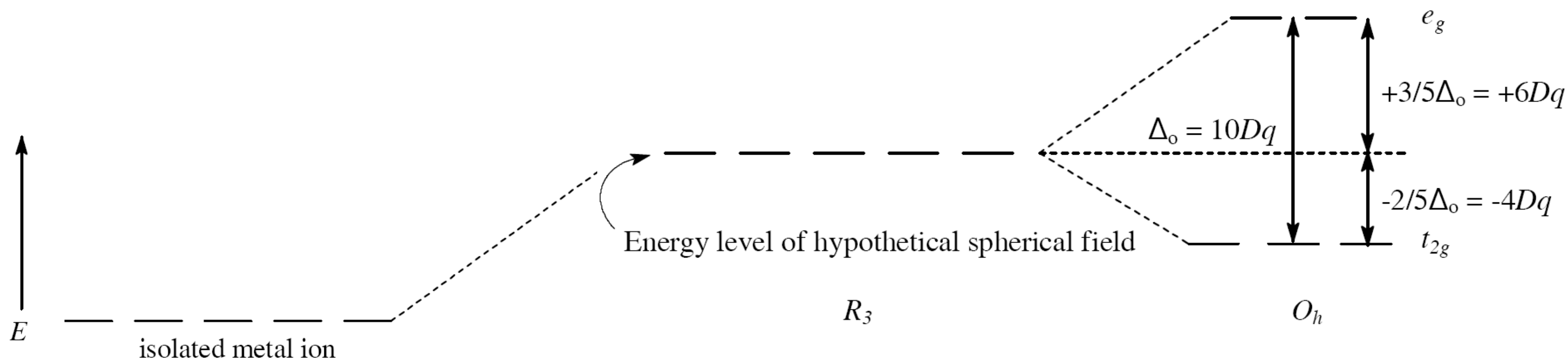
Bonding in transition metal complexes

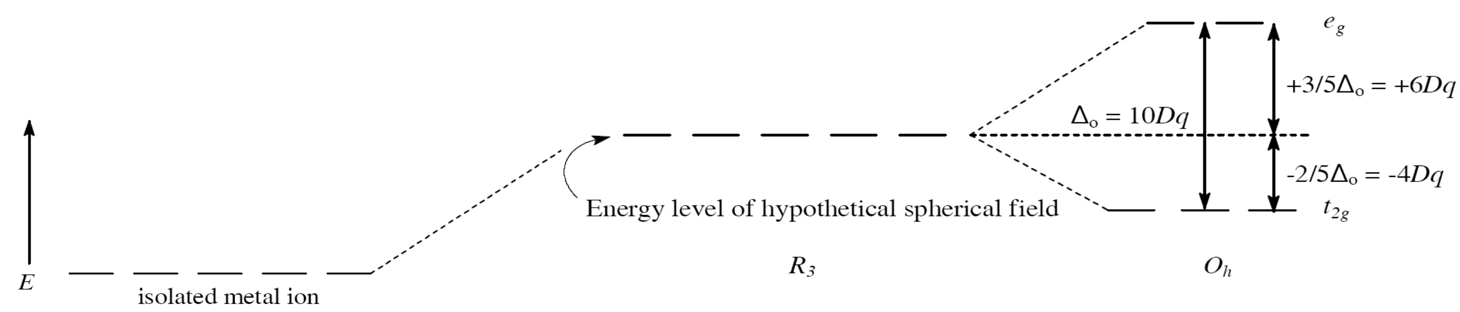
- **Crystal Field Theory (CFT)**
  - ➢ Assumes electrostatic (ionic) interactions between ligands and metal ions
  - ➢ Useful for understanding magnetism and electronic spectra
- **Valence Bond (VB) Theory**
  - ➢ Assumes covalent M–L bonds formed by ligand electron donation to empty metal hybrid orbitals.
  - ➢ Useful for rationalizing magnetic properties, but cannot account for electronic spectra.
  - ➢ Offers little that cannot be covered better by other theories.
- **Molecular Orbital (MO) Theory**
  - ➢ Approach using M–L general MOs
  - ➢ Excellent quantitative agreement, but less useful in routine qualitative discussions
- **Ligand Field Theory (LFT)**
  - ➢ Modified CFT
  - ➢ Makes empirical corrections to account for effects of M–L orbital overlap, improving quantitative agreement with observed spectra

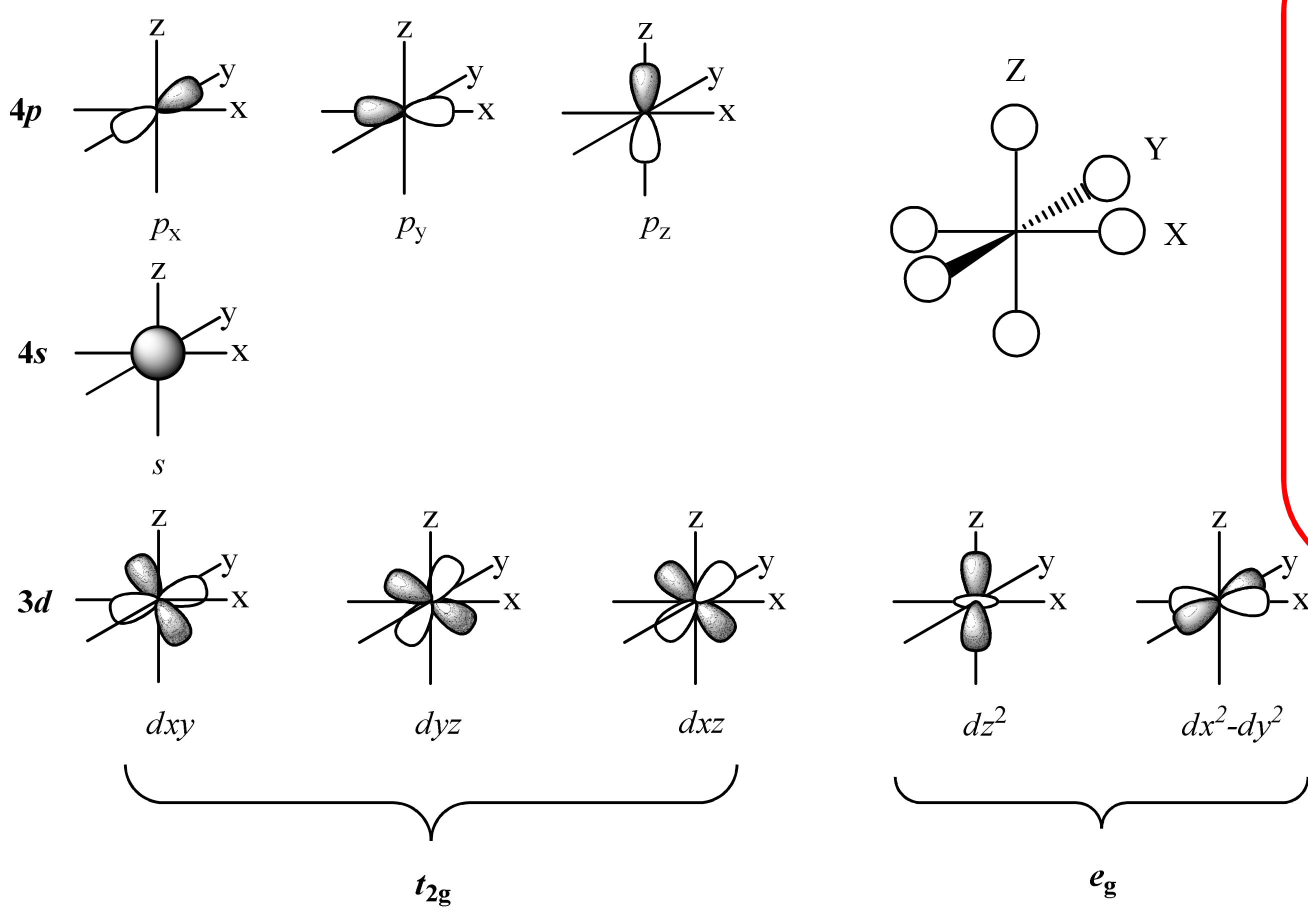
CFT & *d*-subshell Splitting in an O_h Field

- In the octahedral (O_h) environment the fivefold degeneracy among the *d* orbitals is lifted.
- If the ligand field is of O_h symmetry the *d* subshell will separate into a set of three degenerate orbitals (t_{2g} = *d*xy, *d*yz, *d*xz) and a set of two degenerate orbitals (e_g = dx^2–y^2, dz^2).

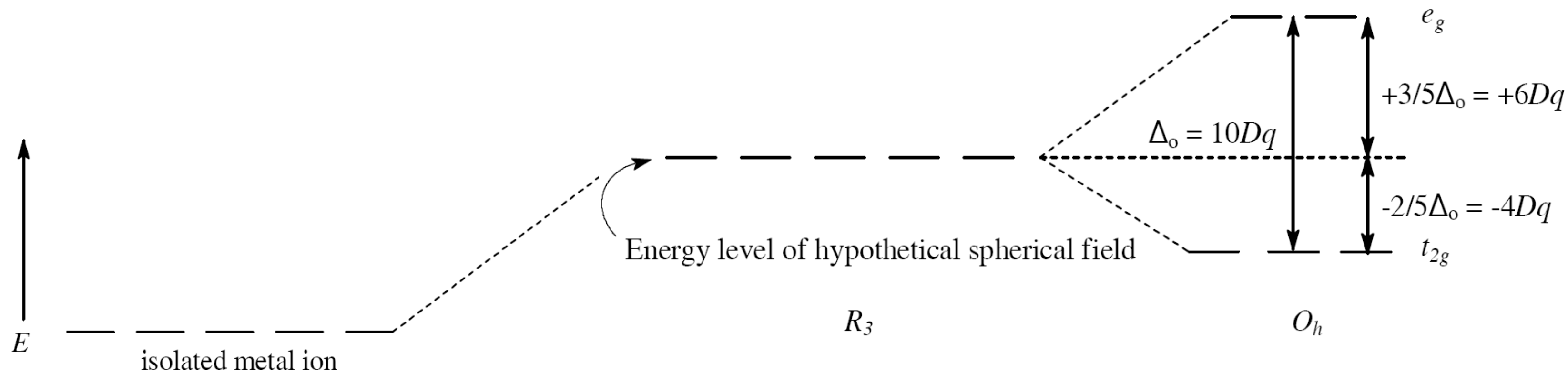


- Relative to the energy of the hypothetical spherical field, the e_g set will rise in energy and the t_{2g} set will fall in energy, creating an energy separation of Δ_o or 10 *Dq* between the two sets of *d* orbitals.





- The t_{2g} orbitals point between ligands.
- The e_g orbitals point directly at the ligands.
- Thus, the t_{2g} set is stabilized and the e_g set is destabilized *(relative to the energy of a hypothetical spherical electric field)*.



- The energy increase of the e_g orbitals and the energy decrease of the t_{2g} orbitals must be balanced relative to the energy of the hypothetical spherical field (*aka* the barycenter).
- The energy of each of the two orbitals of the e_g set rises by +3/5 Δ_o (+6 *Dq*) while the energy of each of the three t_{2g} orbitals falls by -2/5 Δ_o (-4 *Dq*).
- This results in no net energy change for the system:

$$\Delta E = E(e_g) + E(t_{2g})$$

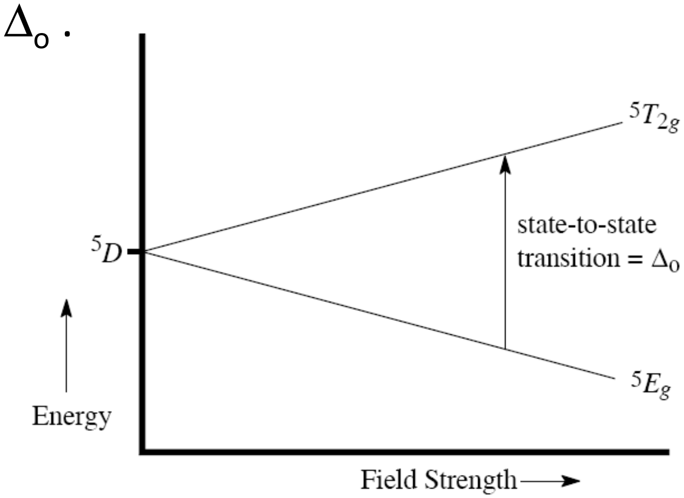
$$= (2)(+3/5\ \Delta_o) + (3)(-2/5\ \Delta_o)$$

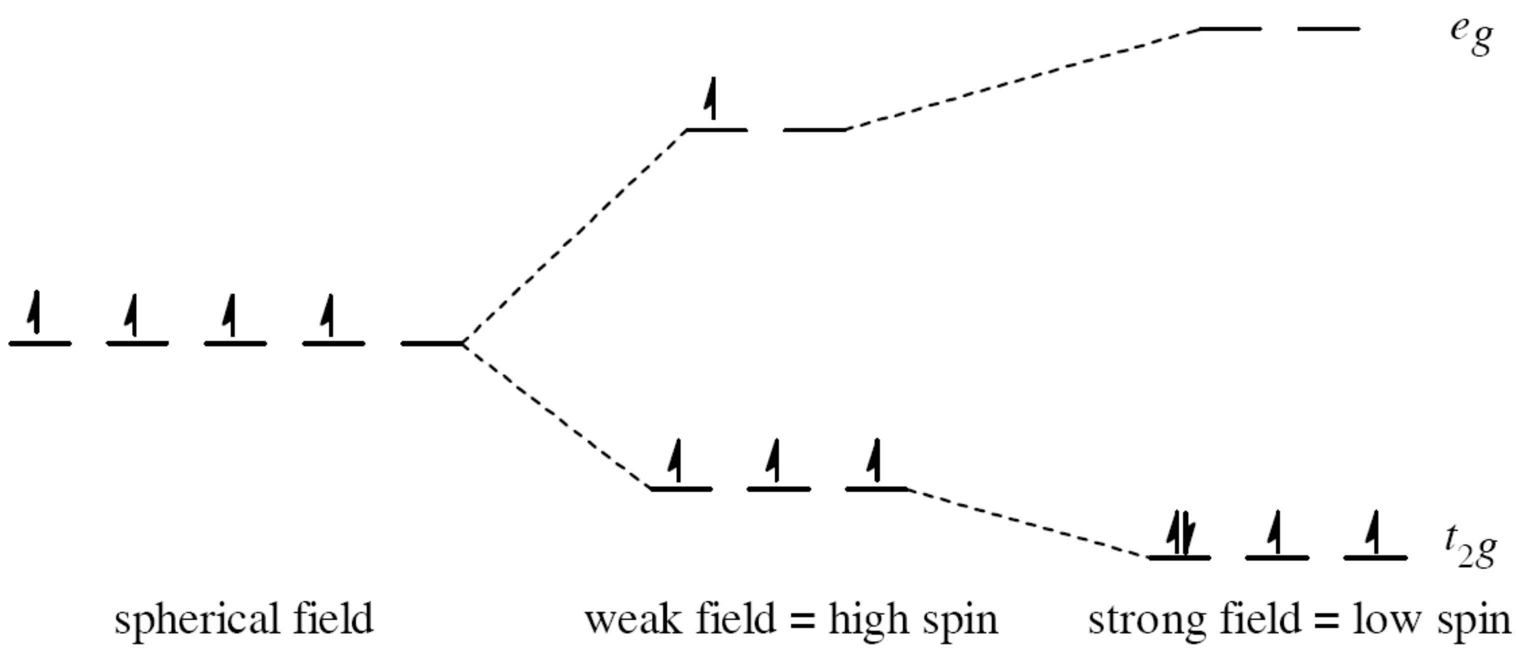
$$= (2)(+6Dq) + (3)(-4Dq) = 0$$

(The magnitude of Δ_o depends upon both the metal ion and the attaching ligands)

High-Spin and Low-Spin Configurations

- In an octahedral complex, electrons fill the t_{2g} and e_g orbitals in an aufbau manner, but for configurations d^4 – d^7 there are two possible filling schemes depending on the magnitude of Δ_o relative to the *mean electron pairing energy*, P.
- A *high-spin configuration* avoids pairing by spreading the electrons across both the t_{2g} and e_g levels.
- A *low-spin configuration* avoids occupying the higher energy e_g level by pairing electrons in the t_{2g} level.
- For a given metal ion, the pairing energy is relatively constant, so the spin state depends upon the magnitude of the field strength, Δ_o .
- Low field strength results in a high-spin state.
- High field strength results in a low-spin state.
- For example, a d^4 configuration, the high-spin state is $t_{2g}{}^3e_g{}^1$, and the low-spin state is $t_{2g}{}^4e_g{}^0$.





- Low field strength results in a high-spin state.
- High field strength results in a low-spin state.
- For a d^4 configuration, the high-spin state is $t_{2g}{}^3e_g{}^1$, and the low-spin state is $t_{2g}{}^4e_g{}^0$.

MO used for most sophisticated and quantitative interpretations

LFT used for semi-quantitative interpretations

CFT used for everyday qualitative interpretations

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:

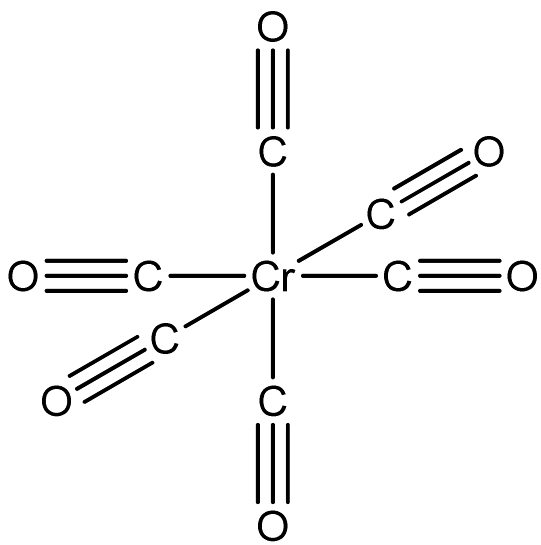
$$\Psi_{MO} = a\,\Psi(\text{Metal AO}) \pm b\,\Psi(\text{SALC } n\text{X})$$

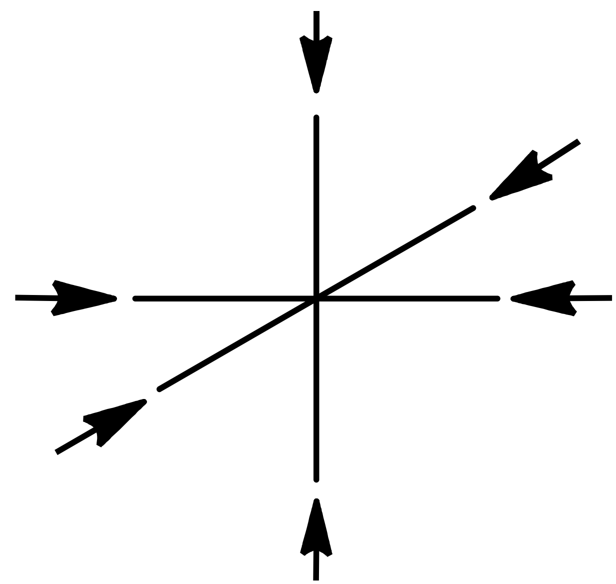
(SALC = Symmetry Adapted Linear Combination)

- 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.**

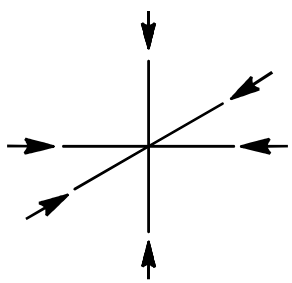




point group = O_h

2. Generate a <u>reducible representation</u> 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										

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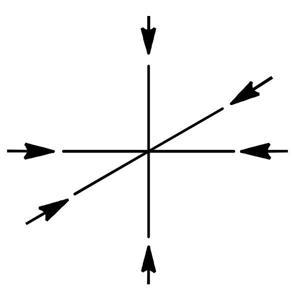


point group = O_h

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

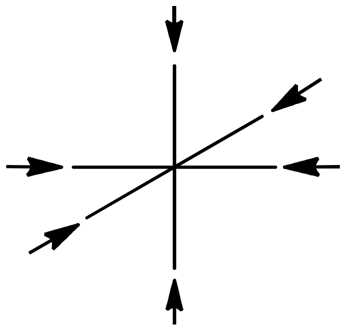
c : class of operations

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.



Character Table for O_h

point group = O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h = 48$	
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 $\chi(C_n) = 1$.
B	:	non-degenerate;	anti-symmetric to C_n where $\chi(C_n) = -1$.
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:

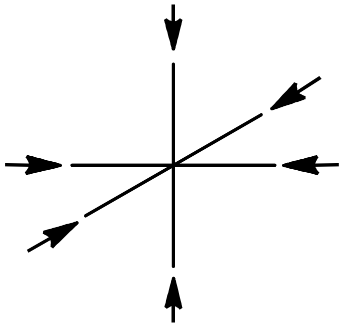
subscript *1* : symmetric with respect to C_m ($m < n$) or σ_v ;
$\chi(C_m) > 0$ or $\chi(\sigma_v) > 0$.

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 $D_{\infty h}$):

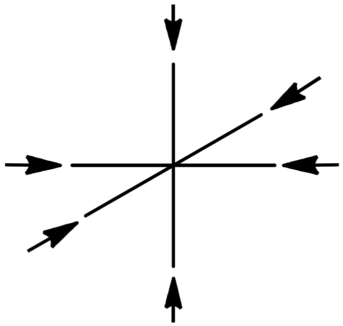
subscript + : symmetric with respect to ∞C_2 or $\infty \sigma_v$;
$\chi(\infty C_2) = 1$ or $\chi(\infty \sigma_h) = 1$.

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

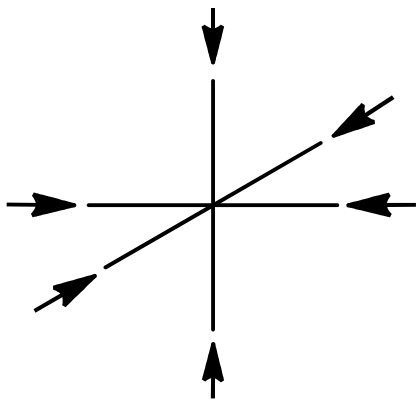
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Σ	$n_i = \Sigma/h$
Γ_σ	6	0	0	2	2	0	0	0	4	2		(h = 48)
A_{1g}												
A_{2g}												
E_g												
T_{1g}												
T_{2g}												
A_{1u}												
A_{2u}												
E_u												
T_{1u}												
T_{2u}												



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.

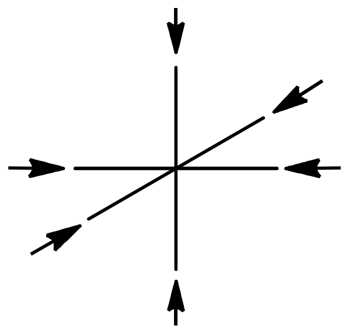


point group = O_h

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

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

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

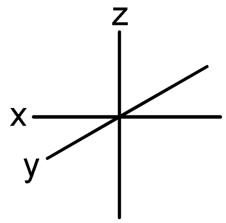
A_{1g} : 4*s*

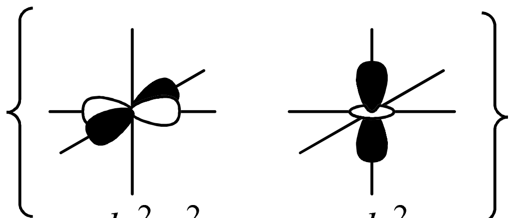
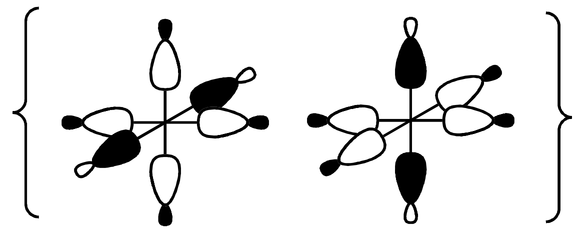
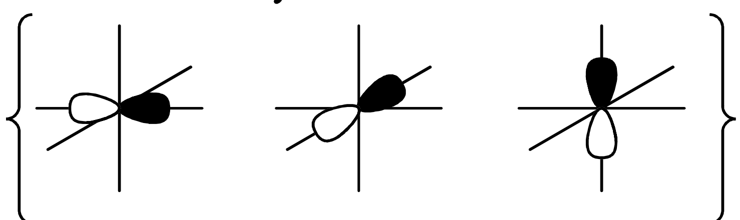
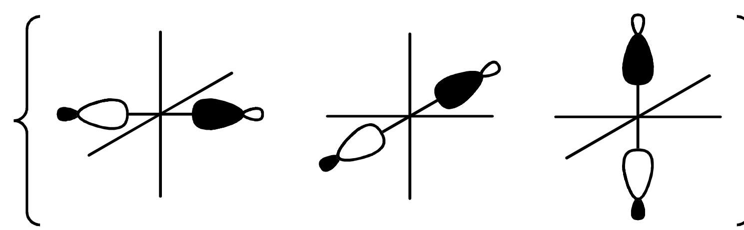
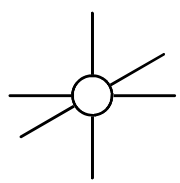
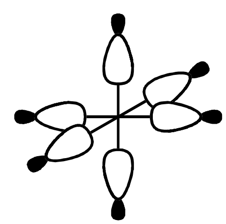
T_{1u} : (4p_x, 4p_y, 4p_z)

E_g : (3*d*x^2-y^2 , 3*d*z^2)

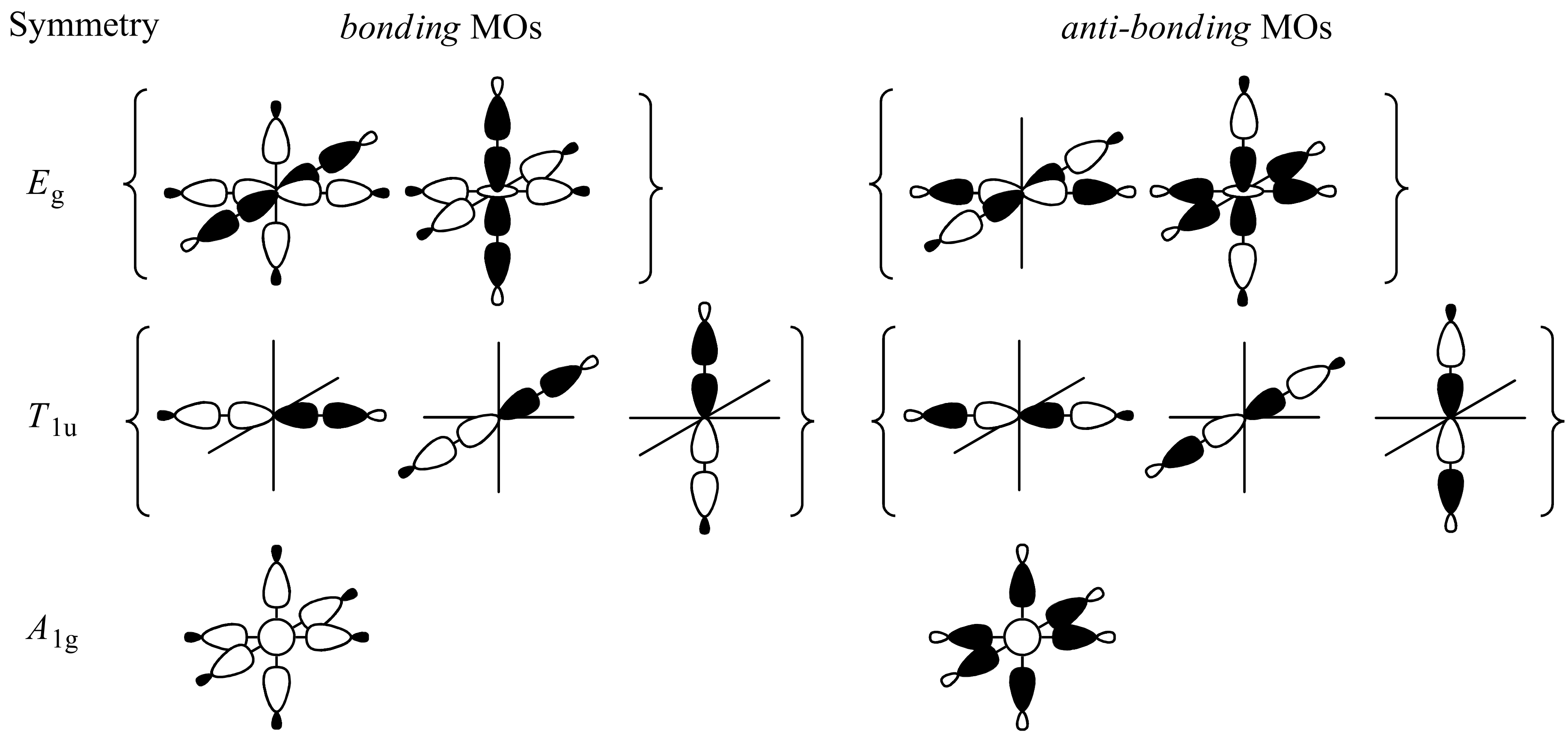
Cr non-bonding AOs

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

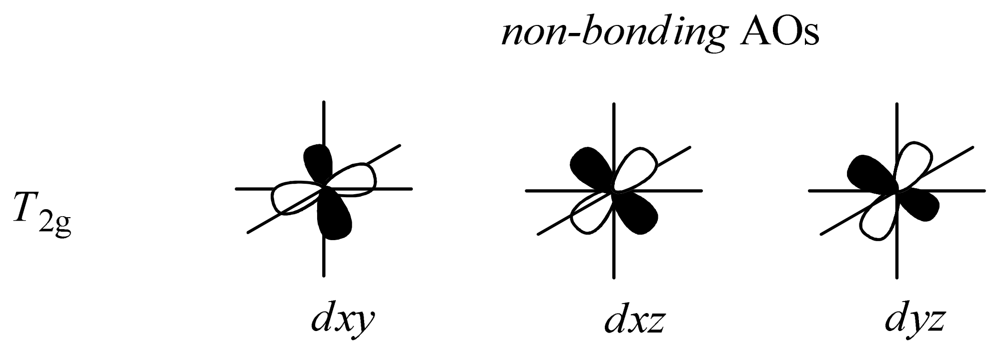
define Cartesian axis 

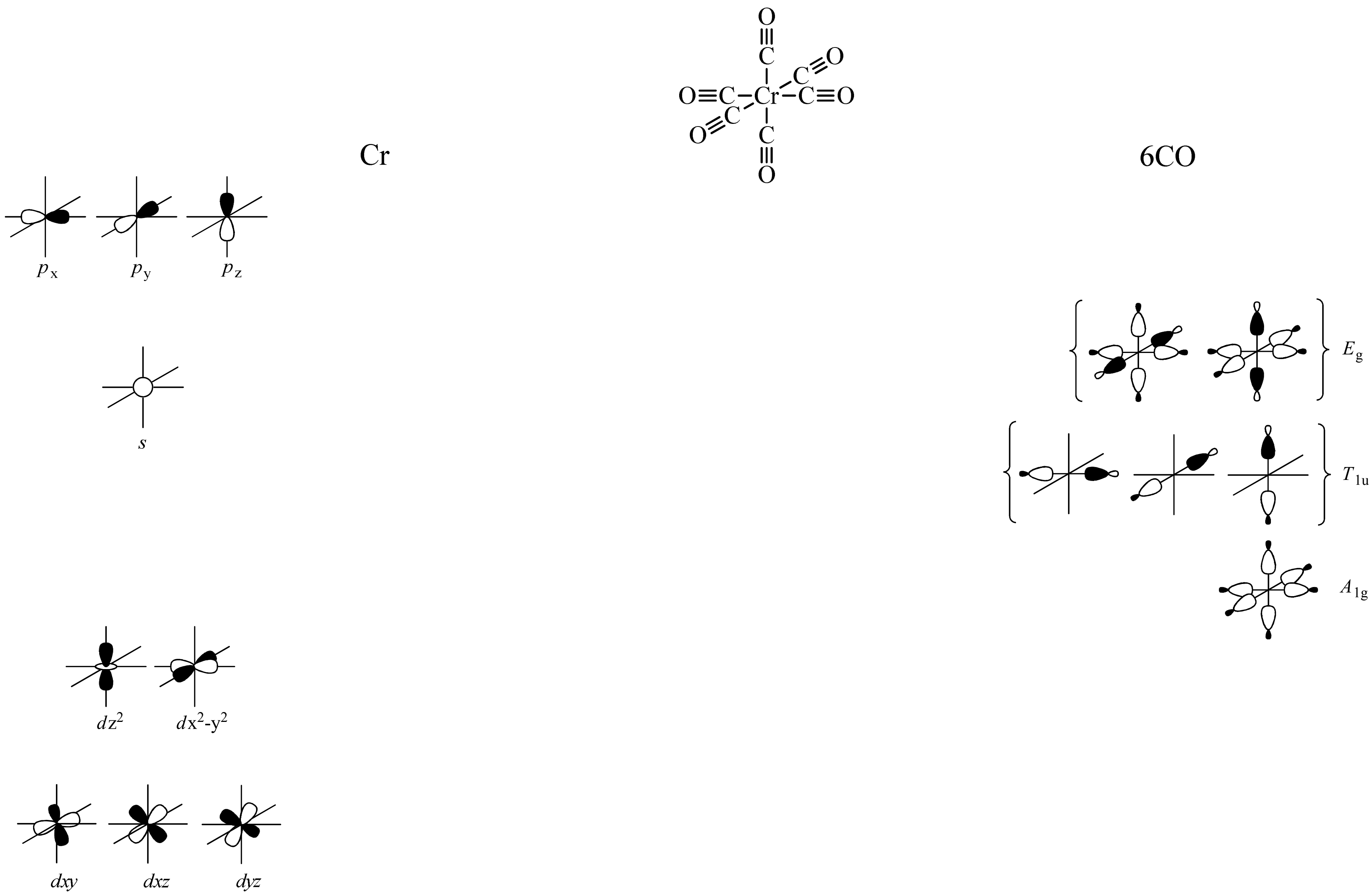
Symmetry	AOs	SALCs
E_g	 dx^2-y^2 dz^2	
T_{1u}	 p_x p_y p_z	
A_{1g}	 s	

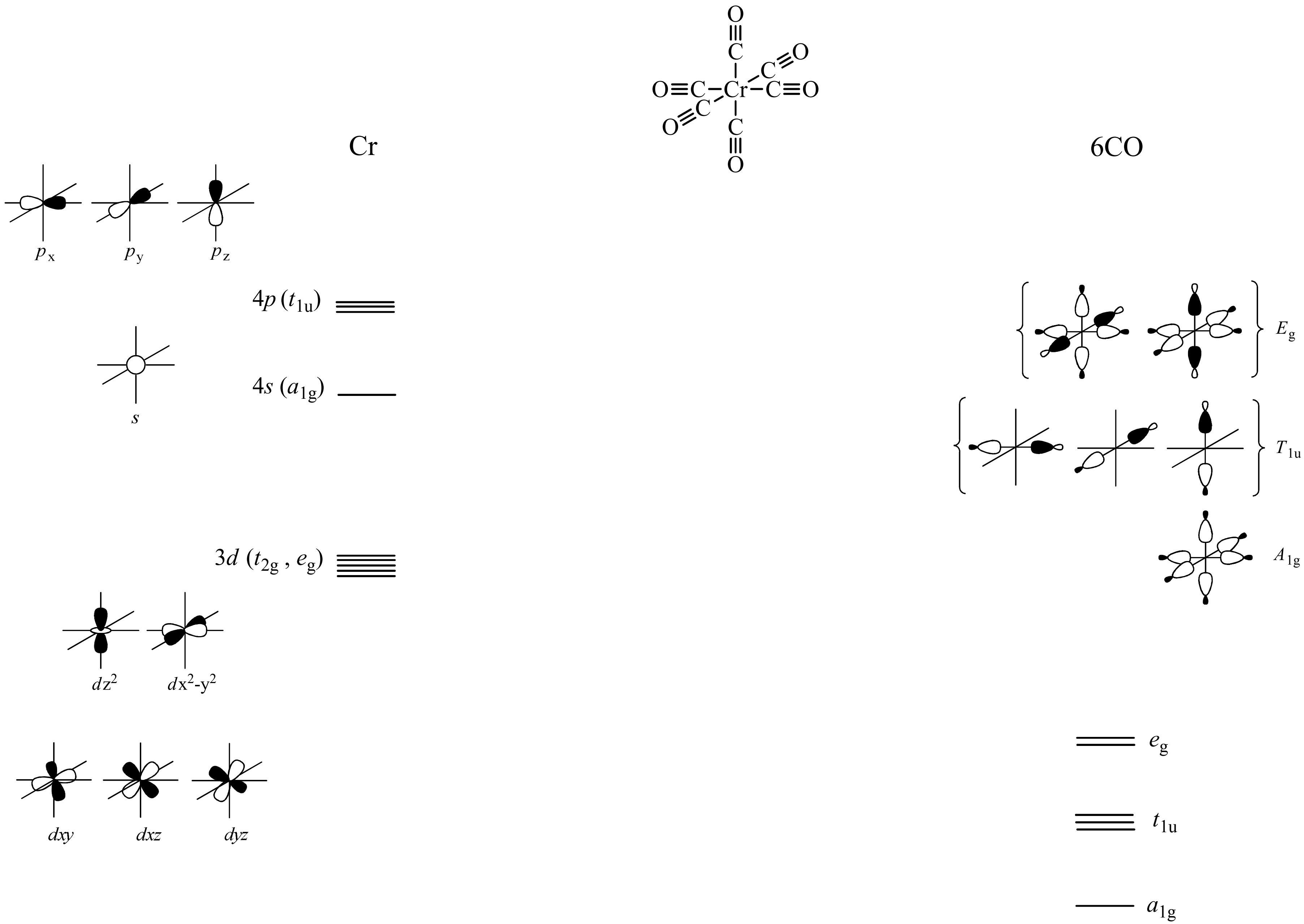
6. **Central-atom AOs and pendant-atom SALCs with the same symmetry species will form both bonding and antibonding LCAO-MOs.**



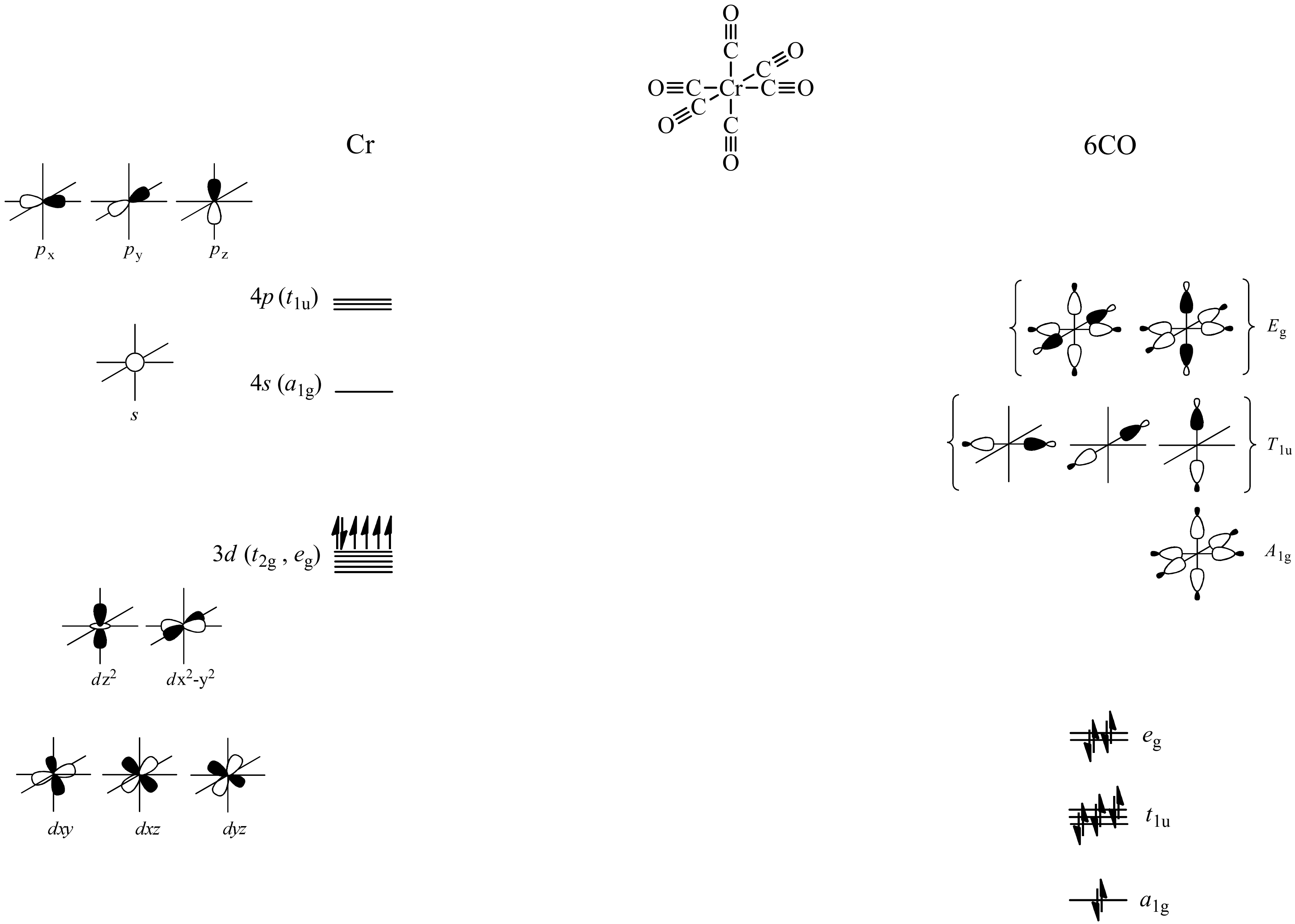
7. **Central-atom AOs or pendant-atom SALCs with unique symmetry (no species match between AOs and SALCs) form nonbonding MOs.**



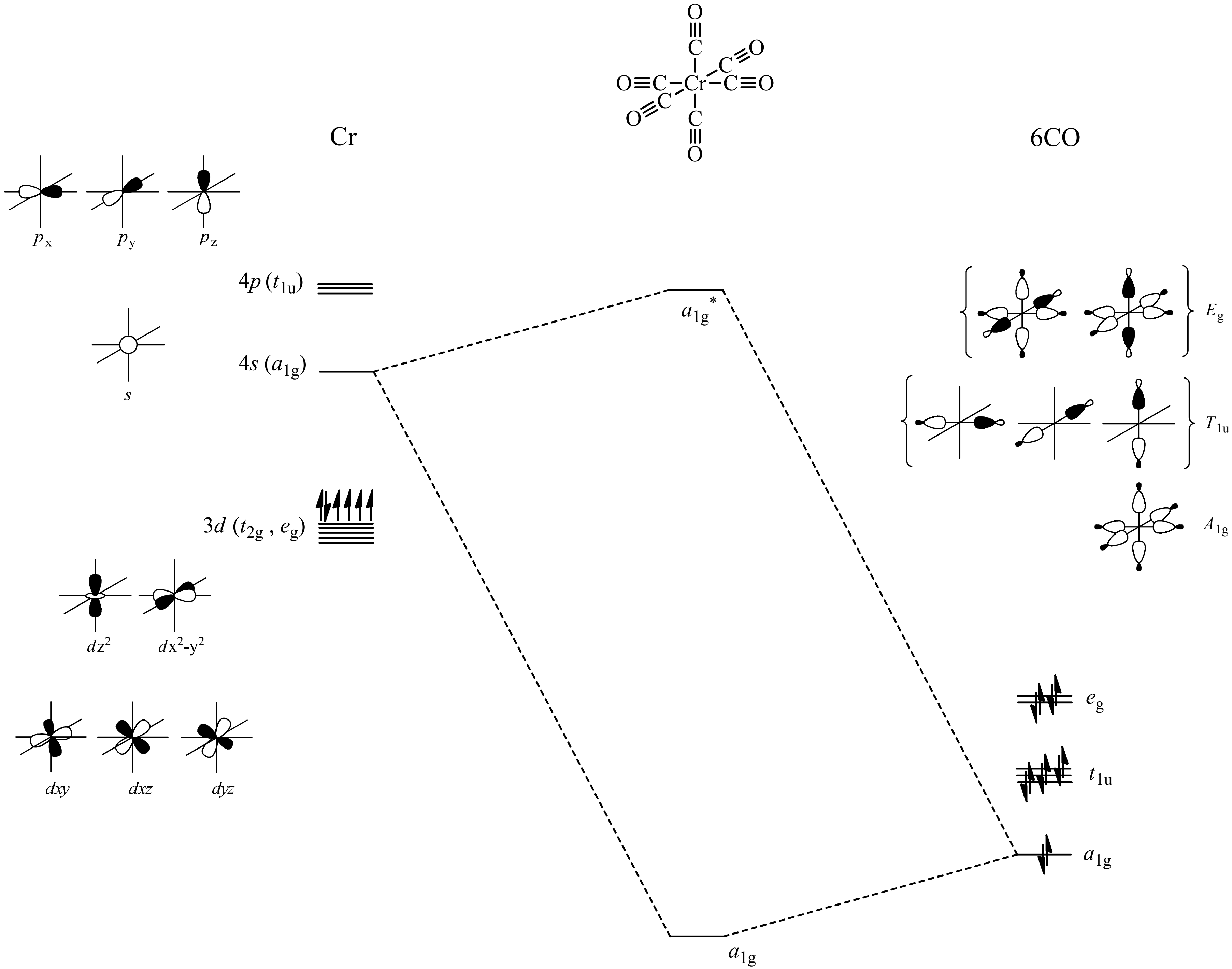

Cr
6CO
O
C
O≡C–Cr–C≡O
C
O
C
O
C
O
px
py
pz
s
dz2
dx2-y2
dxy
dxz
dyz
Eg
T1u
A1g



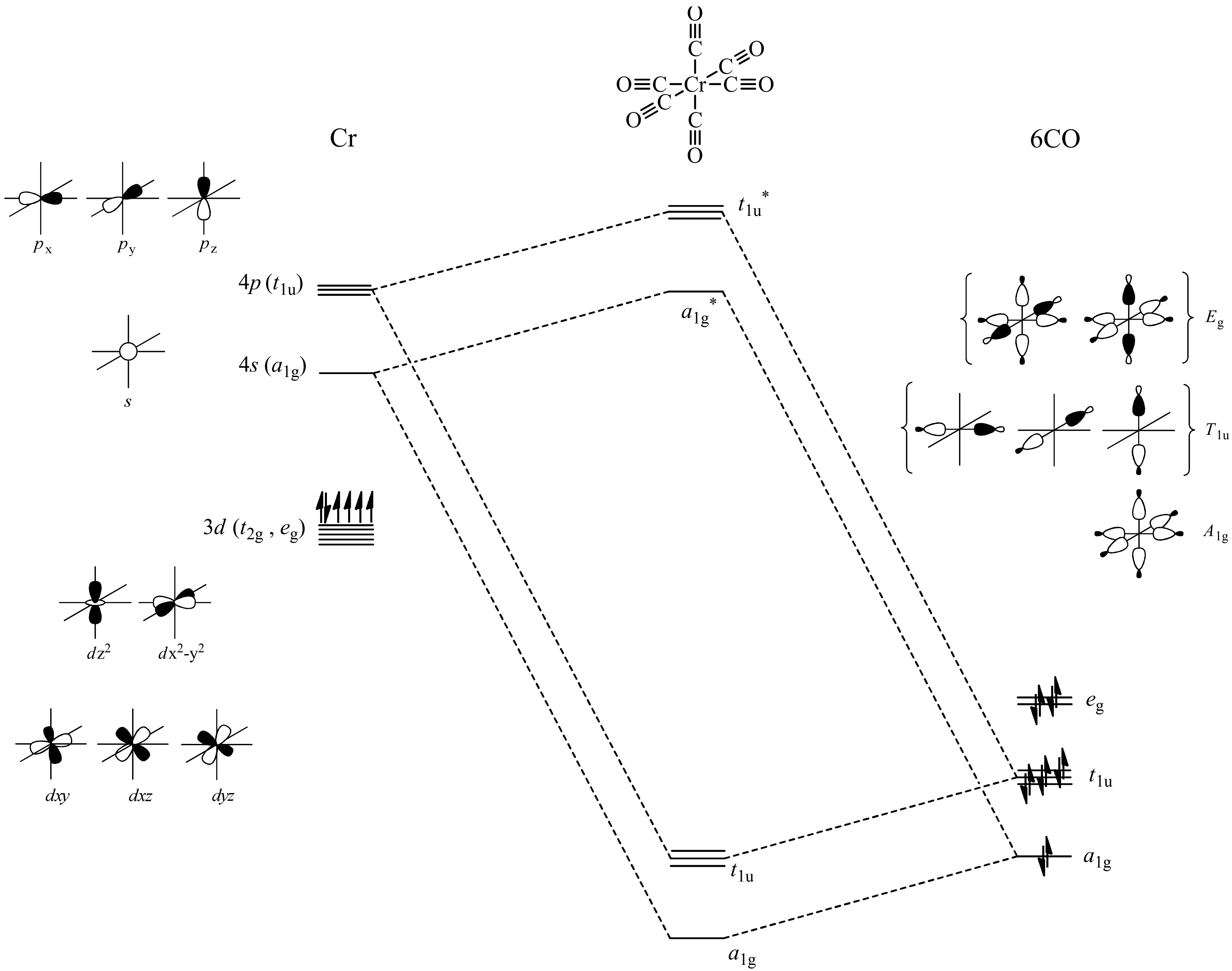
Cr
6CO
O≡C–Cr–C≡O
p_x p_y p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2 $dx^2\text{-}y^2$
dxy dxz dyz
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



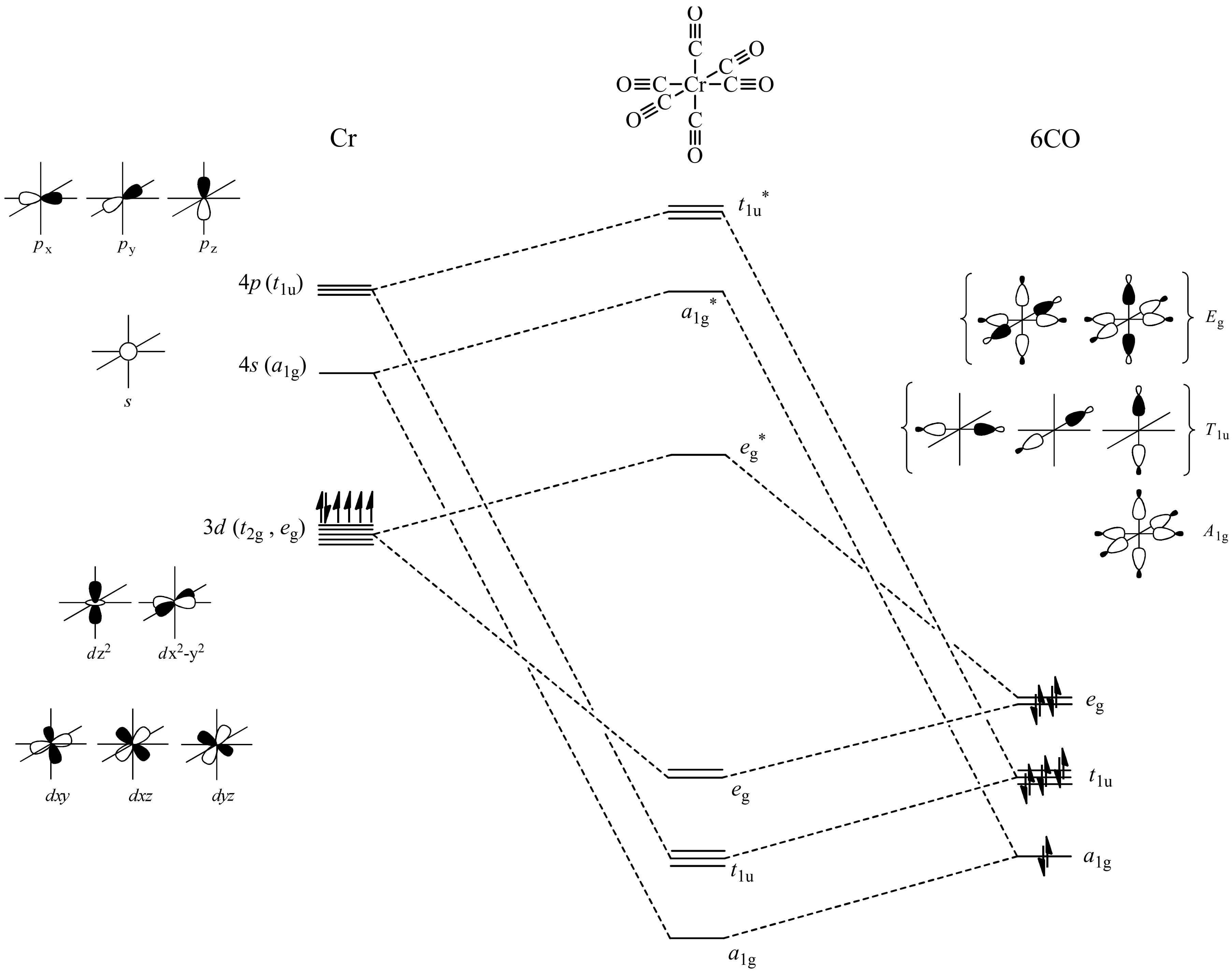
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



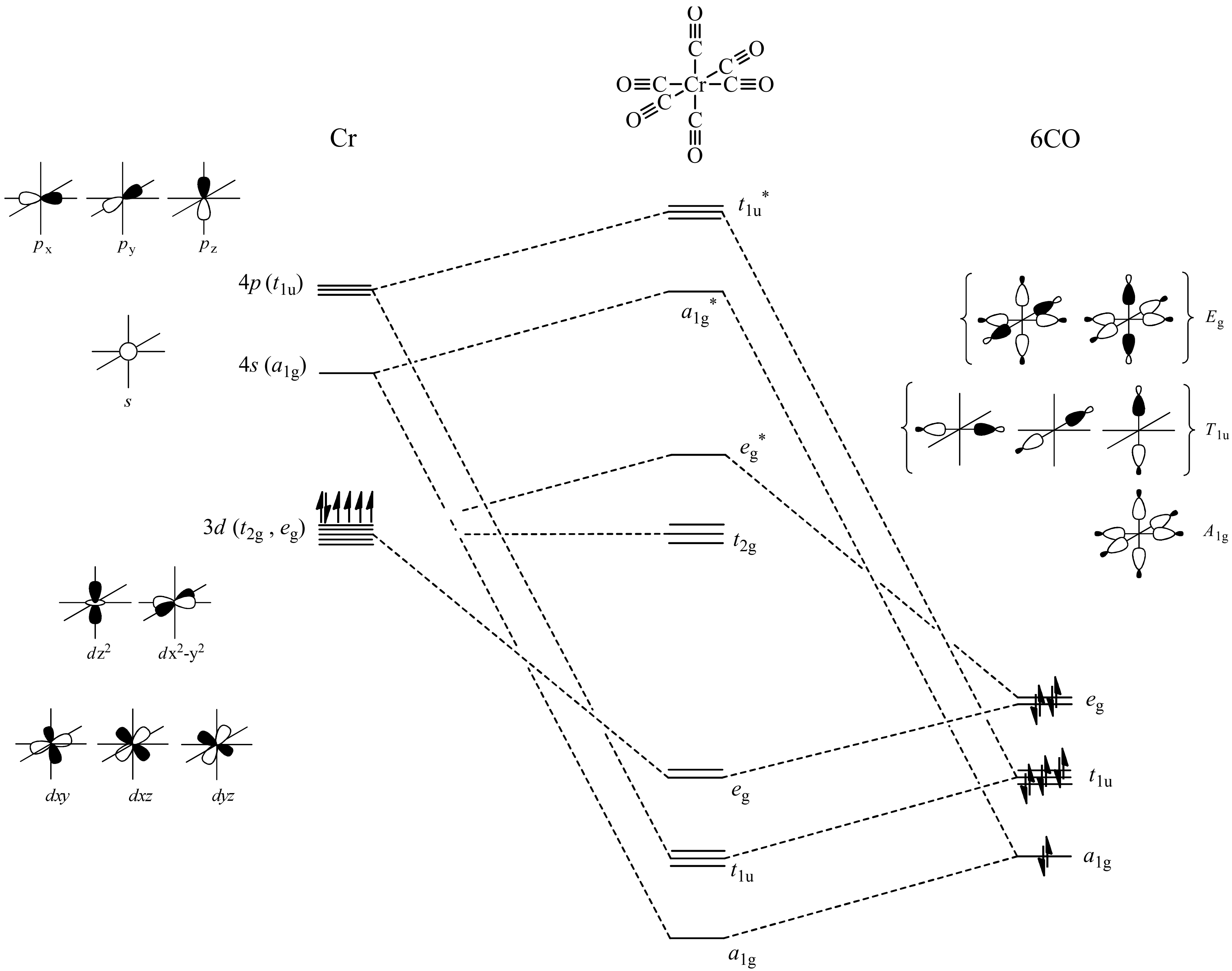
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
a_{1g}^*
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



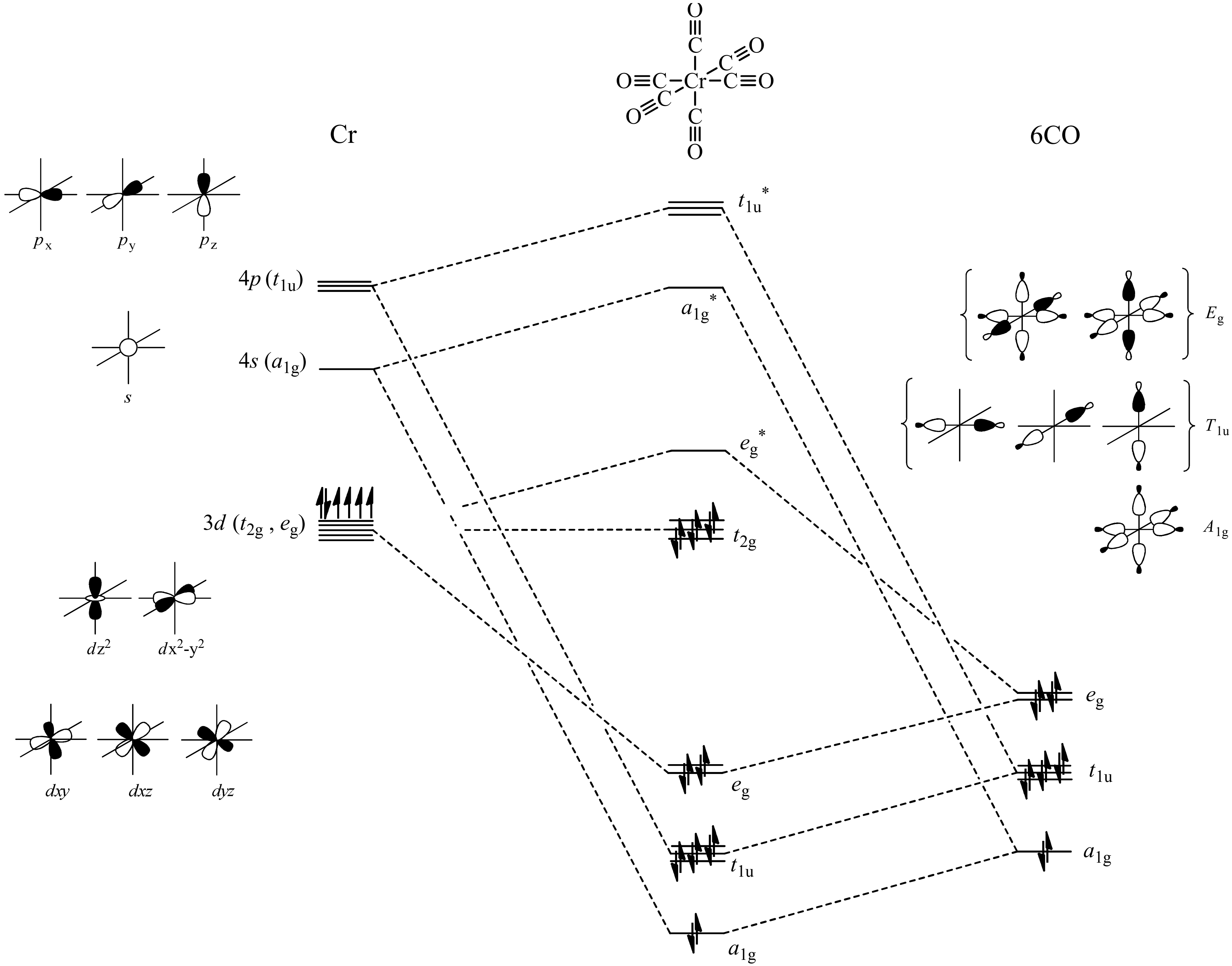
Cr
6CO
p_x p_y p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2 $dx^2\text{-}y^2$
dxy dxz dyz
t_{1u}^*
a_{1g}^*
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



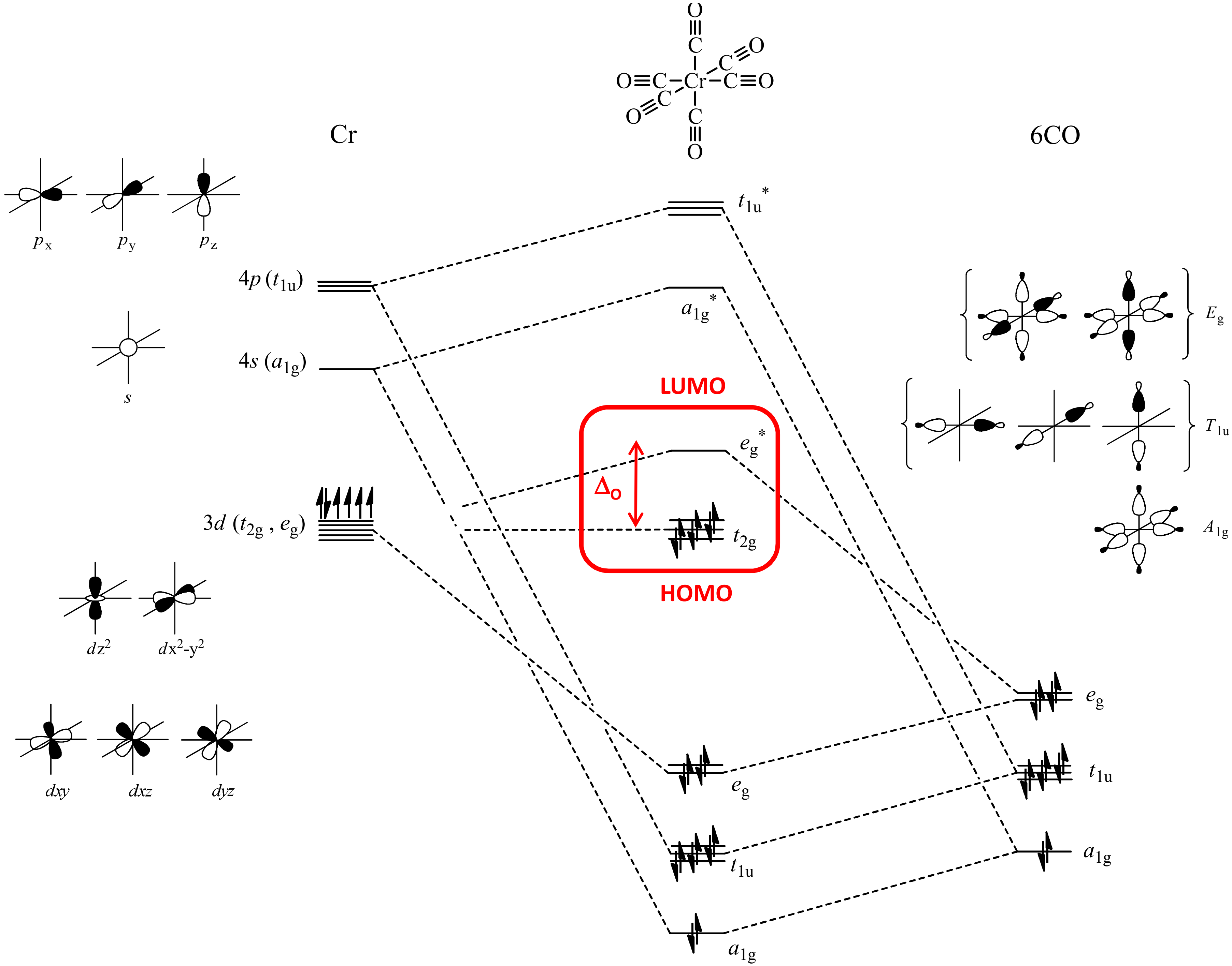
Cr
6CO
p_x p_y p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2 $dx^2\text{-}y^2$
dxy dxz dyz
t_{1u}^*
a_{1g}^*
e_g^*
e_g
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



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}

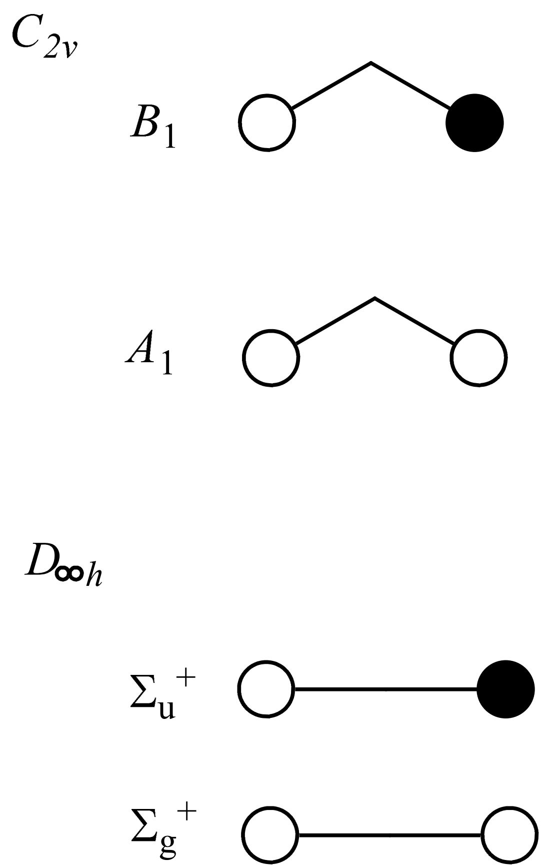


Cr
6CO
O≡C–Cr–C≡O
p_x
p_y
p_z
$4p\ (t_{1u})$
s
$4s\ (a_{1g})$
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
e_g^*
t_{2g}
e_g
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}


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

SALCS for Common Geometries (*σ bonding*)

CN = 2

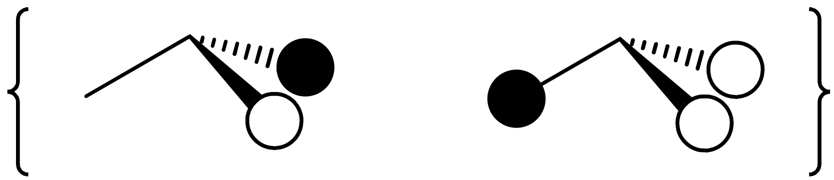


SALCS for Common Geometries *(σ bonding)*

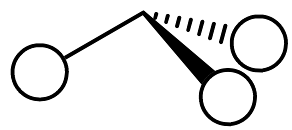
CN = 3

C_{3v}

E

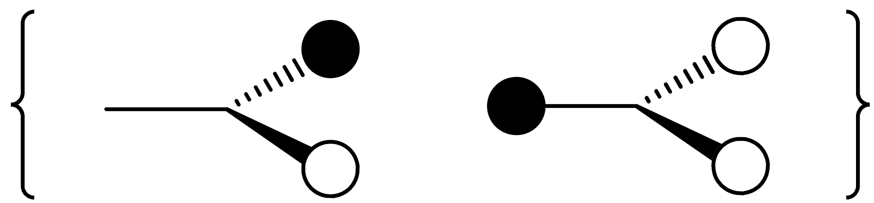


A_1

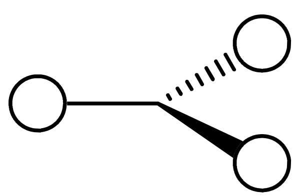


D_{3h}

E'



A_1'

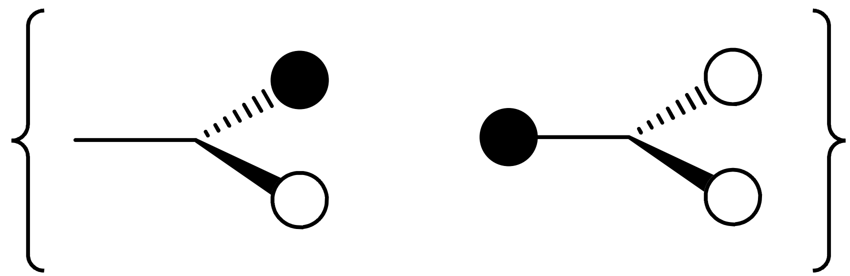


SALCS for Common Geometries (*σ bonding*)

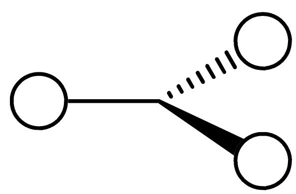
CN = 3

D_{3h}

E



A_1'

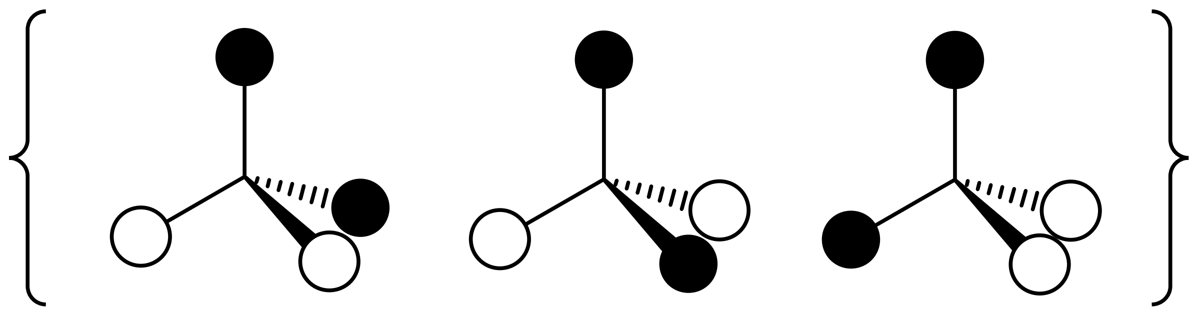


SALCS for Common Geometries (*σ bonding)*

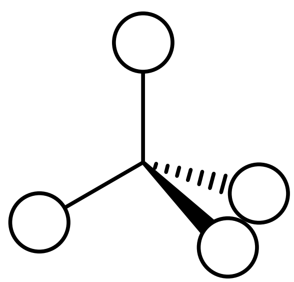
CN = 4

T_d

T_2



A_1

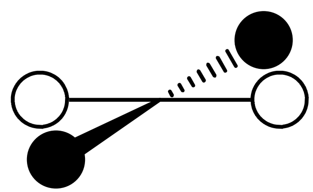


SALCS for Common Geometries *(σ bonding)*

CN = 4

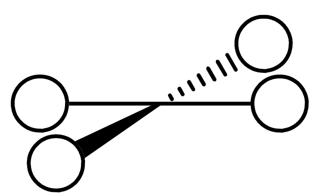
D_{4h}

B_{1g}



E_u

A_{1g}

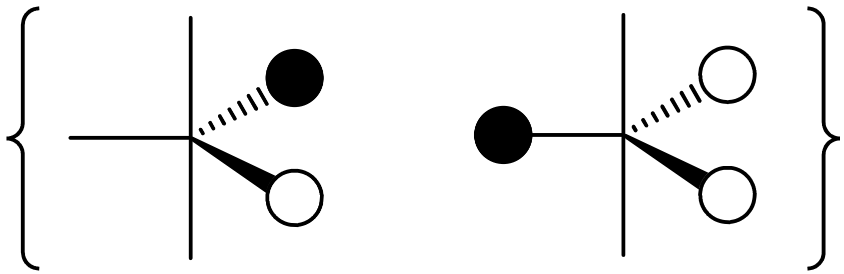


SALCS for Common Geometries (*σ bonding*)

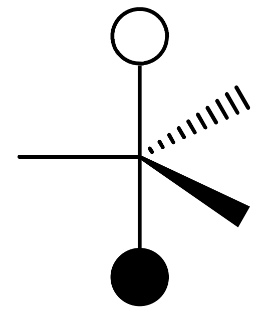
CN = 5

D_{3h}

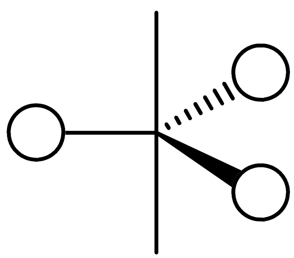
E



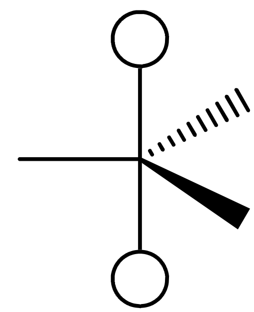
A_2''



A_1'



A_1'

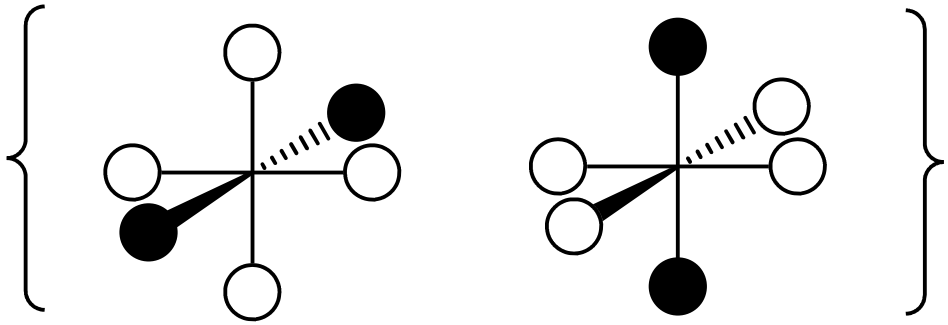


SALCS for Common Geometries (*σ bonding*)

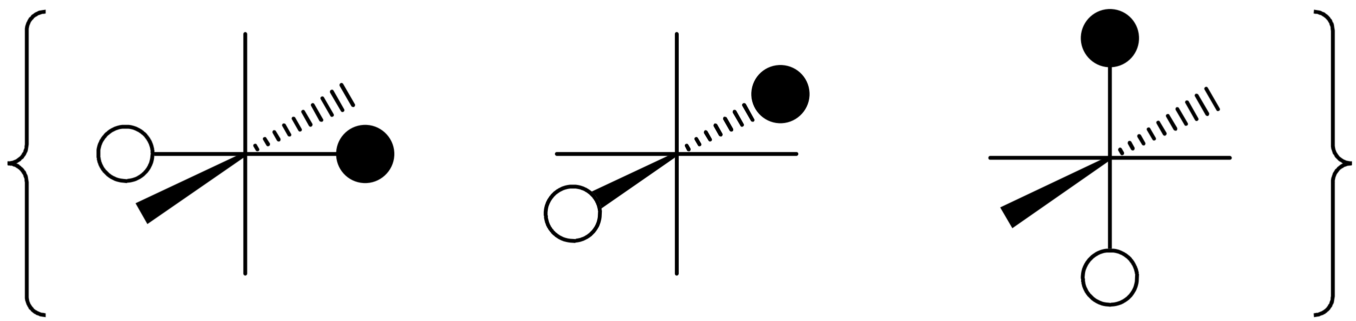
CN = 6

O_h

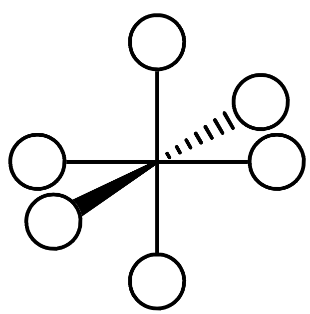
E_g



T_{2g}



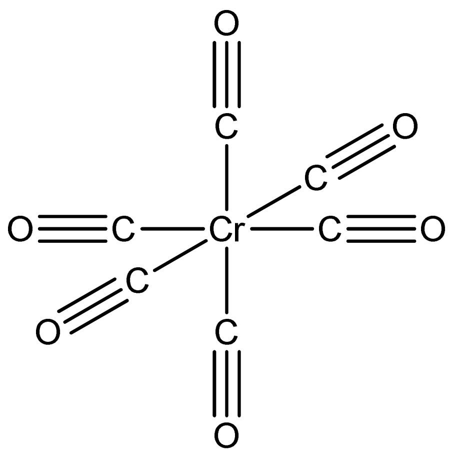
A_{1g}



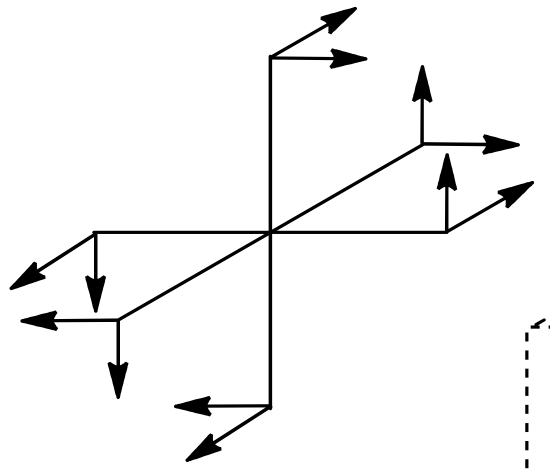
Construction of MO diagrams for Transition Metal Complexes

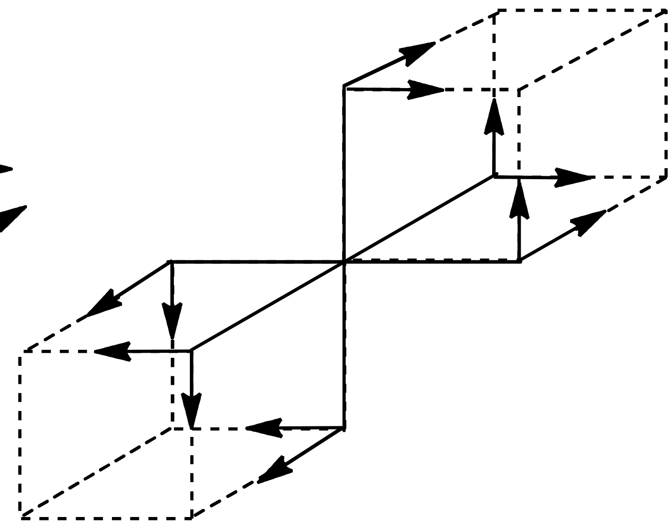
π bonding complexes

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



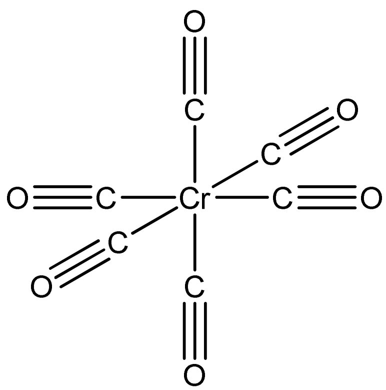
point group = O_h

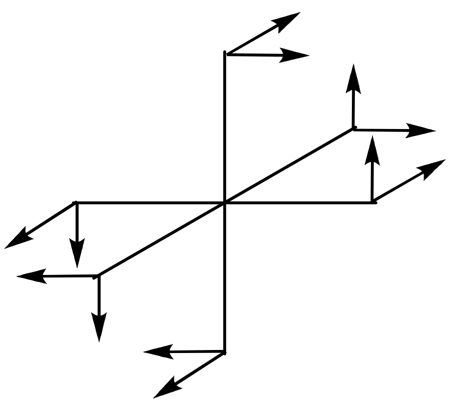




- Each vector shifted through space contributes 0 to the character for the class.
- Each non-shifted vector contributes 1 to the character for the class.
- ***Each vector shifted to the negative of itself (180°) contributes -1 to the character for the class.***

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





point group = O_h

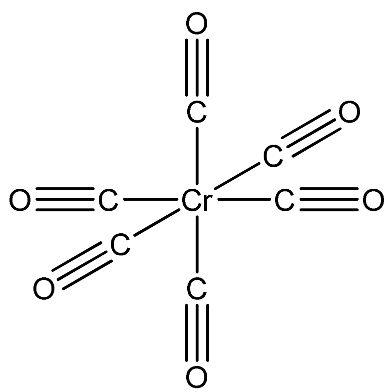
$h =$

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												
A_{1g}												
A_{2g}												
E_g												
T_{1g}												
T_{2g}												
A_{1u}												
A_{2u}												
E_u												
T_{1u}												
T_{2u}												

$\Gamma_\pi =$

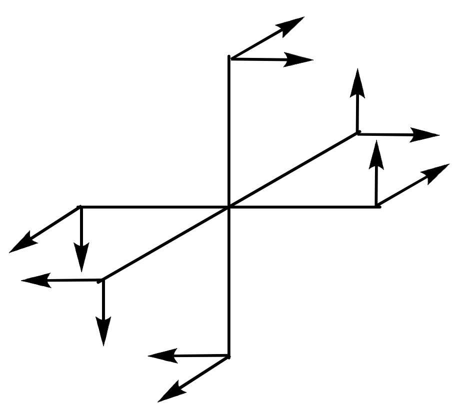
$d_\Gamma =$

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



$h = 48$

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

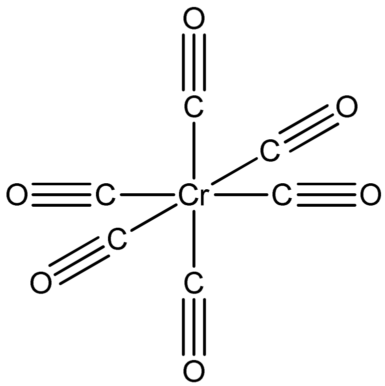


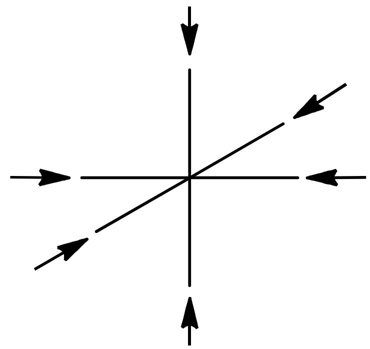
point group = O_h

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

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

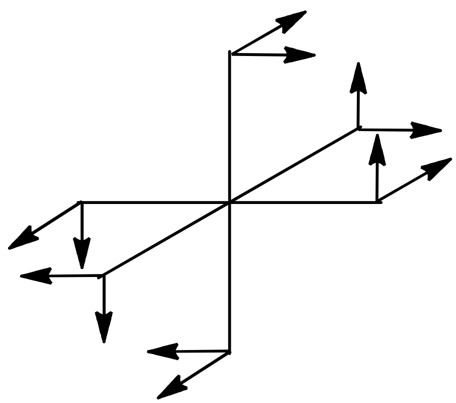
Example: Constructing a MO for Chromium Hexacarbonyl, $Cr(CO)_6$





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, $Cr(CO)_6$

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

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

Cr σ-bonding AOs

Cr π-bonding AOs

Cr non-bonding AOs

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

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

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

Cr σ-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

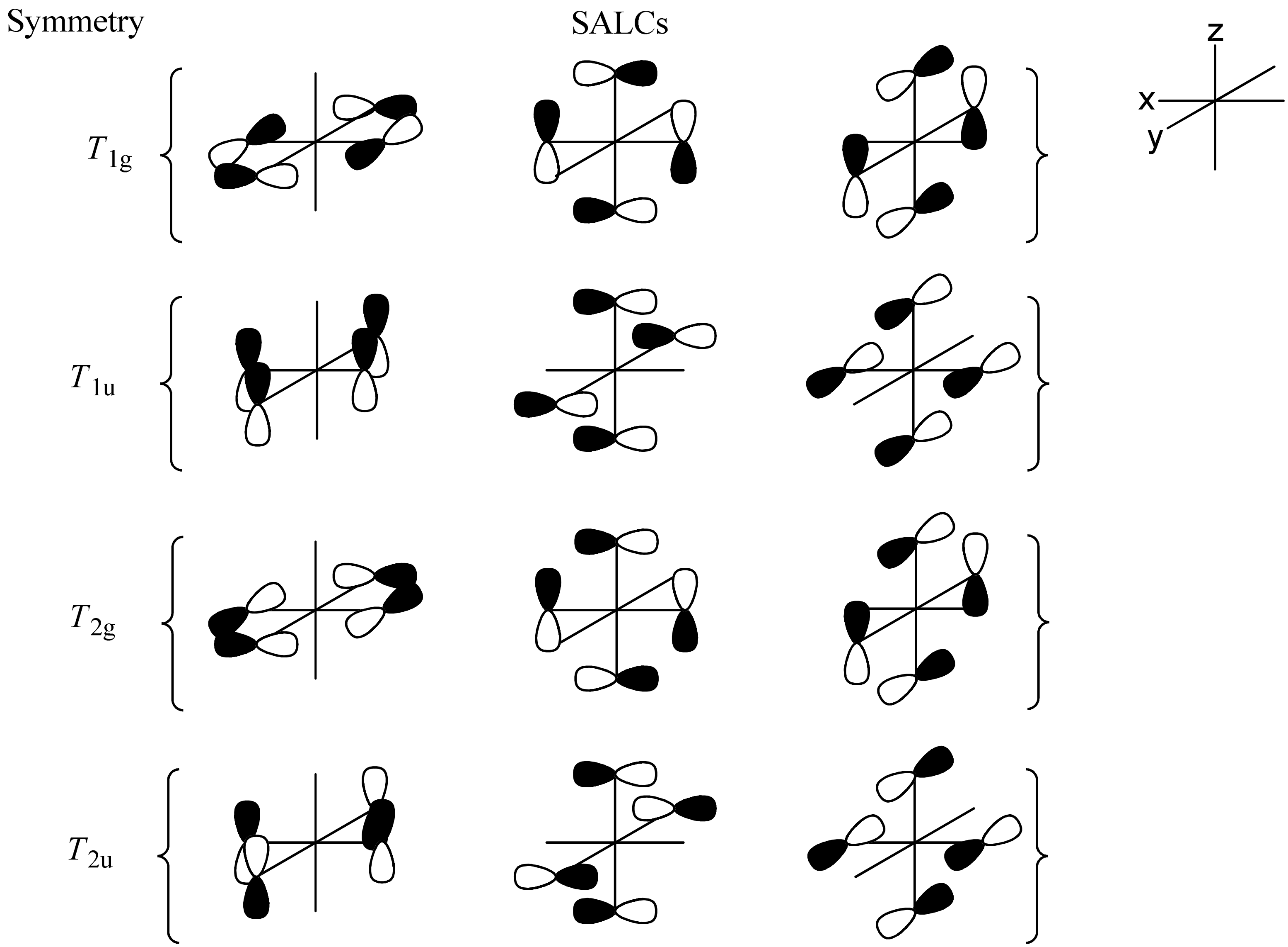
T_{2g} : (3*d*xy, 3*d*xz, 3*d*yz)

Cr π-bonding AOs

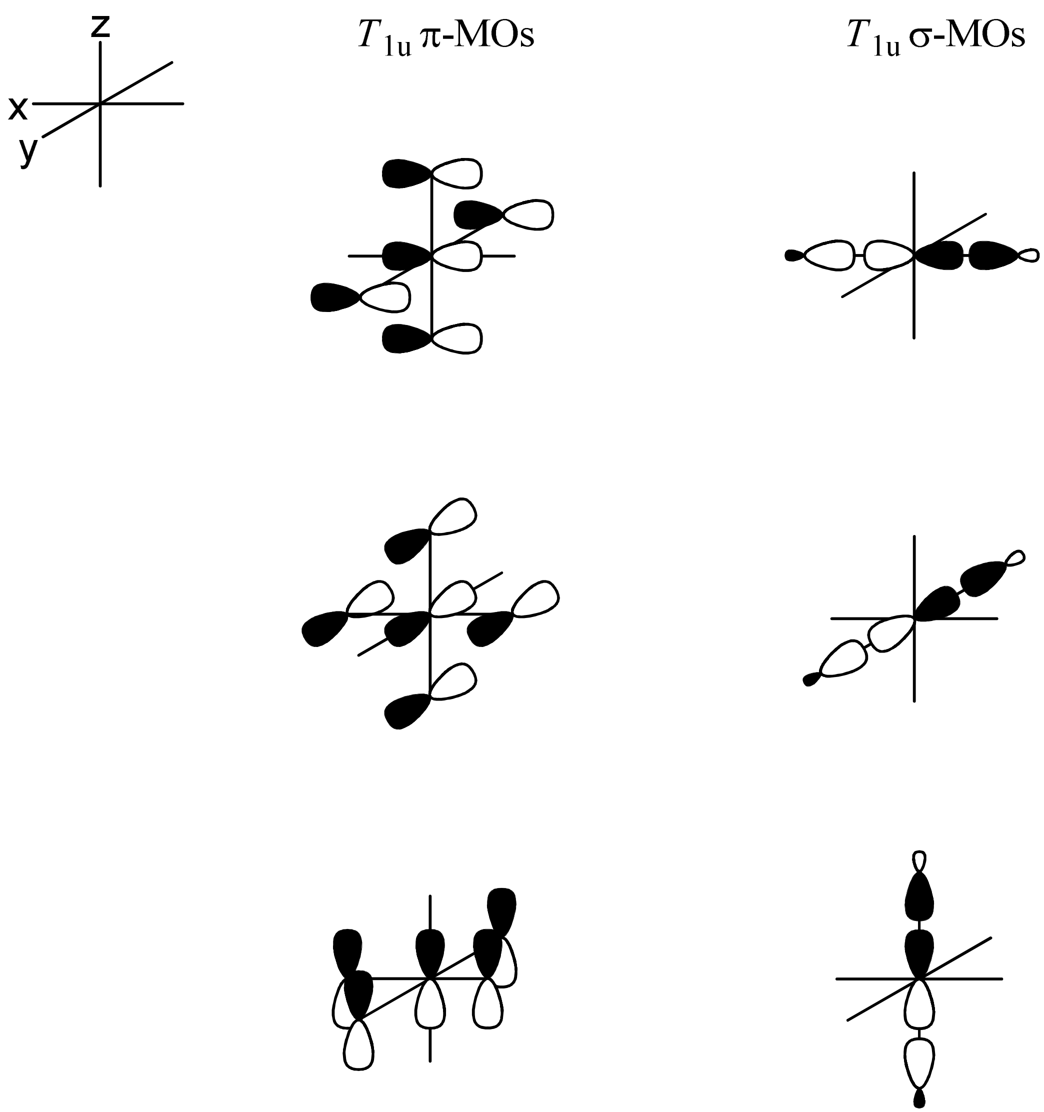
T_{2g} : (3*d*xy, 3*d*xz, 3*d*yz)

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

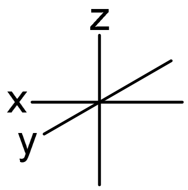
- T_{2g} previously considered non-bonding in σ-bonding scheme
- T_{1u} combines with T_{1u} SALC in in σ-bonding scheme
- T_{1g} , T_{2u} π-SALCs are non-bonding



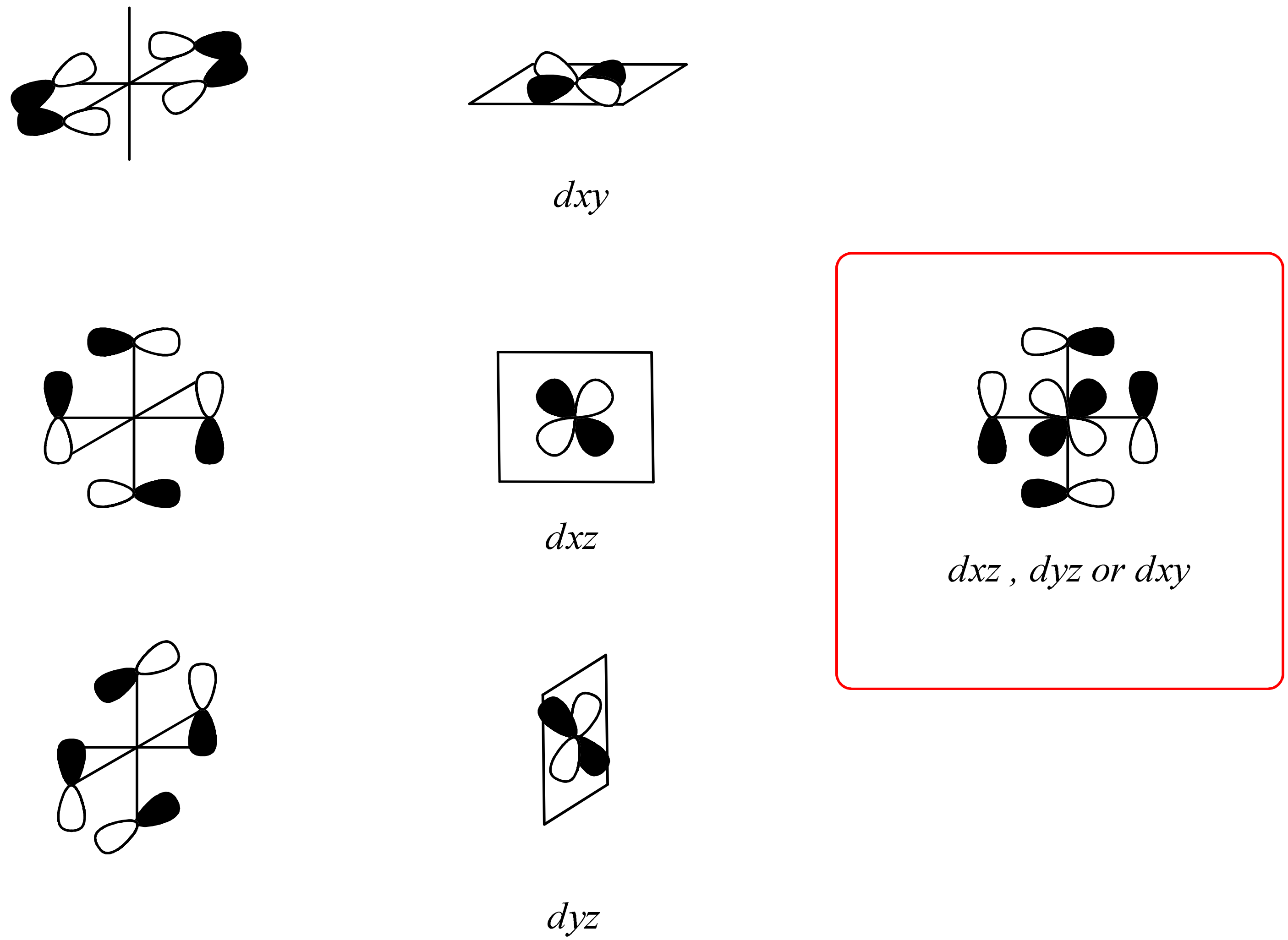
Symmetry
SALCs
z
x
y
T_{1g}
T_{1u}
T_{2g}
T_{2u}

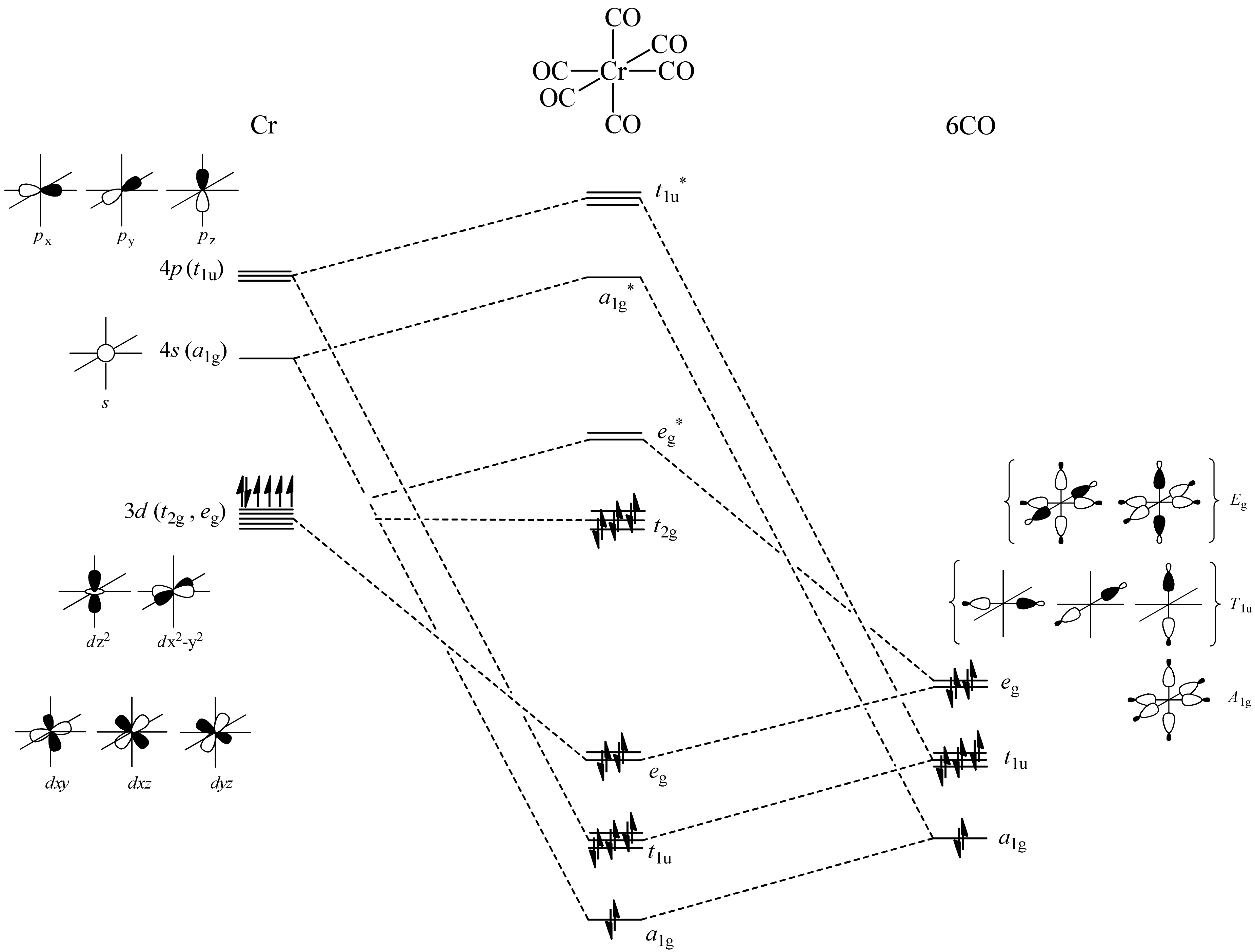


- T_{1u} AOs overlap more effectively with T_{1u} σ-SALC thus the π-bonding interaction is considered negligible or at most only weakly-bonding.

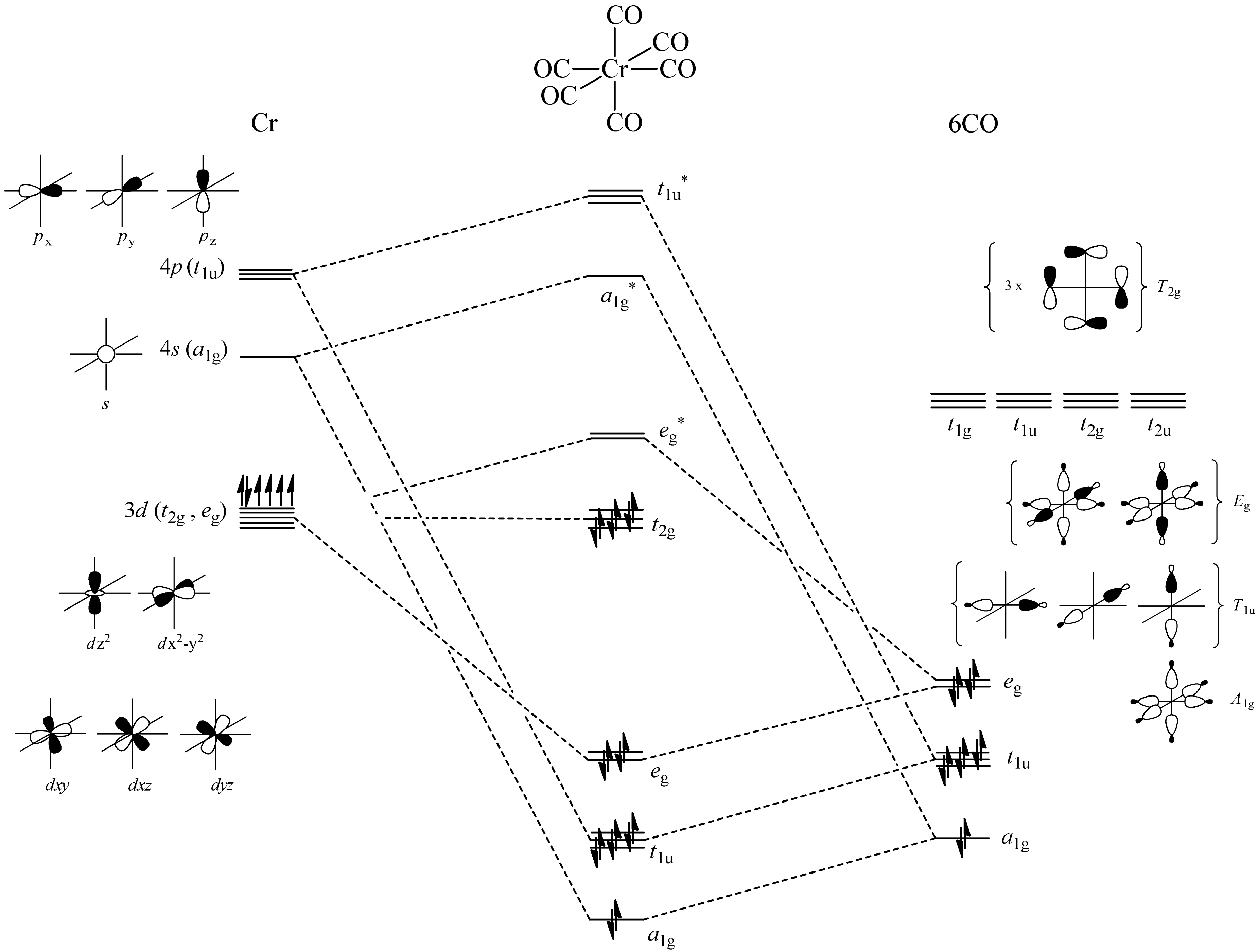


T_{2g} π-MOs

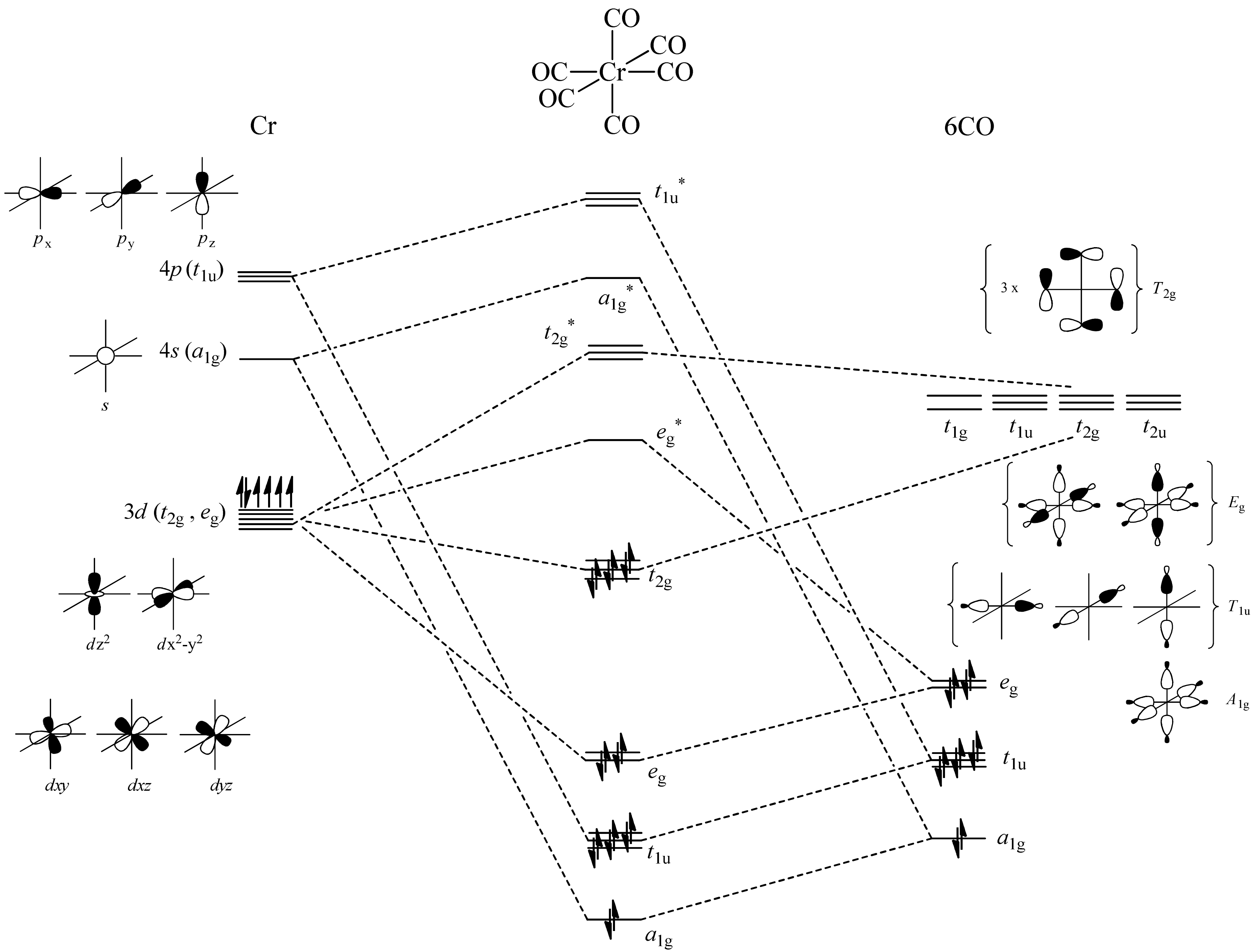




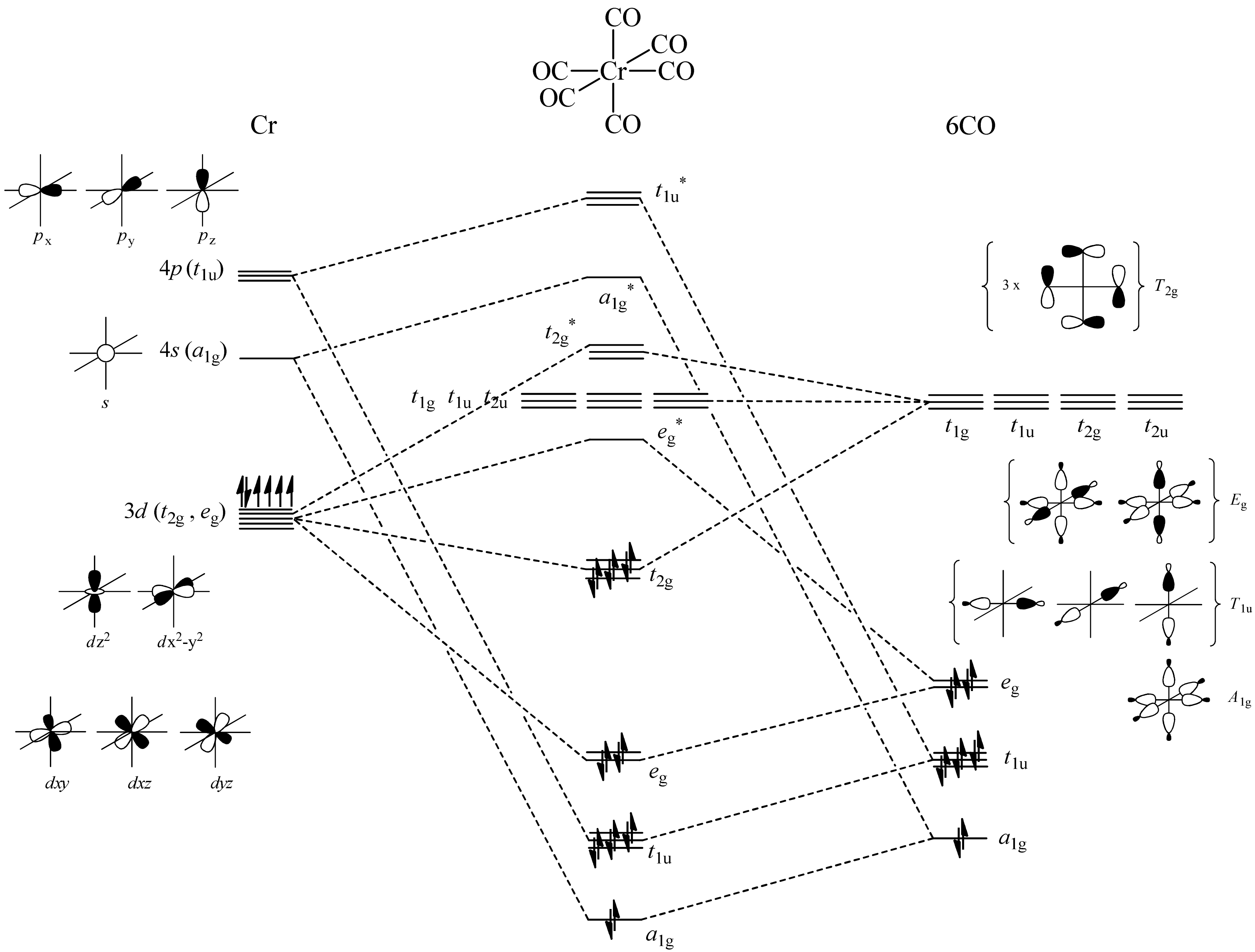
CO
CO
OC
Cr
CO
OC
CO
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
$4s\ (a_{1g})$
s
$3d\ (t_{2g}, e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
e_g^*
t_{2g}
e_g
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



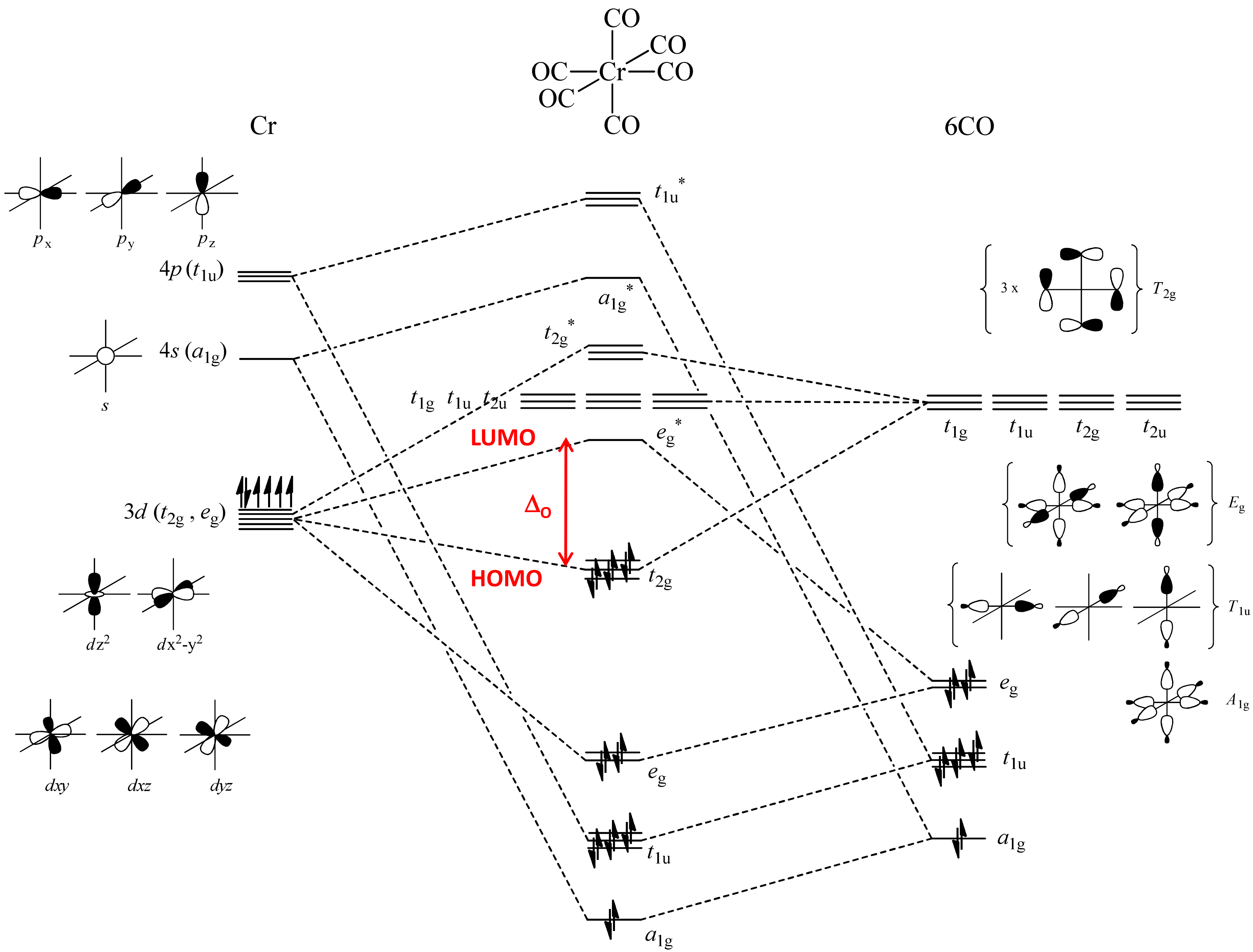
CO
CO
OC
Cr
CO
OC
CO
Cr
6CO
p_x
p_y
p_z
$4p\ (t_{1u})$
$4s\ (a_{1g})$
s
$3d\ (t_{2g}\ ,\ e_g)$
dz^2
$dx^2\text{-}y^2$
dxy
dxz
dyz
$t_{1u}{}^*$
$a_{1g}{}^*$
$e_g{}^*$
t_{2g}
e_g
t_{1u}
a_{1g}
3 x
T_{2g}
t_{1g}
t_{1u}
t_{2g}
t_{2u}
E_g
T_{1u}
e_g
A_{1g}
t_{1u}
a_{1g}



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

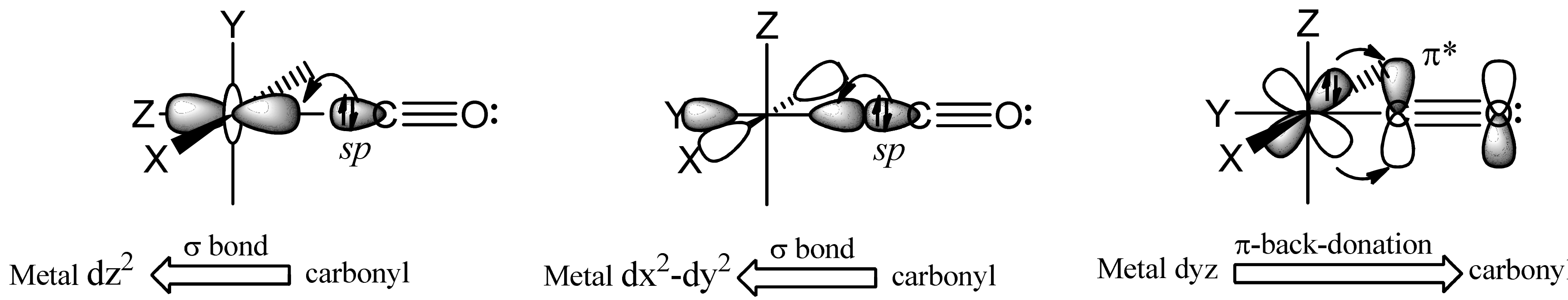


CO
CO
OC—Cr—CO
OC
CO
Cr
6CO
p_x
p_y
p_z
$4p$ (t_{1u})
$4s$ (a_{1g})
s
$3d$ (t_{2g} , e_g)
dz^2
dx^2-y^2
dxy
dxz
dyz
t_{1u}^*
a_{1g}^*
t_{2g}^*
t_{1g} t_{1u} t_{2u}
e_g^*
t_{2g}
e_g
t_{1u}
a_{1g}
3 x
T_{2g}
t_{1g}
t_{1u}
t_{2g}
t_{2u}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}



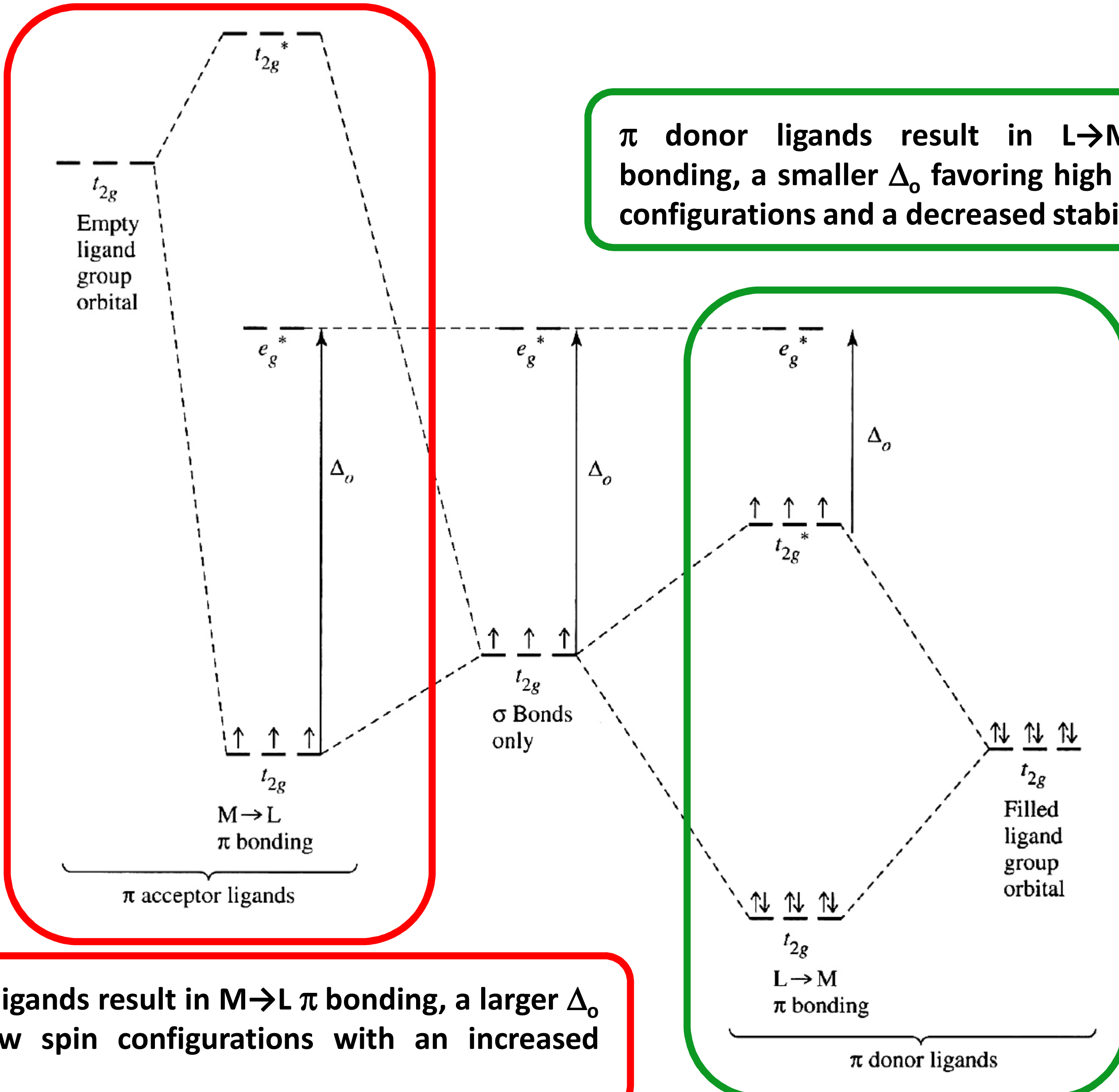
CO
CO
OC—Cr—CO
OC
CO
Cr
6CO
p_x p_y p_z
$4p\ (t_{1u})$
$4s\ (a_{1g})$
s
$3d\ (t_{2g}, e_g)$
dz^2 dx^2-y^2
dxy dxz dyz
t_{1u}^*
a_{1g}^*
t_{2g}^*
t_{1g} t_{1u} t_{2u}
LUMO
e_g^*
Δ_o
HOMO
t_{2g}
e_g
t_{1u}
a_{1g}
3 x
T_{2g}
t_{1g} t_{1u} t_{2g} t_{2u}
E_g
T_{1u}
A_{1g}
e_g
t_{1u}
a_{1g}

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.