{1g}
t_{1u}
a_{1g}

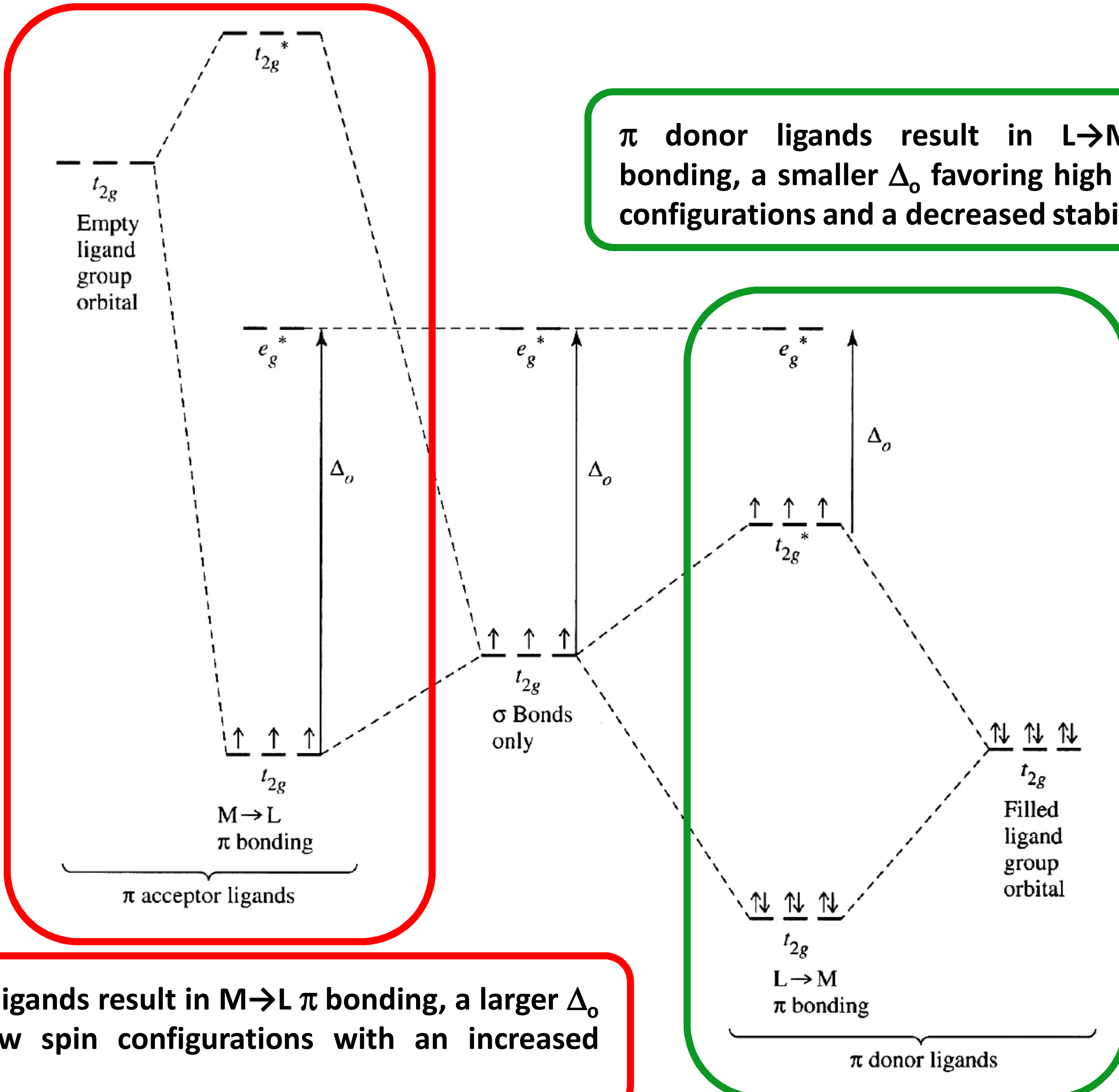
Dewar-Chatt-Duncanson model



	ν(CO) cm^{-1}
$[Ti(CO)_6]^{2-}$	1748
$[V(CO)_6]^{-}$	1859
$Cr(CO)_6$	2000
$[Mn(CO)_6]^{+}$	2100
$[Fe(CO)_6]^{2+}$	2204

Summary of π-bonding in O_h complexes

π donor ligands result in L→M π bonding, a smaller Δ_o favoring high spin configurations and a decreased stability.



π acceptor ligands result in M→L π bonding, a larger Δ_o favoring low spin configurations with an increased stability.