Molecular Orbitals in Inorganic Chemistry

Dr. P. Hunt
p.hunt@imperial.ac.uk
Rm 110F (MSRH)
http://www.ch.ic.ac.uk/hunt/

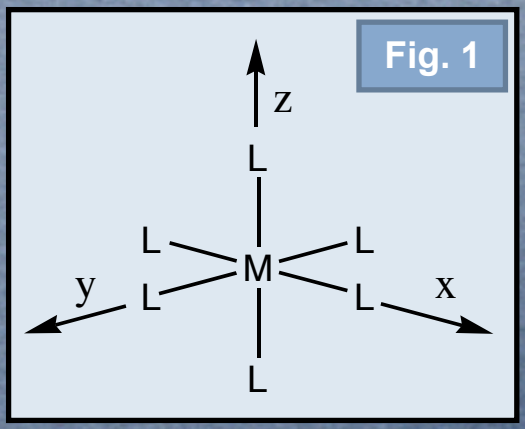
Outline

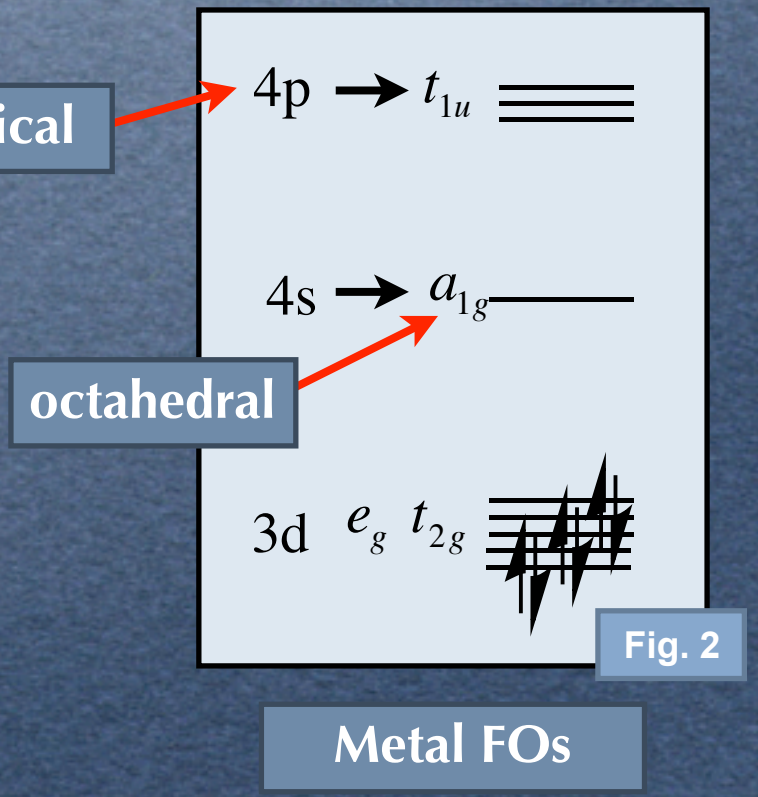
- Metallic dimers
- Ligand symmetry adapted orbitals and the isolobal analogy
- The octahedral point group

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





Octahedral Complexes

- **know how to draw dAOs!**
  - positive lobe in quadrant defining the orbital

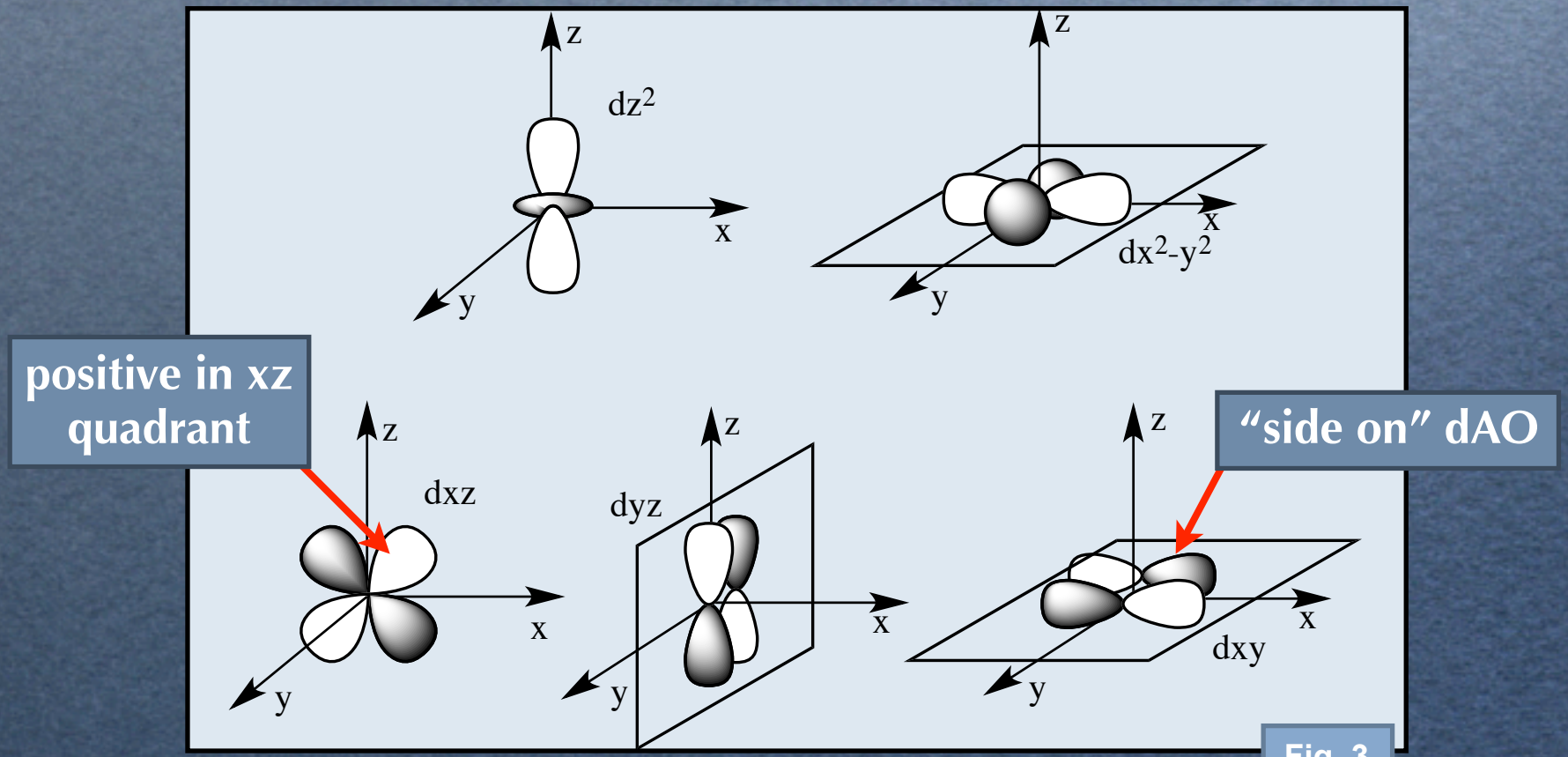


Fig. 3

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-> σ_g^+
  - p_z-> σ_u^+ p_x & p_y-> π_u
  - dz^2-> σ_g^+
  - dxy, dx^2-y^2-> δ_g
  - dyz, dxz -> π_g

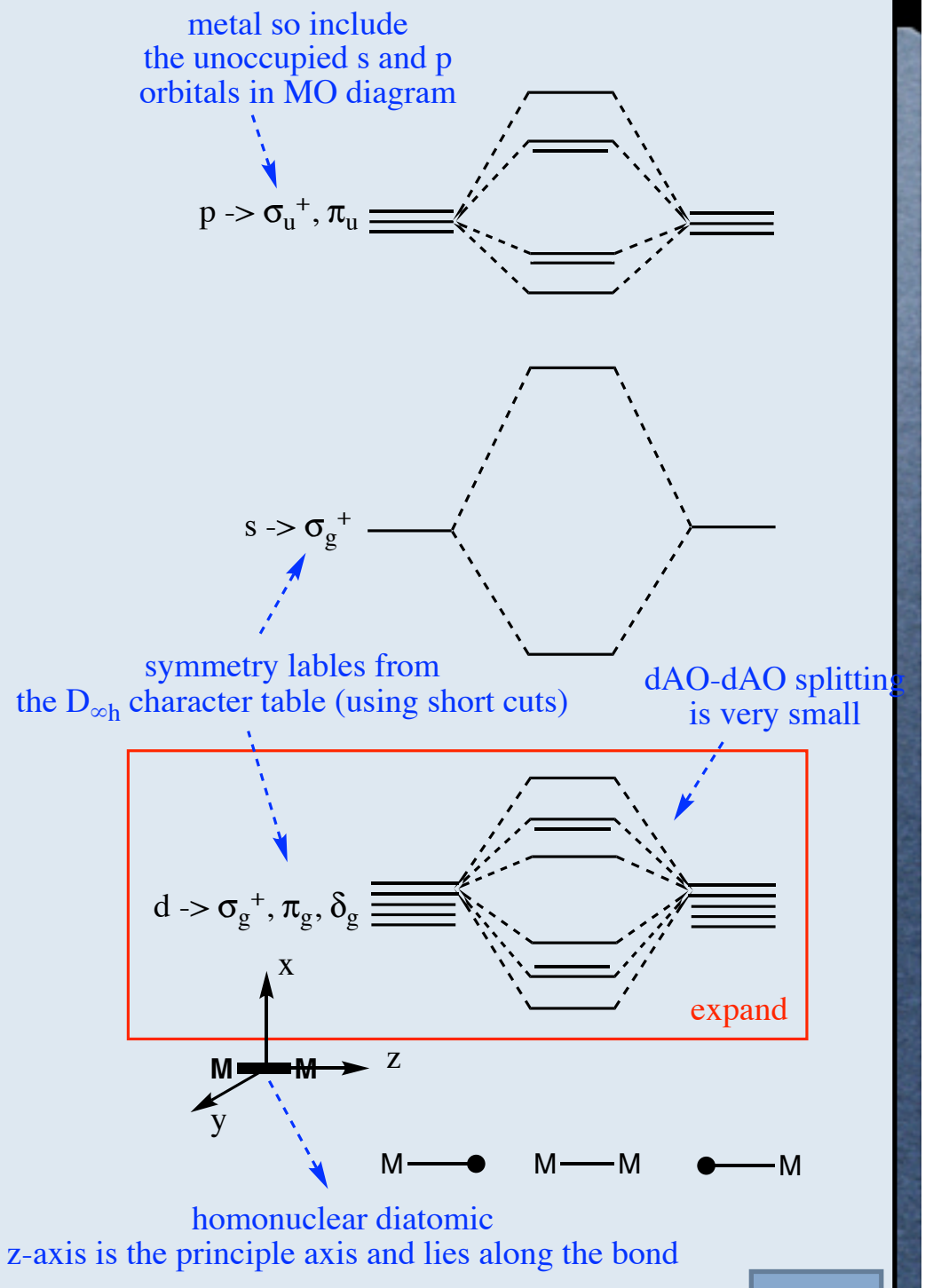


Fig. 4

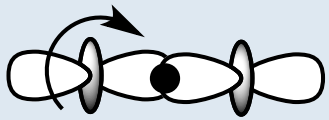
Symmetry Tips

- classify interactions

Important!

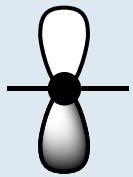
σ-type

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

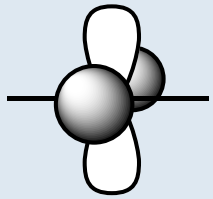


Fig. 6

know your Greek alphabet!

α, β, γ, δ, σ, π
Α, Β, Γ, Δ, Σ, Π

Metallic Dimers

focus dAO region

- combine FO bonding and antibonding pairs
- dz^2-> σ (green)
- dxy, dx^2-y^2-> δ (pink)
- dyz, dxz -> π (blue)

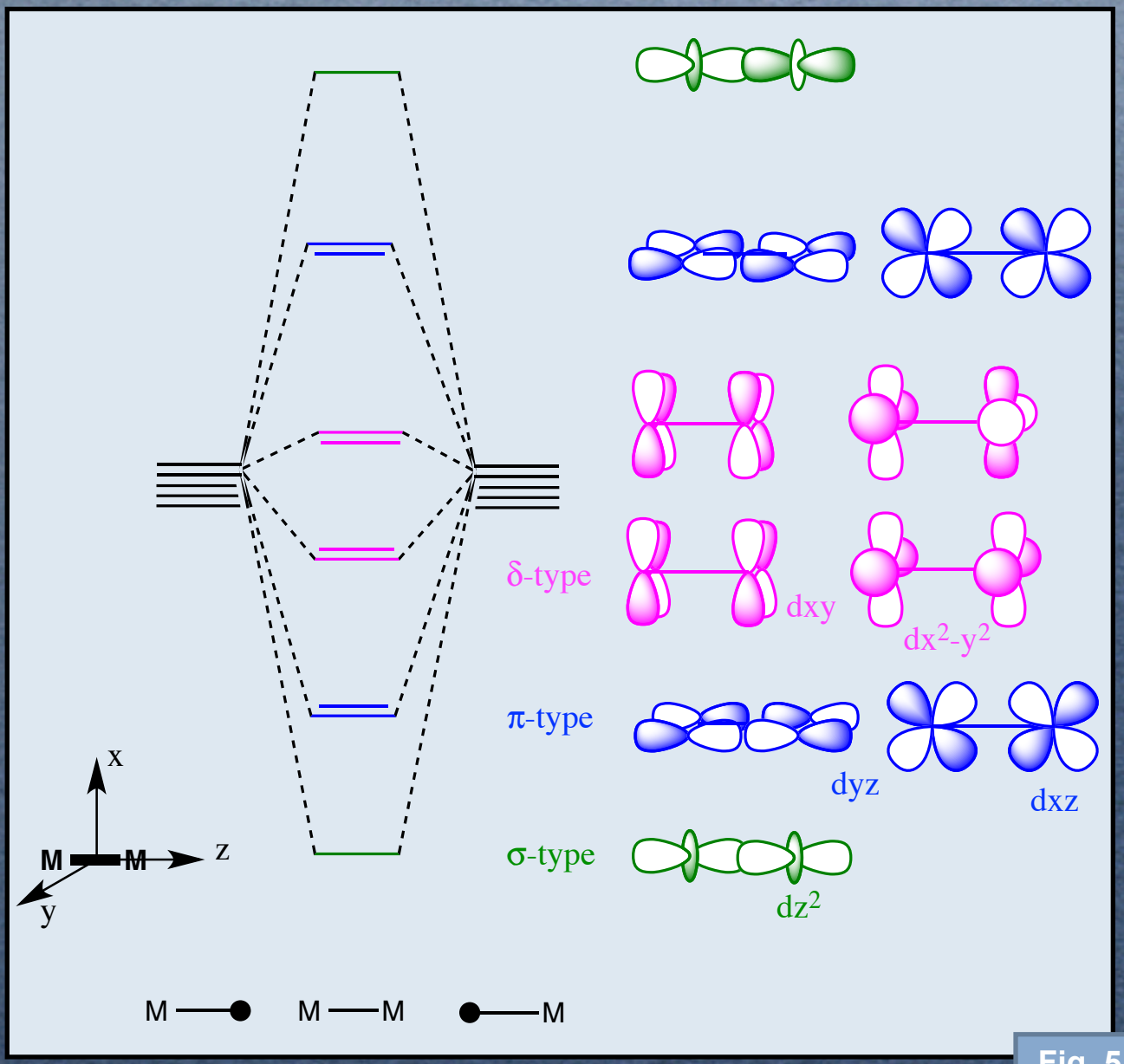


Fig. 5

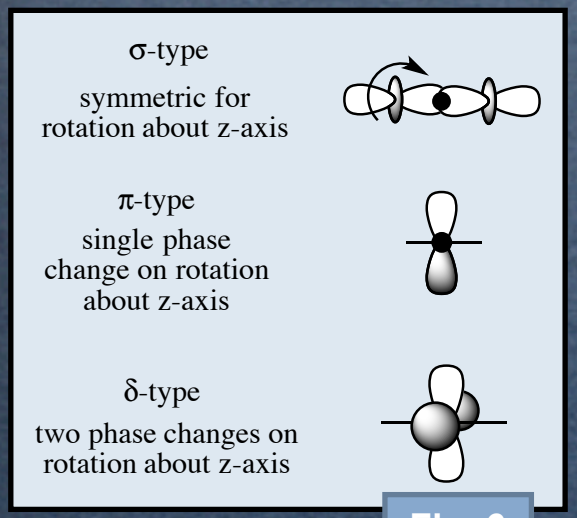


Fig. 6

Metallic Dimers

- **complete the MO symmetry labels**

focus on phase change around center of inversion

looks like z-axis -> σ_u^+

also

along the bond -> σ
inverts through i -> u
no phase change for σ_v -> +

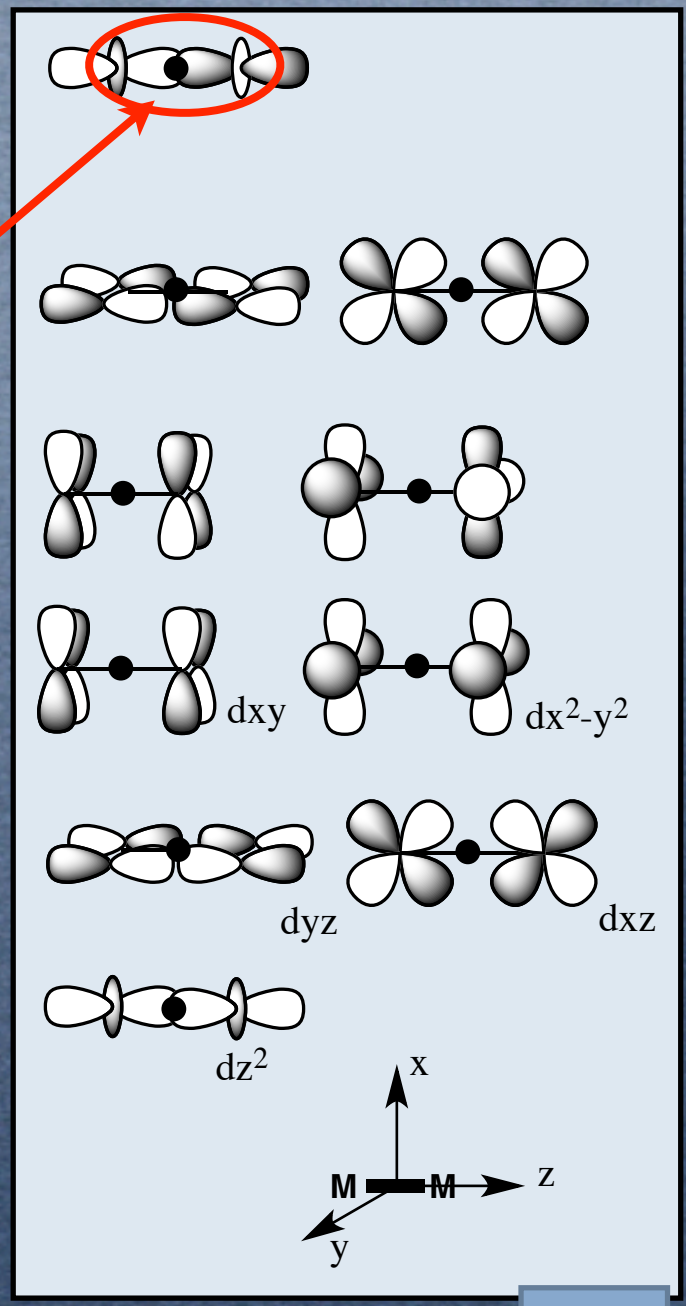


Fig. 7

Metallic Dimers

- **complete the MO symmetry labels**

focus on phase change around center of inversion

looks like dxz & dyz -> π_g

also

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

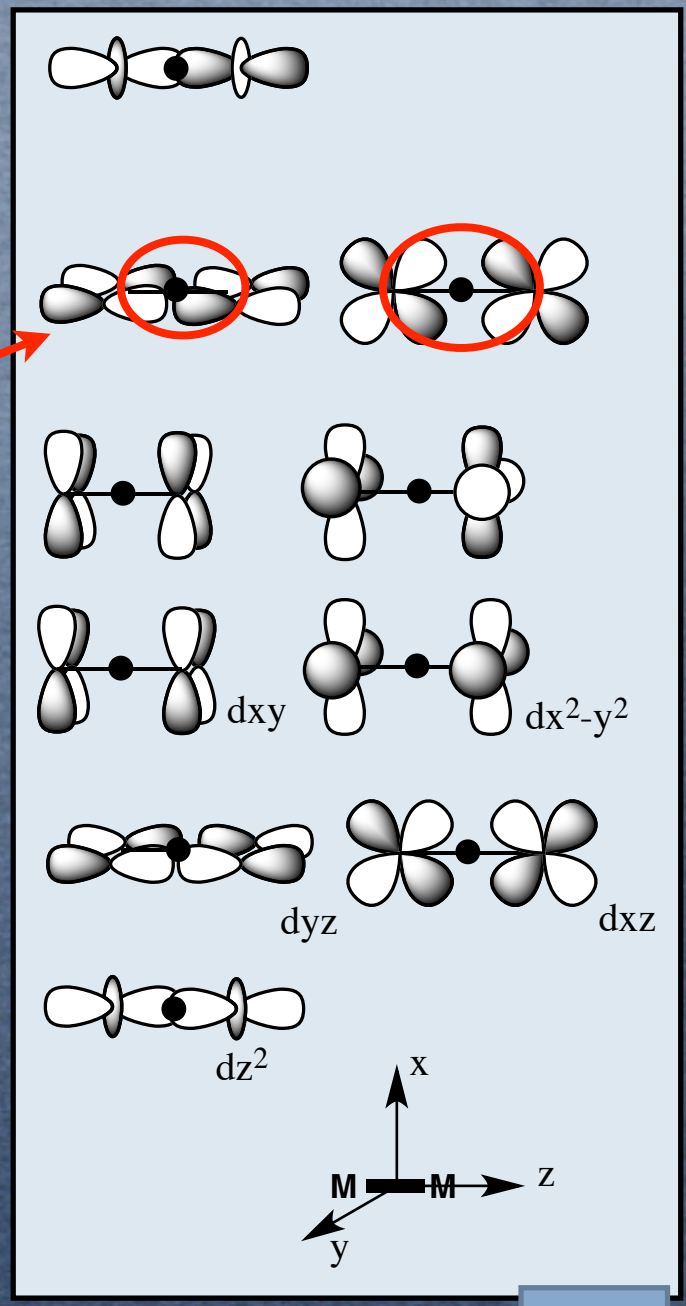


Fig. 7

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 -> u must be δ_u

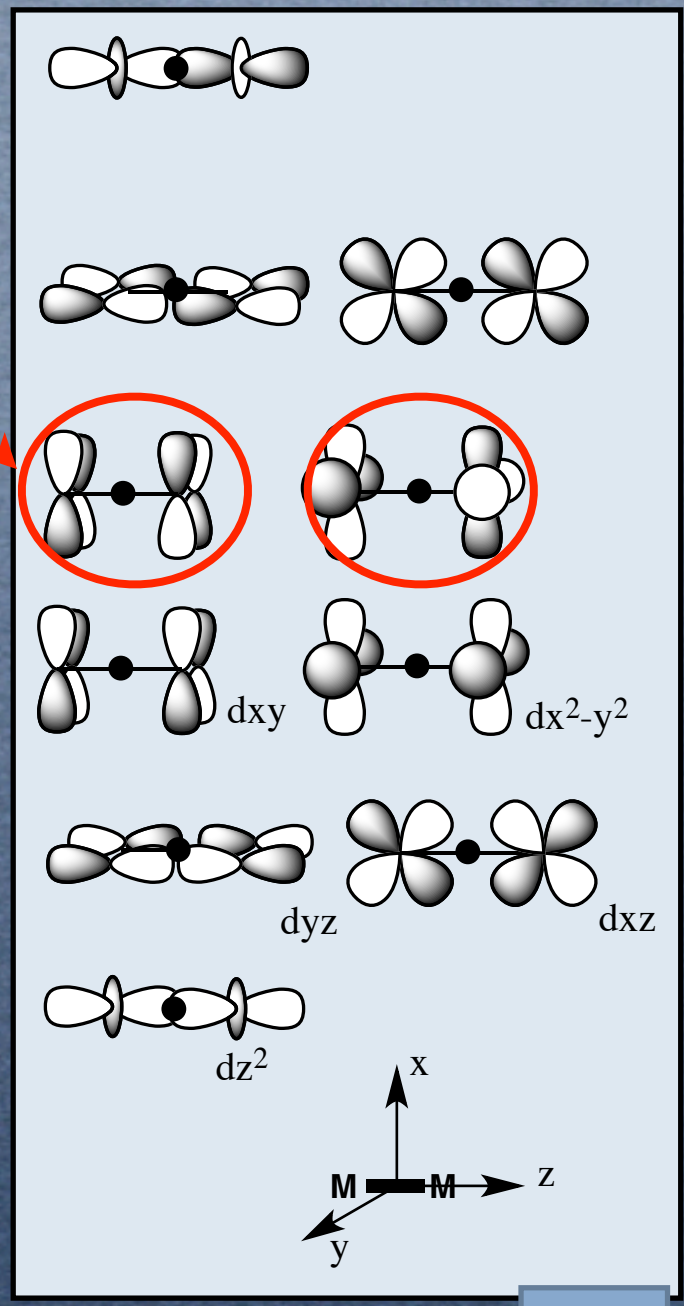


Fig. 7

Metallic Dimers

- complete the MO symmetry labels

focus on phase change around center of inversion

looks like dxy & dx^2-y^2 -> δ_g

also

δ around bond symmetric through i -> g

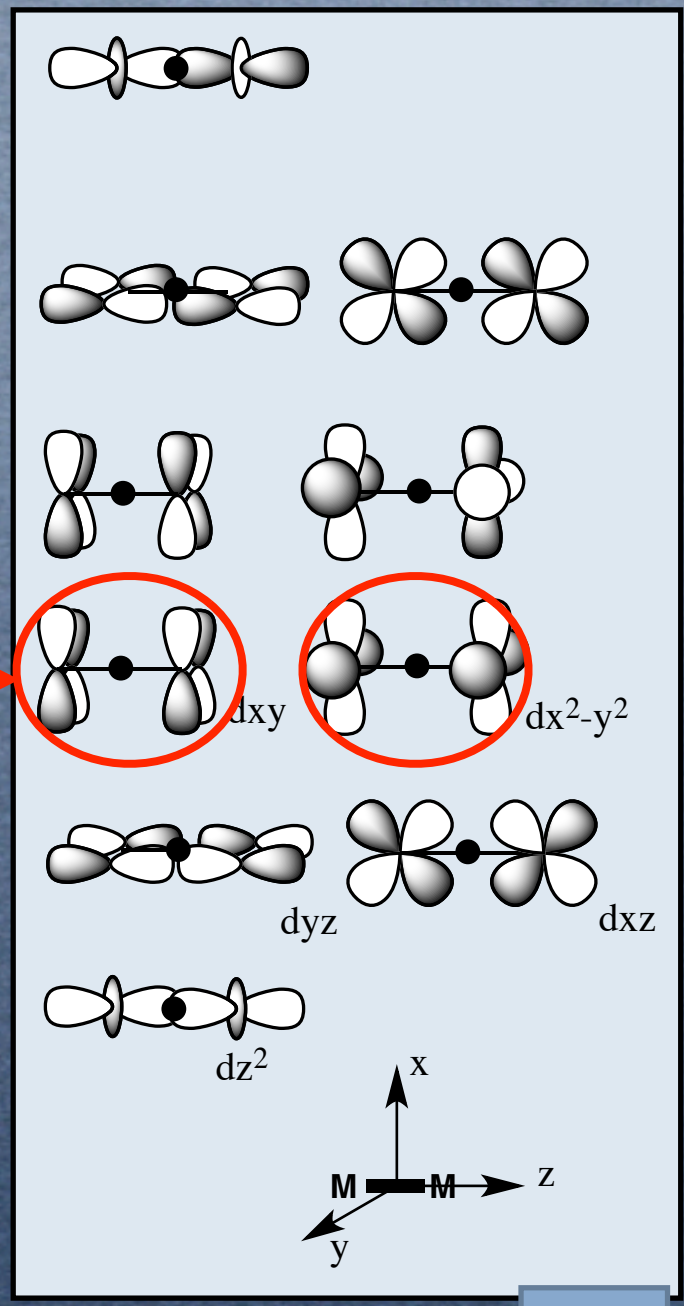


Fig. 7

Metallic Dimers

- complete the MO symmetry labels

focus on phase change around center of inversion

looks like p_x & p_y -> π_u

also

π around bond inverts through i -> u
no +/- label for π

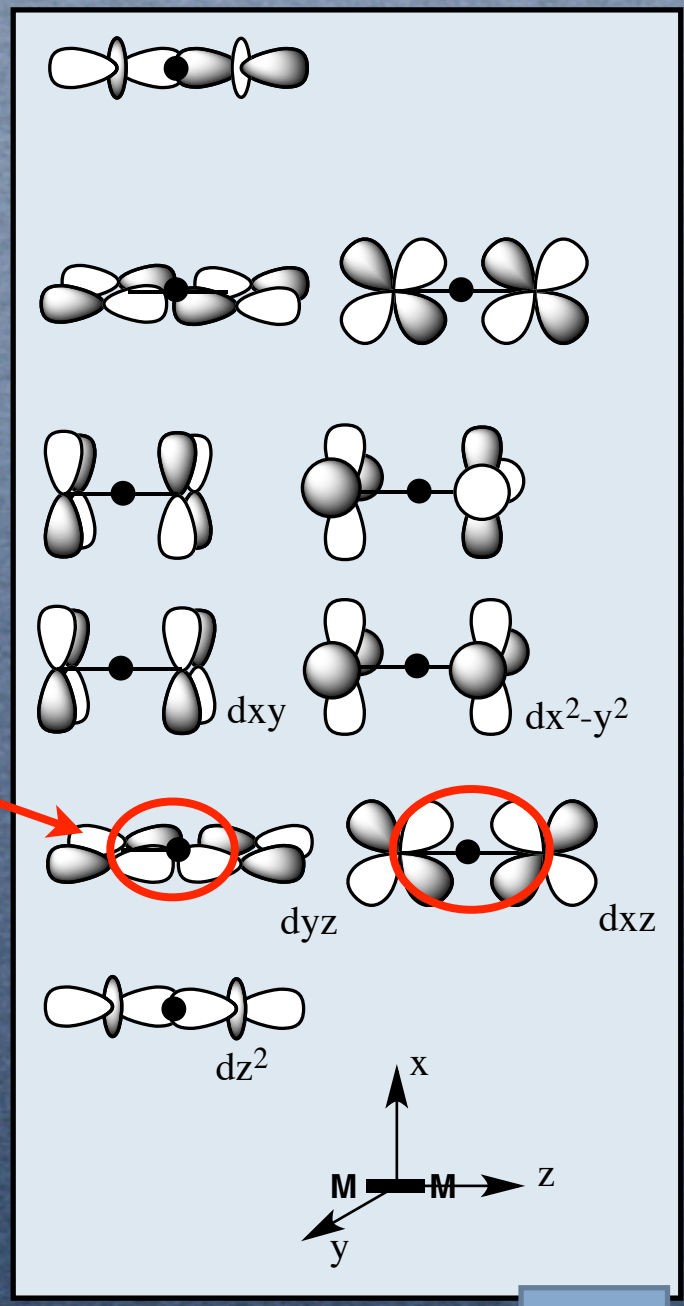
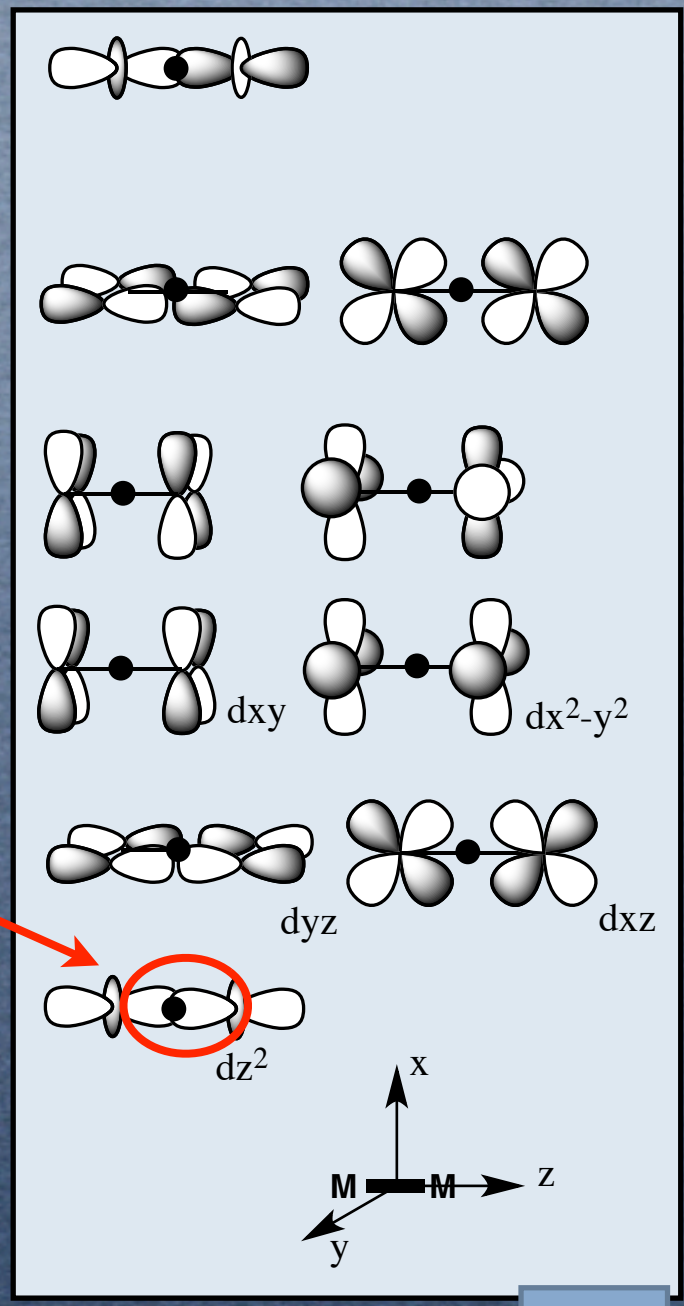


Fig. 7

Metallic Dimers

- complete the MO symmetry labels

focus on phase change around center of inversion



looks like sAO -> σ_g^+

also

along the bond -> σ
symmetric through i -> g
no phase change for σ_v -> +

Fig. 7

Metallic Dimers

bond order

- ONLY applies to diatomics
- fill 5 bonding dAOs

quintiple bond!

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

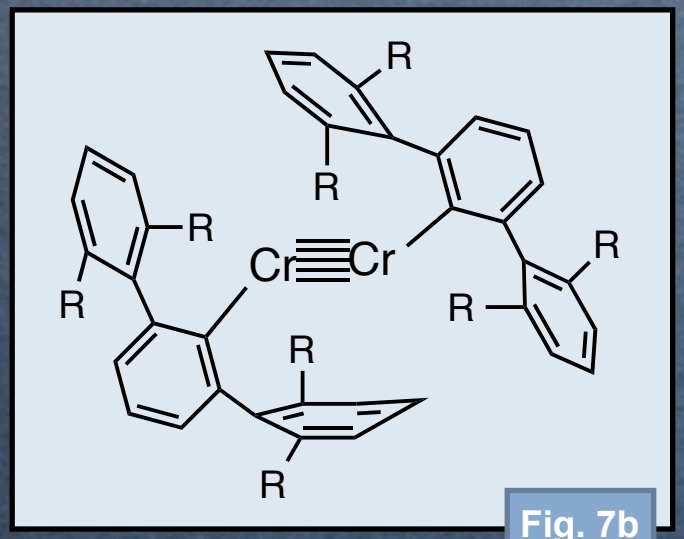


Fig. 7b

Power: 2005 link to paper on web-site

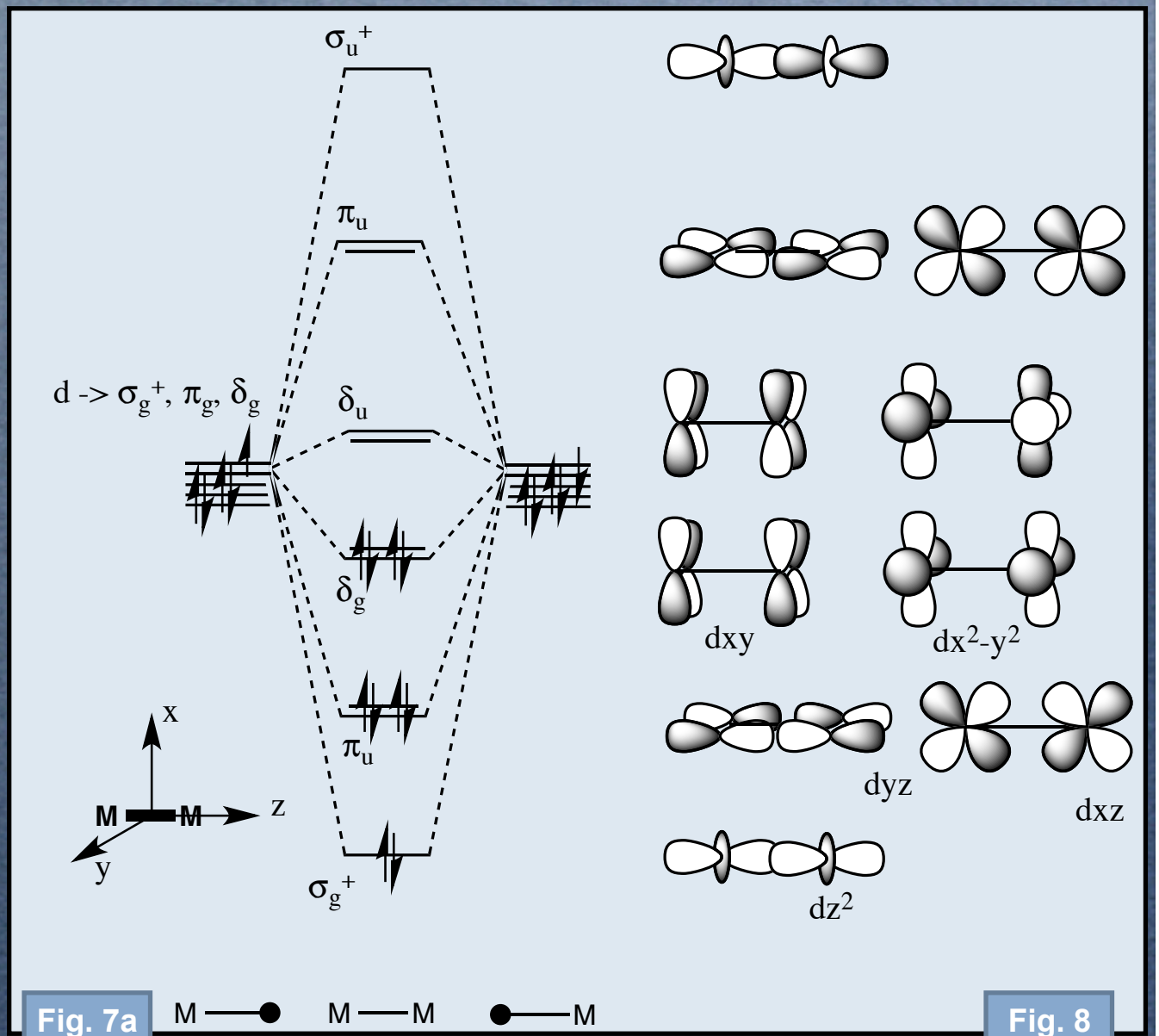


Fig. 7a

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

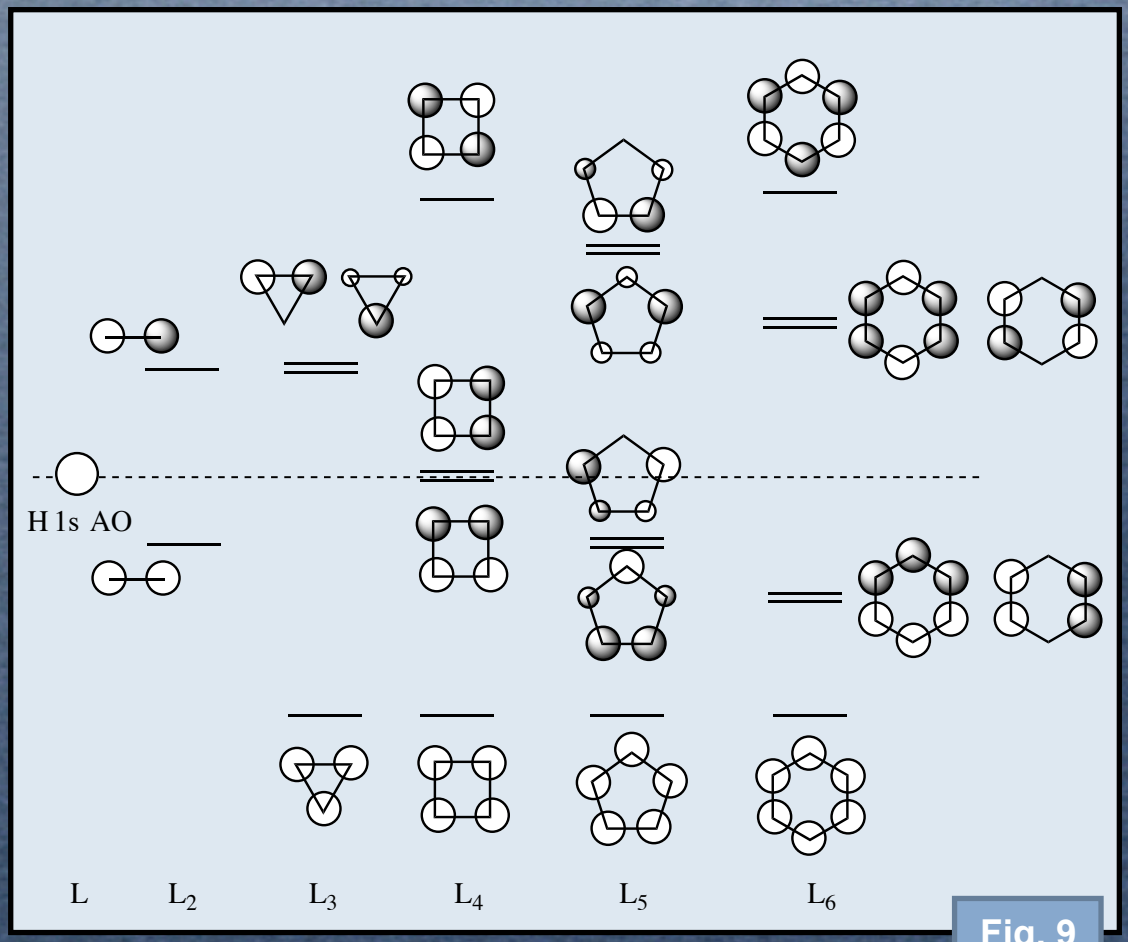


Fig. 9

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

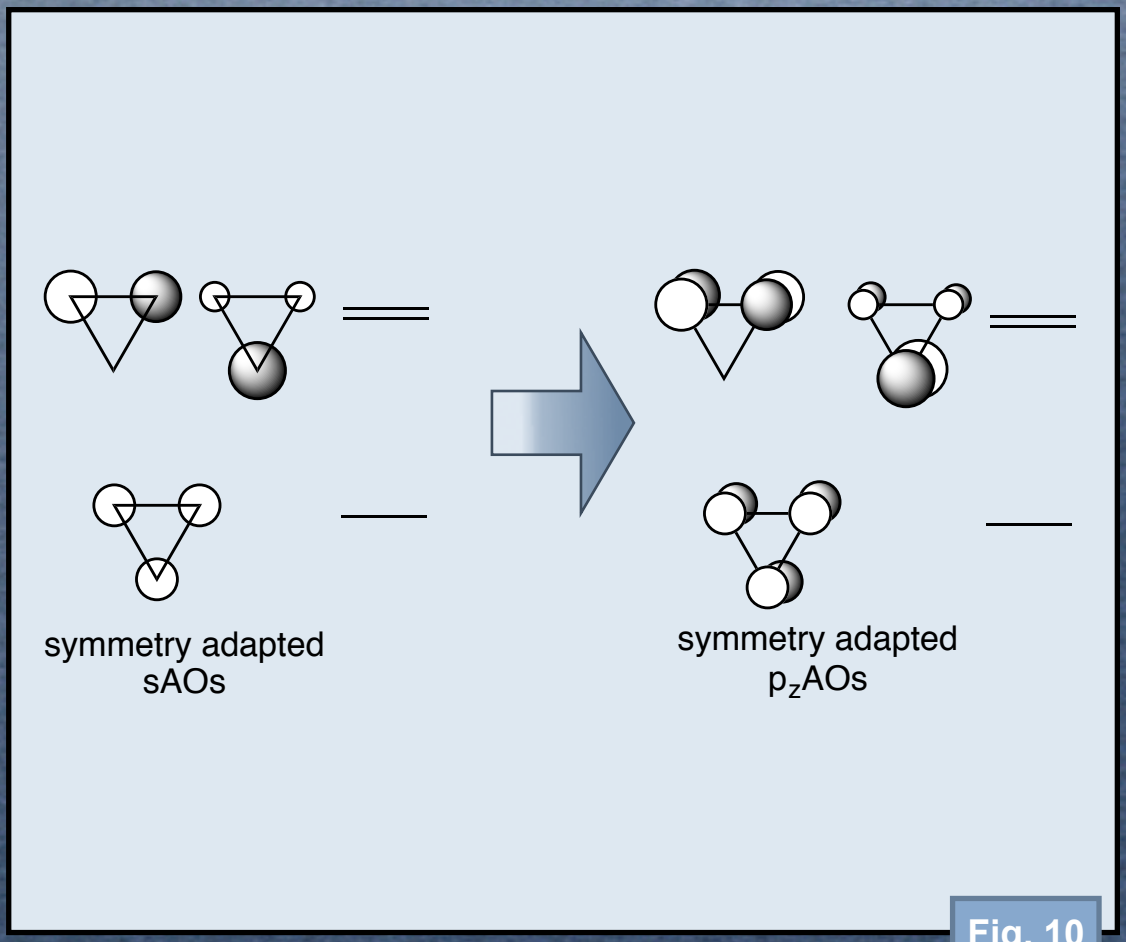
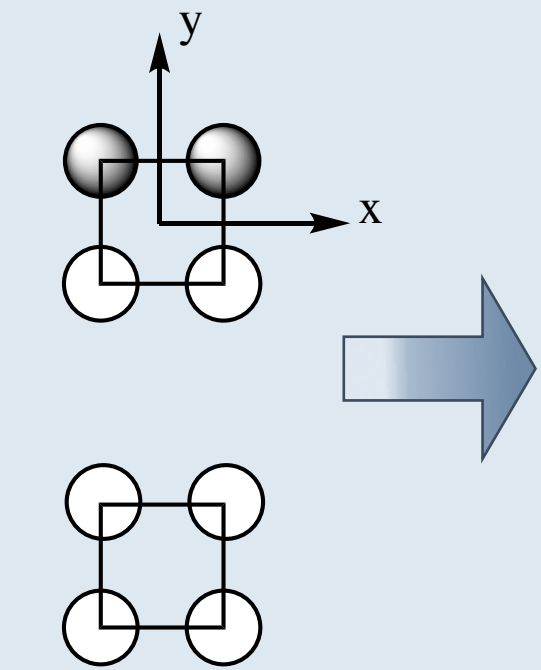


Fig. 10

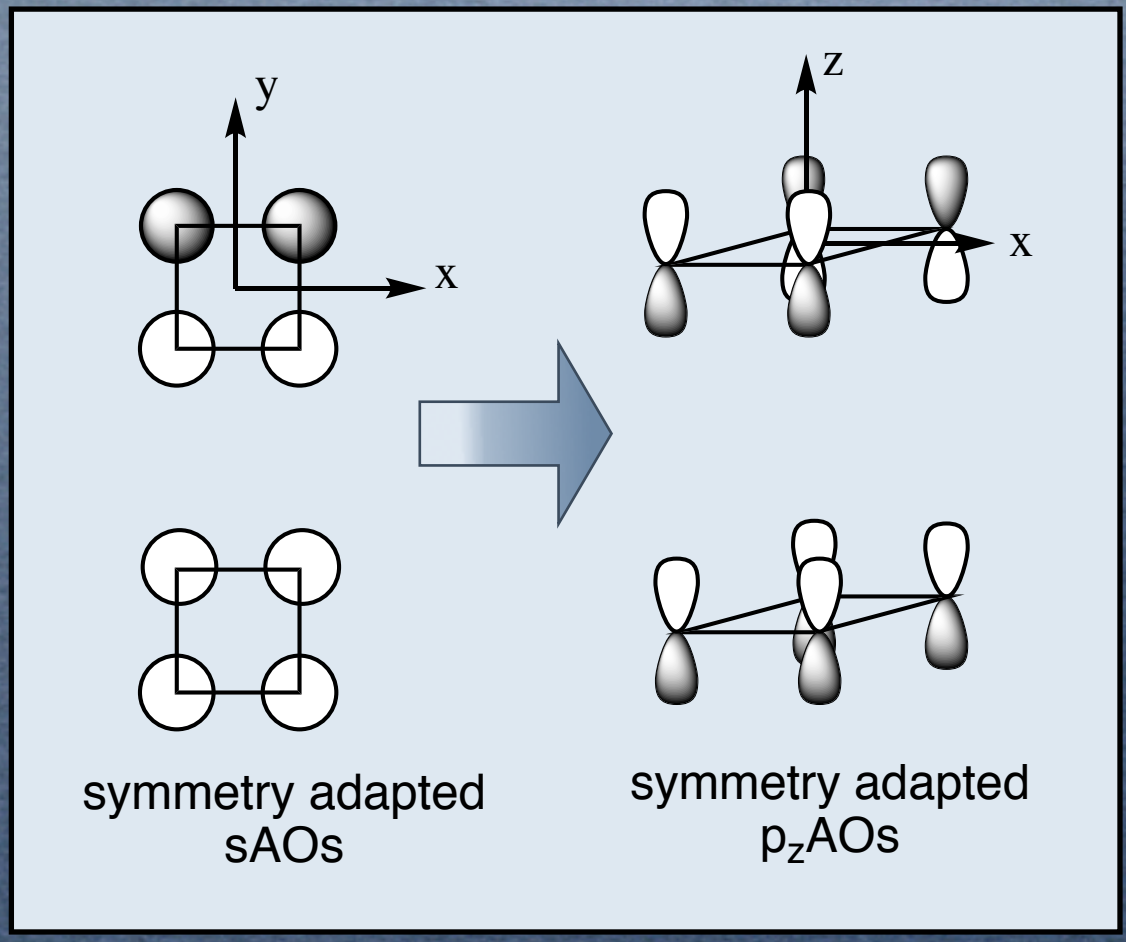
In-Class Activity

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



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 => e_u
  - totally symmetric s orbitals => a_{1g}
  - p orbitals, like e_u but invert under mirror plane =>e_g
  - all in-phase p orbitals, z-axis =>a_{2u} like a_{1g} but invert under mirror plane



Ligand Fragment Orbitals

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

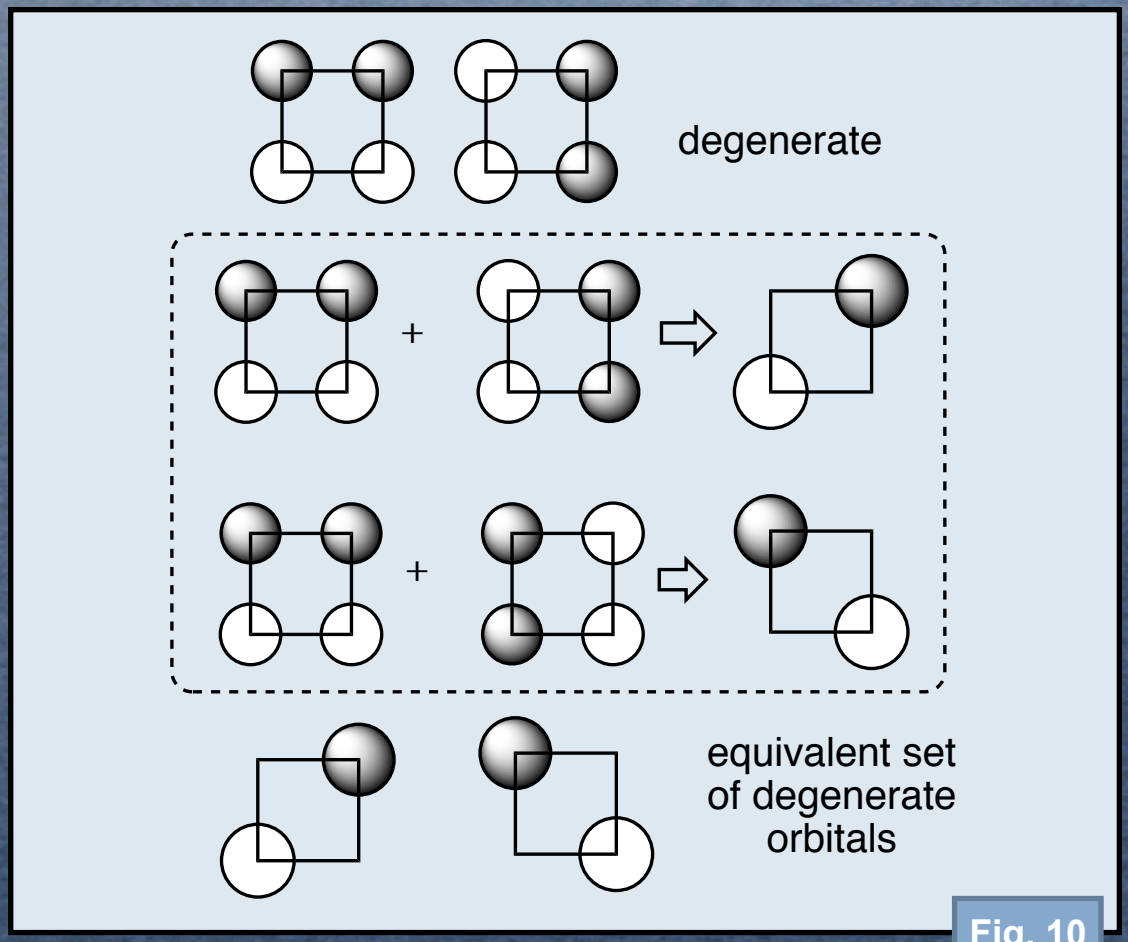
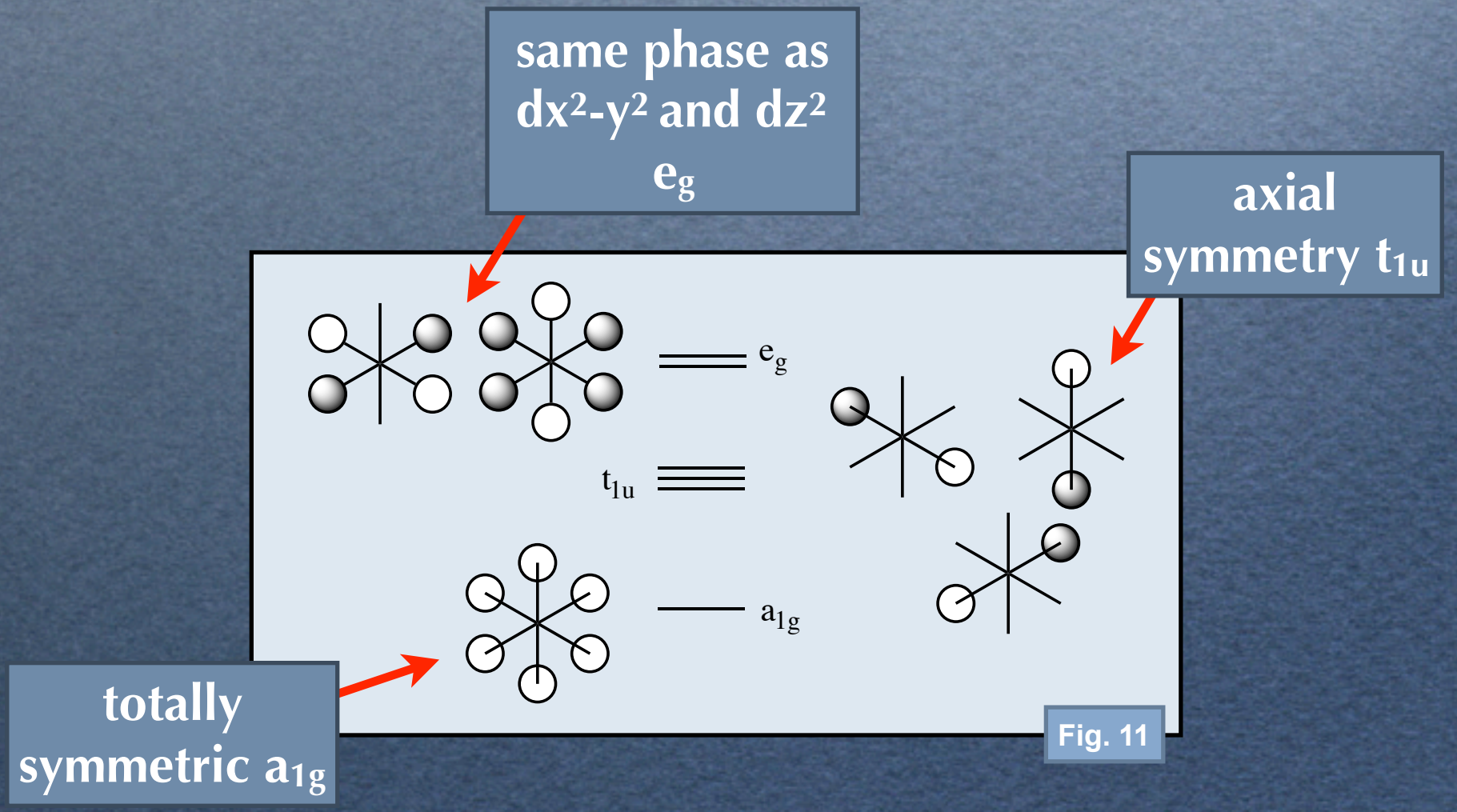


Fig. 10

Octahedral SA Orbitals

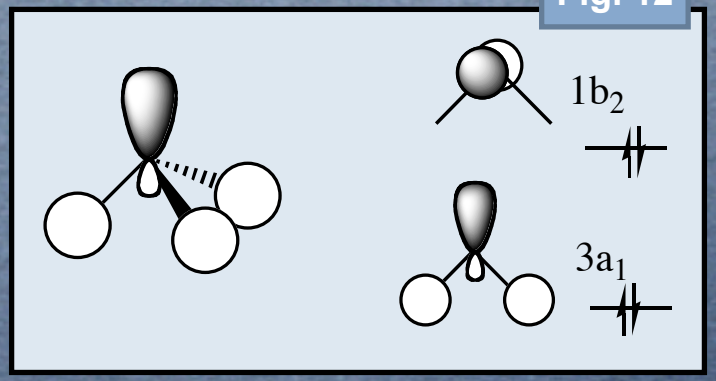
- **symmetry can be used to determine the ligand FOs**
  - use "tricks" to remember the phase patterns



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

Fig. 12



HOMO of NH_3 | HOMO-1 of H_2O

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!

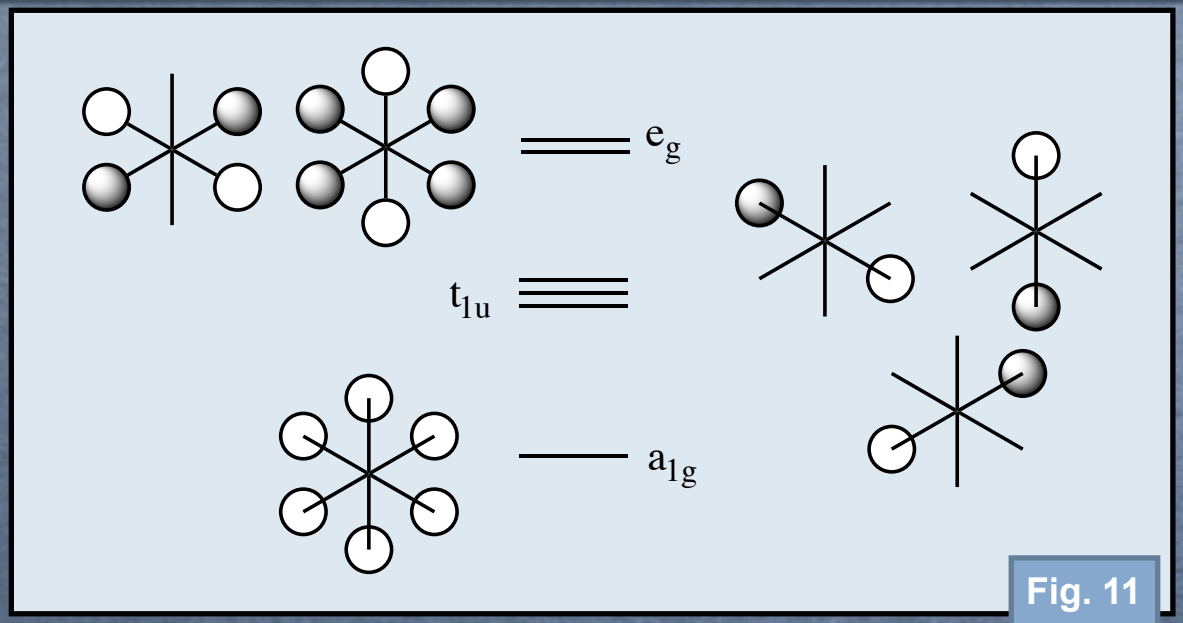


Fig. 11

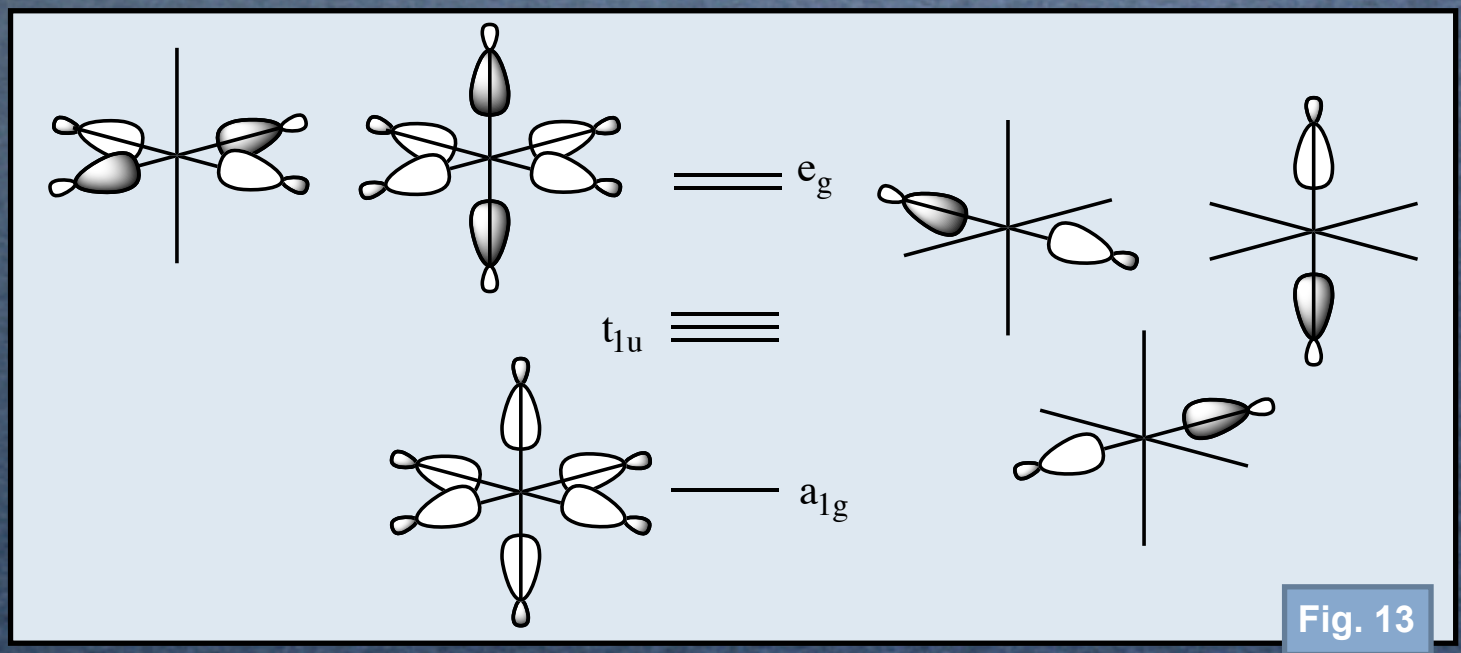


Fig. 13

Ligand Fragment Orbitals

closer through space interactions

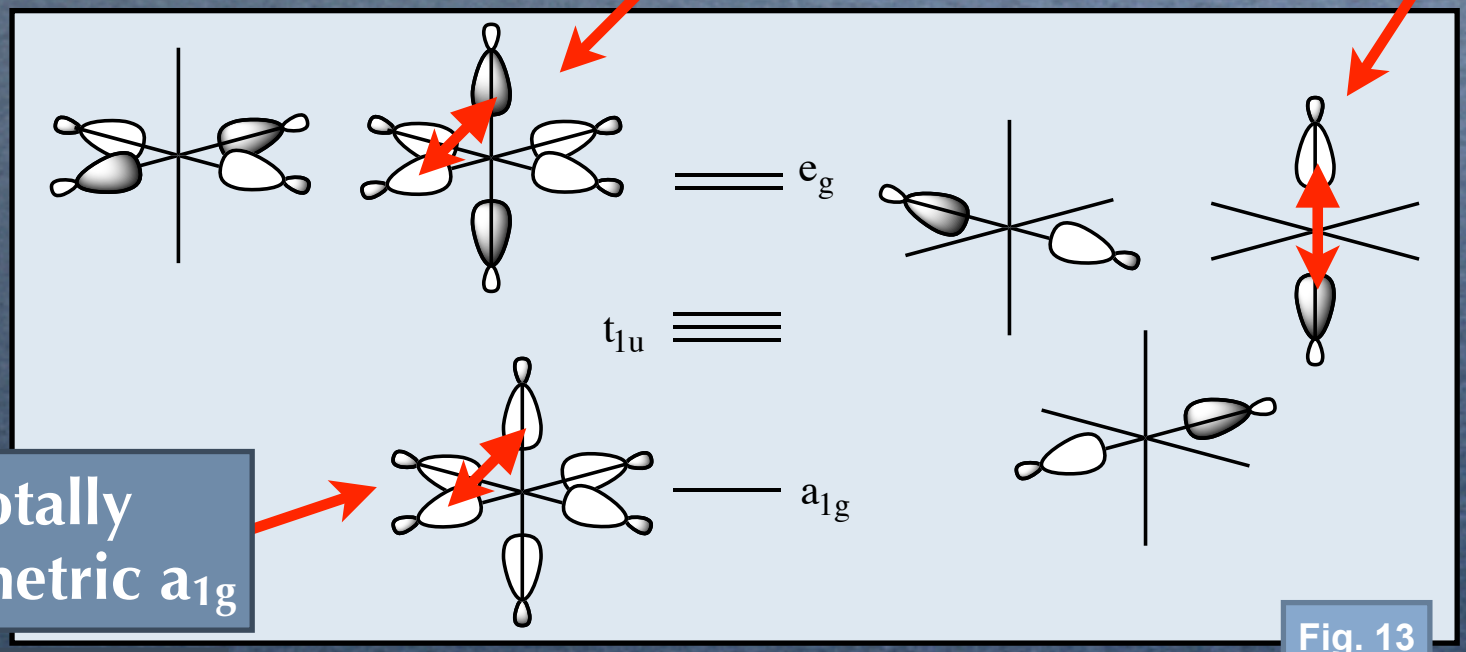
slightly antibonding

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

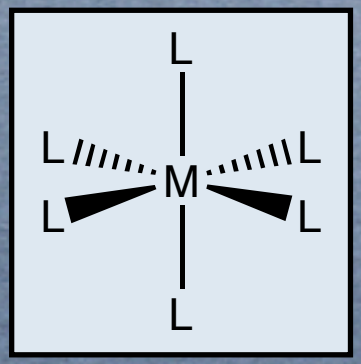
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$(x^2+y^2+z^2)$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
Eg	2	-1	0	0	2	2	0	-1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
Eu	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_x)
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



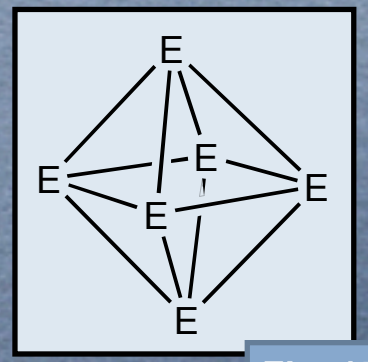


Fig. 15

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Δoct
$Ni(OH_2)_6$ green
$Ni(NH_3)_6$ purple

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

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Emerald: Cr^{3+} in the octahedral sites of Beryl $Be_3Al_2Si_6O_{18}$

http://www.gemstone.org/gem-by-gem/english/
http://www.uncp.edu/home/mcclurem/ptable/ni.htm

Visualisation

- **Focus on cube**
  - emphasis on C_2 and C_4 axes

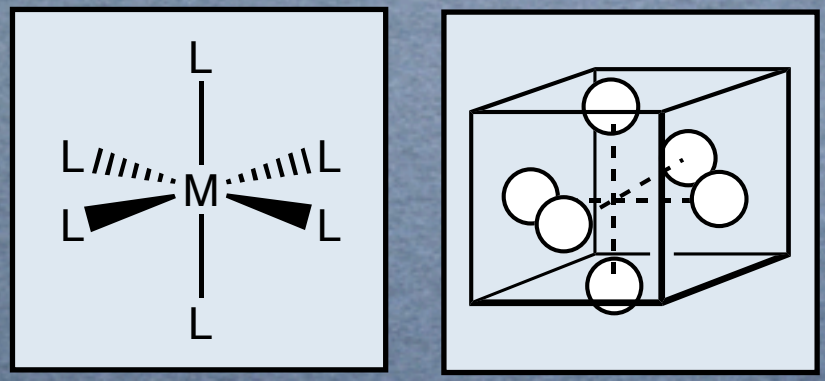
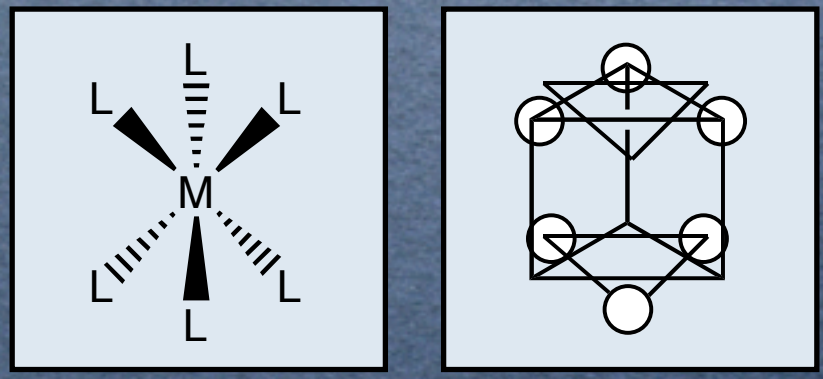


Fig. 16

- **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
- **$6C_4$ and $3C_2$ operations (axes coincident)**
  - C_4 axis through center of each pair of faces
  - three pairs of faces
  - thus 3 C_4 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 C_4 axes with 2 operations each
  - therefor 3 C_2 axes with 1 operation each
  - =$6C_4$ and =$3C_2$

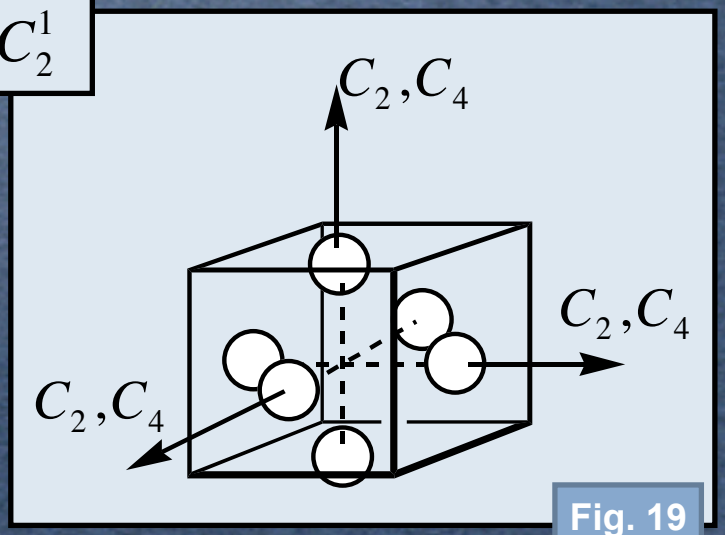


Fig. 19

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-> bent

MOs remain very similar BUT symmetry labels change

Important!

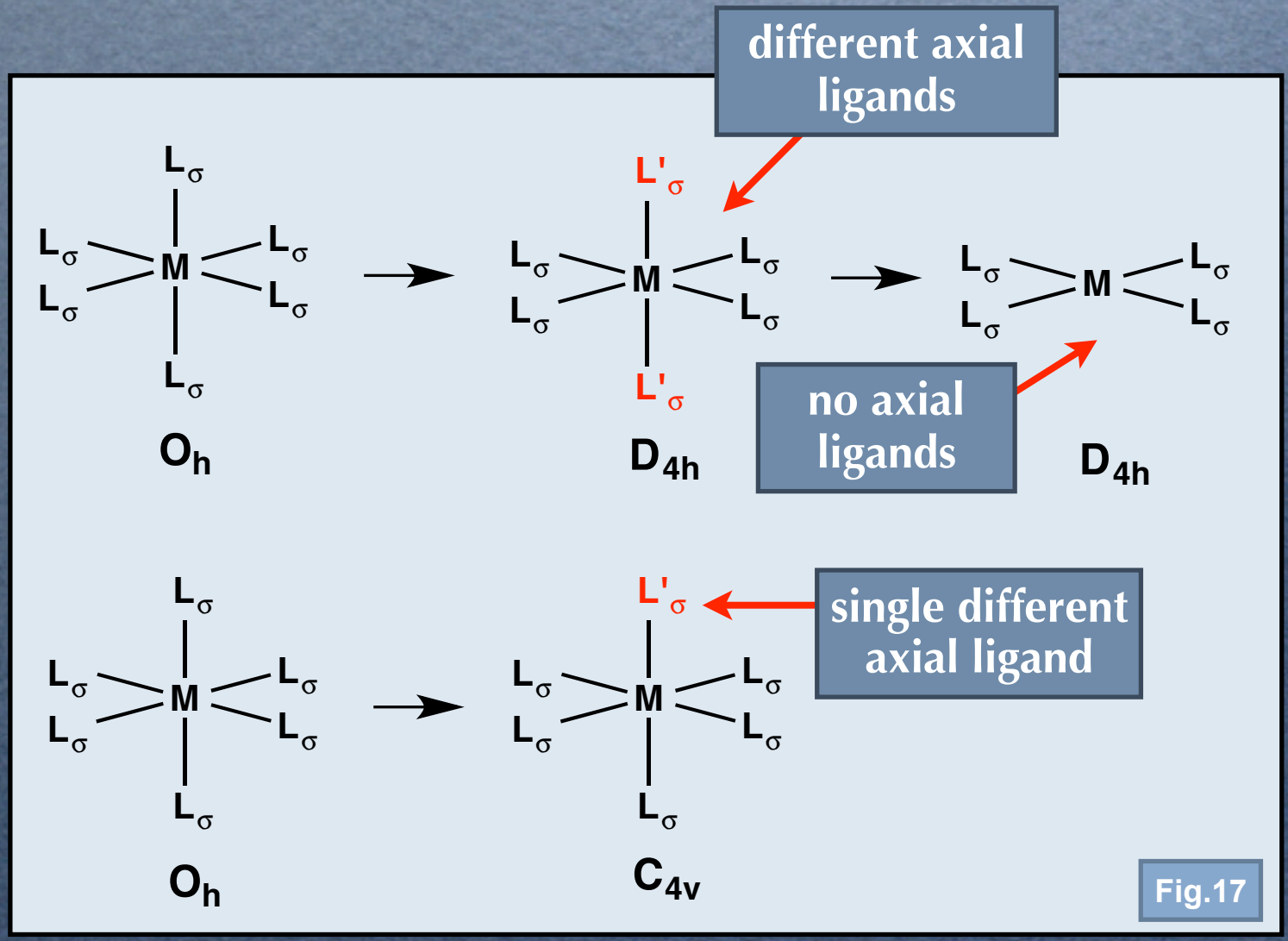


Fig.17

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 days
- 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!!