

Molecular Orbitals in Inorganic Chemistry

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Outline

- octahedral complexes
- forming the MO diagram for O_h
- colour, selection rules
- Δ_{oct} , spectrochemical series
- forming the MO diagram for C_{4v}

Octahedral Complexes

- **very large and important class of transition metal complexes**
- **TM complexes act as catalysts**
 - ◆ to control and improve catalysts we need to understand the underlying electronic structure
- **magnetic properties, colour!**

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Image from p16 of Metal Ligand Bonding by R. Janes and E. Moore RSC, Cambridge, 2004.

MO checklist

Steps to construct a MO diagram

- ✦ determine the molecular shape and identify the point group of the molecule
- ✦ define the axial system and find all of the symmetry operations on the molecule
- ✦ identify the chemical fragments, and put them along the bottom of the diagram
- ✦ determine the energy levels and symmetry labels of the fragment orbitals (use H1s as a reference)
- ✦ combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs (in pencil!)
- ✦ determine the number of electrons in each fragment and hence the central MO region, add them to the diagram
- ✦ identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
- ✦ annotate your diagram
- ✦ use the MO diagram to understand the structure, bonding and chemistry of the molecule

work through for
an octahedral
molecule

Steps 1-2: Point Group

● determine molecular shape: octahedral

● determine the point group of the molecule

✦ find O_h in your character tables

● define the axial system

● find all of the symmetry operations

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	$(2z^2-x^2-y^2, x^2-y^2)$
E_g	2	-1	0	0	2	2	0	-1	2	0	
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. 1

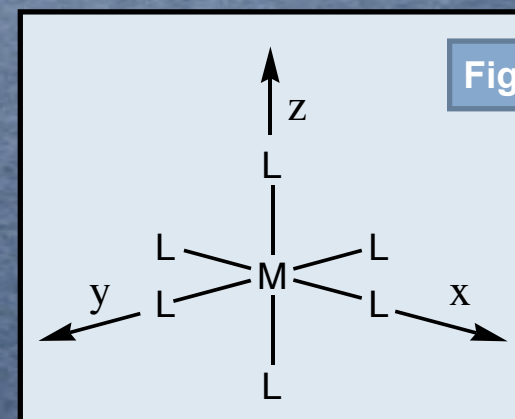
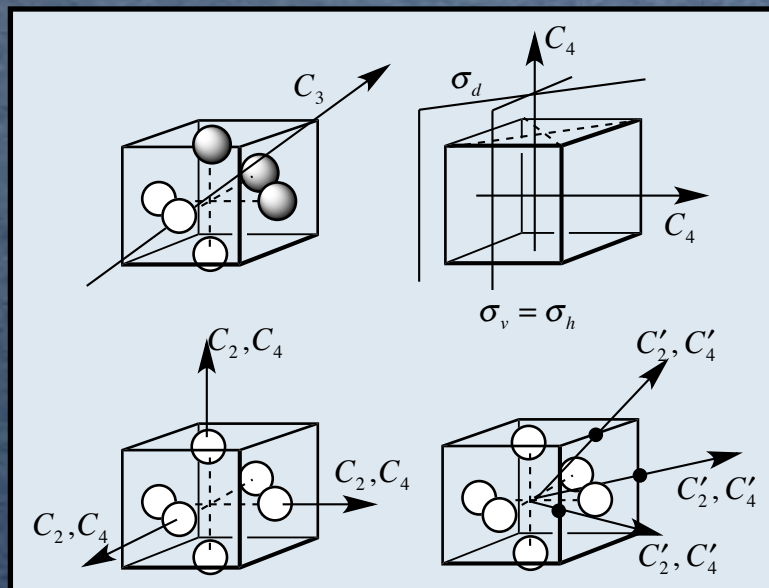


Fig. 2



Steps 3-4: Fragment Orbitals

determine the fragments

♦ central metal and the symmetry adapted fragment orbitals for L_6

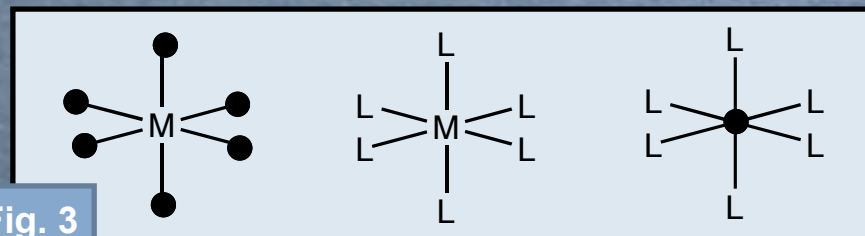


Fig. 3

determine the energy levels and symmetry labels of the fragments

♦ covered last lecture => tricks to help remember

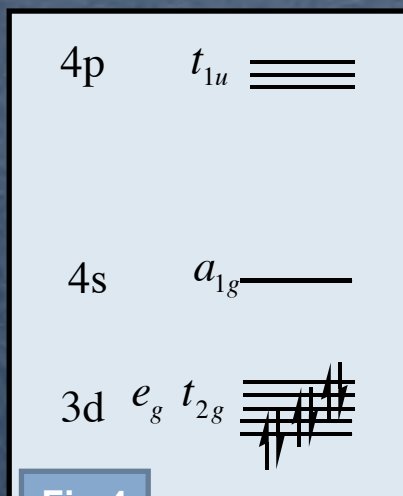


Fig.4

metal

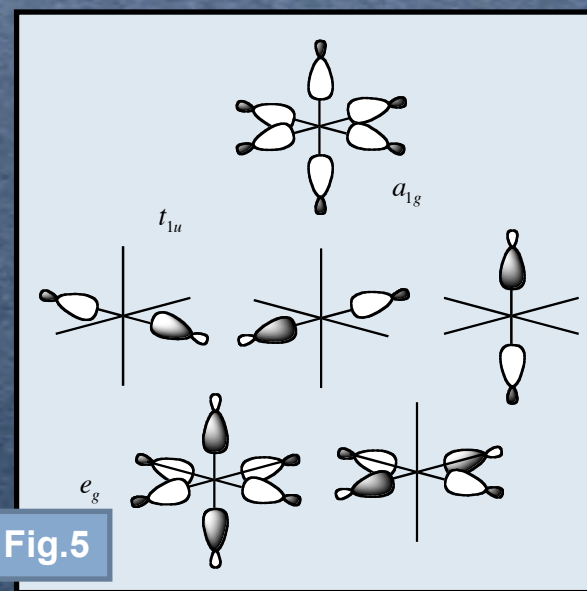
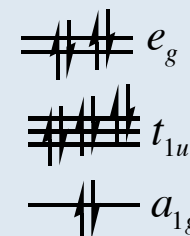


Fig.5

ligands



Set up MO Diagram

● draw the fragments and chemical structure

◆ use place holders!

Fig 7 Page 3
colour the
place holders
in on your
notes!

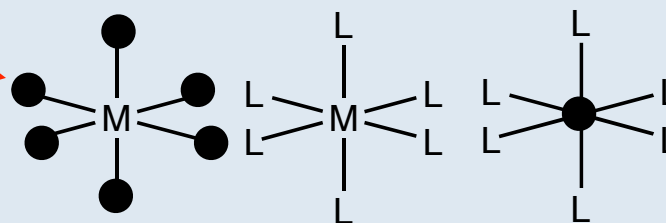


Fig.6

Set up MO Diagram

add the fragment orbitals

- ♦ metal is electropositive dAOs are higher in energy
- ♦ ligand orbitals are bonding FOs lie deeper in energy

Important!

4p t_{1u}

4s a_{1g}

3d $e_g t_{2g}$

e_g
 t_{1u}
 a_{1g}

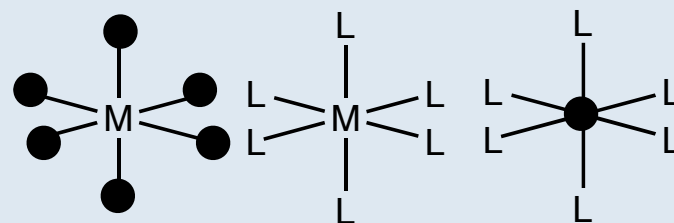
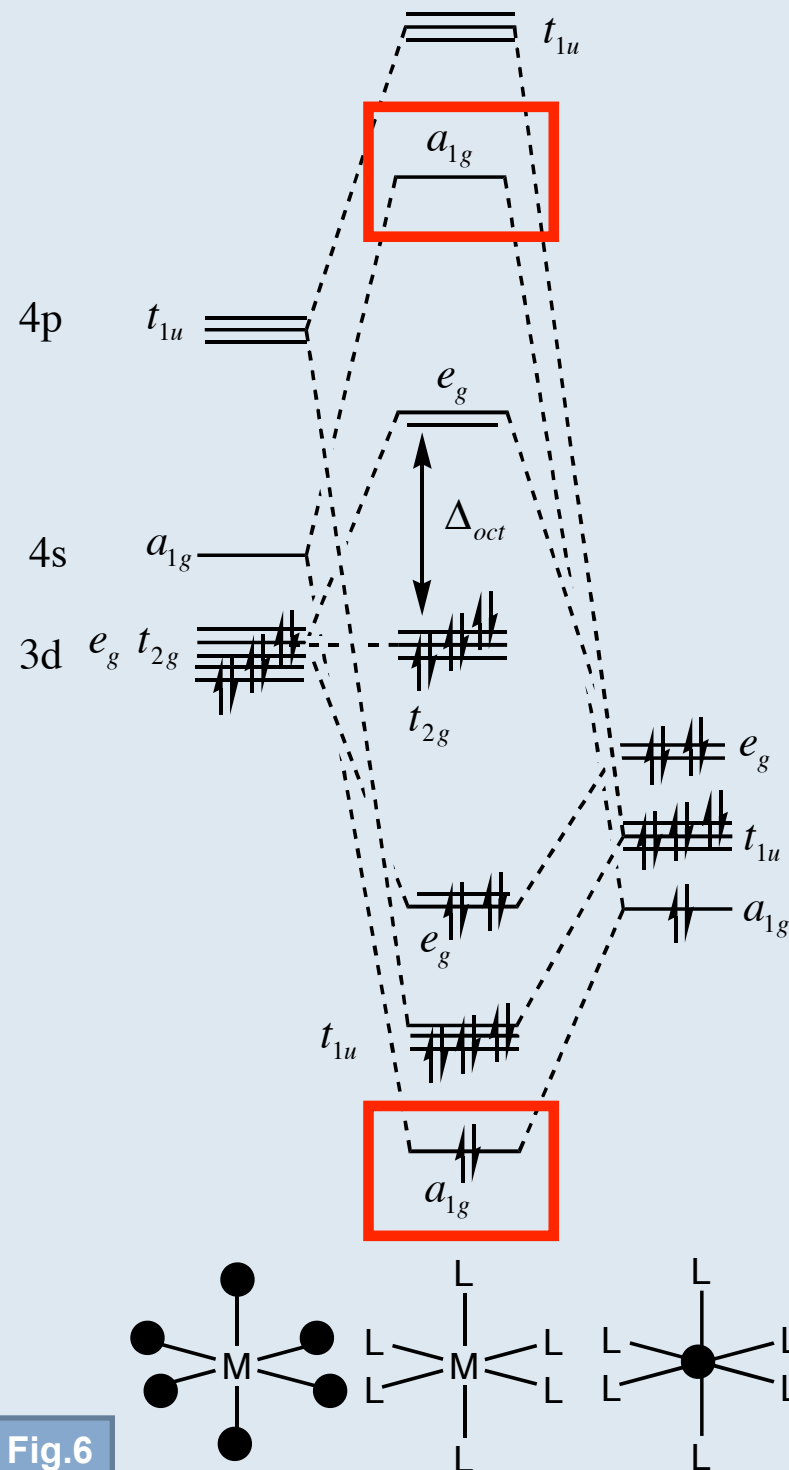
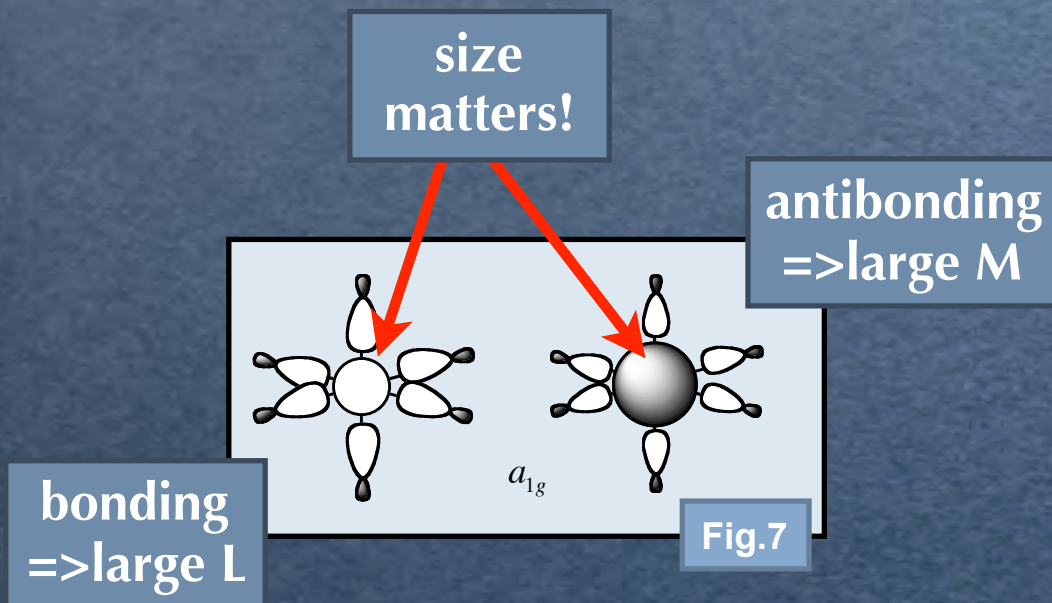


Fig.6

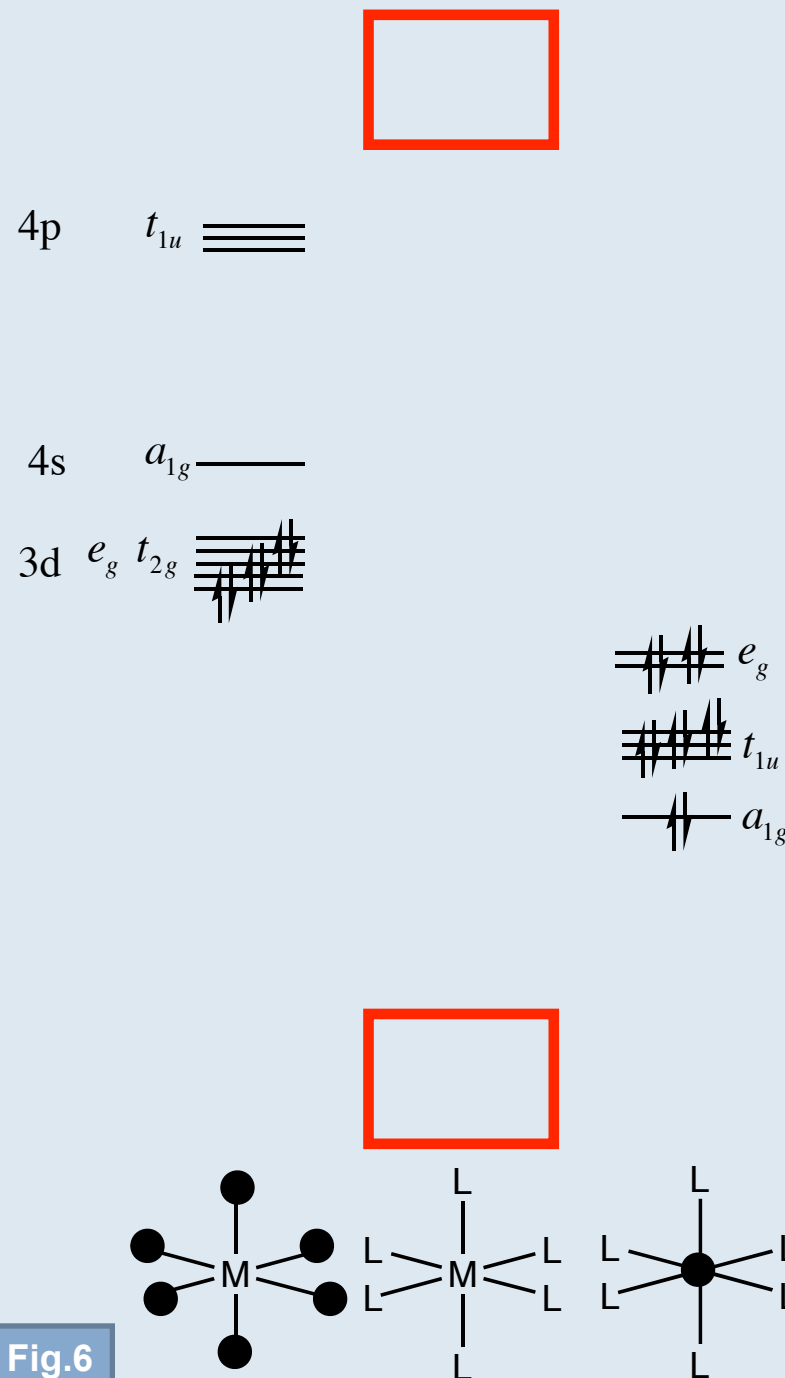
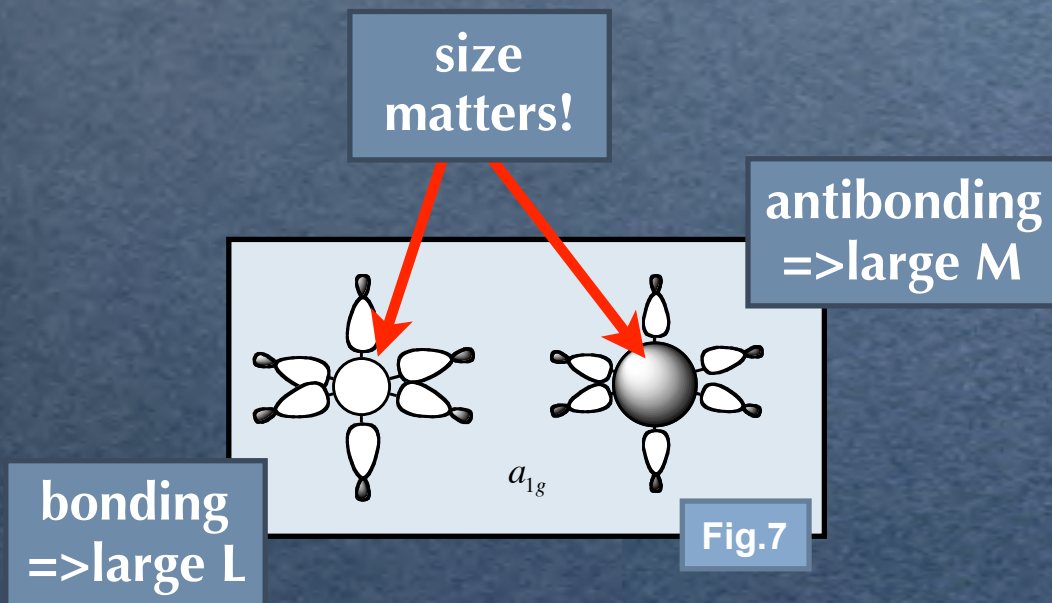
Energy Diagram

- combine orbitals of the same symmetry
- estimate the extent of energy splitting
 - ♦ a_{1g} are s- σ => strong splitting energy
 - ♦ a_{1g} are far apart in energy => reduces splitting



Energy Diagram

- combine orbitals of the same symmetry
- estimate the extent of energy splitting
 - ♦ a_{1g} are s- σ => strong splitting energy
 - ♦ a_{1g} are far apart in energy => reduces splitting



Combine Orbitals

estimate the extent of energy splitting

- ♦ t_{1u} interaction is p- $\sigma \Rightarrow$ medium
- ♦ t_{1u} energy difference is very large $\Rightarrow$ decreases splitting

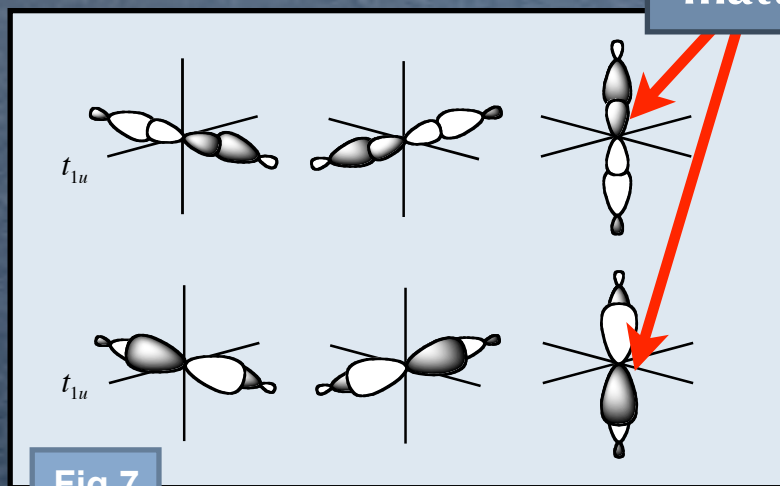


Fig.7

size matters!

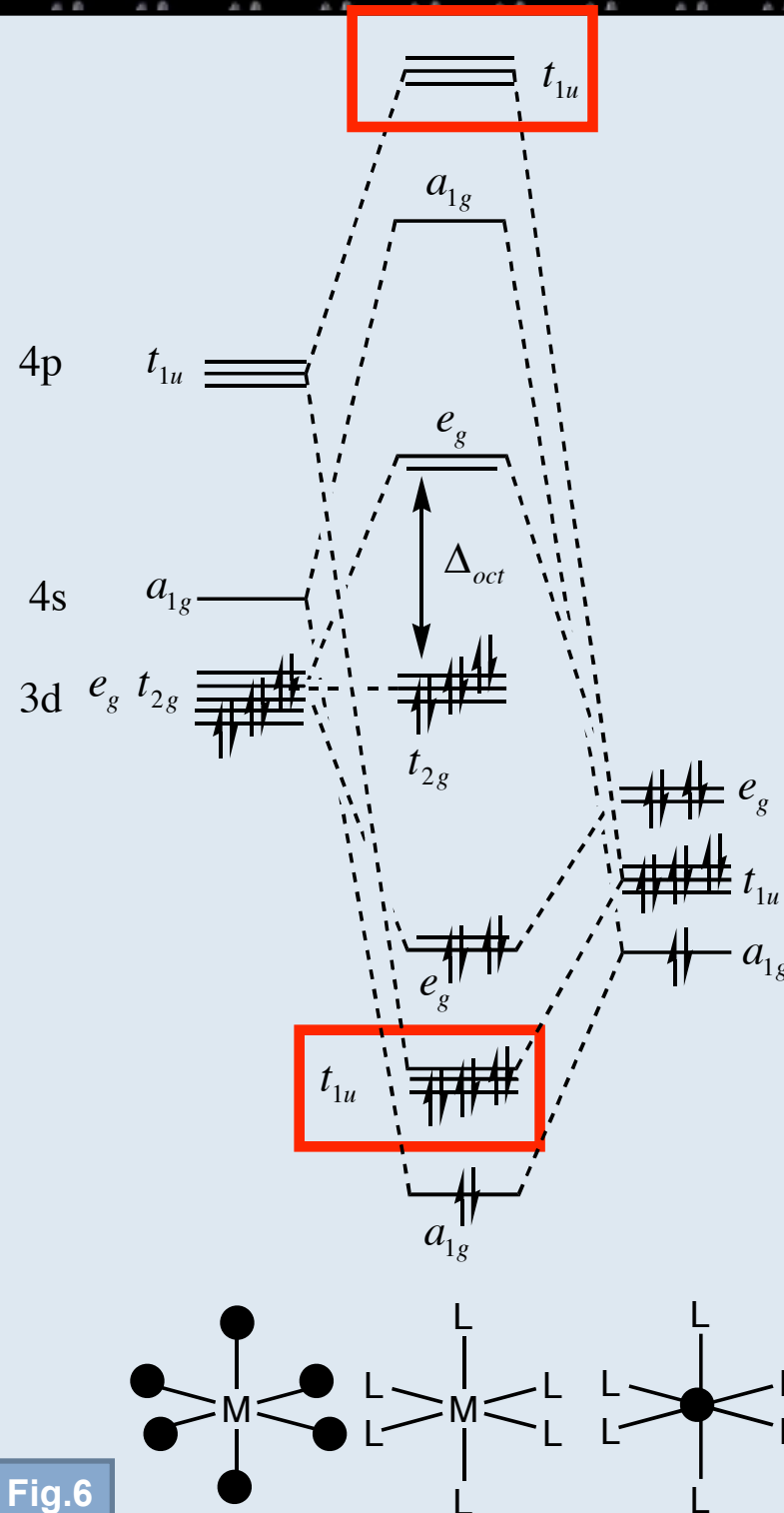


Fig.6

Combine Orbitals

estimate the extent of energy splitting

- ♦ e_g interaction is d- $\sigma \Rightarrow$ small
- ♦ e_g close in energy $\Rightarrow$ increases splitting

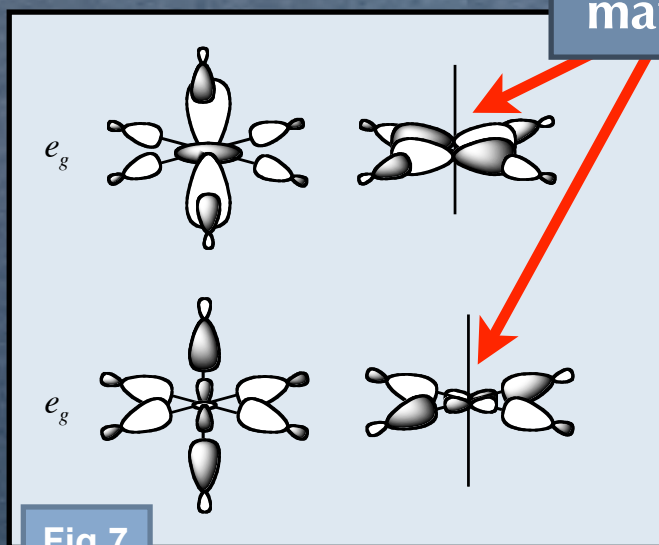


Fig.7

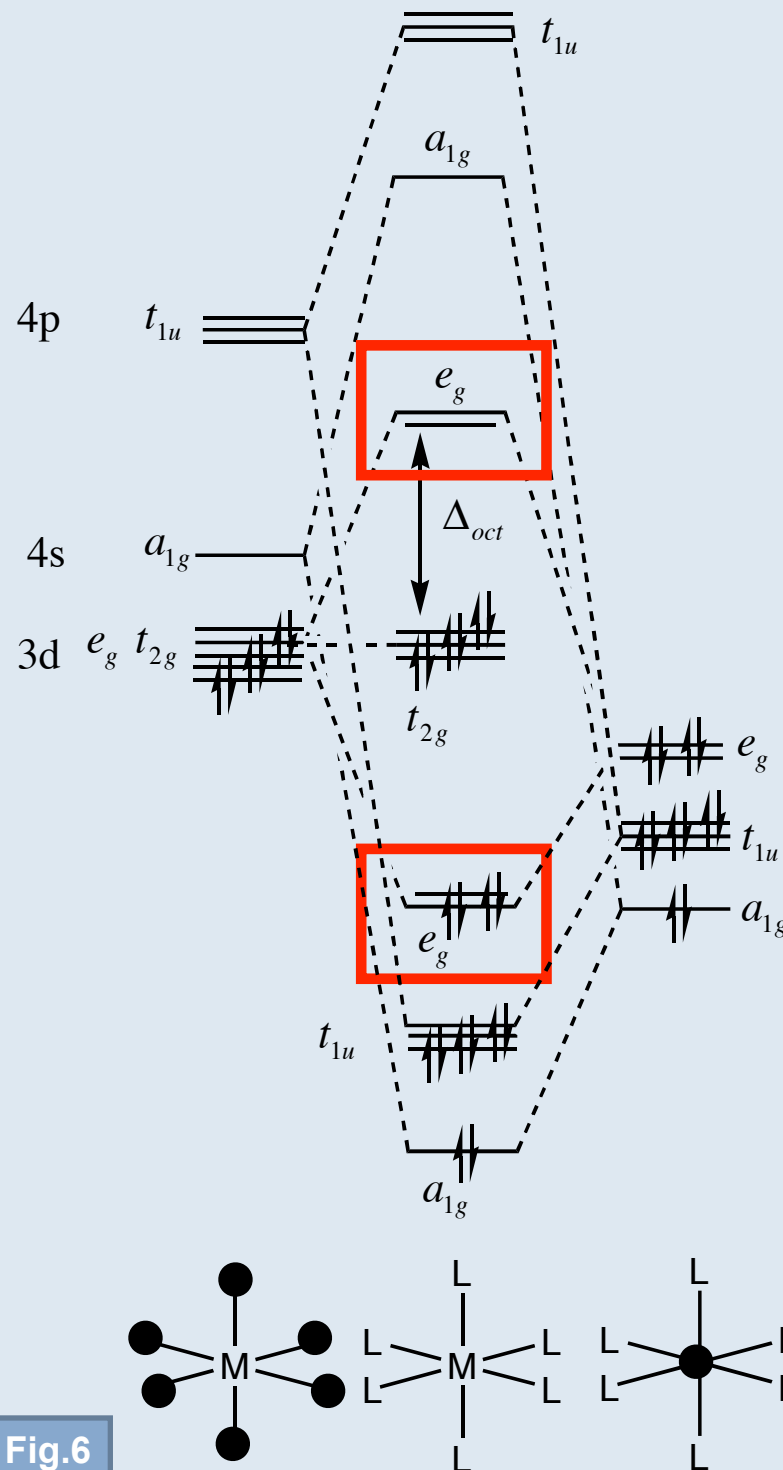


Fig.6

Combine Orbitals

estimate the extent of energy splitting

- metal t_{2g} remain non-bonding as there are no ligand orbitals of this symmetry

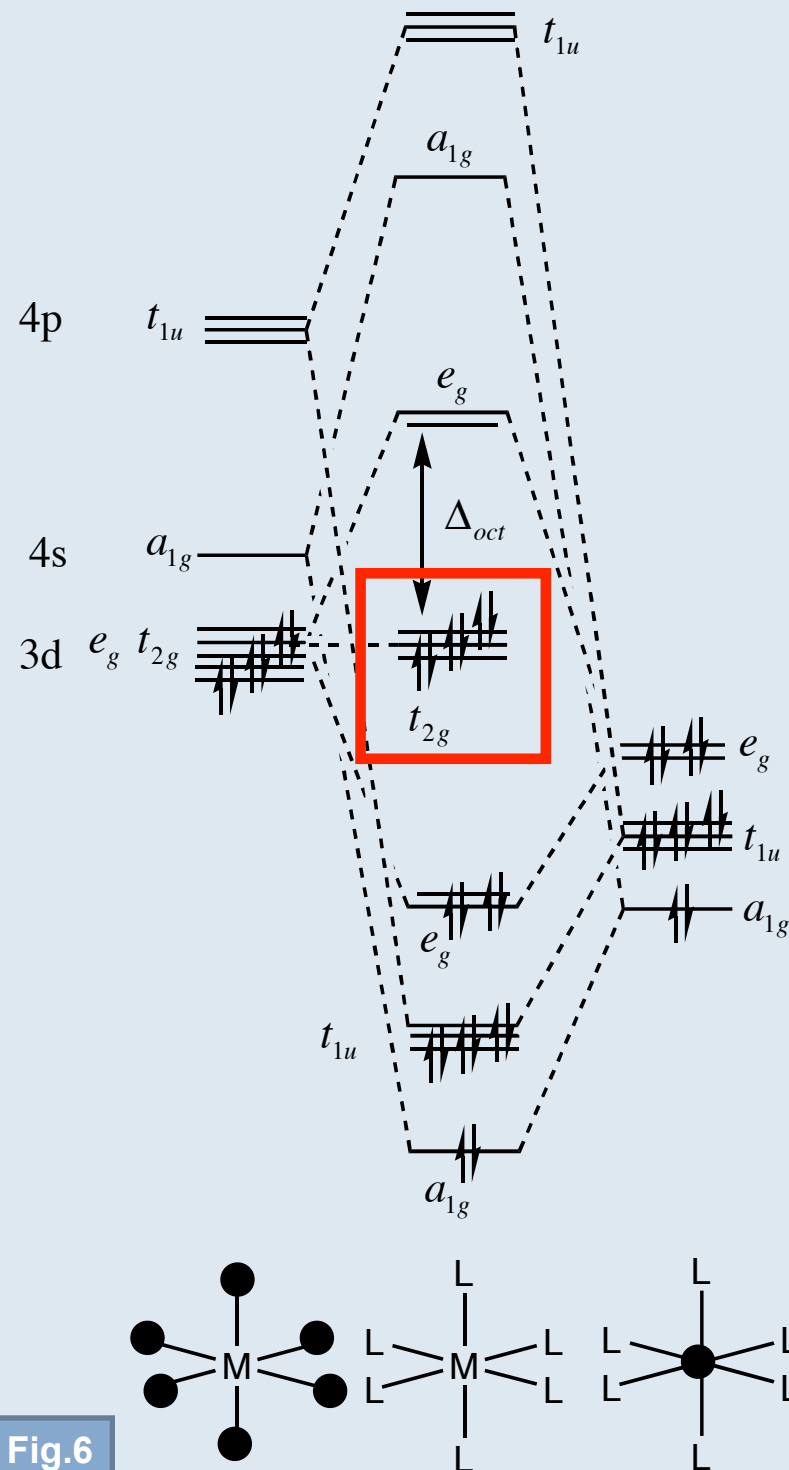


Fig.6

Steps: 6-8

electronic configuration

- ✦ six 2e donor ligands = 12e
- ✦ number d electrons depends on the metal and oxidation state
- ✦ I've used six here

determine if there is mixing

- ✦ no mixing occurs

use MO diagram checklist!

Energy Diagram

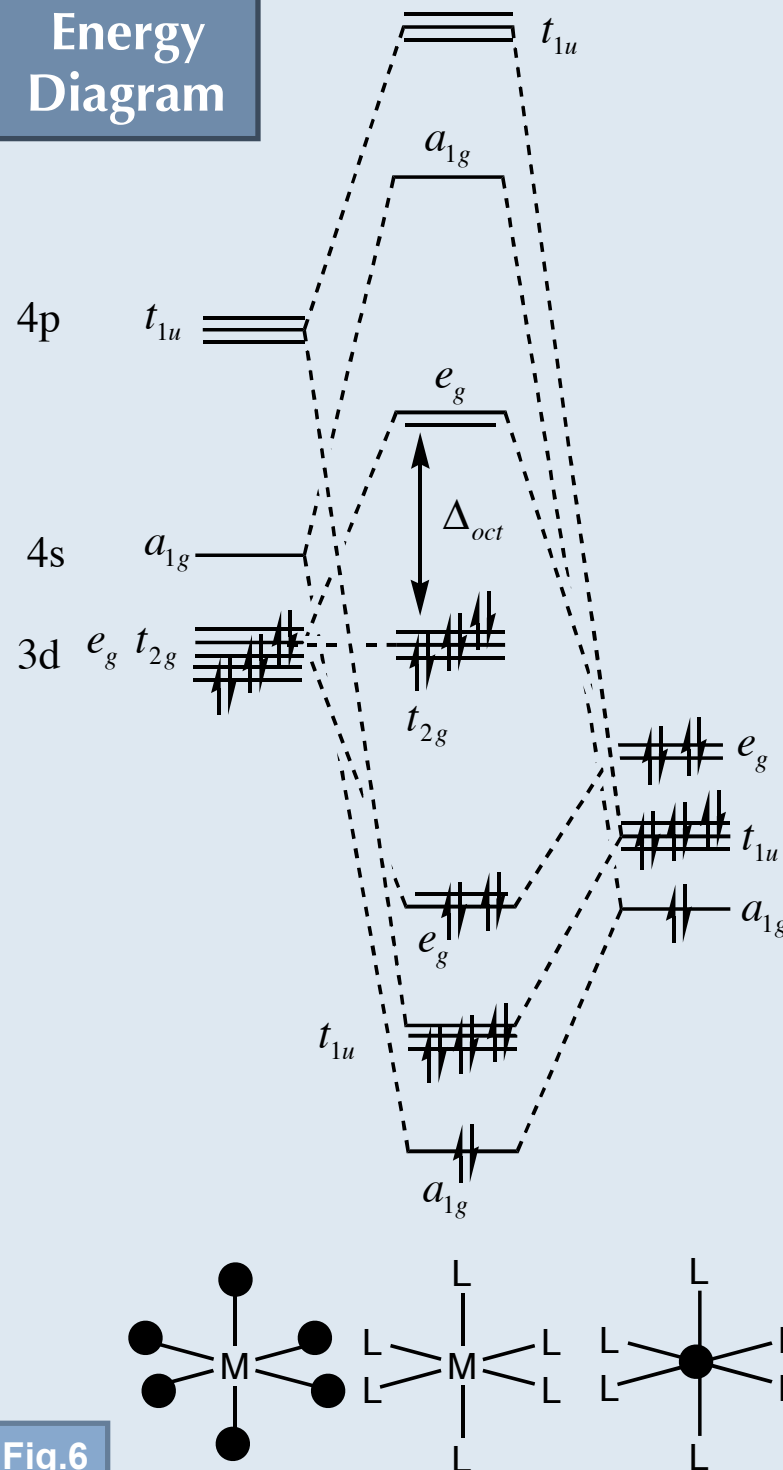


Fig.6

The full MO diagram!

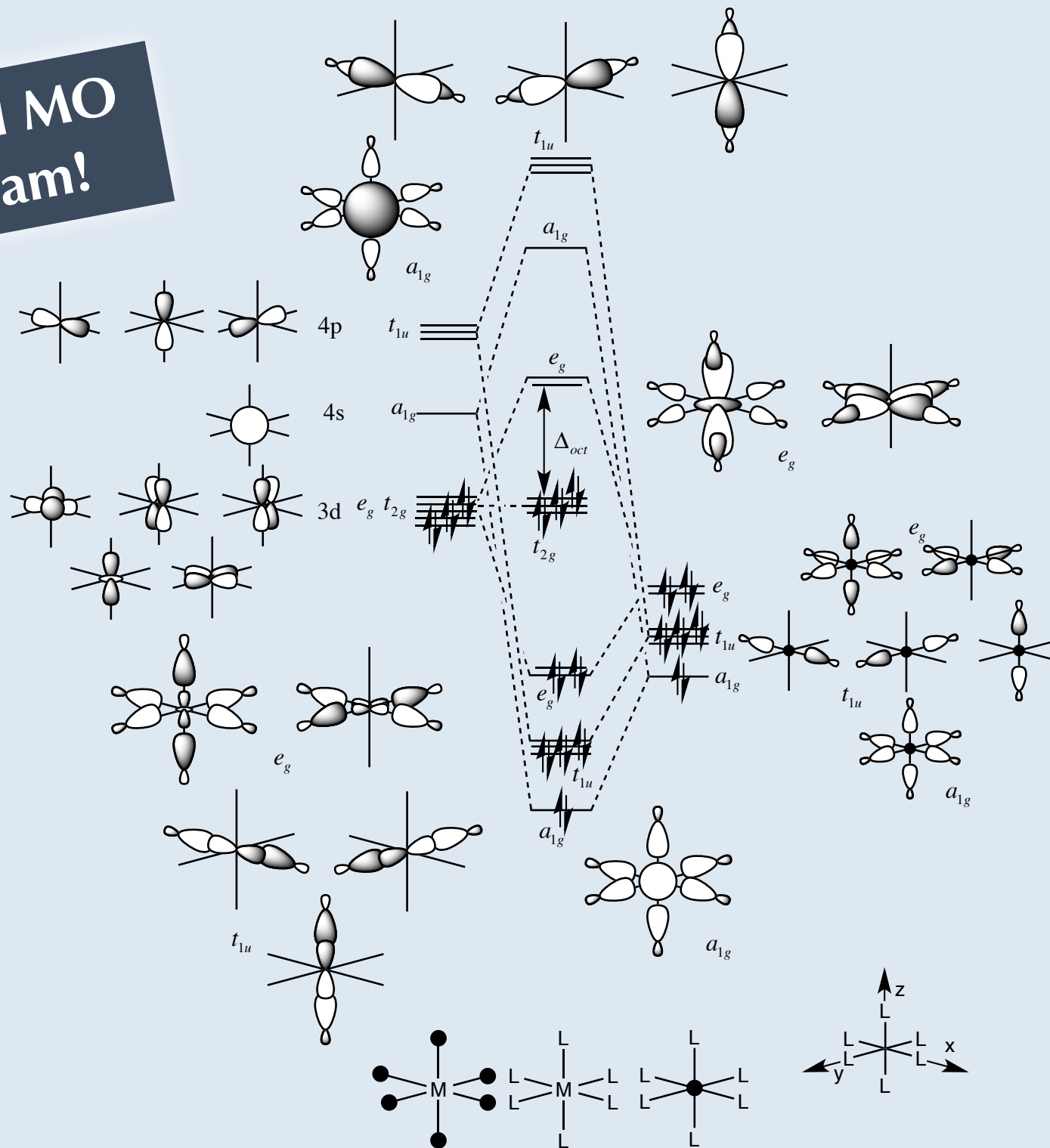


Fig.8

Step 9: Analysis

- three lowest energy sets of orbitals are ligand based

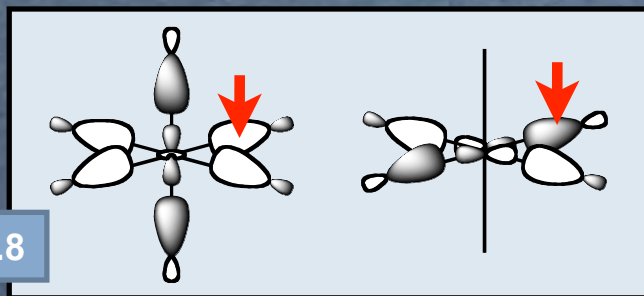
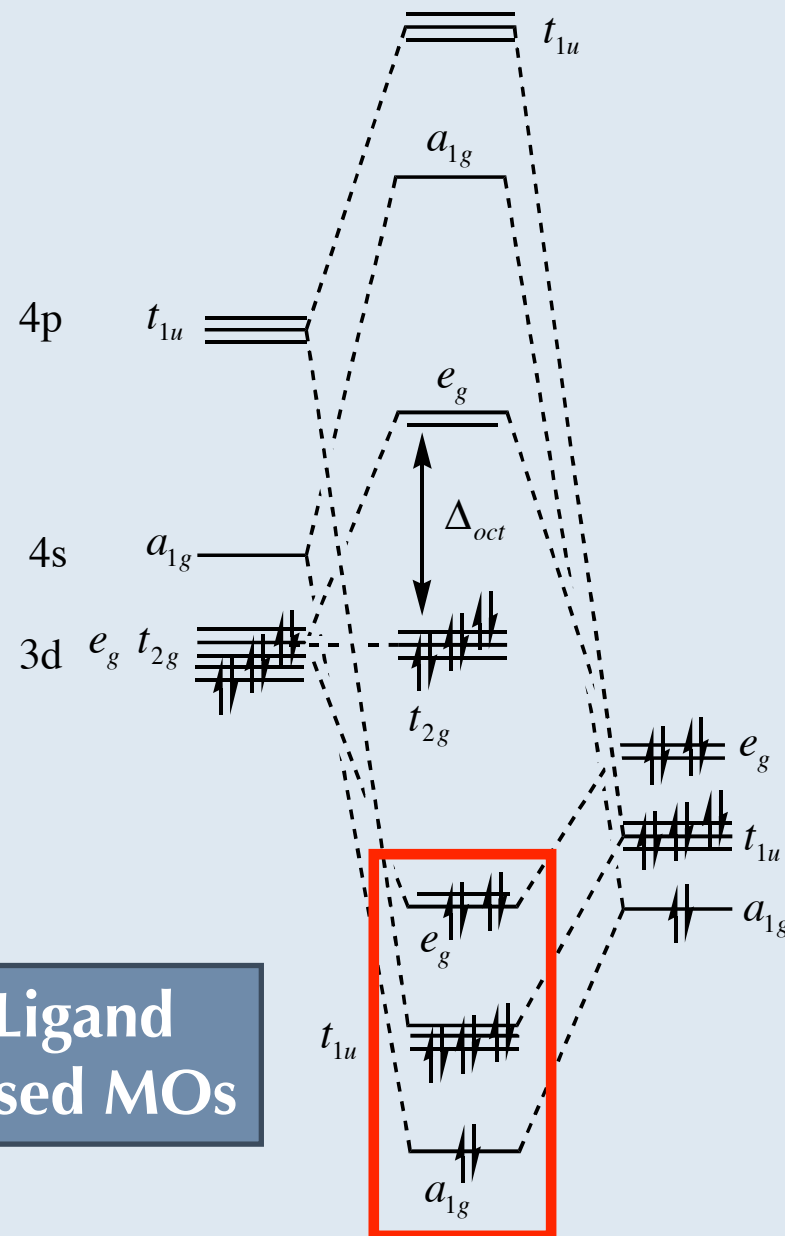


Fig.8

for example the e_g MOs

Important!



**Ligand
based MOs**

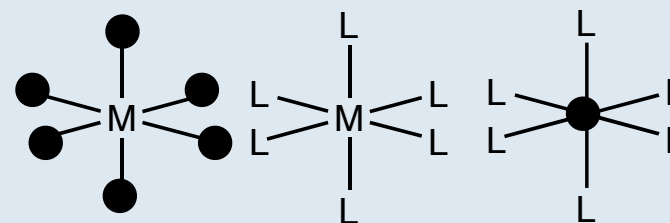


Fig.8

Step 9: Analysis

- three lowest energy sets of orbitals are ligand based
- higher energy MOs are metal based

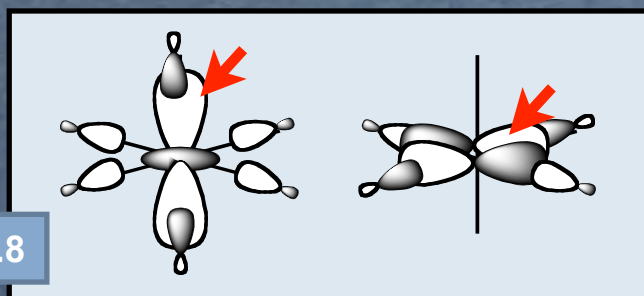


Fig.8

for example the e_g MOs

Important!

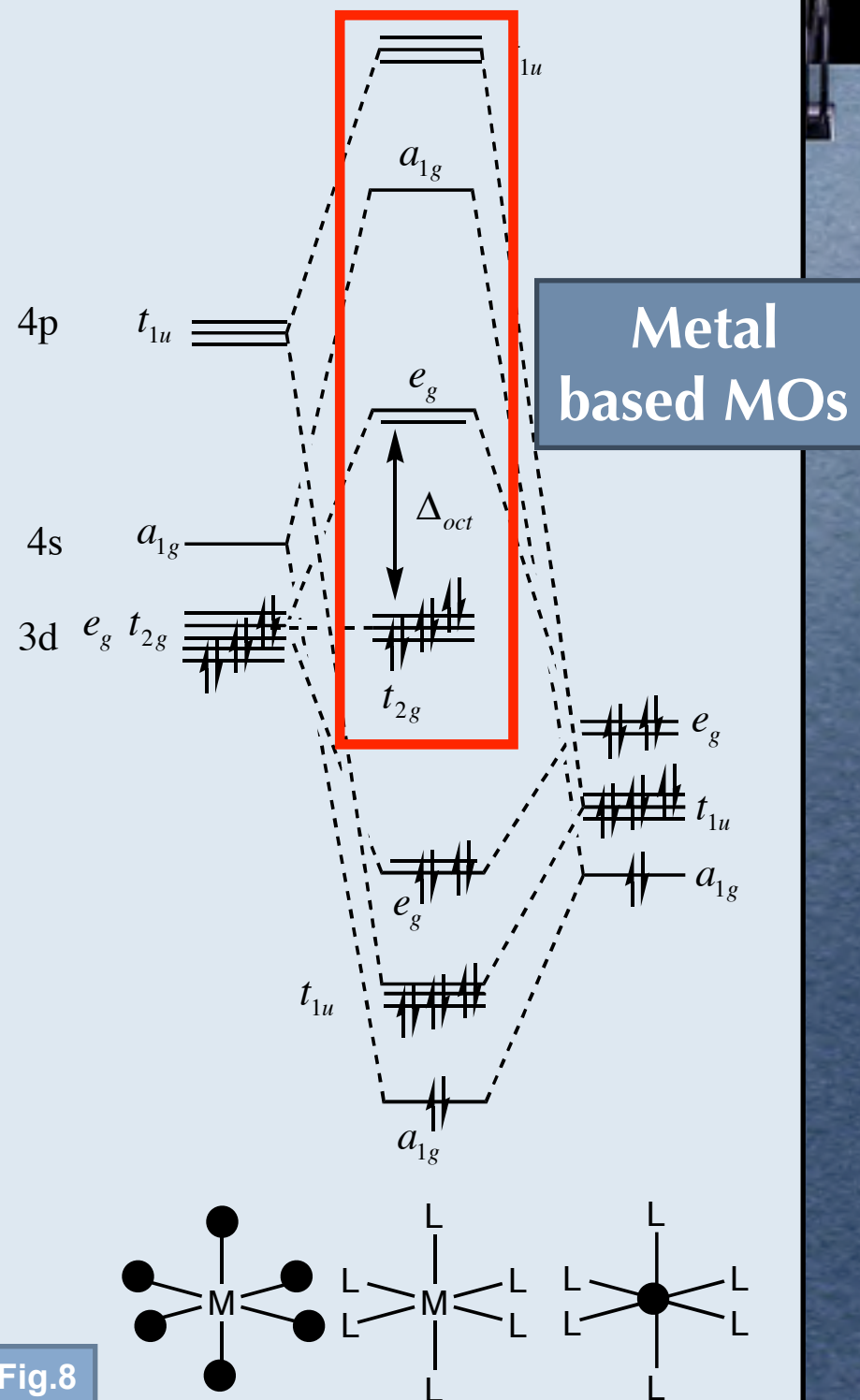


Fig.8

Note!

- leave off some of the “lines” for the metal dominated (s & p FOs) and the ligand dominated (low energy) FOs
- keep all the lines for the dAOs!

Important!

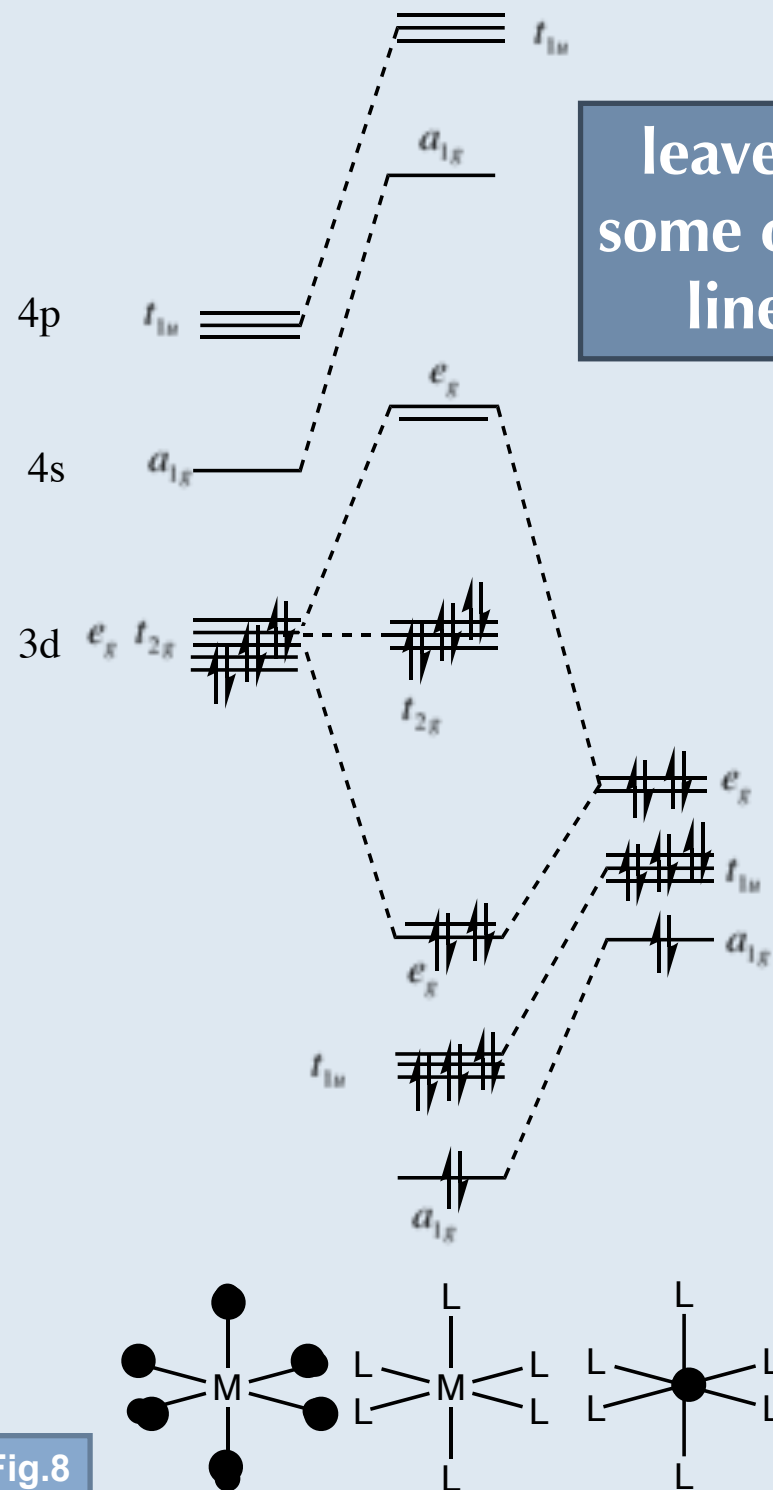


Fig.8

Δ_{oct} parameter

● Δ_{oct} energy span of the dAO dominated MOs

● σ -ligands

◆ t_{2g} is non-bonding

◆ e_g is antibonding!

● Δ_{oct} depends on strength of interaction:

- ◆ $\Delta\varepsilon$ energy between M and L FOs
- ◆ S_{ij} strength/density of overlap of FOs
- ◆ H_{ij} which is hard to estimate!
- ◆ total charge on complex
- ◆ oxidation state of the M (charge on M)

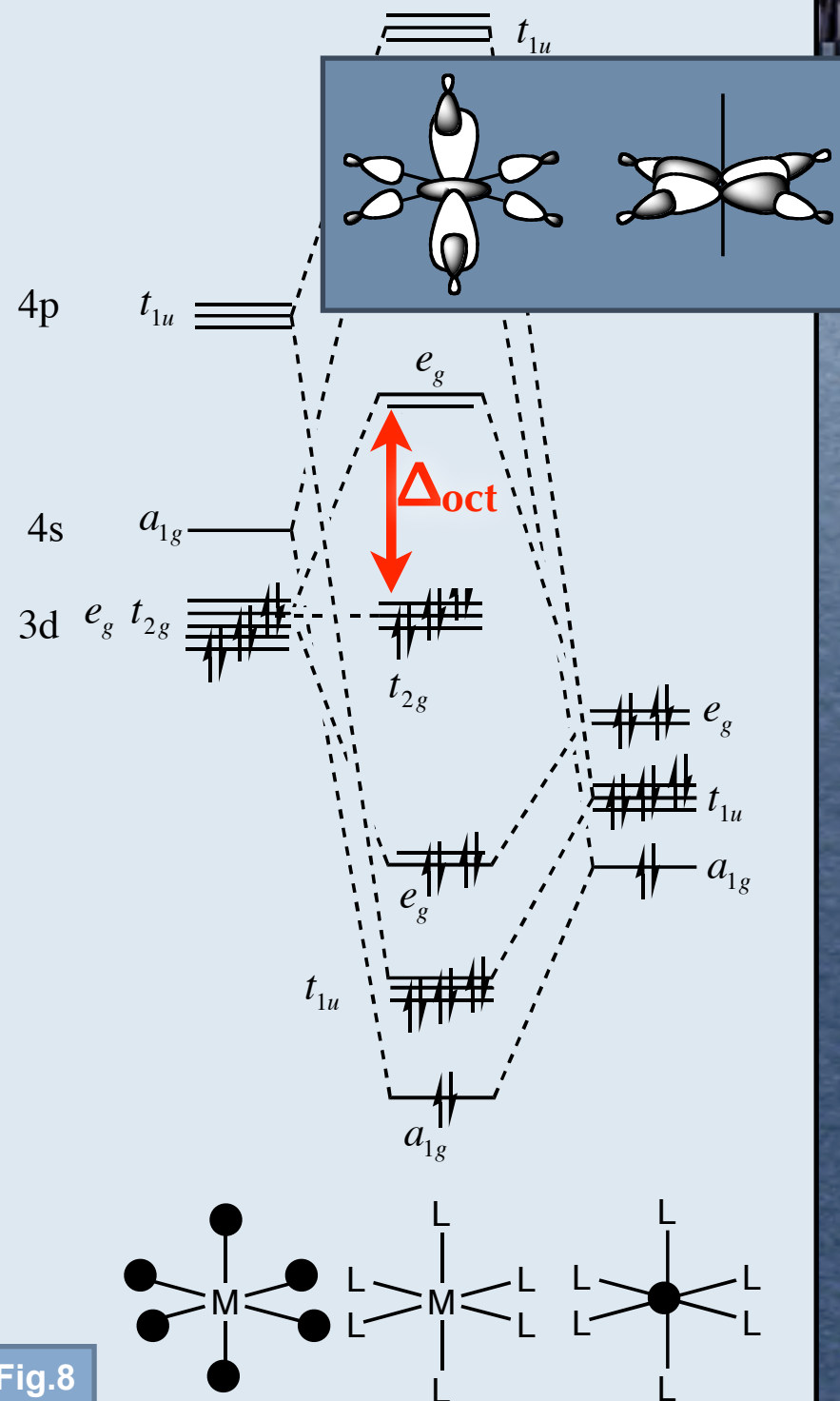


Fig.8

Δ_{oct} parameter

higher in energy the ligand FOs the better the interaction

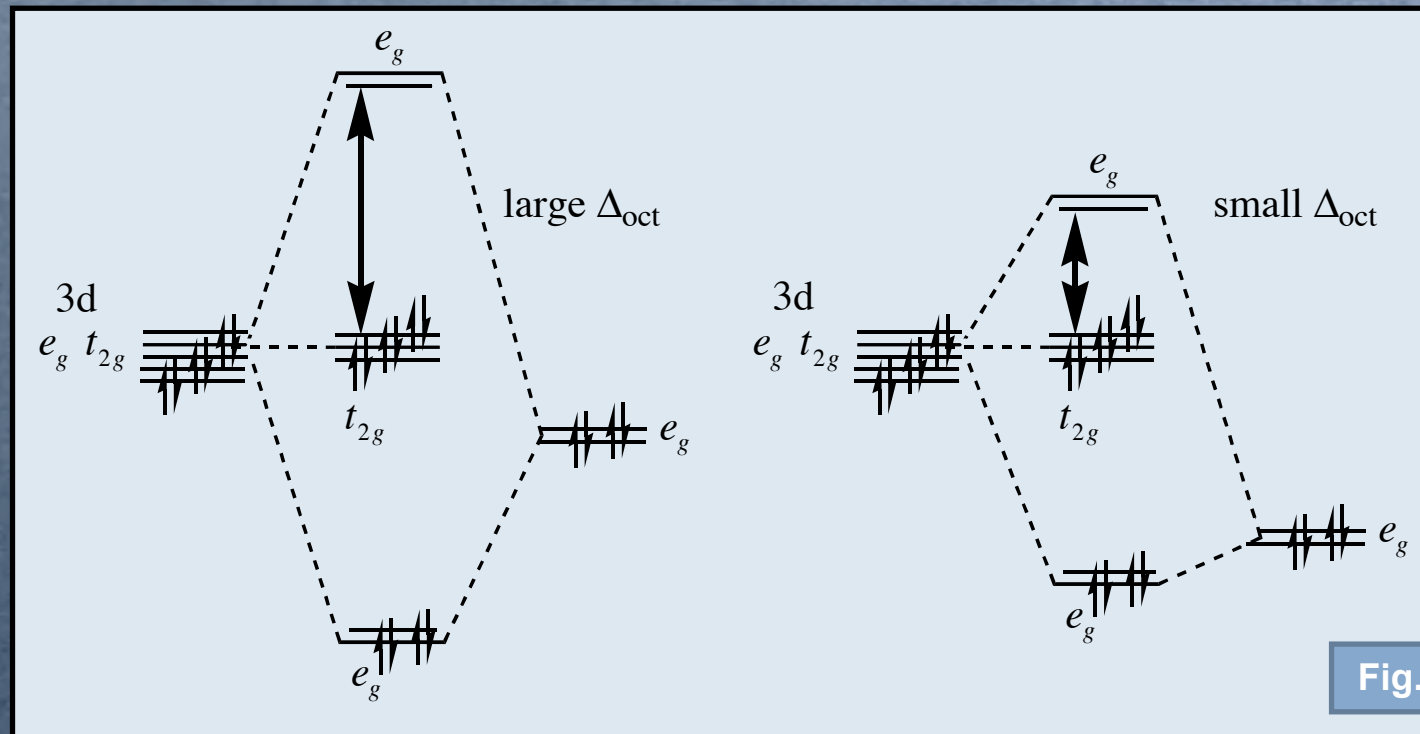


Fig.9

=> larger interaction
=> higher e_g orbital
=> a larger Δ_{oct}

Important!

Colour and d-d Transitions

colour

- ✦ molecule absorbs light
- ✦ electron is excited
- ✦ d-d transition right wavelength for colour
- ✦ $[\text{Ti}(\text{OH}_2)_6]^{3+}$ absorbs in yellow/green and appears red/violet

reminder

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Fig.10

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Fig.13

Coordination Chemistry

Colour and d-d Transitions

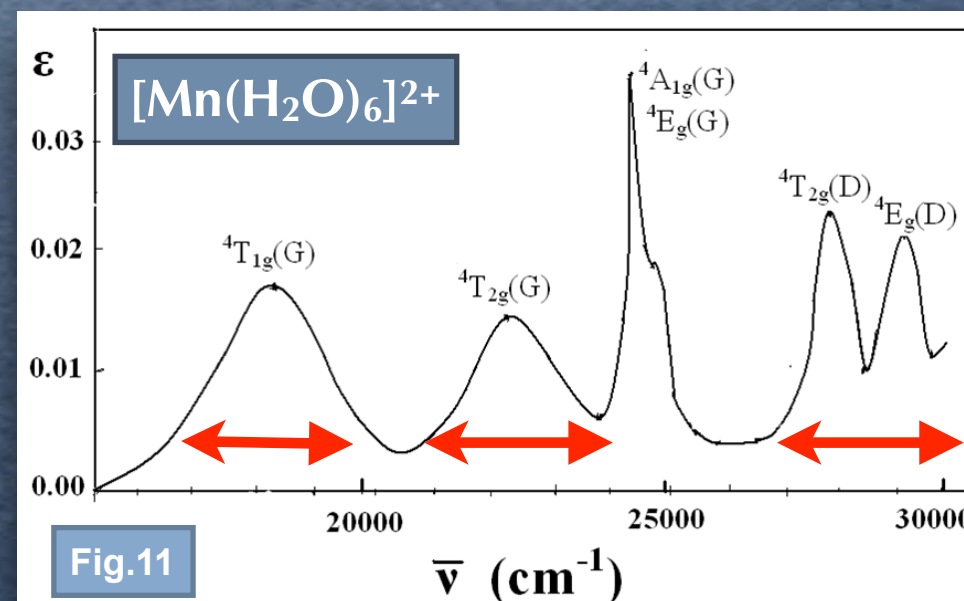
Selection Rules

- ♦ d-d transitions are forbidden
- ♦ Laporte selection rule : only ± 1 for angular quantum number
- ♦ s $\rightarrow$ p or p $\rightarrow$ d NOT d $\rightarrow$ d
- ♦ another form rule : must have a change of parity
- ♦ u $\rightarrow$ g or g $\rightarrow$ u NOT g $\rightarrow$ g (d $\rightarrow$ d transition involves $t_{2g} \rightarrow e_g$)
- ♦ spin selection rule : cannot change spin state

reminder

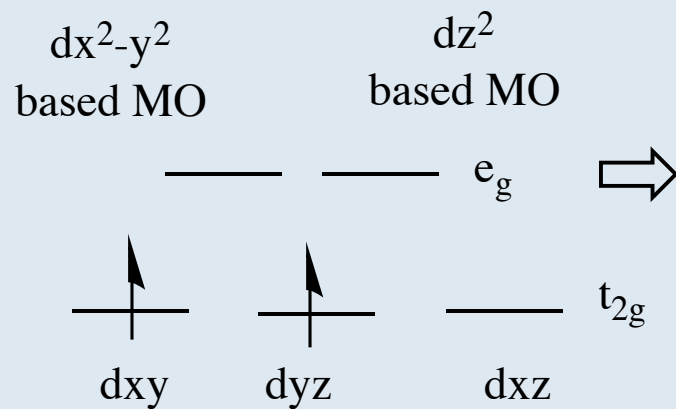
d $\rightarrow$ d transitions

- ♦ rule is broken!
- ♦ weak transitions due to vibronic coupling
- ♦ vibrations and electronic structure couple
- ♦ low intensity
- ♦ broad due to vibrations (move energy levels slightly)



Colour and d-d Transitions

States or configurations



start d² ground state

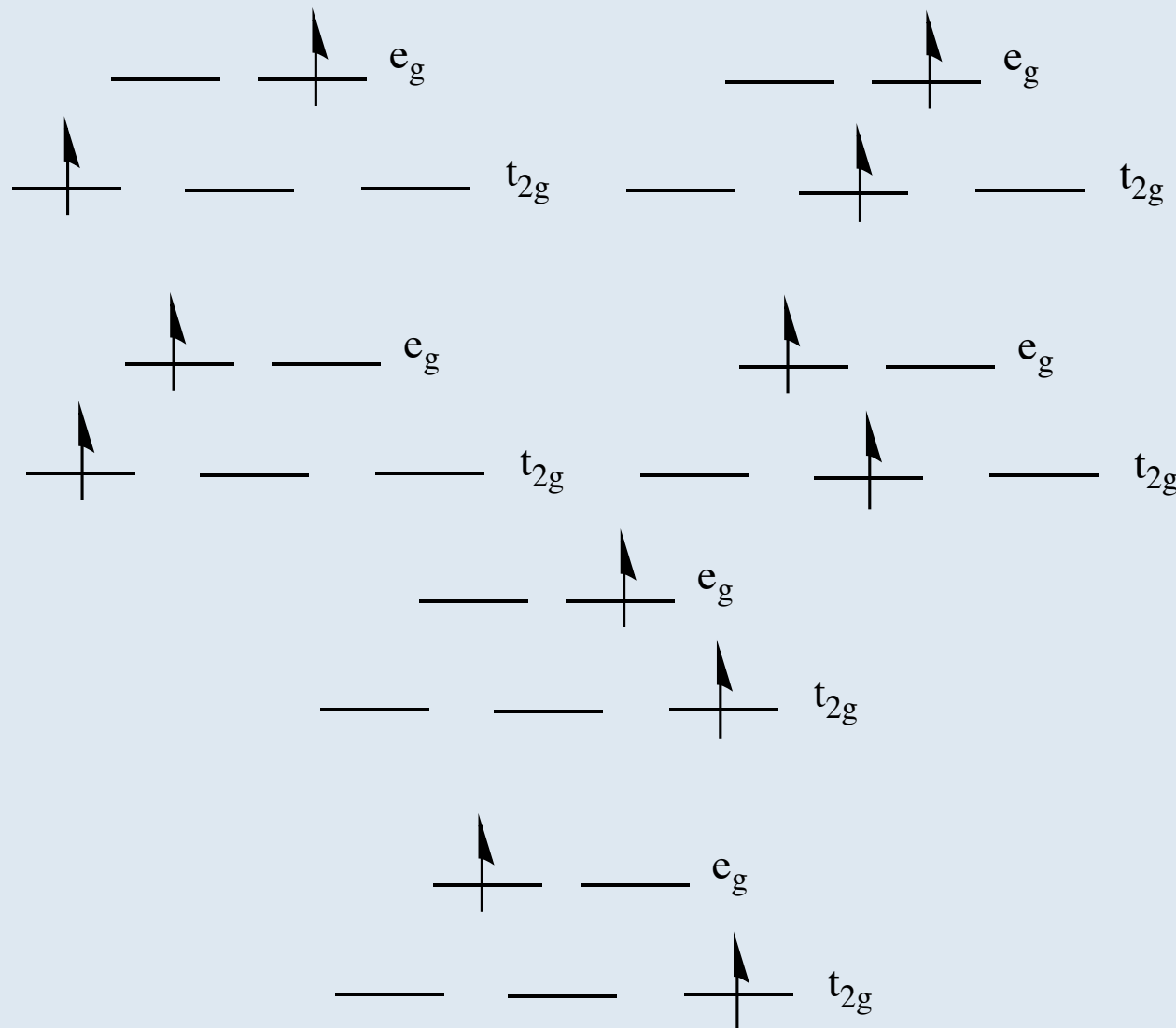
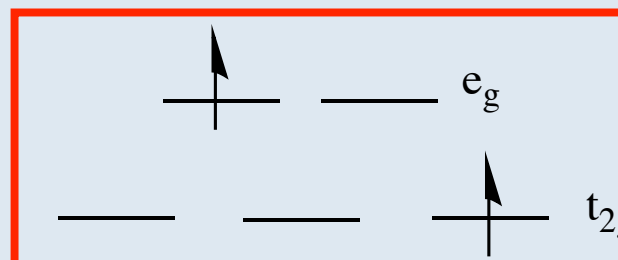
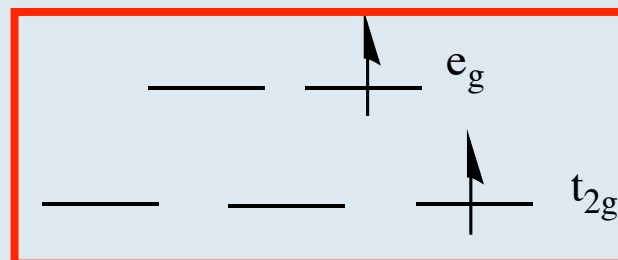
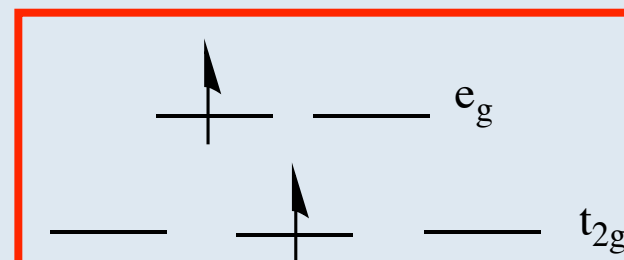
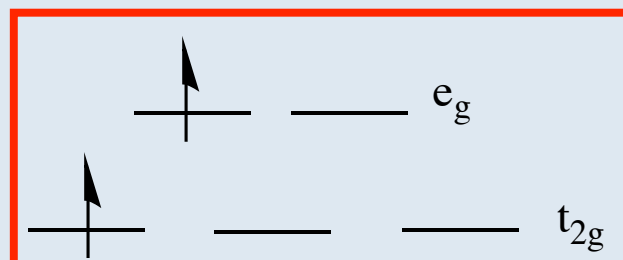
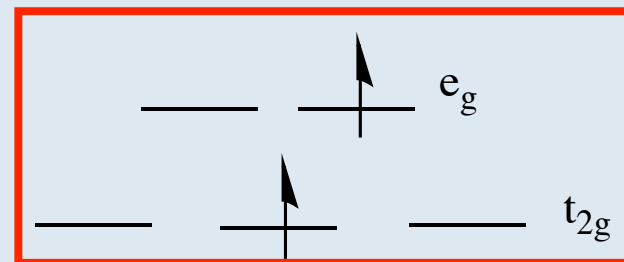
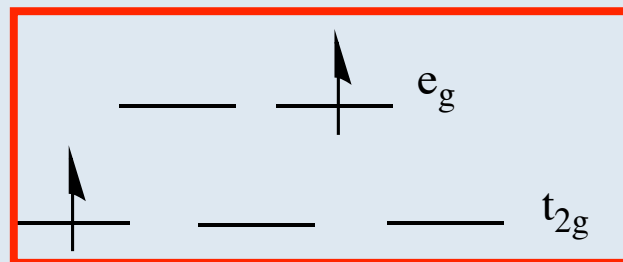
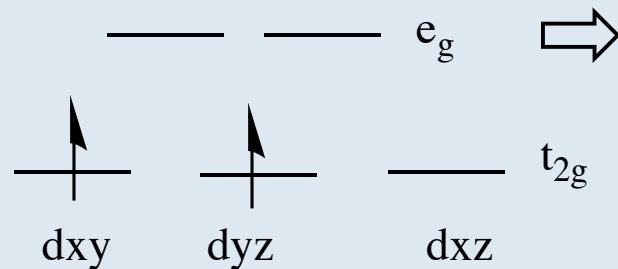


Fig.12

Colour and d-d Transitions

States or configurations

dx^2-y^2 based MO dz^2 based MO



Many initial and final states!

Fig.12

Colour and d-d Transitions

- each state has slightly different energy
 - ✦ different electron distribution
 - ✦ different Coulomb interactions
 - ✦ different electron correlation
- multiple states = multiple peaks in spectra

Term symbols:
define symmetry, multiplicity,
total angular momentum
of the state

important for
lectures next year!

Absorption spectrum of
 $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, downloaded from
http://en.wikipedia.org/wiki/Tanabe-Sugano_diagram, Dec 8
2014

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$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

Fig.12

Spectrochemical Series

uv-Vis experimentally measures Δ_{oct}

order ligands according to size Δ_{oct}

strong field ligand large Δ_{oct}

♦ for example CO

weak field ligand small Δ_{oct}

♦ for example Cl^-



reminder

Spectrochemical series

weak field

$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- <$

$\text{OH}^- < \text{O}^{2-} < \text{H}_2\text{O} <$

$\text{py} < \text{NR}_3 < \text{NH}_3 < \text{en} < \text{NO}_2^-$

$< \text{CH}_3^- < \text{C}_6\text{H}_5^- <$

$\text{CN}^- < \text{CO} < \text{NO}^+$

strong field

Spectrochemical Series

example!

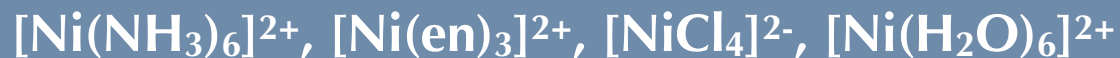
replace NiL_6 ligands from stronger field to weaker field change Δ_{oct} and the colour

- ♦ $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ has low energy, small Δ_{oct}
- ♦ absorbs in the red and is green

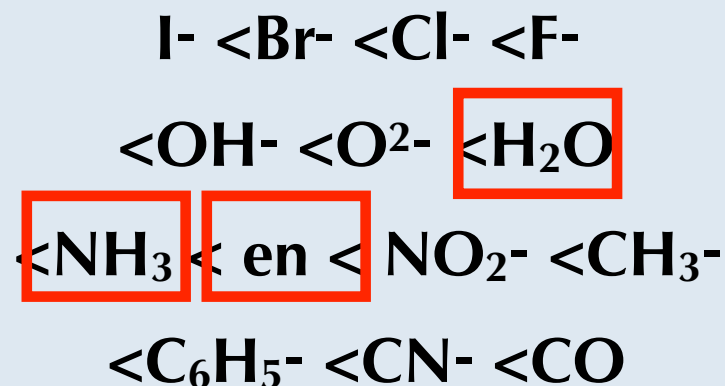
Colour of various Ni(II) complexes in aqueous solution.

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Fig.13



Spectrochemical series



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Fig.13

Image from http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Crystal_Field_Theory/Colors_of_Coordination_Complexes, downloaded 1 Dec 2014

Image from [http://en.wikipedia.org/wiki/Nickel\(II\)_chloride](http://en.wikipedia.org/wiki/Nickel(II)_chloride), LHchem, downloaded 1 Dec 2014

TM-Colour!

 Info-graphics from <http://www.compoundchem.com/>

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Other Factors

● not only the ligands effect the size of Δ_{oct}

- ◆ overall charge on the the complex
- ◆ oxidation state metal
- ◆ charge on the metal / ligands
- ◆ density of overlapping orbitals
- ◆ radius of metal (row)
- ◆ steric congestion ligands

● high charge on M

- ◆ draws ligands in
- ◆ increases overlap
- ◆ increases interaction
- ◆ increases Δ_{oct}

● large ligand

- ◆ cannot approach metal
- ◆ poor overlap
- ◆ reduced interaction
- ◆ decreases Δ_{oct}

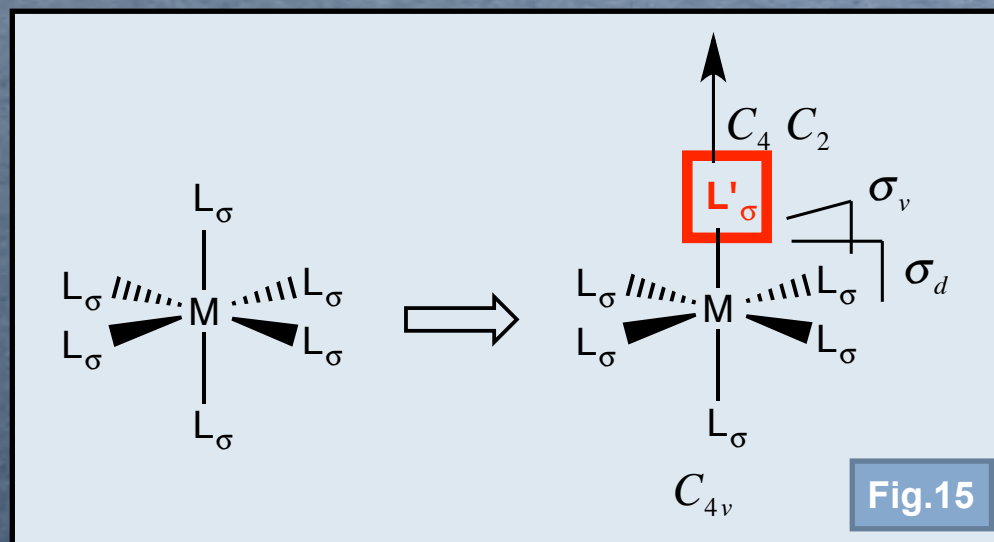
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Fig.14

Reduce the Symmetry

- replace 1 ligand with a different σ -ligand
- loss of symmetry $O_h \rightarrow C_{4v}$



● process simple:

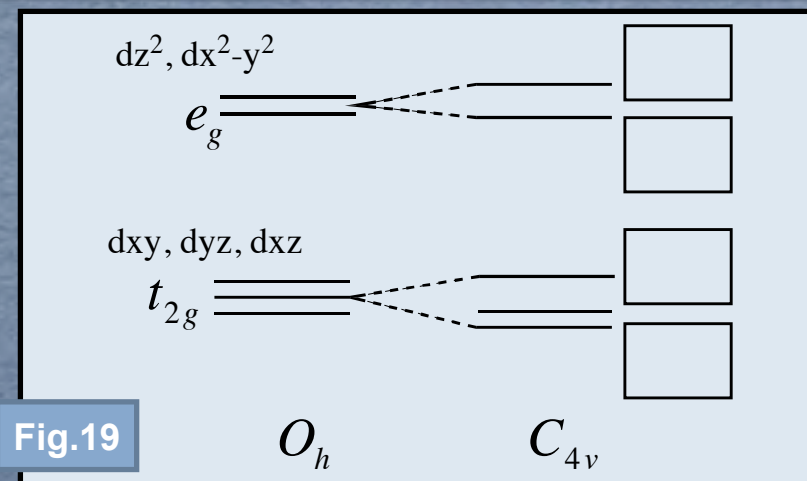
- ◆ MOs remain the same
- ◆ just need to work out reduced symmetry labels!
- ◆ watch for degeneracy breaking

In-Class Activity

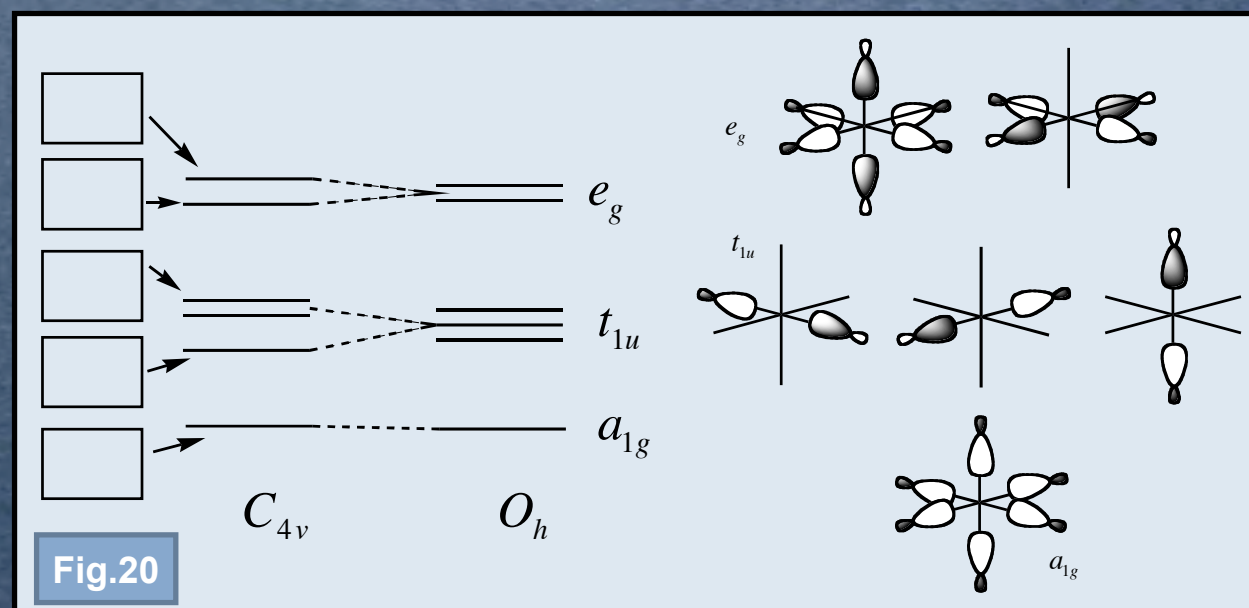
- determine new symmetry labels for metal AOs
- determine the new symmetry labels for the ligand FOs

VERY Important!

use short-cuts and your character table for C_{4v}



degenerate levels remain degenerate, I've split them for ease of interpretation



In-Class Activity

- now combine the TM dAOs and the ligand FO to form the energy level diagram for a C_{4v} TM complex

Fig.18, page 10 of your notes

In-Class Activity

now combine the TM dAOs and the ligand FO to form the energy level diagram for a C_{4v} TM complex

hint 1

add the fragment orbital energy levels

4p e a_1 $\equiv$

4s a_1 —

3d b_1 a_1 b_2 e

b_1 a_1
 e a_1
 a_1

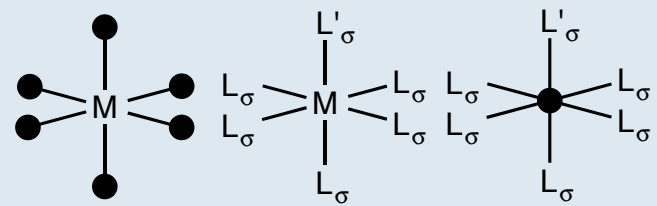


Fig.19

In-Class Activity

- now combine the TM dAOs and the ligand FO to form the energy level diagram for a C_{4v} TM complex

hint 1

add the fragment orbital energy levels

hint 2

combine levels of the same symmetry

4p $\begin{matrix} e \\ a_1 \end{matrix} \equiv \equiv \equiv$

4s $a_1 \text{ ———}$

3d $\begin{matrix} b_1 \\ a_1 \\ b_2 \\ e \end{matrix}$

degenerate spread out to illustrate different symmetries

$\begin{matrix} b_1 & a_1 \\ e & a_1 \\ a_1 \end{matrix}$

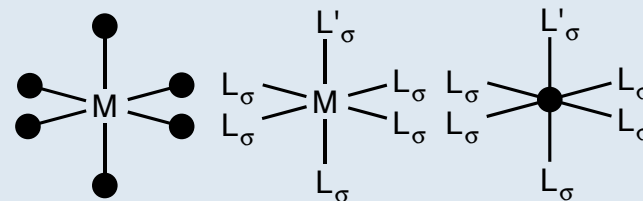


Fig.19

C_{4v} Diagram

completed!

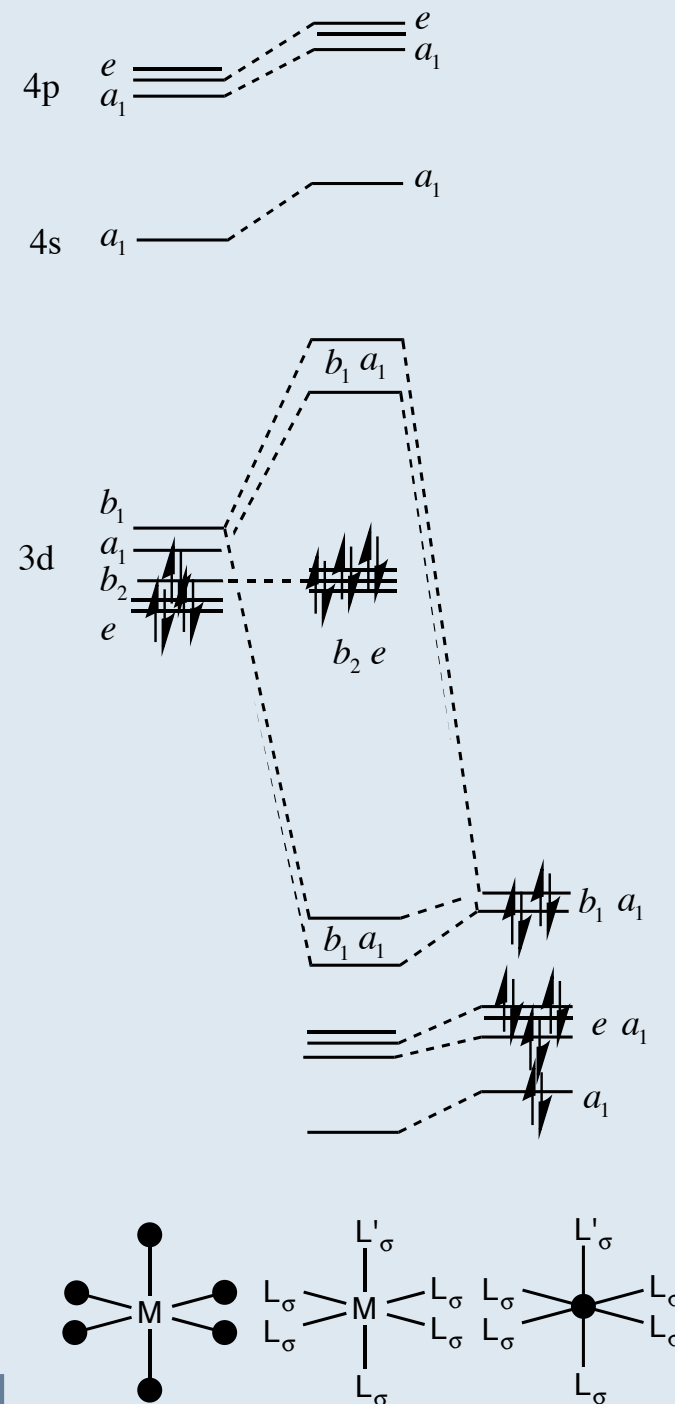
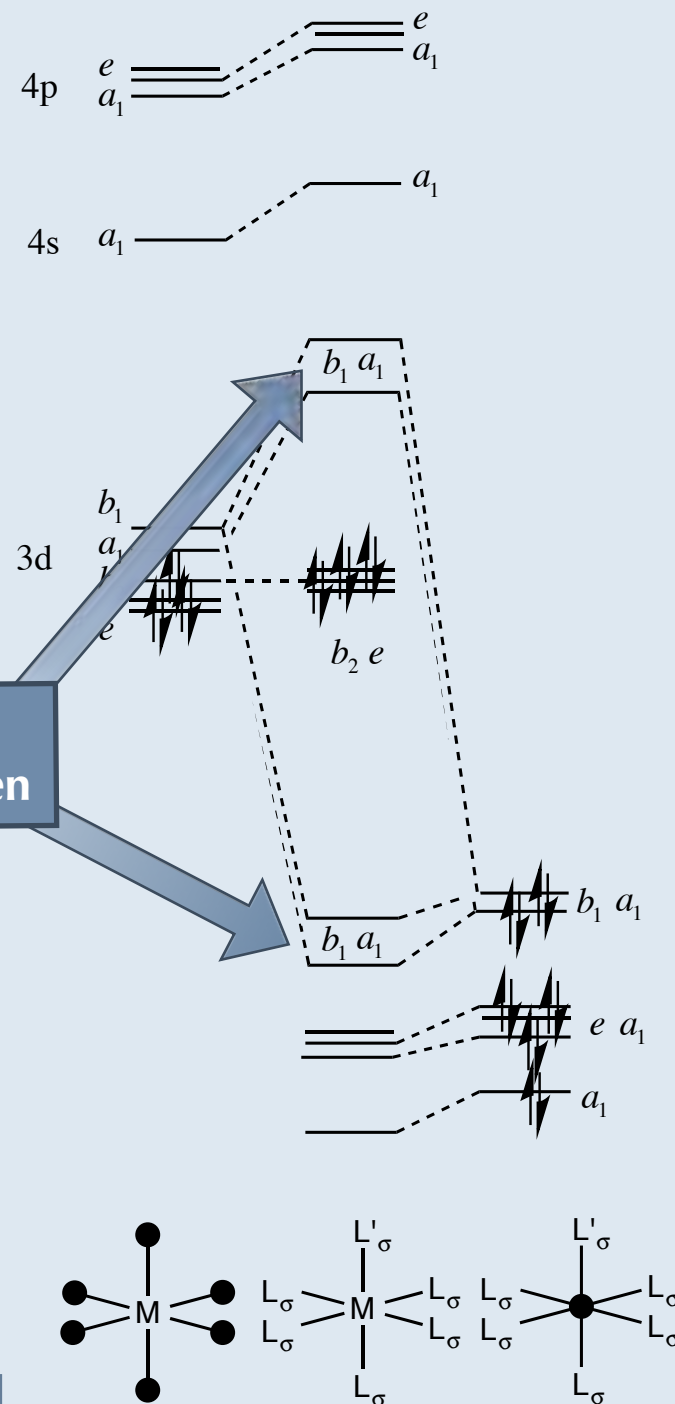


Fig.19

C_{4v} Diagram

completed!

was e_g now
degeneracy is broken



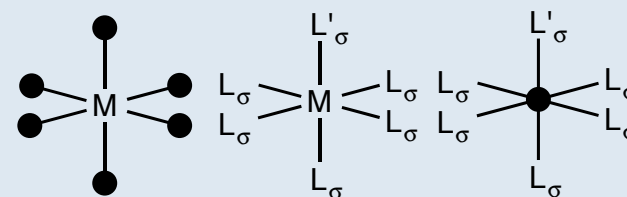
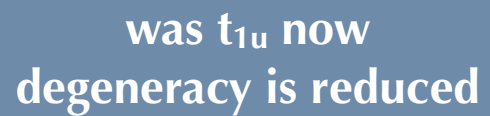
 completed!

Fig.19

C_{4v} Diagram

completed!

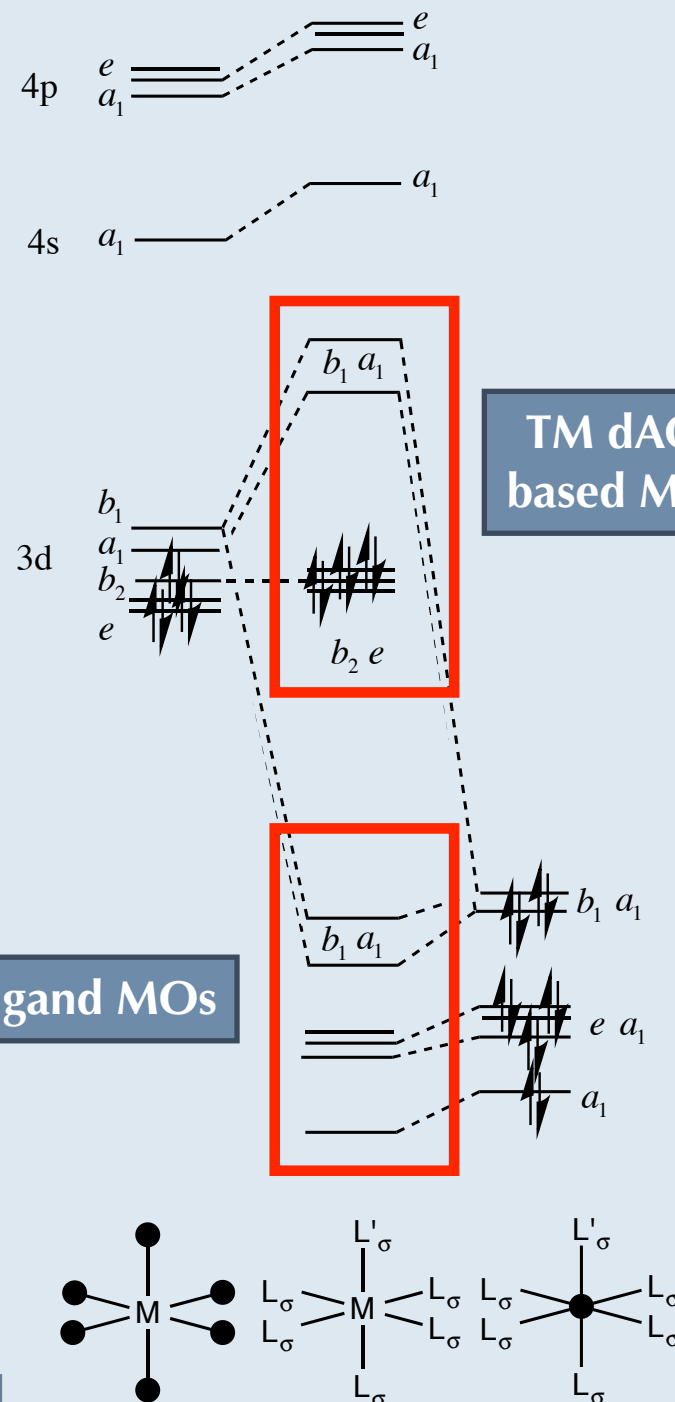


Fig.19

C_{4v} TM Diagram

- primary effect of the reduction in symmetry $\Rightarrow$ split the e_g energy levels
- ordering of a_1 and b_1 will depend on the ligands
- Δ_{oct} is splitting of dAO manifold (group of orbitals!)

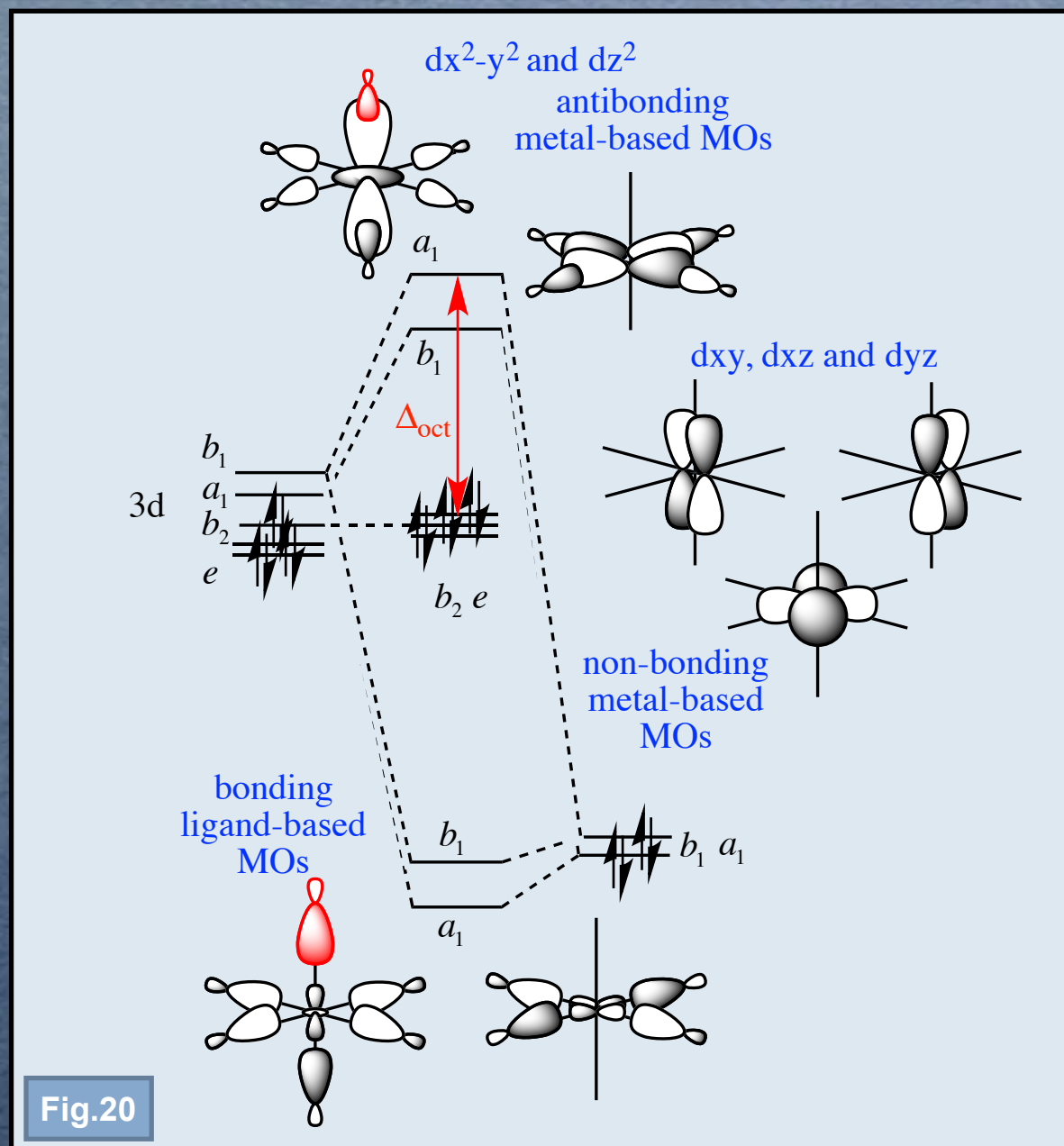


Fig.20

Key Points

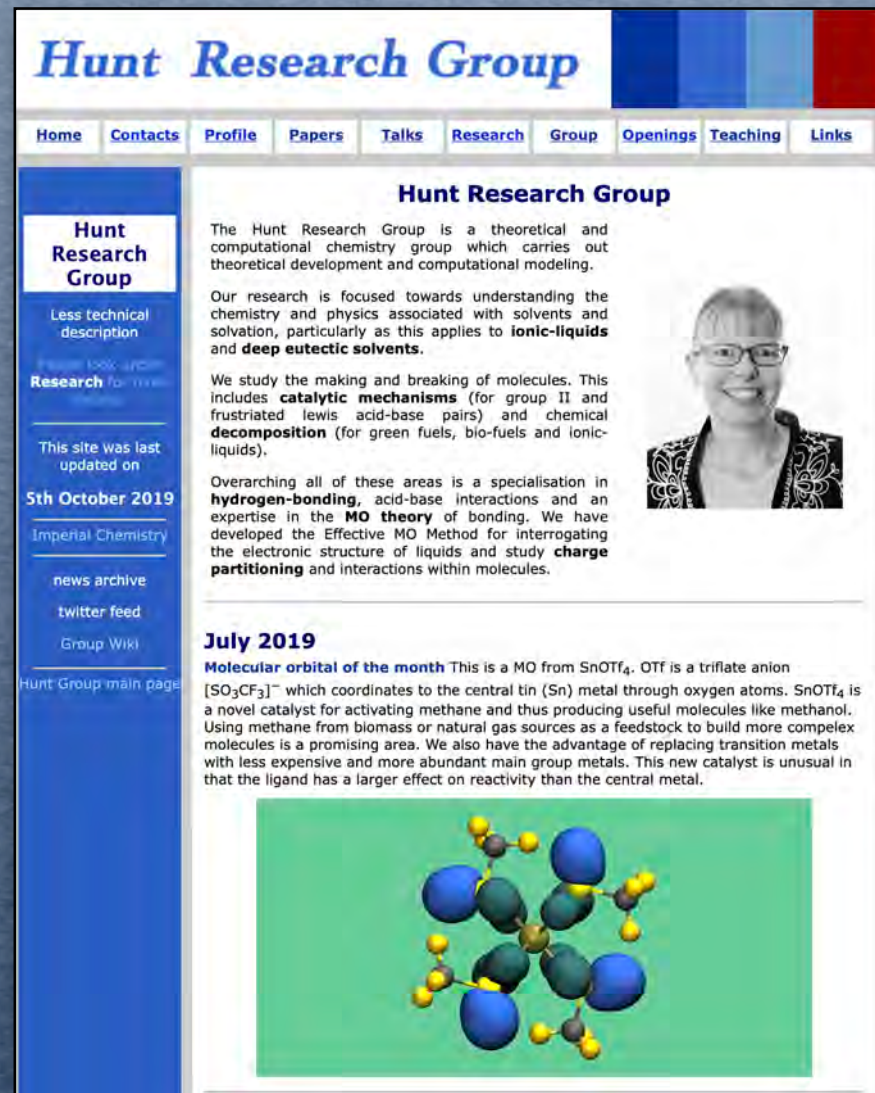
- be able to draw energy level diagrams for octahedral TM complexes with L_σ
- be able to draw and describe the important MOs
- be able to discuss key features of the diagrams, especially features relating to the character of the MOs
- be able to define the octahedral splitting parameter and be able to discuss key properties that impact on or effect Δ_{oct}
- be able to draw the energy diagram for a lower symmetry TM complex with σ -bonding ligands, including square planar

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!!



The screenshot shows the homepage of the Hunt Research Group website. The header features the group's name in a large blue font, followed by a navigation bar with links: Home, Contacts, Profile, Papers, Talks, Research, Group, Openings, Teaching, and Links. The main content area is divided into two columns. The left column contains a sidebar with links to 'Less technical description', 'Research for...', 'This site was last updated on 5th October 2019', 'Imperial Chemistry', 'news archive', 'twitter feed', and 'Group Wiki'. The right column contains the main text, which includes a welcome message, a description of the group's research focus (theoretical and computational chemistry), a list of research areas (ionic-liquids, deep eutectic solvents, catalytic mechanisms, frustrated Lewis acid-base pairs, and chemical decomposition), and a section for 'Molecular orbital of the month' featuring a molecular orbital diagram of a tin complex.

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.

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.

