

Molecular Orbitals in Inorganic Chemistry

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Outline

- **Metallic dimers**
- **Ligand symmetry adapted orbitals and the isolobal analogy**
- **The octahedral point group**

next lecture combine all this information
to form the MO diagram for a
TM Octahedral complex!

Octahedral Complexes

● transition metal surrounded by six σ -donor ligands L in an octahedral geometry

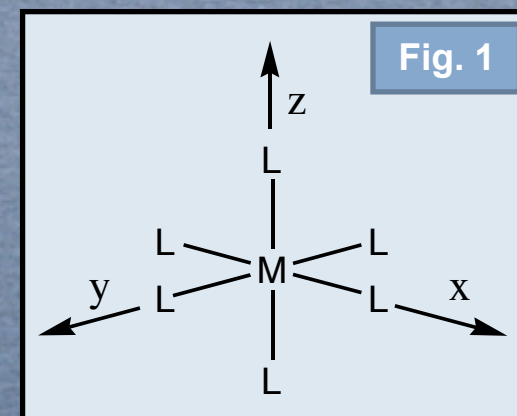
● MO diagram describes the interaction between the metal AOs and ligand FOs

● Metal orbitals

- ◆ different from main group metals
- ◆ include the 3d (or 4d) AOs
- ◆ AND the 4s and 4p (or 5s and 5p) unoccupied AOs

● AO symmetry

- ◆ assume O_h symmetry (initially!)
- ◆ use short-cuts!
- ◆ dAOs use binary functions
- ◆ pAOs use T_x, T_y, T_z
- ◆ sAO is totally symmetric



spherical

4p \rightarrow t_{1u} \equiv \equiv

4s \rightarrow a_{1g} ---

octahedral


3d e_g t_{2g} 

Fig. 2

Metal FOs

Octahedral Complexes

● know how to draw dAOs!

- ◆ positive lobe in quadrant defining the orbital

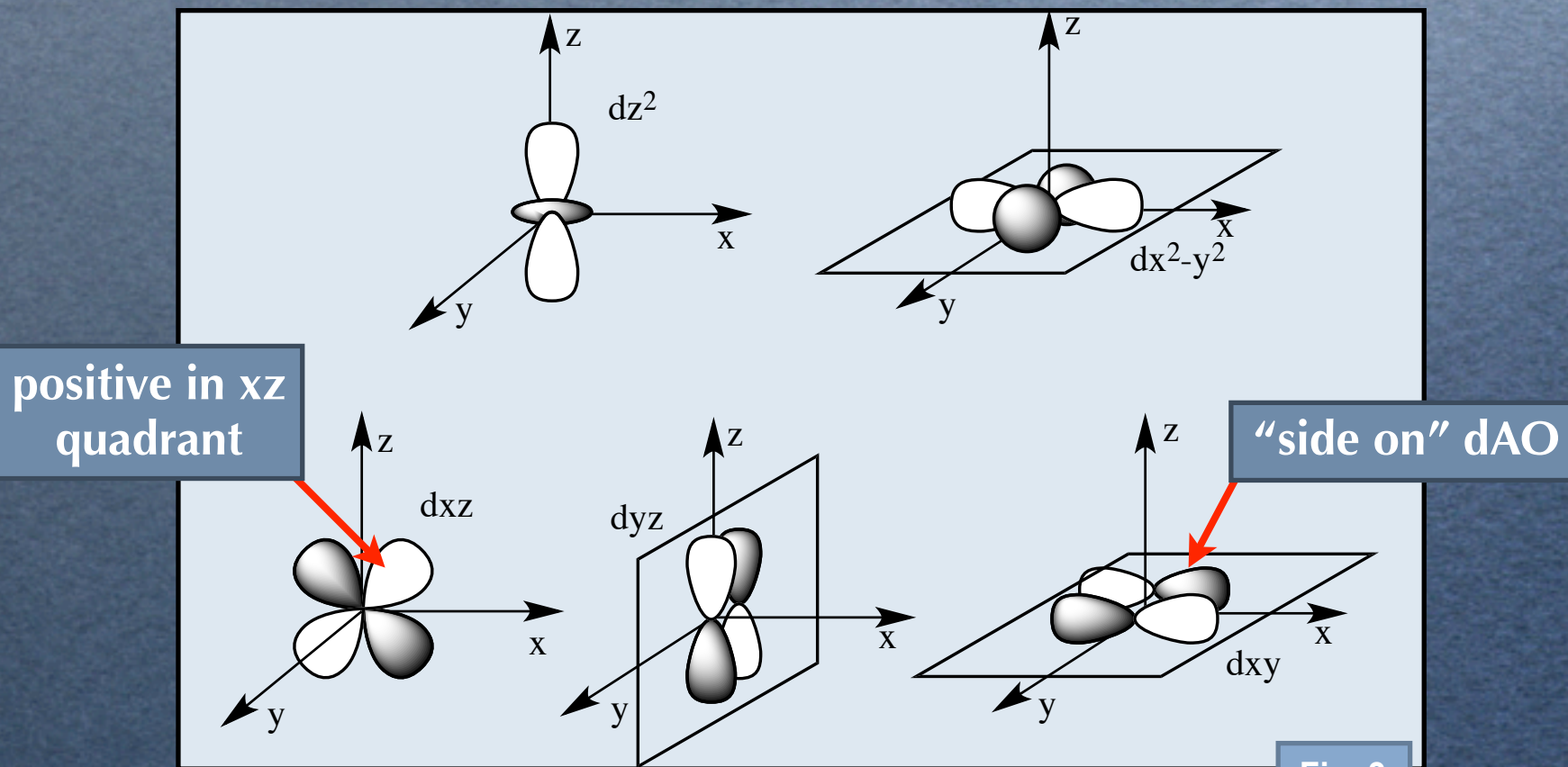


Fig. 3

Metallic Dimers

M_2 homonuclear diatomic

Energy diagram

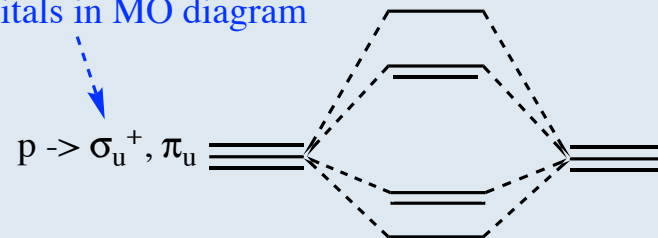
- ◆ has energy levels
- ◆ only include key MOs

$D_{\infty h}$ point group

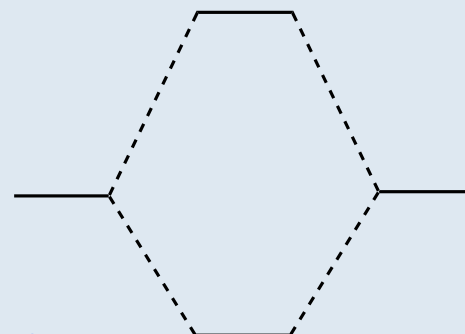
read FO symmetry off character table

- ◆ $s \rightarrow \sigma_g^+$
- ◆ $p_z \rightarrow \sigma_u^+$ p_x & $p_y \rightarrow \pi_u$
- ◆ $d_{z^2} \rightarrow \sigma_g^+$
- ◆ $d_{xy}, d_{x^2-y^2} \rightarrow \delta_g$
- ◆ $d_{yz}, d_{xz} \rightarrow \pi_g$

metal so include
the unoccupied s and p
orbitals in MO diagram

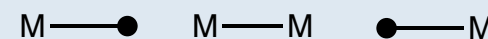
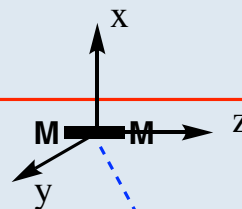
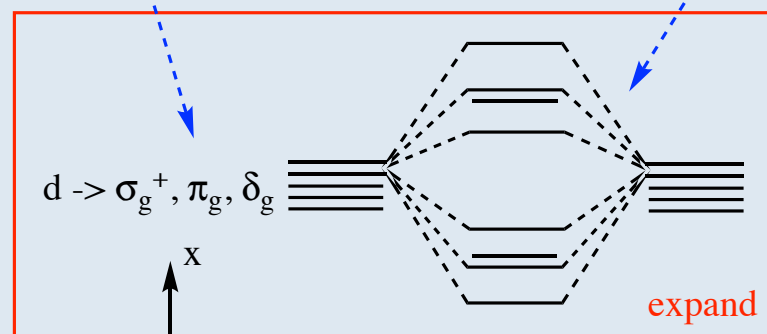


$s \rightarrow \sigma_g^+$



symmetry labels from
the $D_{\infty h}$ character table (using short cuts)

dAO-dAO splitting
is very small



homonuclear diatomic
z-axis is the principle axis and lies along the bond

Fig. 4

Symmetry Tips

 **classify interactions**

Important!

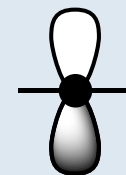
σ -type

symmetric for
rotation about z-axis



π -type

single phase
change on rotation
about z-axis



δ -type

two phase changes on
rotation about z-axis

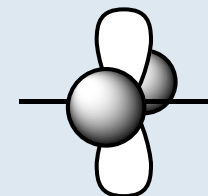


Fig. 6

know your Greek
alphabet!

$\alpha, \beta, \gamma, \delta, \sigma, \pi$
A, B, $\Gamma, \Delta, \Sigma, \Pi$

Metallic Dimers

focus dAO region

- ◆ combine FO bonding and antibonding pairs
- ◆ $dz^2 \rightarrow \sigma$ (green)
- ◆ $dxy, dx^2-y^2 \rightarrow \delta$ (pink)
- ◆ $dyz, dxz \rightarrow \pi$ (blue)

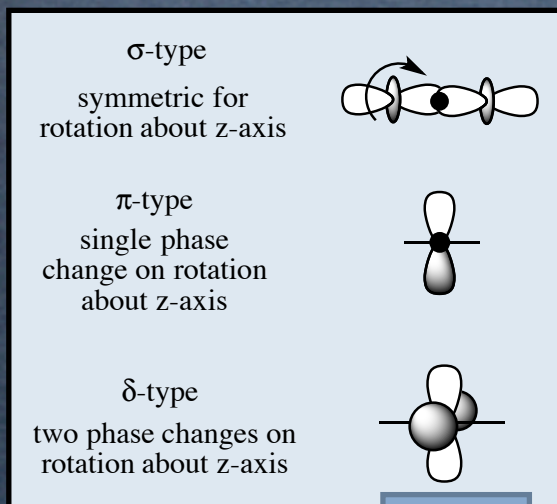


Fig. 6

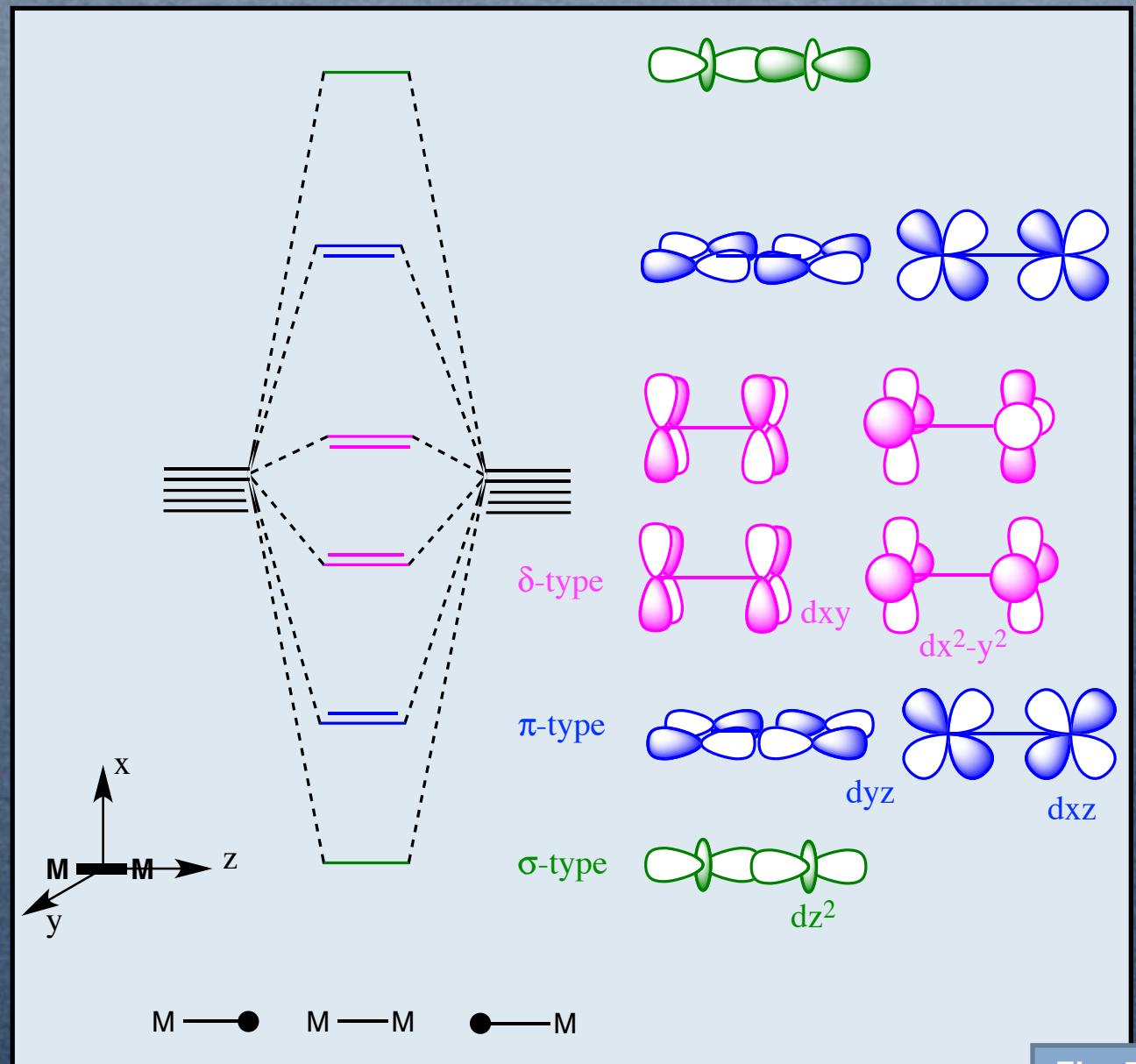


Fig. 5

Metallic Dimers

complete the MO symmetry labels

focus on phase change around center of inversion

looks like z-axis $\rightarrow \sigma_u^+$

also

along the bond $\rightarrow \sigma$
inverts through i $\rightarrow u$
no phase change for $\sigma_v \rightarrow +$

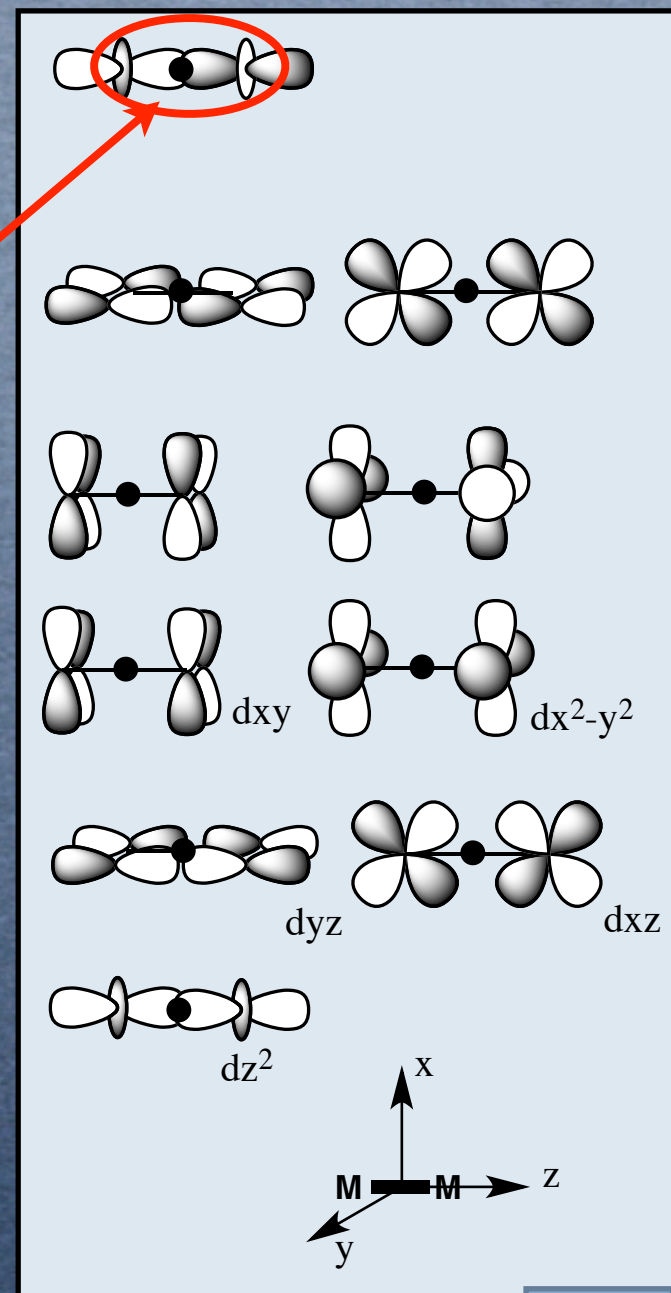


Fig. 7

Metallic Dimers

complete the MO symmetry labels

focus on phase change around center of inversion

looks like dxz & dyz \rightarrow
 π_g

also

π around bond
symmetric through i \rightarrow g
no +/- label for π

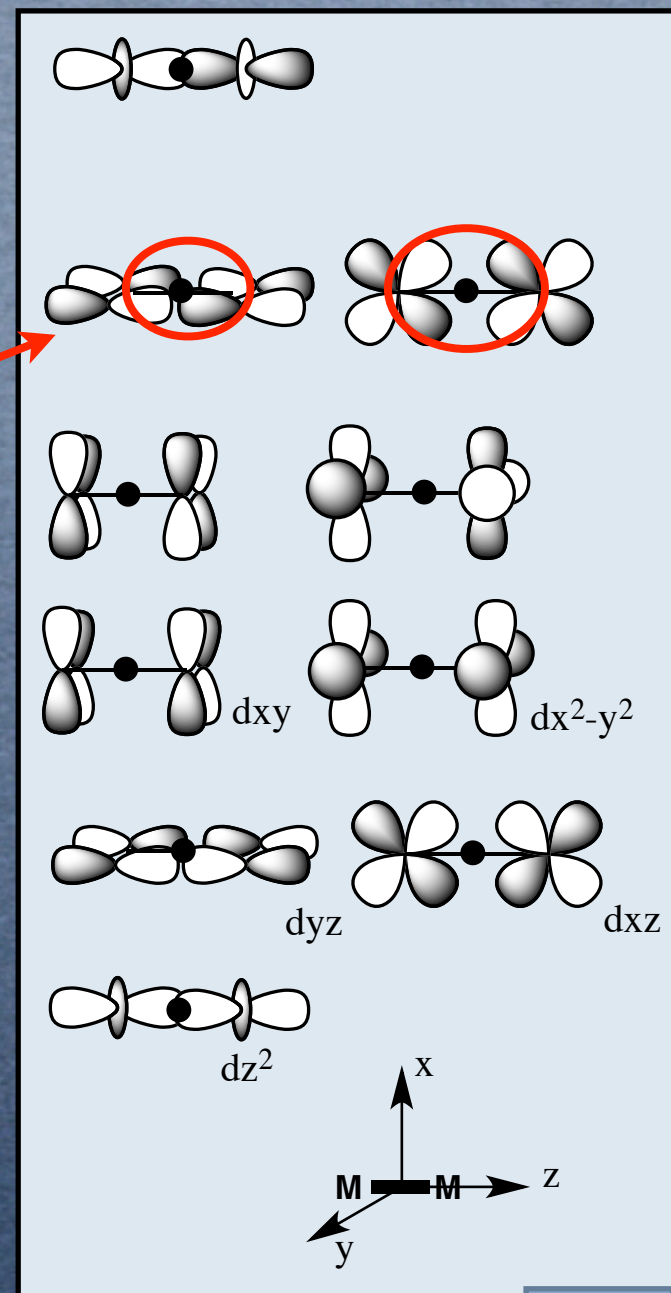


Fig. 7

Metallic Dimers

complete the MO symmetry labels

focus on phase change around center of inversion

no dAO analogy

but

δ around bond inverts through $i \rightarrow u$ must be δ_u

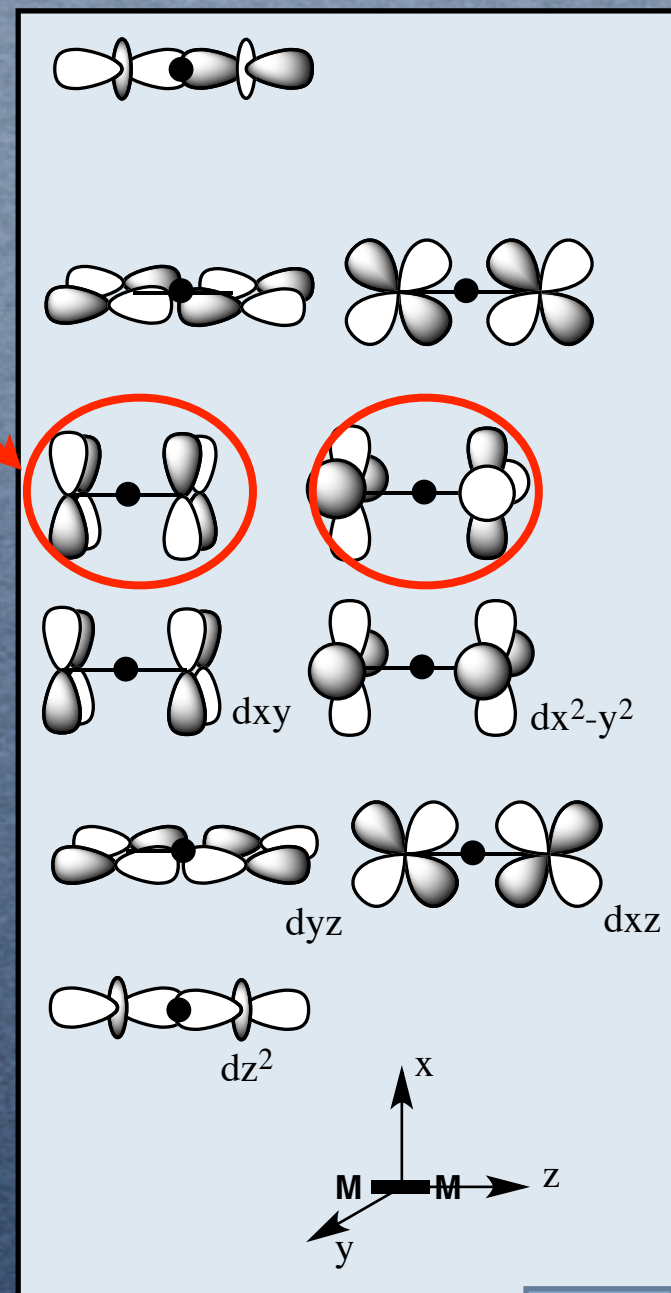


Fig. 7

Metallic Dimers

complete the MO symmetry labels

focus on phase change around center of inversion

looks like d_{xy} & $d_{x^2-y^2} \rightarrow \delta_g$

also

δ around bond symmetric through i $\rightarrow g$

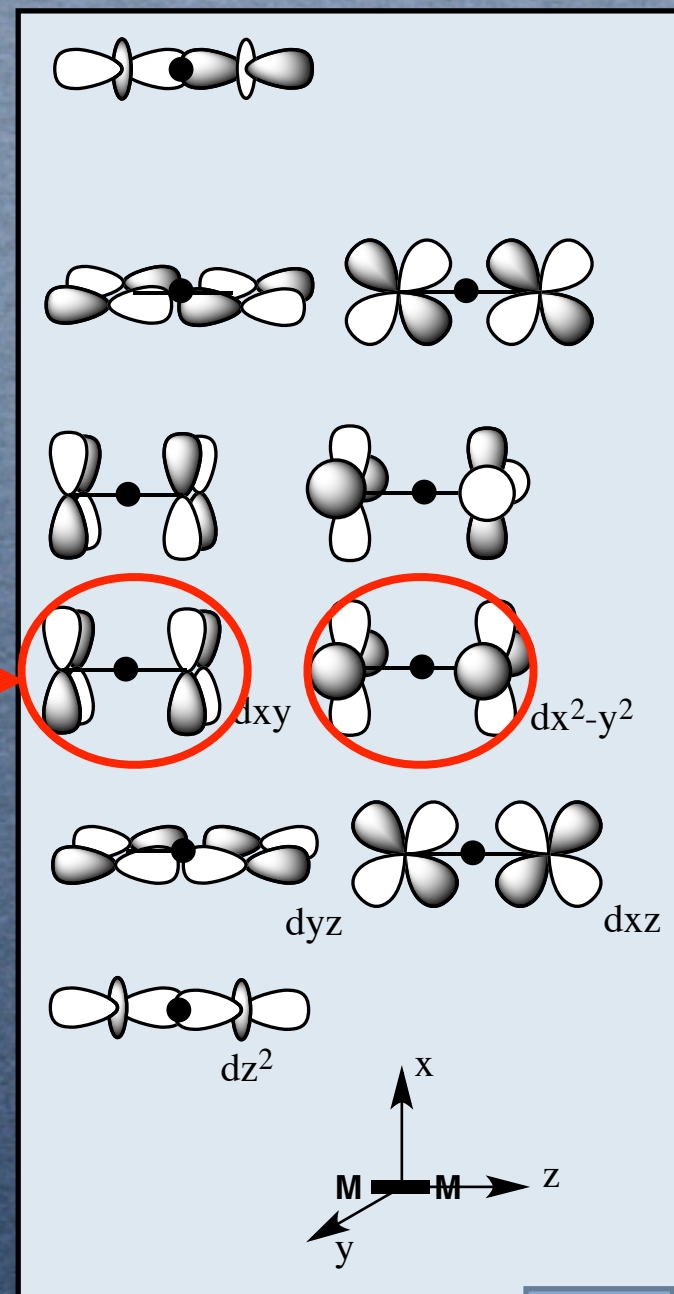


Fig. 7

Metallic Dimers

complete the MO symmetry labels

focus on phase change around center of inversion

looks like p_x & $p_y \rightarrow \pi_u$

also

π around bond inverts through $i \rightarrow u$
no +/- label for π

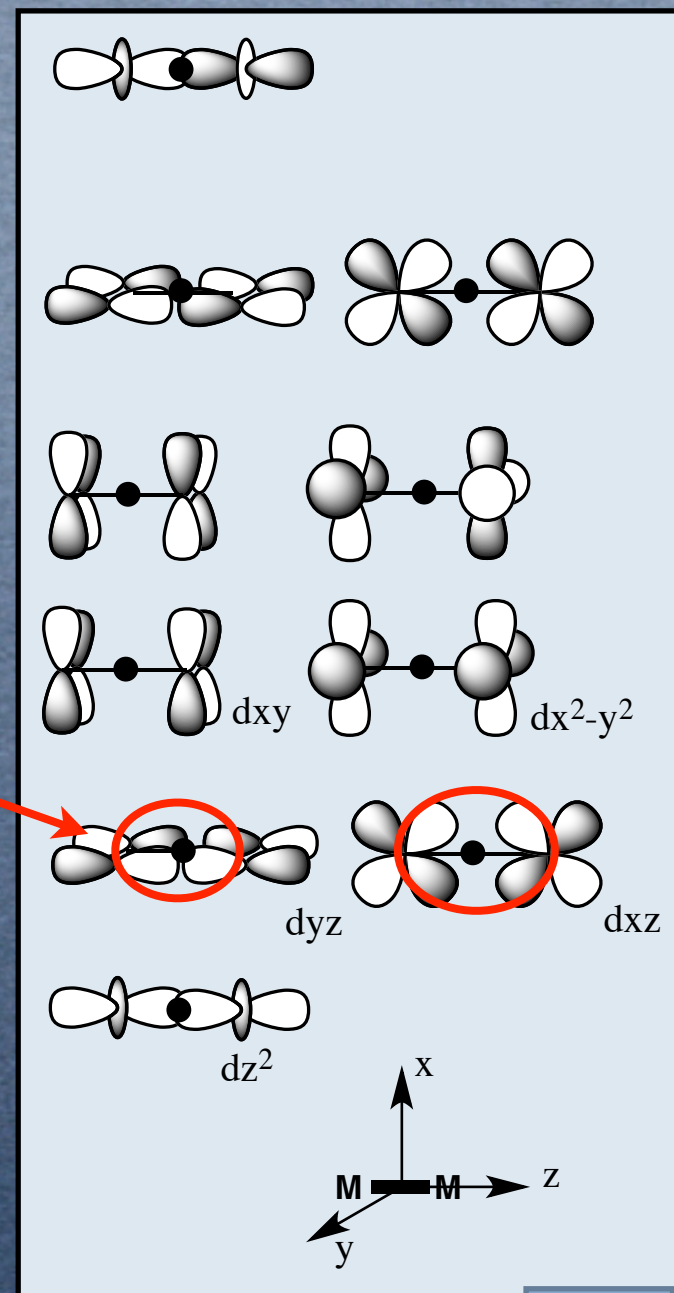


Fig. 7

Metallic Dimers

complete the MO symmetry labels

focus on phase change around center of inversion

looks like sAO $\rightarrow \sigma_g^+$

also

along the bond $\rightarrow \sigma$
symmetric through i $\rightarrow g$
no phase change for $\sigma_v \rightarrow +$

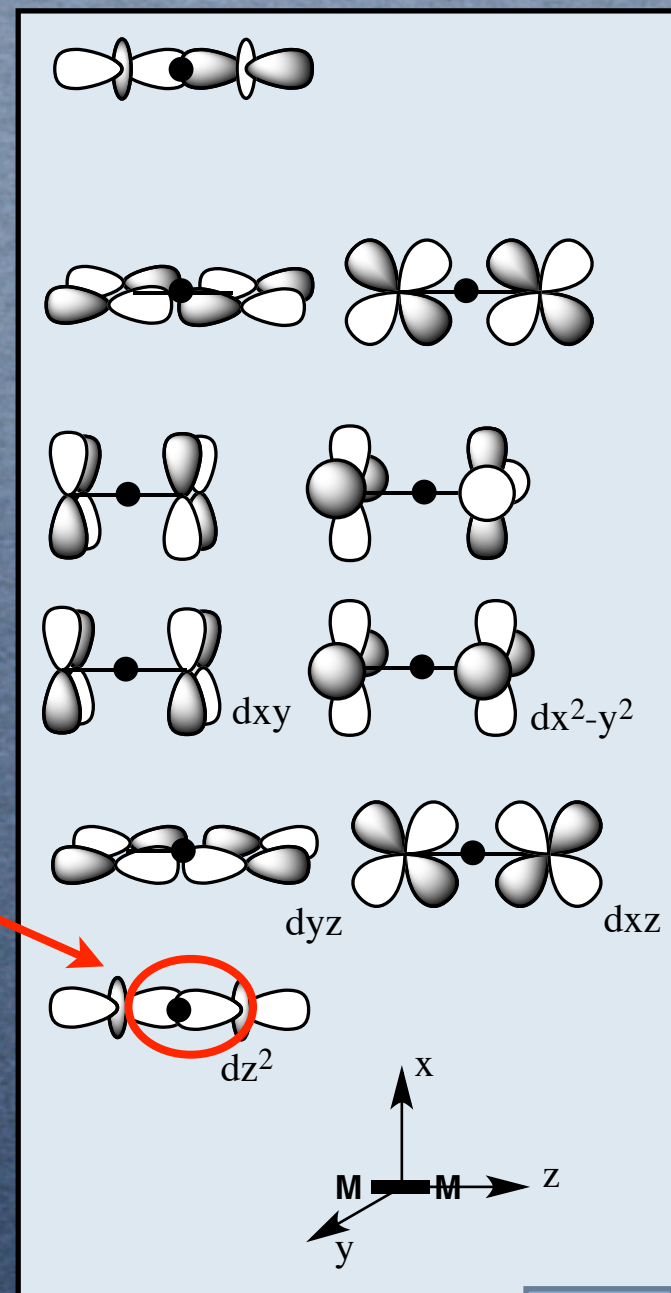


Fig. 7

Metallic Dimers

● bond order

- ◆ ONLY applies to diatomics
- ◆ fill 5 bonding dAOs

quintuple bond!

- ◆ configuration: $\sigma^2\pi^4\delta^4$

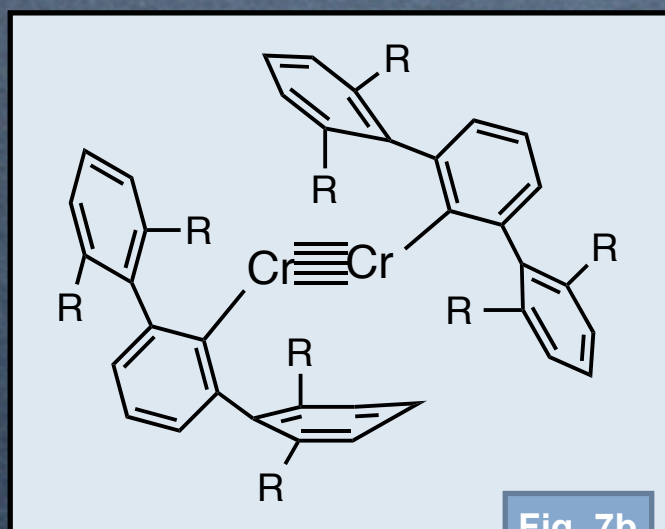


Fig. 7b

Power: 2005
link to paper on
web-site

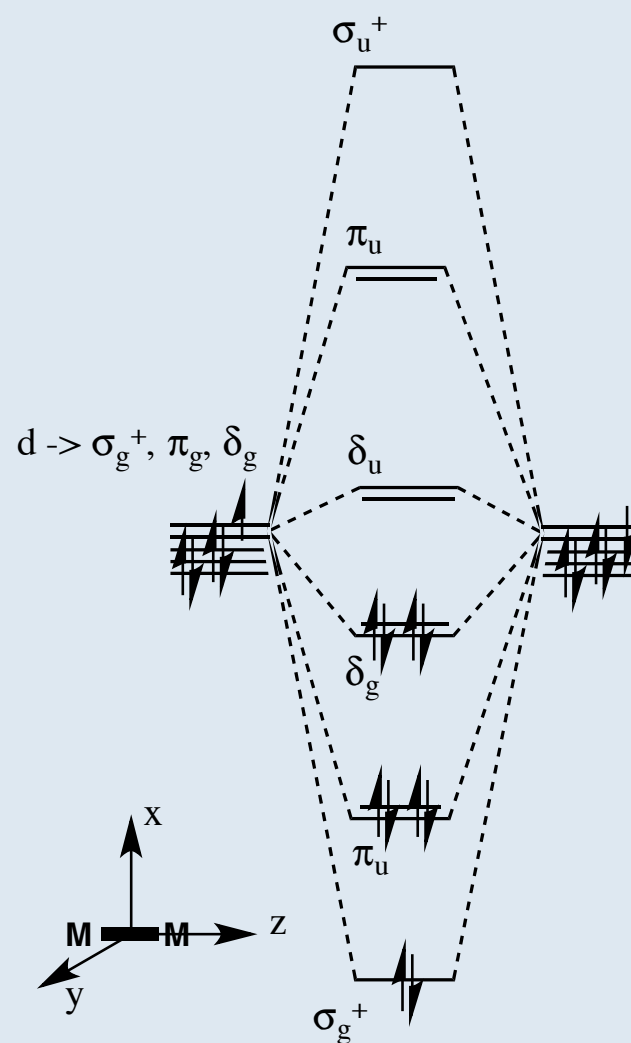


Fig. 7a

M —● M — M ● — M

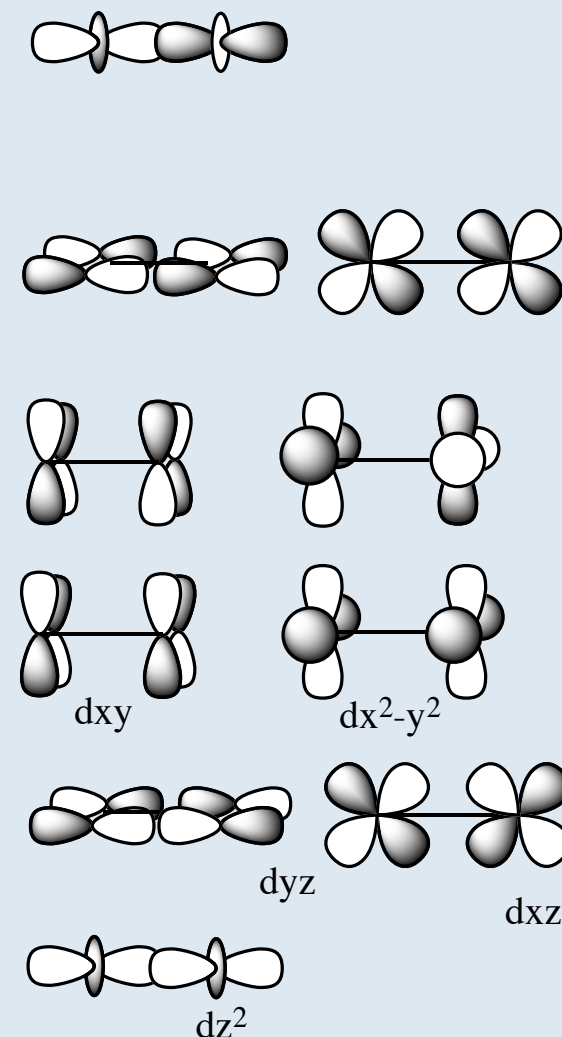


Fig. 8

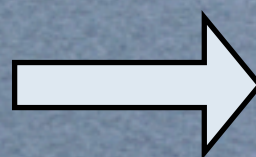
Ligand Fragment Orbitals

● **symmetry can be used to determine the ligand FOs**

- ◆ not covered this year, but notes are available on-line if you are interested

● **SA orbitals are general**

- ◆ you should know L_2 , L_3 , L_4
- ◆ you should be familiar with L_5 , L_6



Symmetry Adapted orbitals

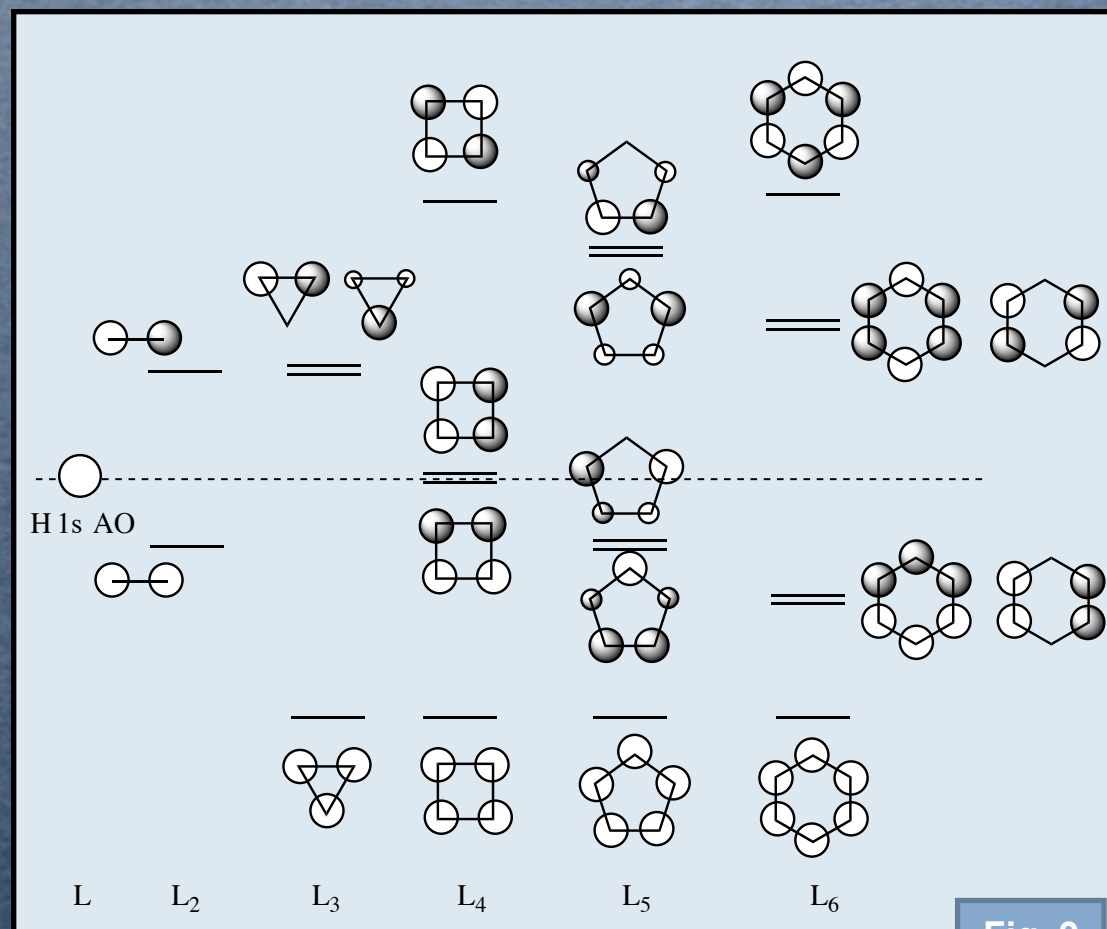


Fig. 9

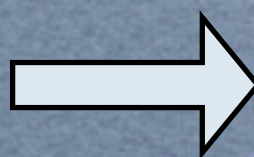
Ligand Fragment Orbitals

● symmetry can be used to determine the ligand FOs

- ◆ not covered this year, but notes are available on-line if you are interested

● SA orbitals are general

- ◆ you should know L_2 , L_3 , L_4
- ◆ you should be familiar with L_5 , L_6
- ◆ can also be used to predict some of the pAO combinations



Symmetry Adapted orbitals

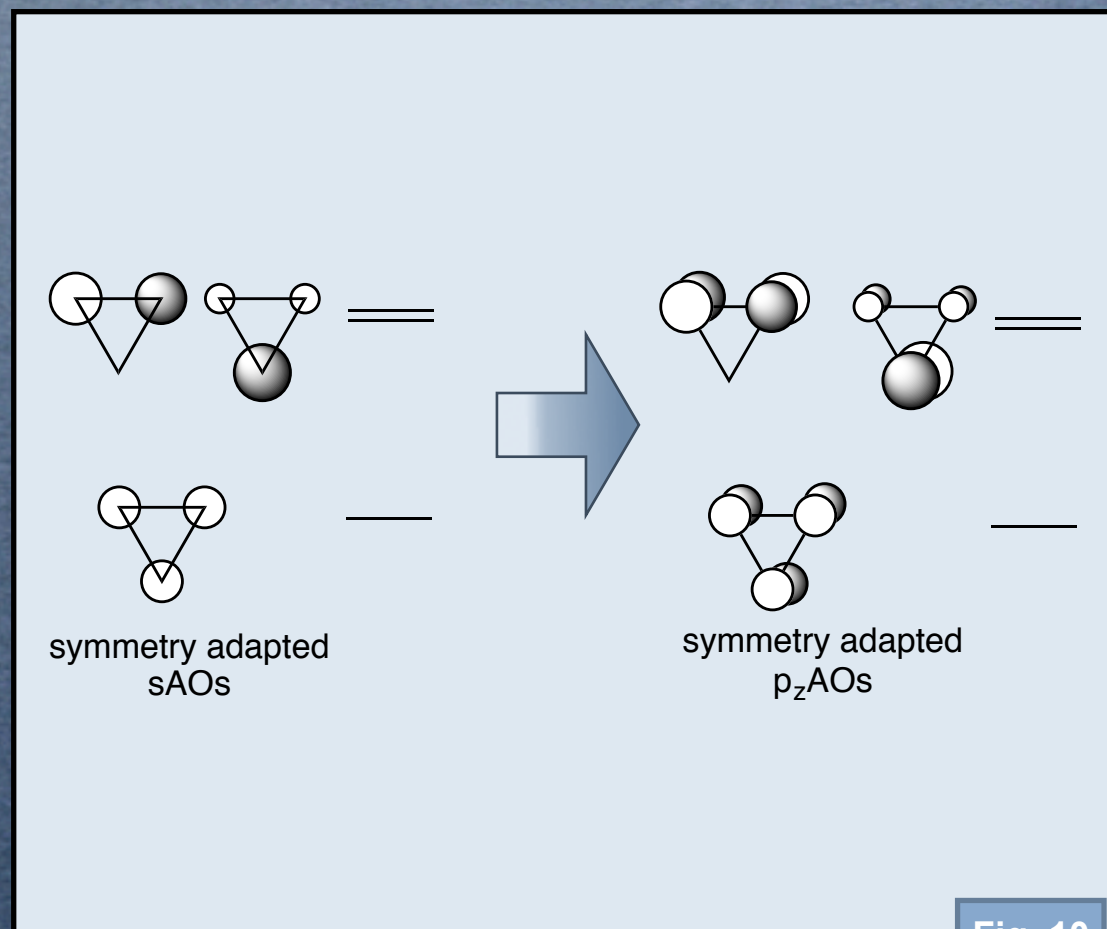
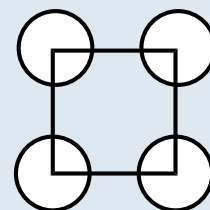
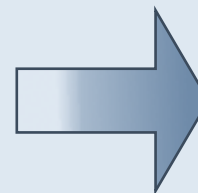
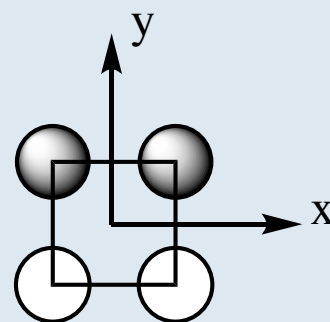


Fig. 10

In-Class Activity

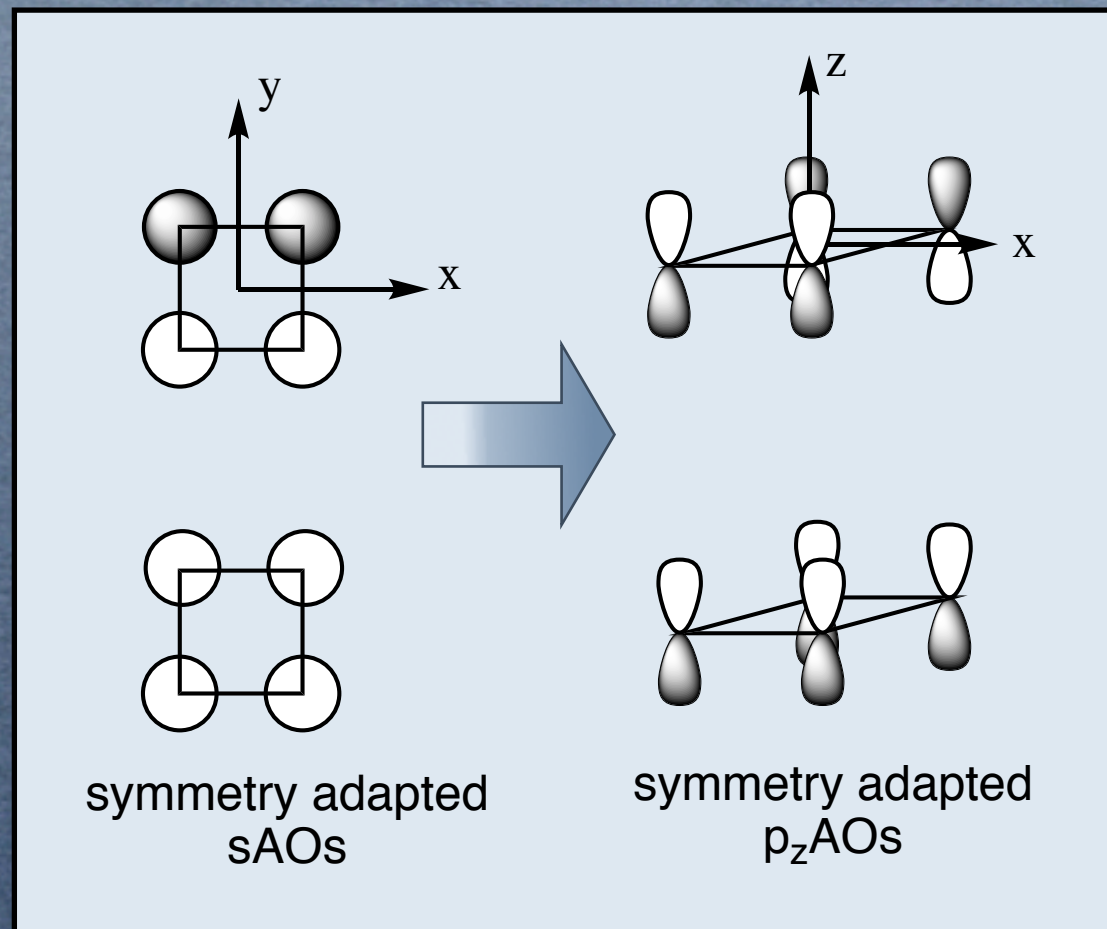
- draw the pAOs that correspond to the following sAO patterns
- what is the symmetry of all FOs under D_{4h}



symmetry adapted
sAOs

In-Class Activity

- draw the pAOs that correspond to the following sAO patterns
- what is the symmetry of all FOs under D_{4h}
 - ◆ y-axis s orbitals $\Rightarrow e_u$
 - ◆ totally symmetric s orbitals $\Rightarrow a_{1g}$
 - ◆ p orbitals, like e_u but invert under mirror plane $\Rightarrow e_g$
 - ◆ all in-phase p orbitals, z-axis $\Rightarrow a_{2u}$ like a_{1g} but invert under mirror plane



Ligand Fragment Orbitals

- degenerate orbitals can rotate among themselves
 - ◆ draw it out for yourself!

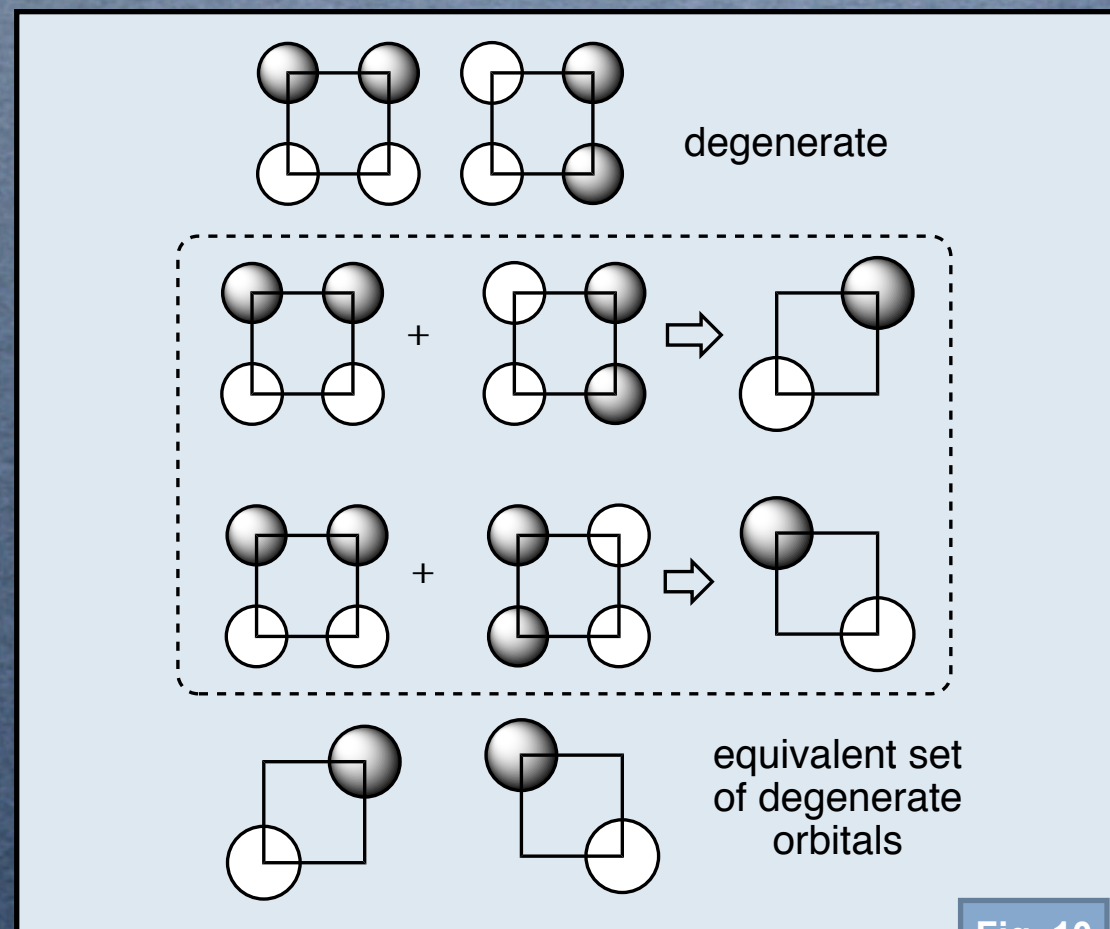
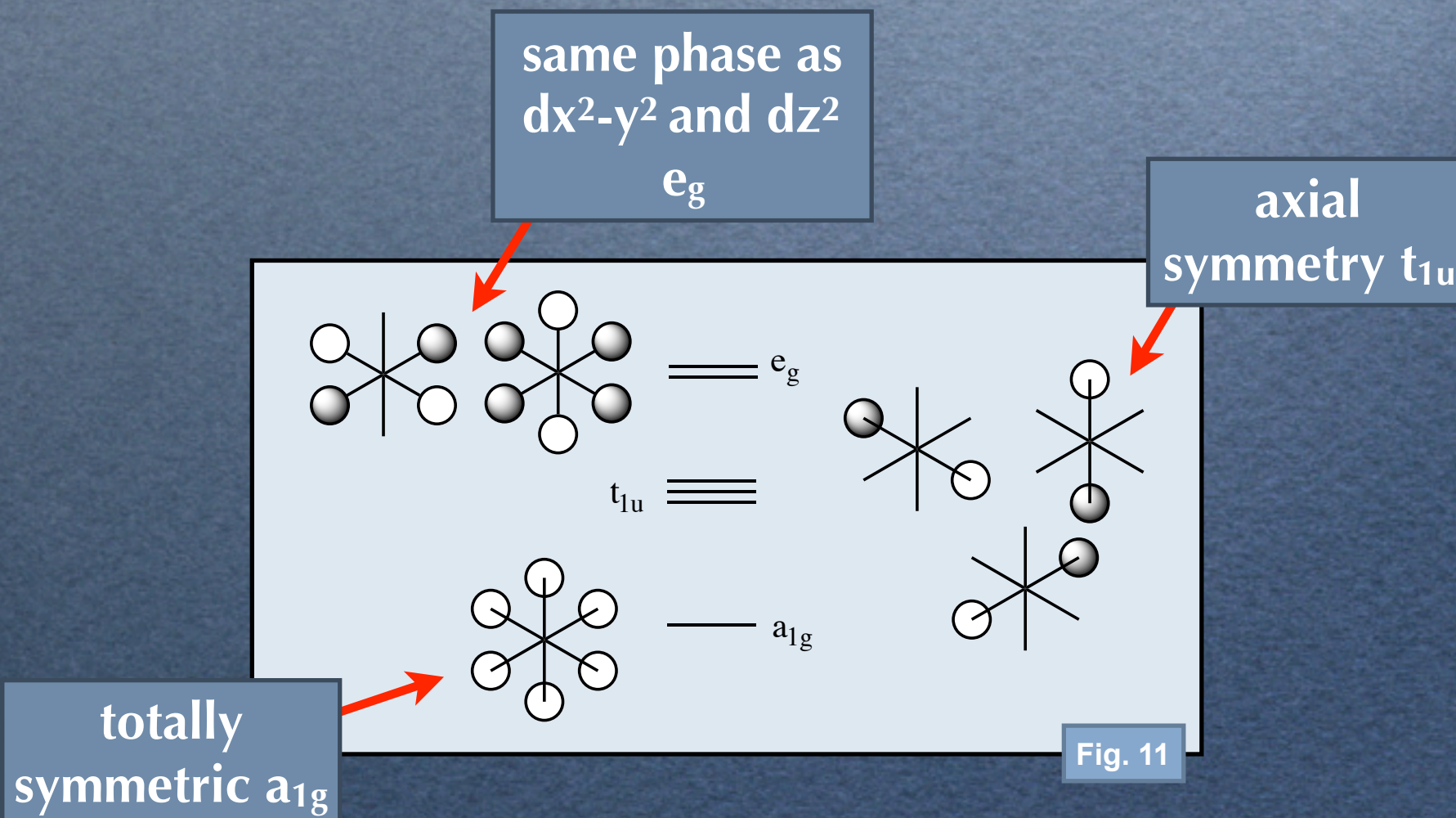


Fig. 10

Octahedral SA Orbitals

● symmetry can be used to determine the ligand FOs

◆ use “tricks” to remember the phase patterns



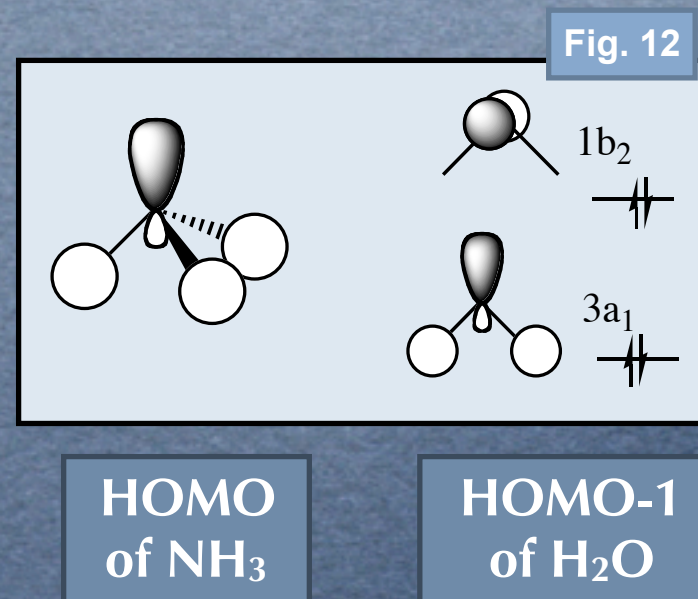
Isolobal Analogy

Ligand fragment orbitals

- ◆ only some orbitals are important

key orbital has σ like characteristics

- ◆ these “mimic” the 1sAO orbital of H
- ◆ looking from the metal orbital appears as sAO
- ◆ isolobal to sAOs
- ◆ typically the HOMO of the ligand
- ◆ BUT not always, can be a deeper MO



σ -type ligands:
all have σ -type FOs which interact with the TM
 NH_3 , NR_3 , PH_3 , PR_3 , OH_2 , R^- , CR_3 , SiR_3

Ligand Fragment Orbitals

**VERY
Important!**

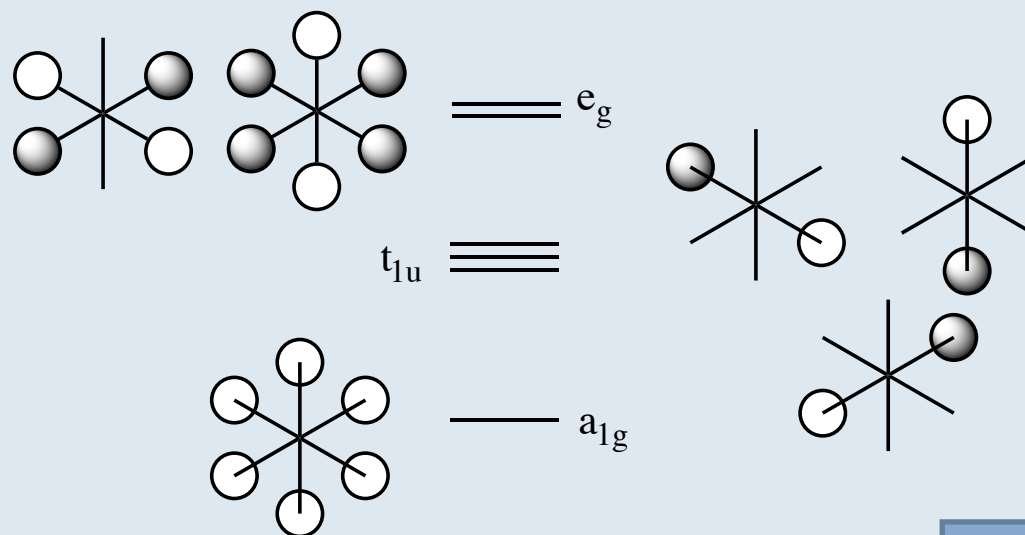


Fig. 11

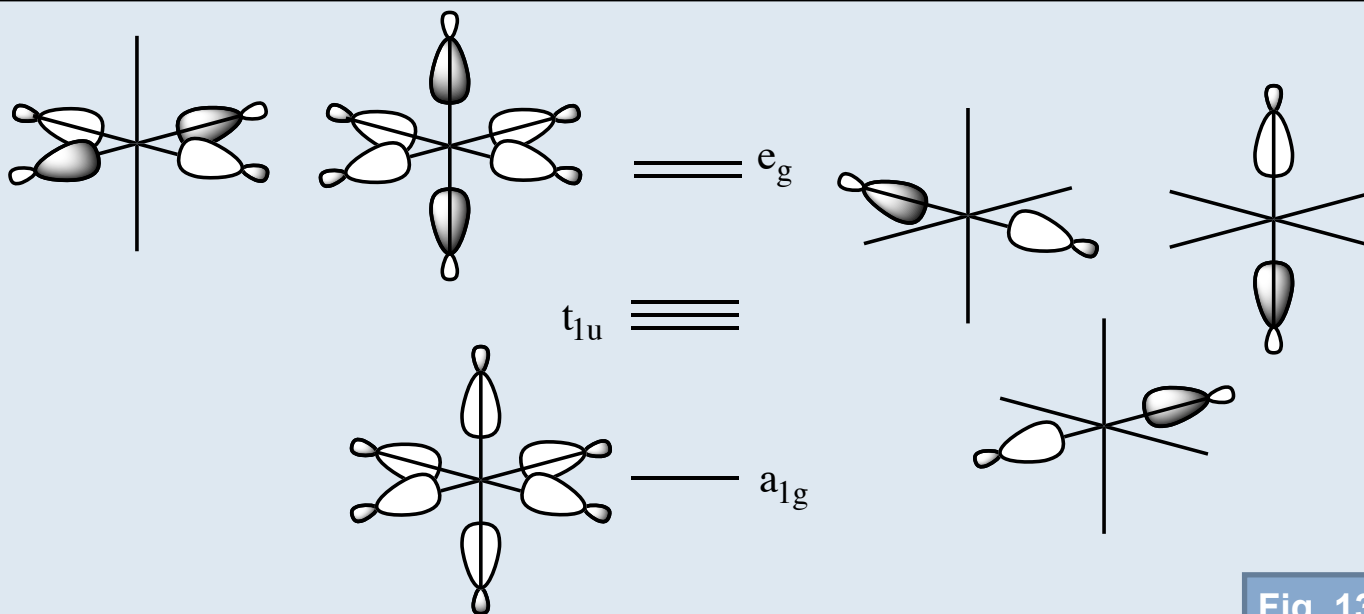


Fig. 13

Ligand Fragment Orbitals

closer through space interactions

slightly antibonding

same phase as dx^2-y^2 and dz^2
 e_g

axial symmetry t_{1u}

essentially non-bonding

2-bonds apart very weak interactions

totally symmetric a_{1g}

totally bonding

closer through space interactions

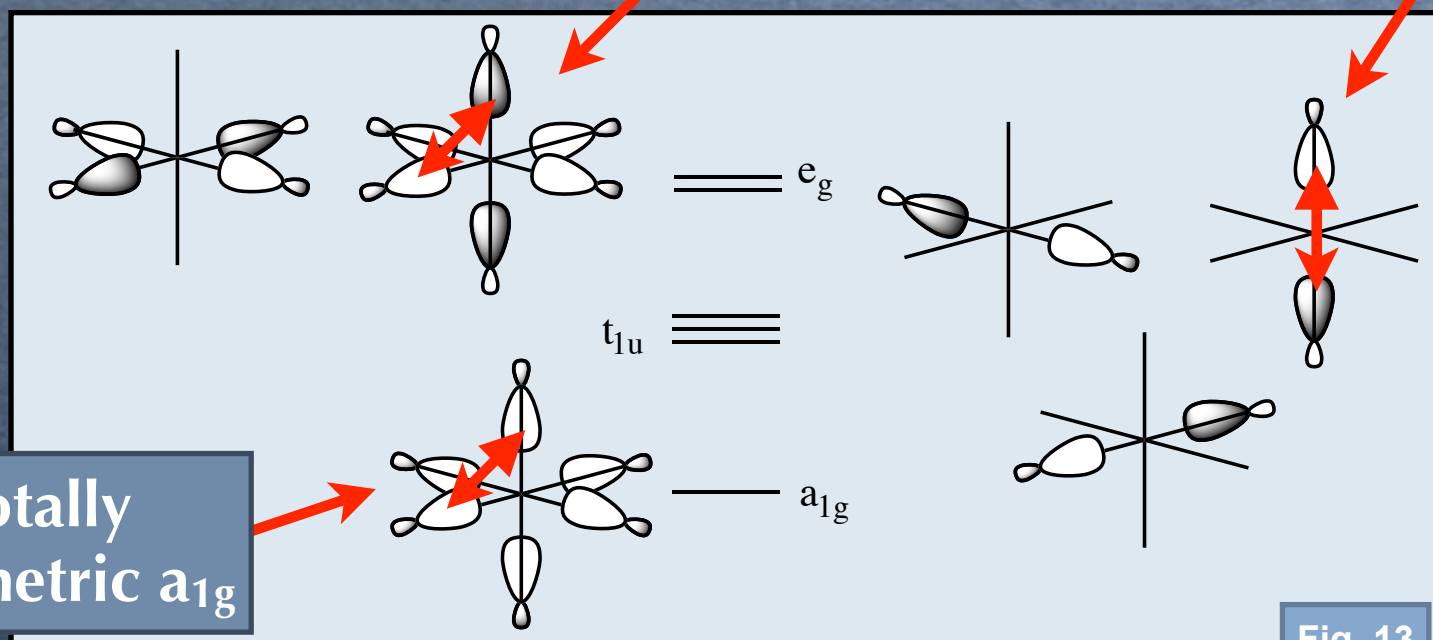


Fig. 13

Octahedral Point Group

- we know orbitals on the metal
- we know the FOs for the ligand

combined in
TM complexes

one more piece to
the puzzle

- **octahedral point group!**
 - ◆ feedback has been that this is a tough point group
 - ◆ there is information online going through each symmetry operation for you
- **related point groups D_{4h} and C_{4v}**
 - ◆ key for TM complexes
 - ◆ if you can conquer O_h then the rest are easy

Octahedral Point Group

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
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	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, xz, yz)
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	(T_x, T_y, T_z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

Fig. 14

Octahedral Point Group

Important!

- ♦ transition metal octahedral complexes
- ♦ clusters
- ♦ solids: unit cells and interstitial sites

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Ruby: Cr^{3+}
replaces Al^{3+}
in Al_2O_3

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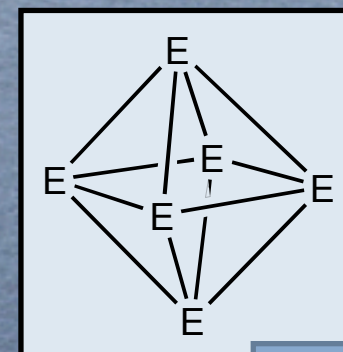
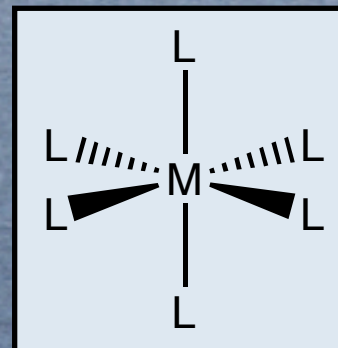


Fig. 15

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Δ_{oct}
 $\text{Ni}(\text{OH}_2)_6$ green
 $\text{Ni}(\text{NH}_3)_6$ purple

Emerald: Cr^{3+} in the
octahedral sites of
Beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

Visualisation

Focus on cube

- ◆ emphasis on C_2 and C_4 axes

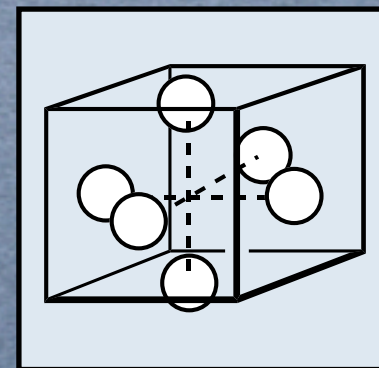
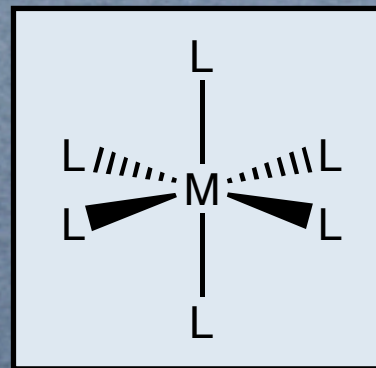
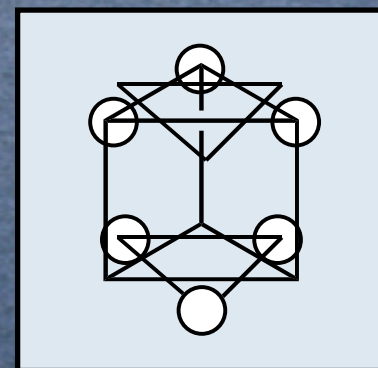
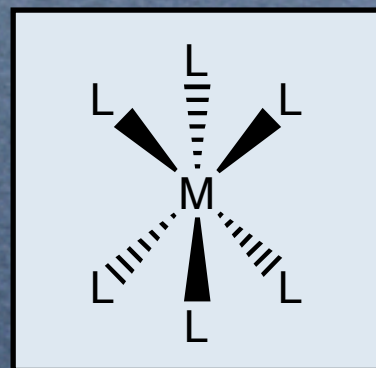


Fig. 16

Focus on double prism

- ◆ emphasis on C_3 axes



Key Symmetry Operations

$$E \ 8C_3 \ 6C_2 \ 6C_4 \ 3C_2 \ i \ 6S_4 \ 8S_6 \ 3\sigma_h \ 6\sigma_d$$

remember D_{3h}

- ♦ difference between elements and operations

6C₄ and 3C₂ operations (axes coincident)

- ♦ C₄ axis through center of each pair of faces
- ♦ three pairs of faces
- ♦ thus 3 C₄ axes
- ♦ each has 4 rotation operations
- ♦ but one is already counted → $C_4^4 = E$
- ♦ and one is associated with a lower n axis → $C_4^2 = C_2^1$
- ♦ therefor 3 C₄ axes with 2 operations each
- ♦ therefor 3 C₂ axes with 1 operation each
- ♦ =6C₄ and =3C₂

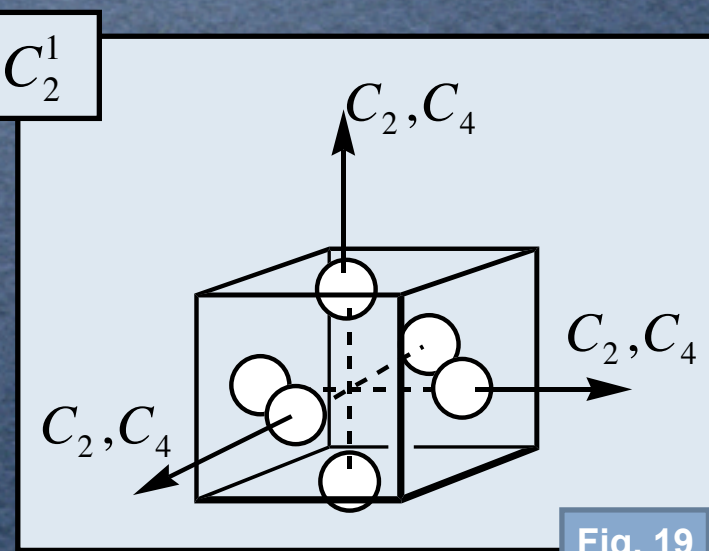


Fig. 19

Descent in Symmetry

- TM complexes can be almost octahedral but have a lower symmetry due to having a mixture of ligands
- higher symmetry group => more operations
 - lower symmetry group => fewer operations
 - lower group is called a sub-group
 - as we eliminate symmetry elements from a group we descend in symmetry
 - complex!
 - see Table 1 in your notes

C _{2v}	C ₂	C _s							
C _{3v}	C ₃	C _s							
C _{4v}	C ₄	C _{2v}							
D _{3h}	C _{3h}	C _{3v}							
	D ₃	C ₃	also	C _{2v}					
D _{4h}	D _{2d}	D _{2h}	D ₂	C _{4h}	C _{4v}	C _{2v}			
	D ₄	C ₄	S ₄	C _{2h}	C ₂	C _s	C _i		
D _{6h}	D _{3d}	D _{2h}	C _{6v}	C _{3v}	C _{2v}	C _{2h}			
	D ₆	D _{3h}	C _{6h}	C ₆	C _{3h}	D ₃	S ₆	D ₂	C ₃
T _d	D _{2d}	C _{3v}	C _{2v}	also	S ₄	D ₂	C ₃	C ₂	C _s
O _h	T _d	D _{4h}	D ₄	D _{2d}	C _{4h}	C _{4v}	D _{2h}	D ₂	C _{2h}
	D _{3d}	D ₃	C _{3v}	S ₆	C ₃	also	C ₄	S ₄	C _{2v}

Table 1 A selection of examples showing descent in symmetry, descent after C_{2v}, C_{3v} are assumed for the higher point groups.

Descent in Symmetry

- TM complexes can be almost octahedral but have a lower symmetry due to having a mixture of ligands

similar to forming the correlation diagrams:
 H_2O
linear \rightarrow bent

MOs remain very similar
BUT
symmetry labels change

Important!

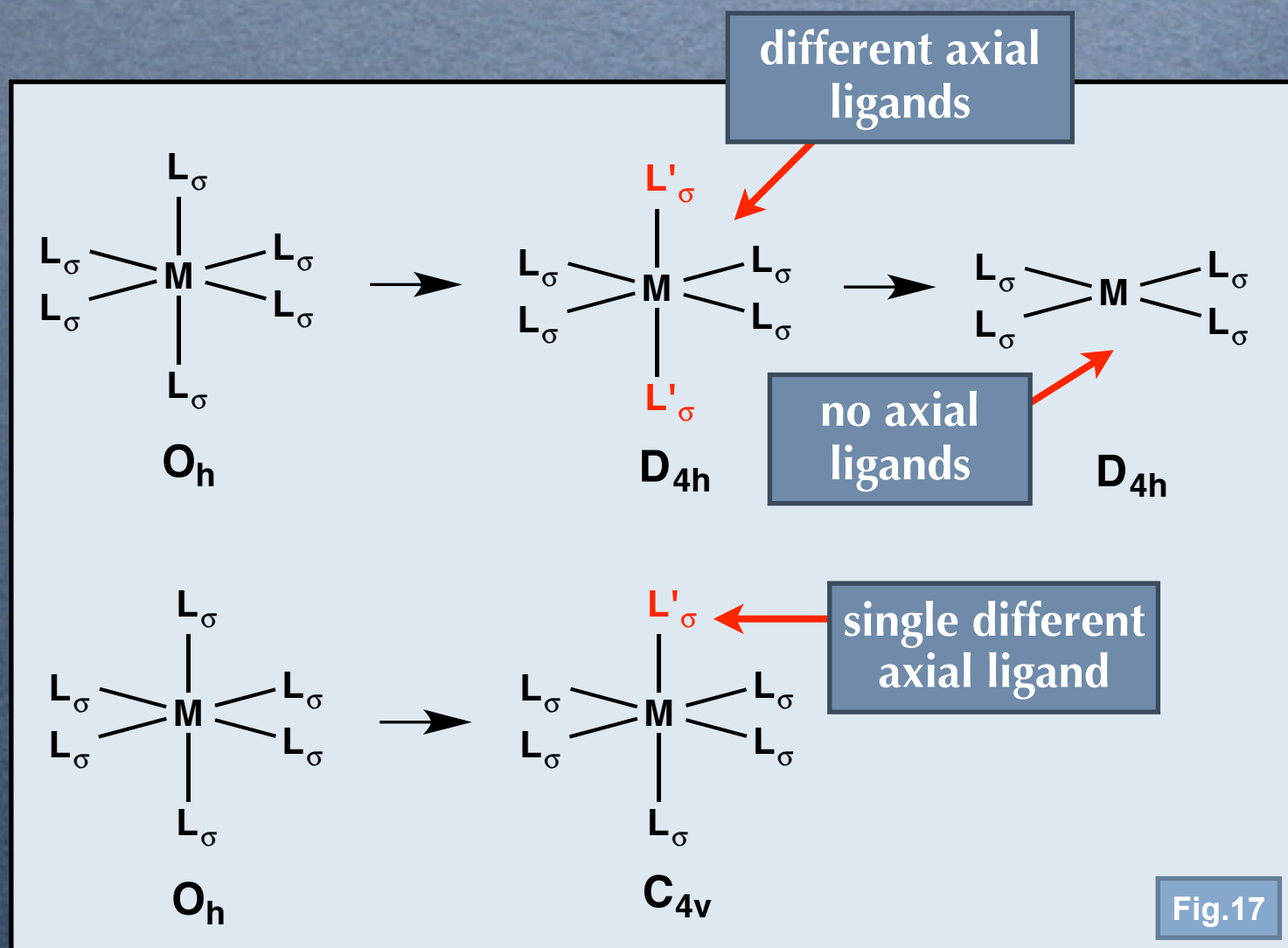


Fig.17

Descent in Symmetry

● example D_{3h} has symmetry elements: E $2C_3$ $3C_2$ σ_h $2S_3$ $3\sigma_v$

● D_3 has: E , $2C_3$, $3C_2$

◆ “lost” σ_h , $2S_3$, $3\sigma_v$

● C_{3v} has: E , $2C_3$, $2S_3$

◆ “lost” σ_h , $3C_2$, $3\sigma_v$

In Class Activity

● List the elements in D_{4h}

● List the elements in C_{4v}

● which elements have been lost?

Key Points

- be able to draw MO diagrams that include dAOs
- be able to explain σ , π and δ interactions for diatomic molecules
- be able to draw MO diagrams for M_2 , MM' , ME
- be able to discuss bond order with respect to diatomic molecules
- be able to draw and use ligand symmetry adapted fragment orbitals for L_n $n=1-4$ (rings) and O_h L_6
- be able to explain and use the isolobal analogy
- be able to locate and describe all of the Octahedral point group symmetry elements and operations
- be able to describe and use descent in symmetry

Finally

<http://www.huntresearchgroup.org.uk/>

See my web-site

- ♦ notes AND slides
- ♦ link to panopto when it becomes available
- ♦ optional background support for beginners
- ♦ optional material to take you a little further
- ♦ links to interesting people and web-sites
- ♦ links to relevant research papers on MOs
- ♦ model answers!!

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Hunt Research Group

The Hunt Research Group is a theoretical and computational chemistry group which carries out theoretical development and computational modeling.

Our research is focused towards understanding the chemistry and physics associated with solvents and solvation, particularly as this applies to **ionic-liquids** and **deep eutectic solvents**.

We study the making and breaking of molecules. This includes **catalytic mechanisms** (for group II and frustrated Lewis acid-base pairs) and chemical **decomposition** (for green fuels, bio-fuels and ionic-liquids).

Overarching all of these areas is a specialisation in **hydrogen-bonding**, acid-base interactions and an expertise in the **MO theory** of bonding. We have developed the Effective MO Method for interrogating the electronic structure of liquids and study **charge partitioning** and interactions within molecules.



5th October 2019

Imperial Chemistry

news archive

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July 2019

Molecular orbital of the month This is a MO from SnOTf_4 . OTf is a triflate anion $[\text{SO}_3\text{CF}_3]^-$ which coordinates to the central tin (Sn) metal through oxygen atoms. SnOTf_4 is a novel catalyst for activating methane and thus producing useful molecules like methanol. Using methane from biomass or natural gas sources as a feedstock to build more complex molecules is a promising area. We also have the advantage of replacing transition metals with less expensive and more abundant main group metals. This new catalyst is unusual in that the ligand has a larger effect on reactivity than the central metal.

