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!

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

MO checklist

work through for an octahedral molecule

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

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	
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. 1

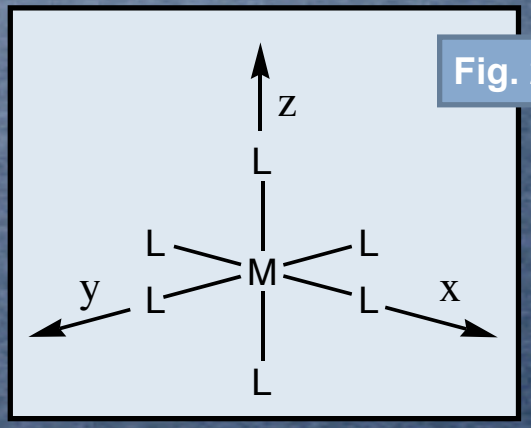
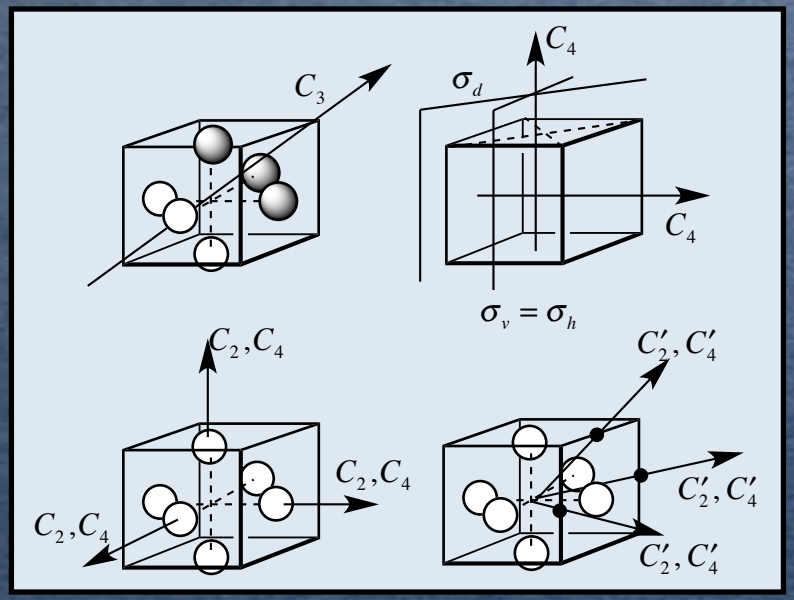


Fig. 2



Steps 3-4: Fragment Orbitals

- **determine the fragments**
  - ✦central metal and the symmetry adapted fragment orbitals for L_6

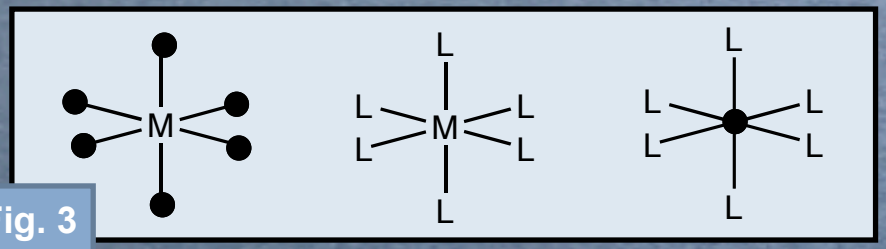


Fig. 3

- **determine the energy levels and symmetry labels of the fragments**
  - ✦covered last lecture => tricks to help remember

metal

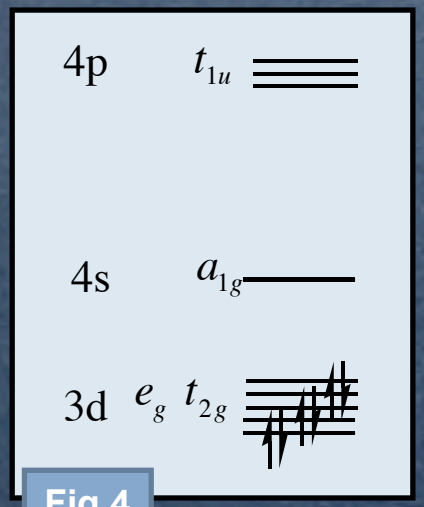


Fig.4

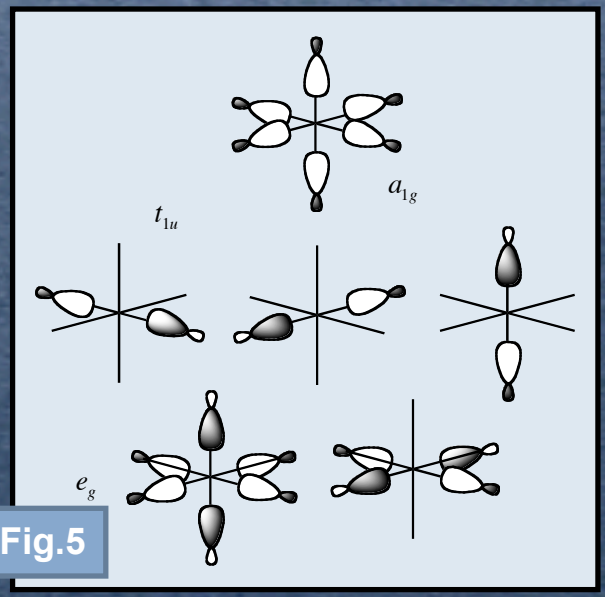
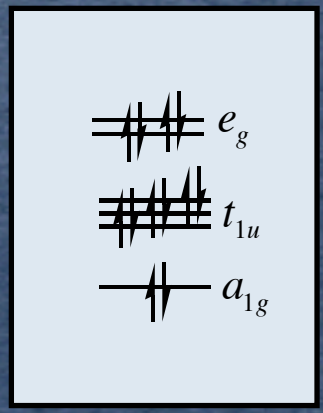


Fig.5

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!

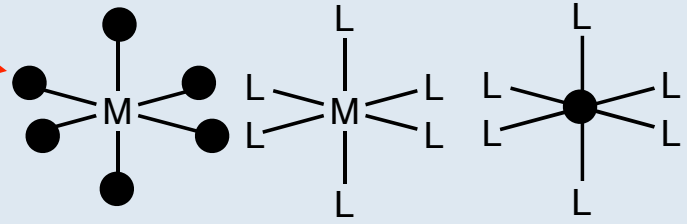
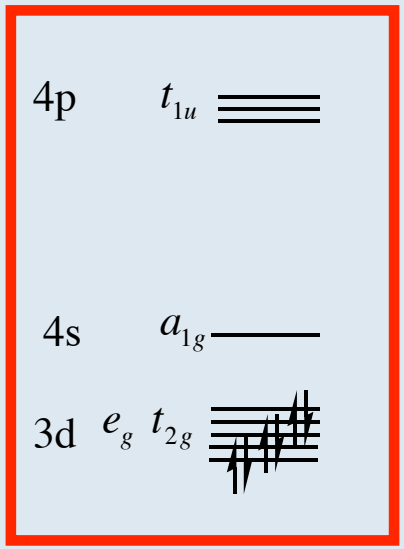


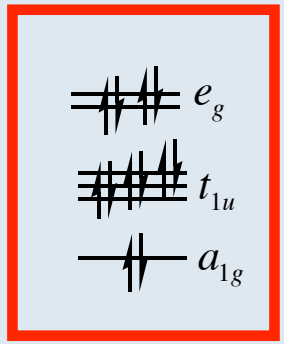
Fig.6

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!





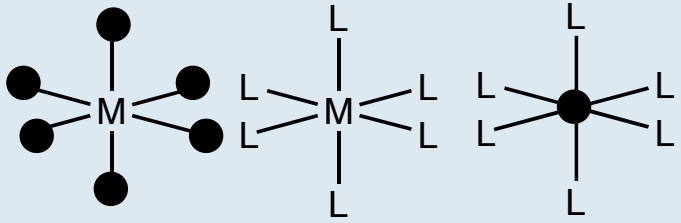


Fig.6

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

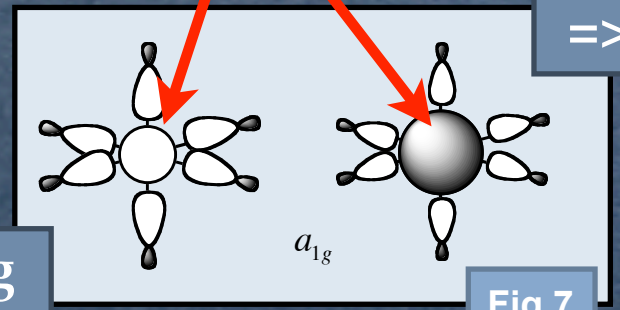
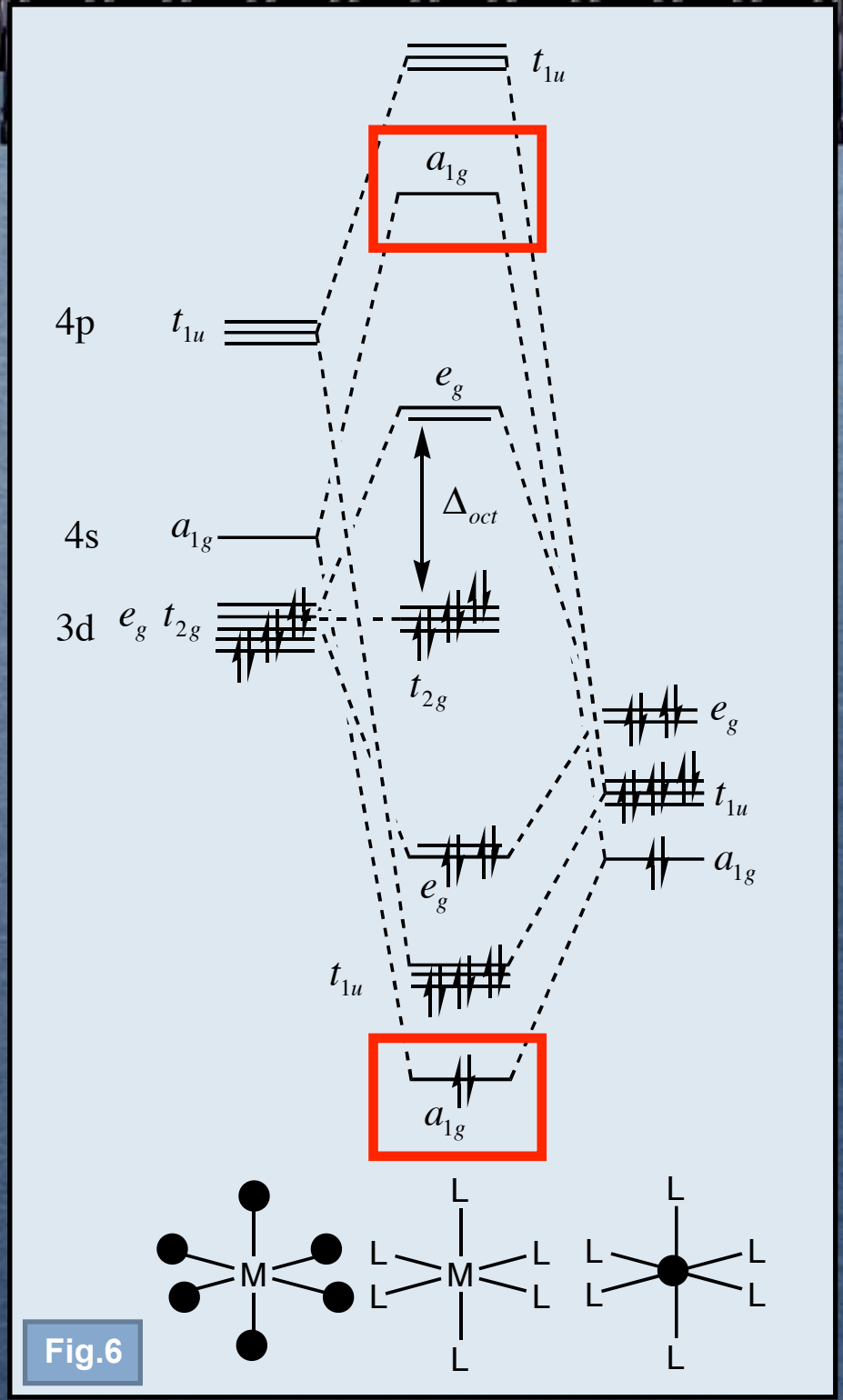


Fig.7



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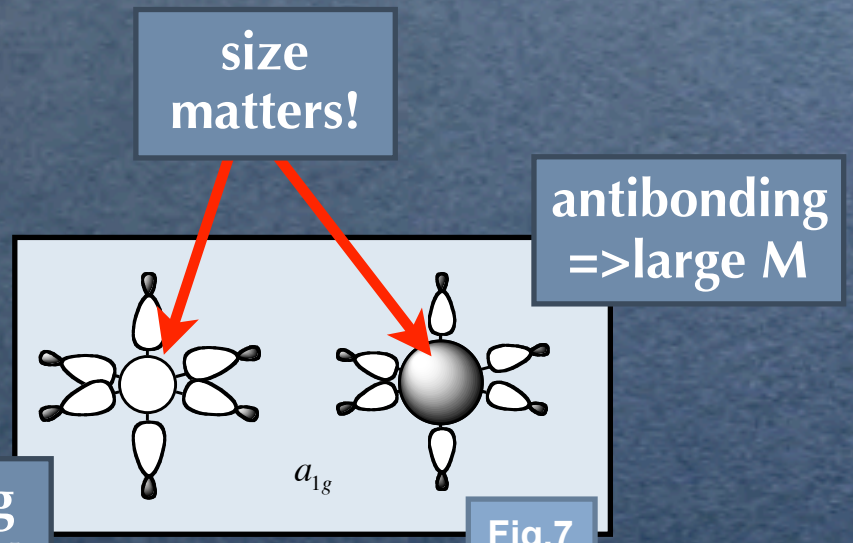


Fig.7

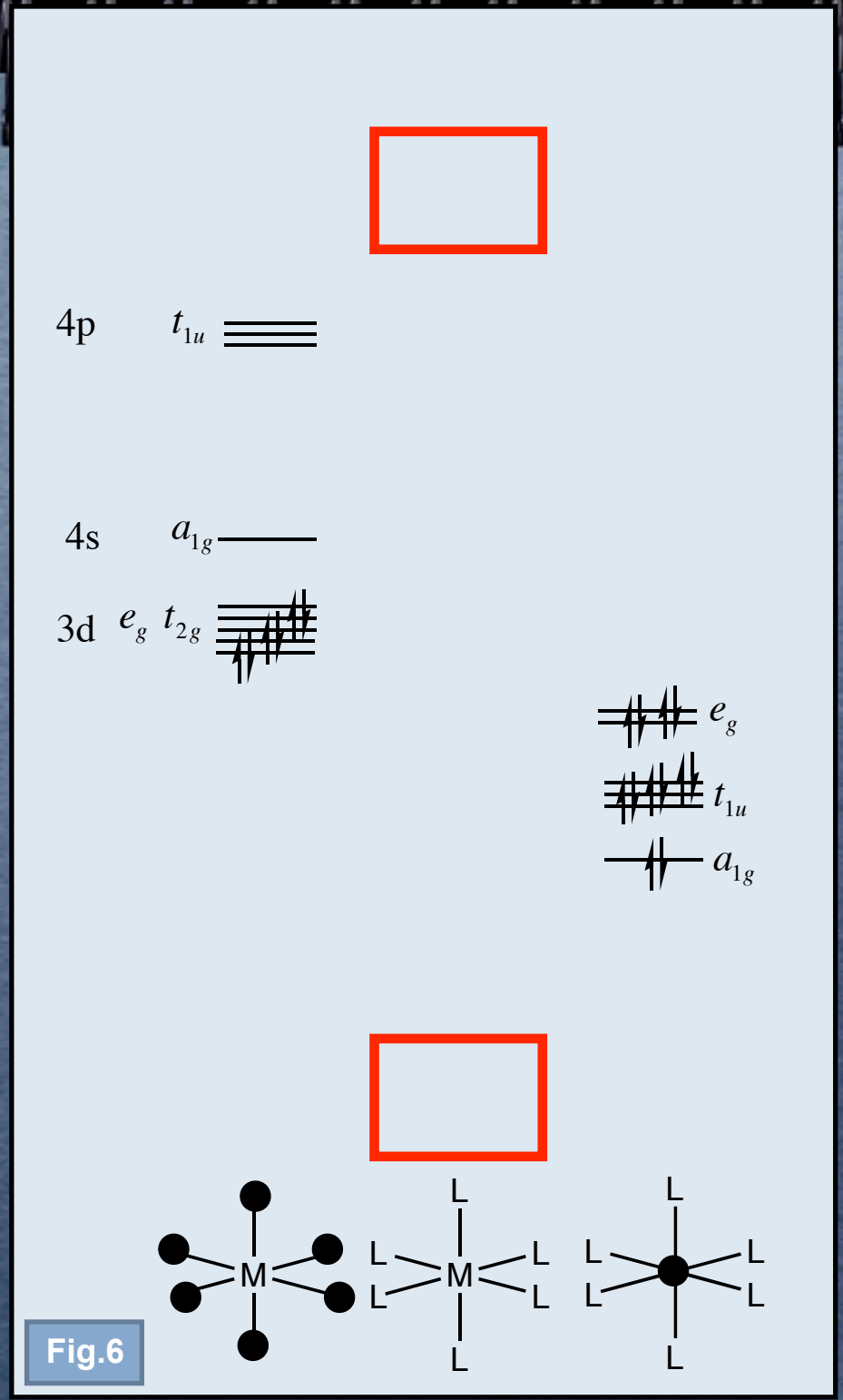


Fig.6

Combine Orbitals

- **estimate the extent of energy splitting**
  - ✦ t_{1u} interaction is p-σ => medium
  - ✦ t_{1u} energy difference is very large => decreases splitting

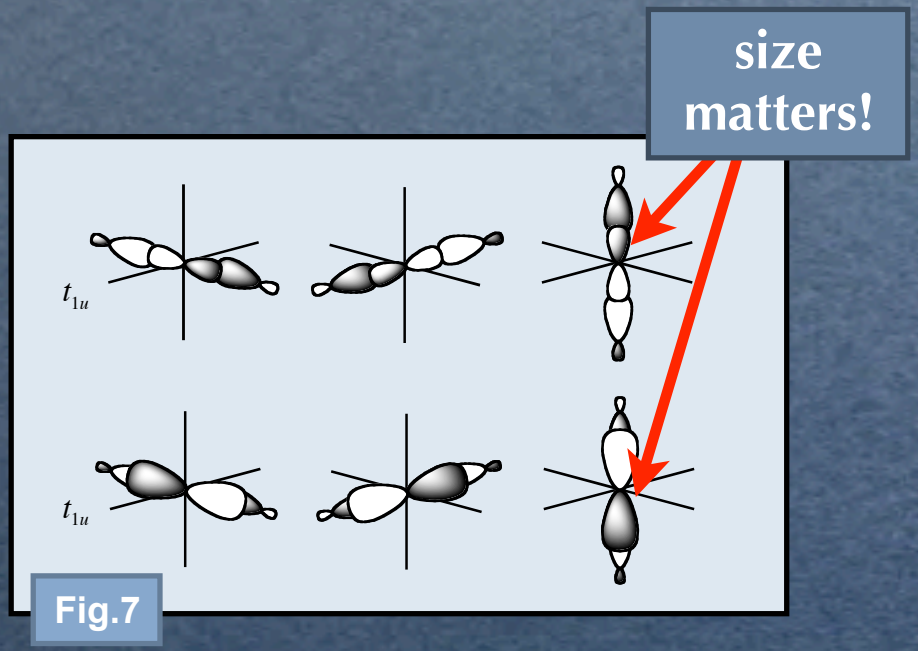


Fig.7

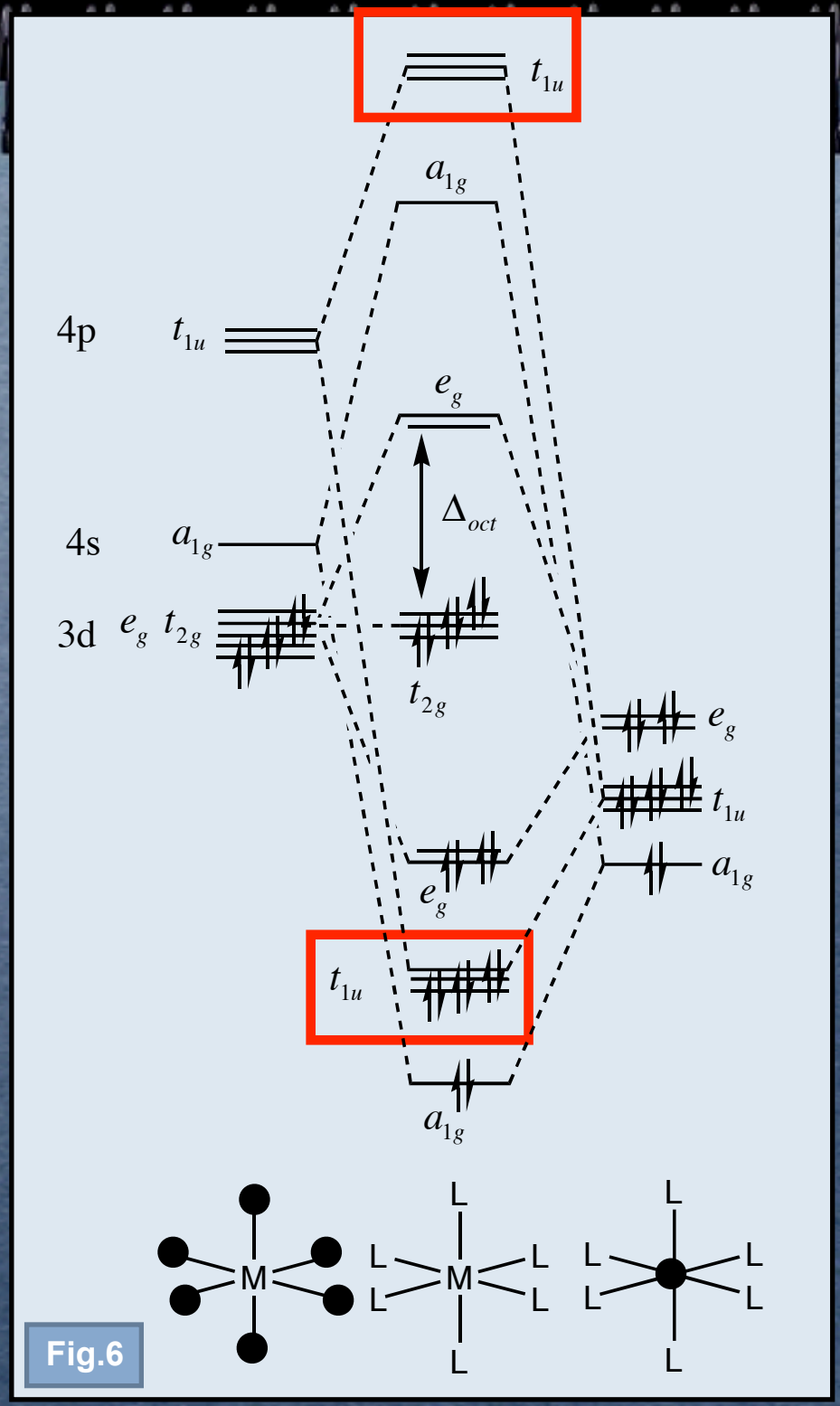


Fig.6

Combine Orbitals

- **estimate the extent of energy splitting**
  - ✦e_g interaction is d-σ => small
  - ✦e_g close in energy => increases splitting

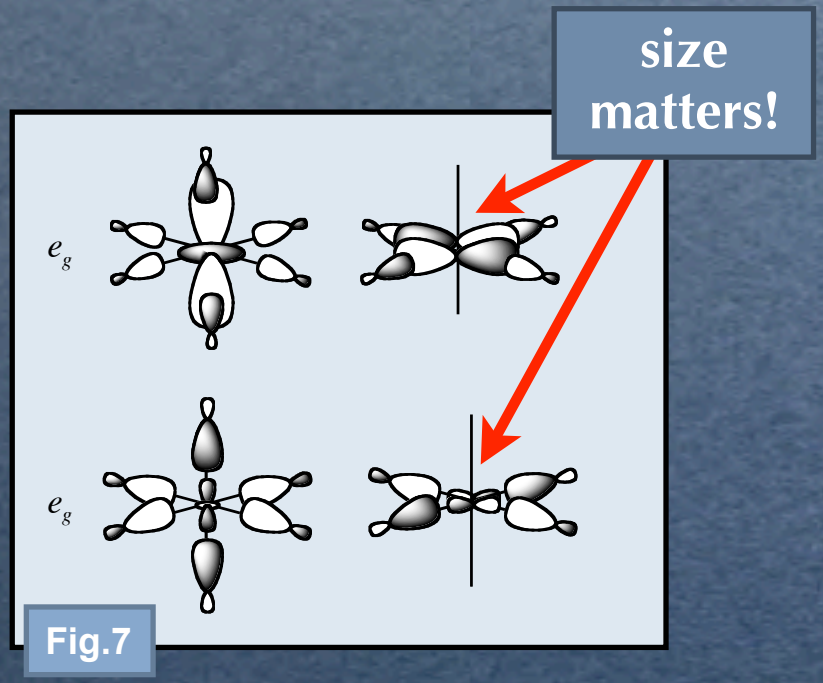


Fig.7

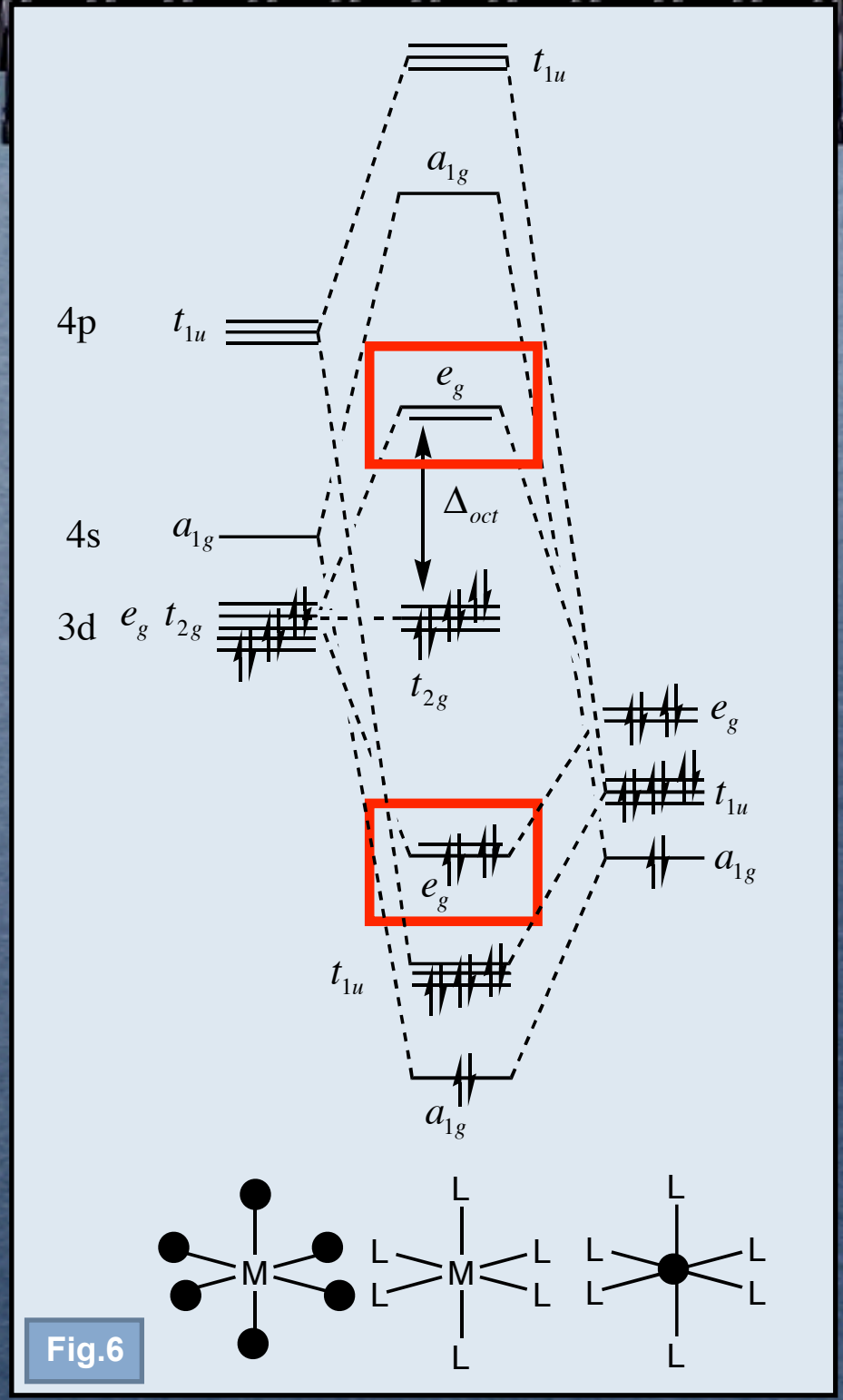


Fig.6

Combine Orbitals

- **estimate the extent of energy splitting**
  - ✦ metal t_{2g} remain non-bonding as there are no ligand orbitals of this symmetry

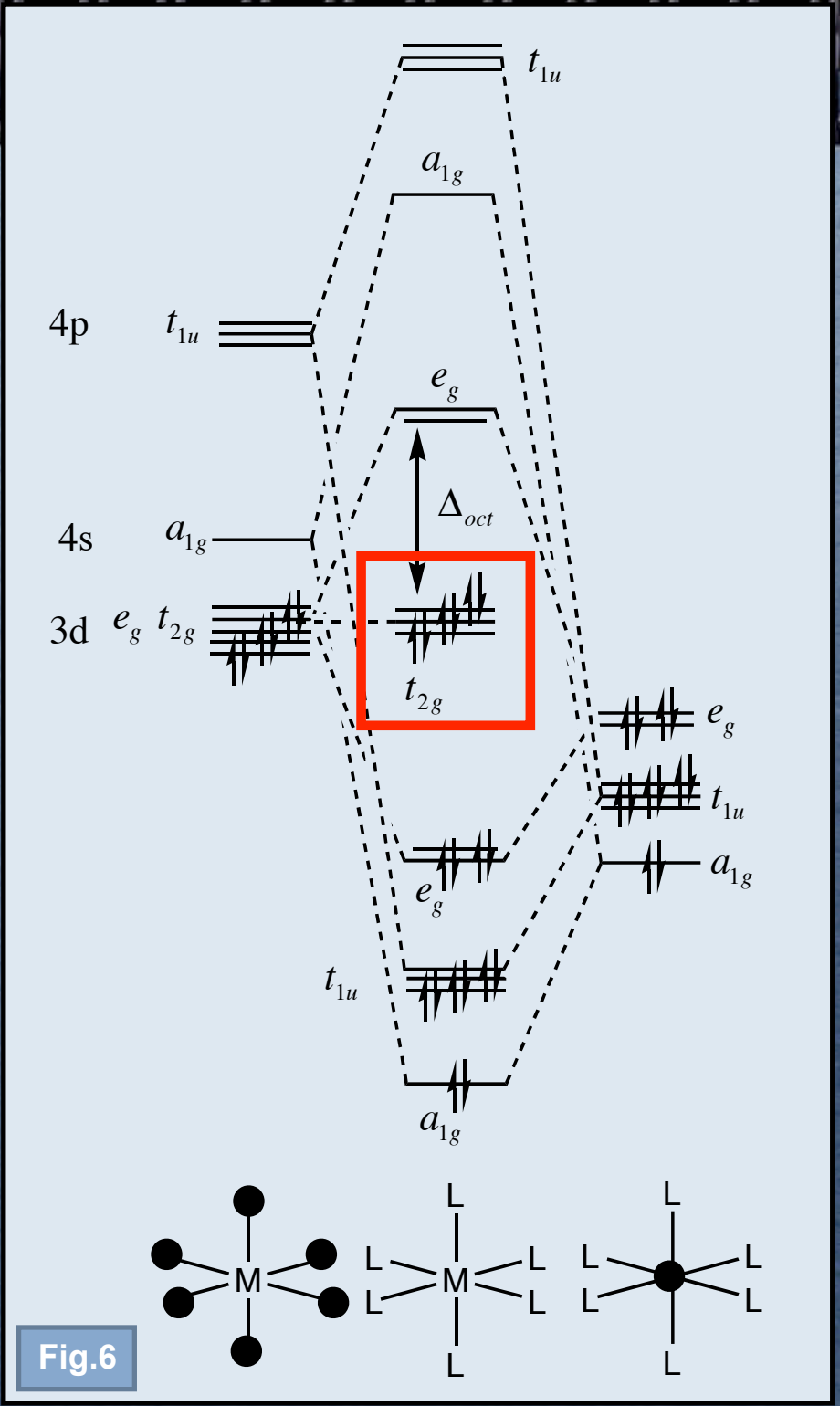
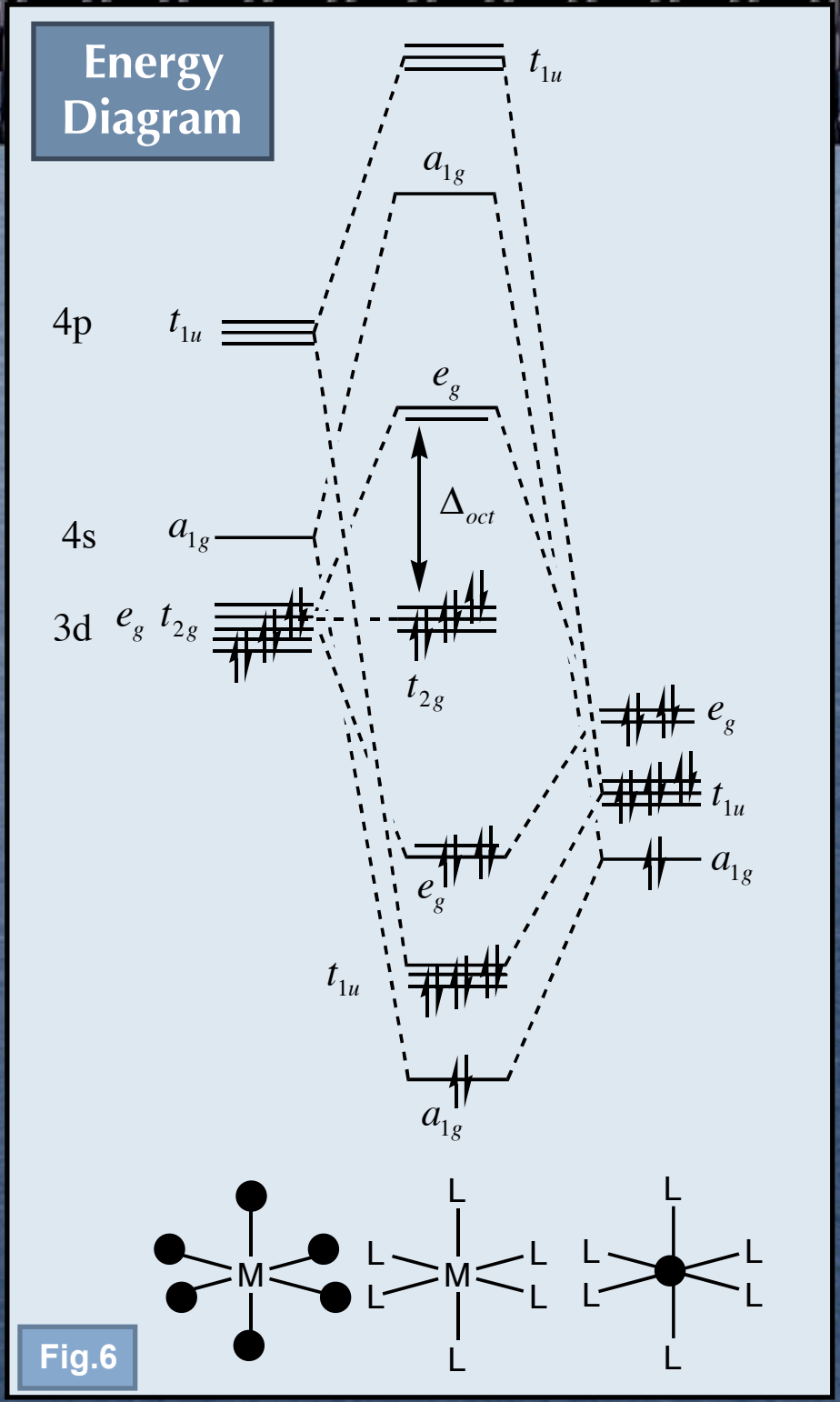


Fig.6

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!**



The full MO diagram!

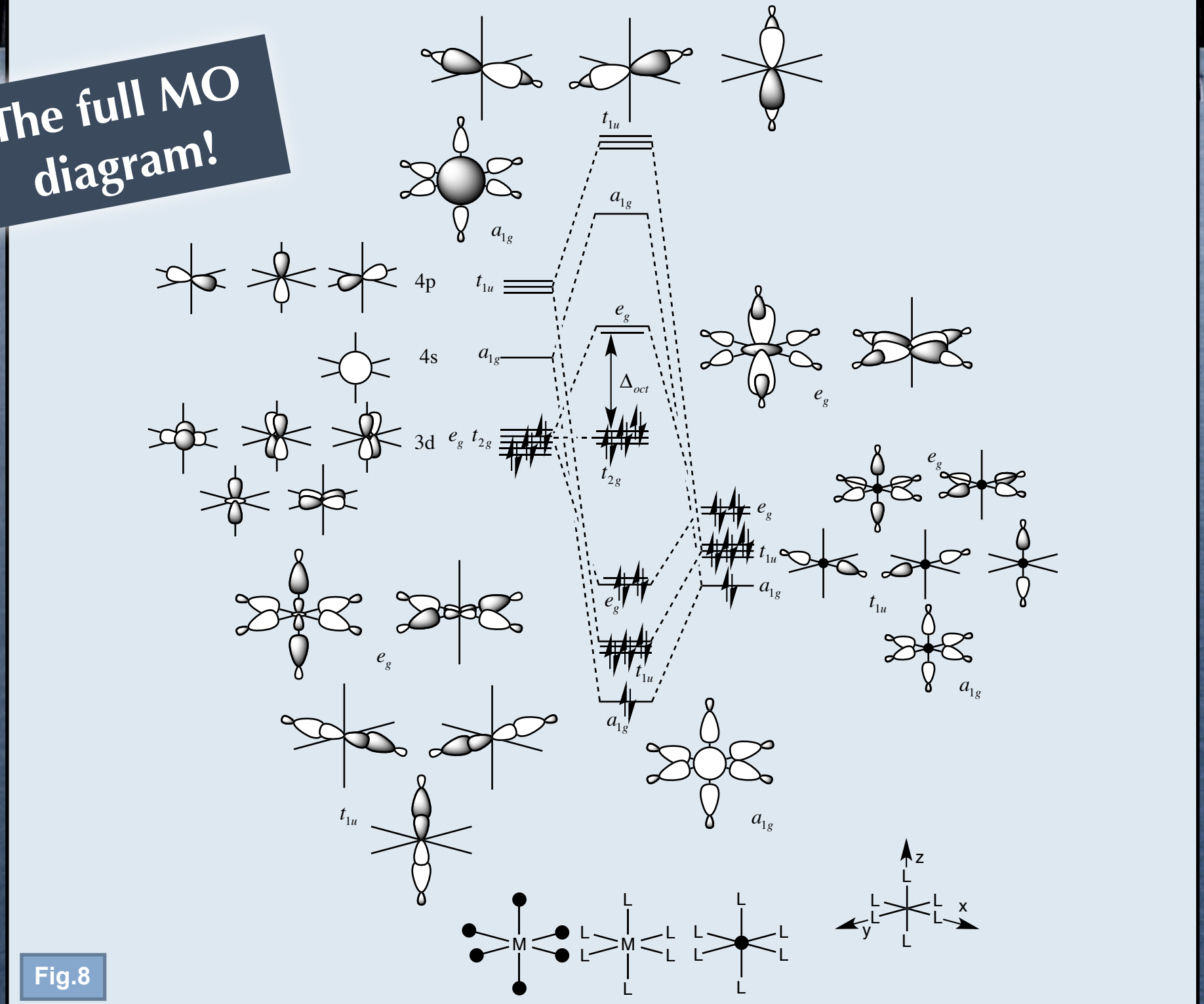


Fig.8

Step 9: Analysis

- three lowest energy sets of orbitals are ligand based

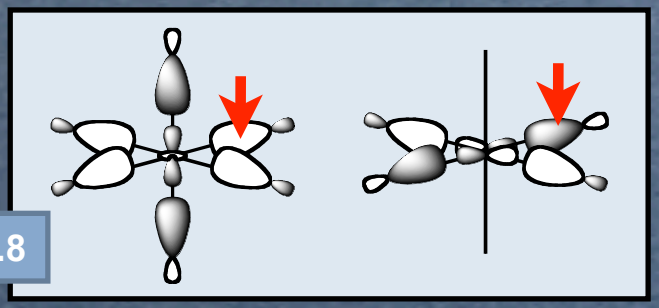
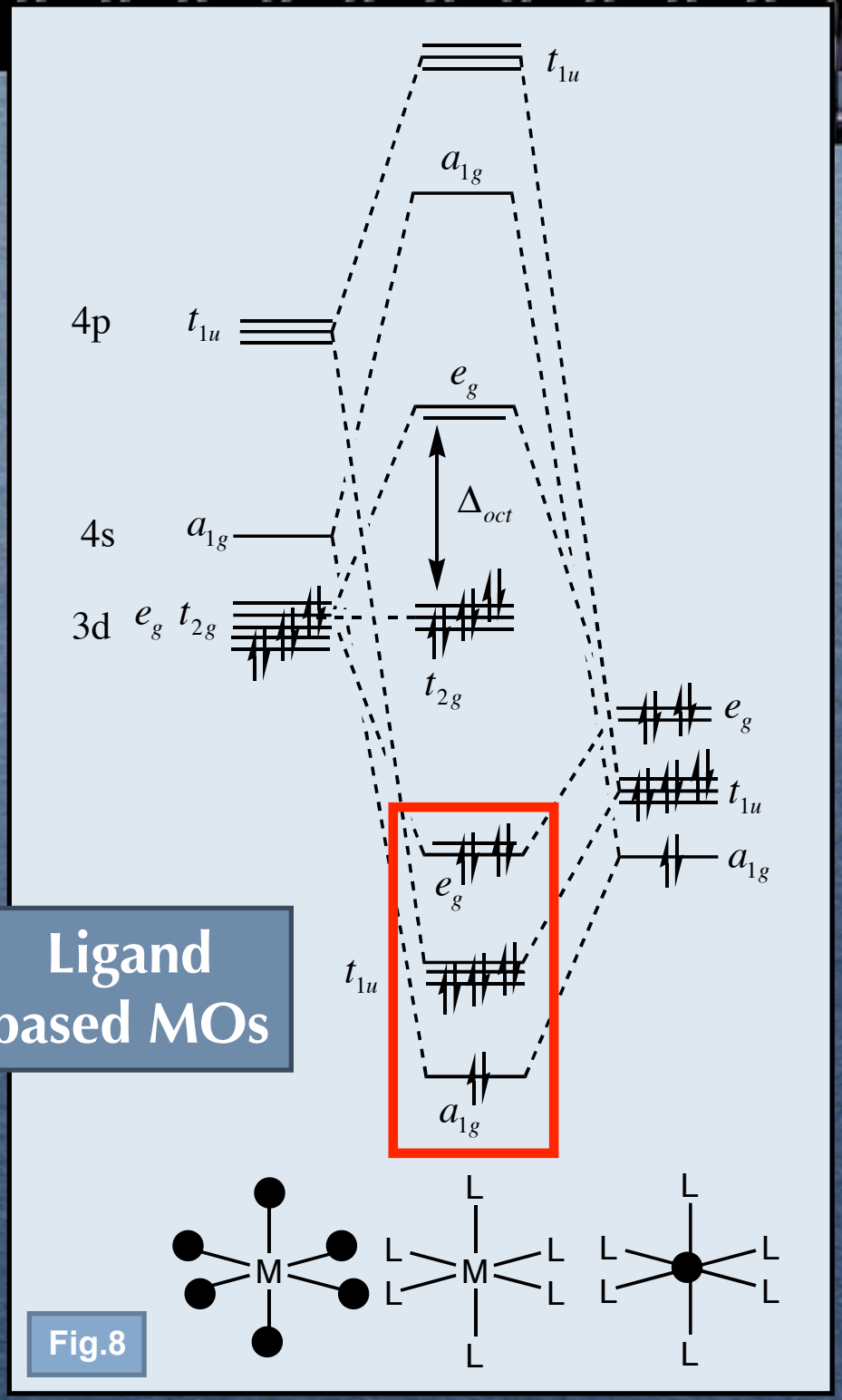


Fig.8

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

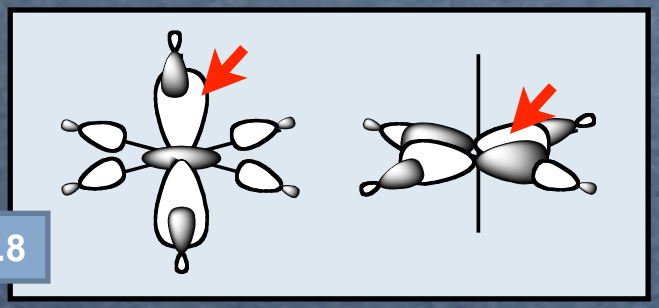


Fig.8

for example the e_g MOs

Important!

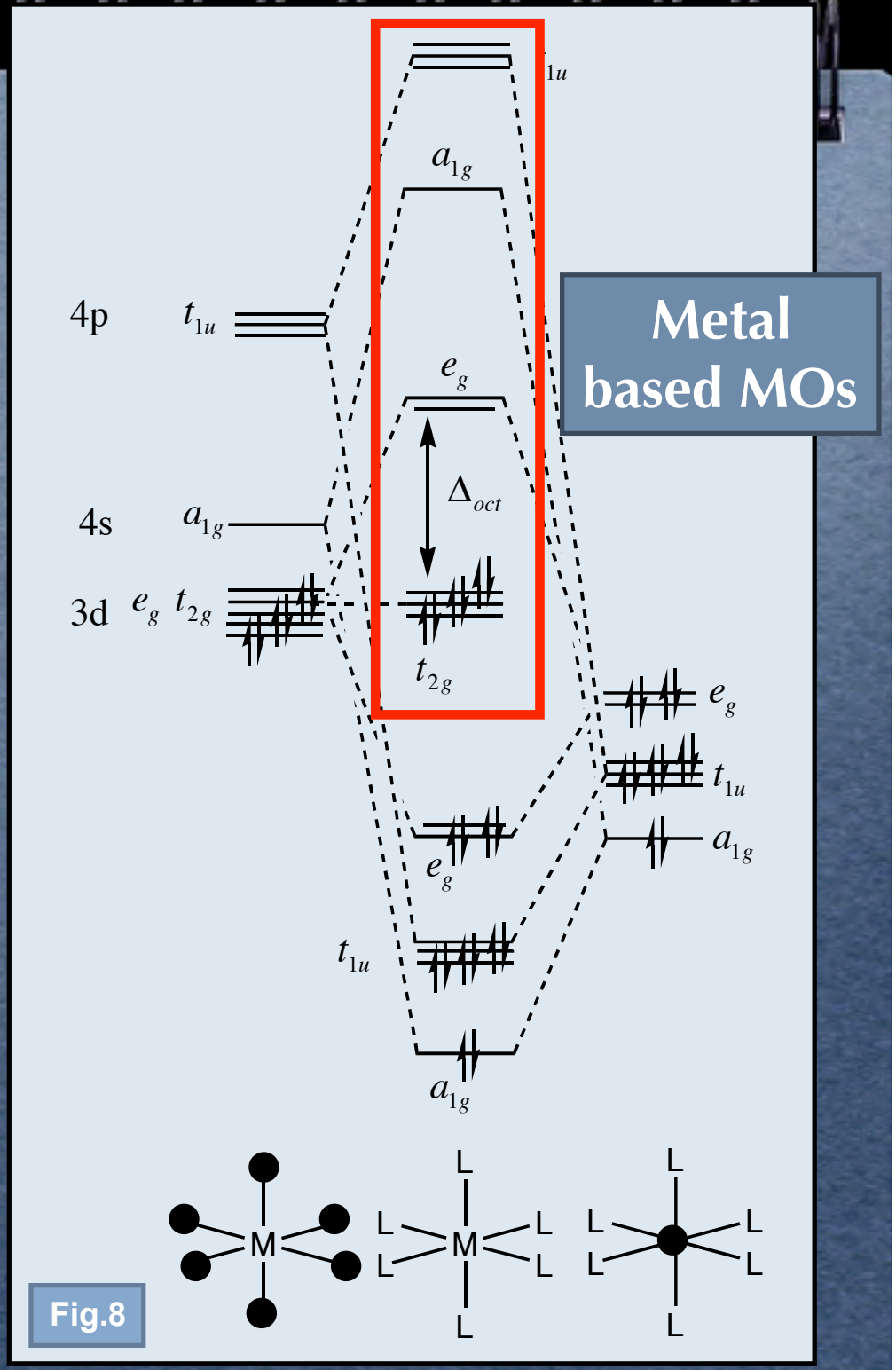
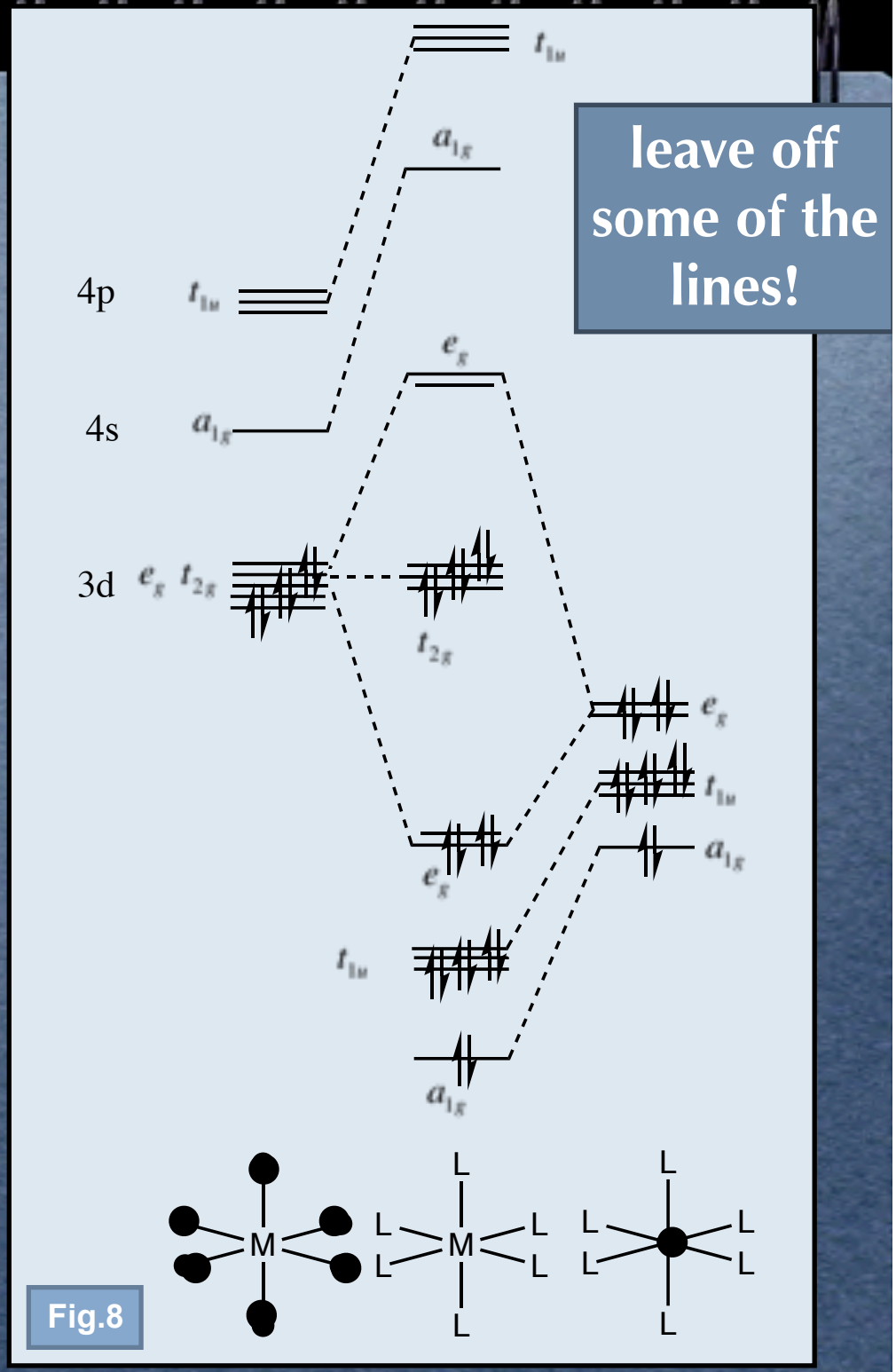


Fig.8

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!



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:**
  - ✦ Δε 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)

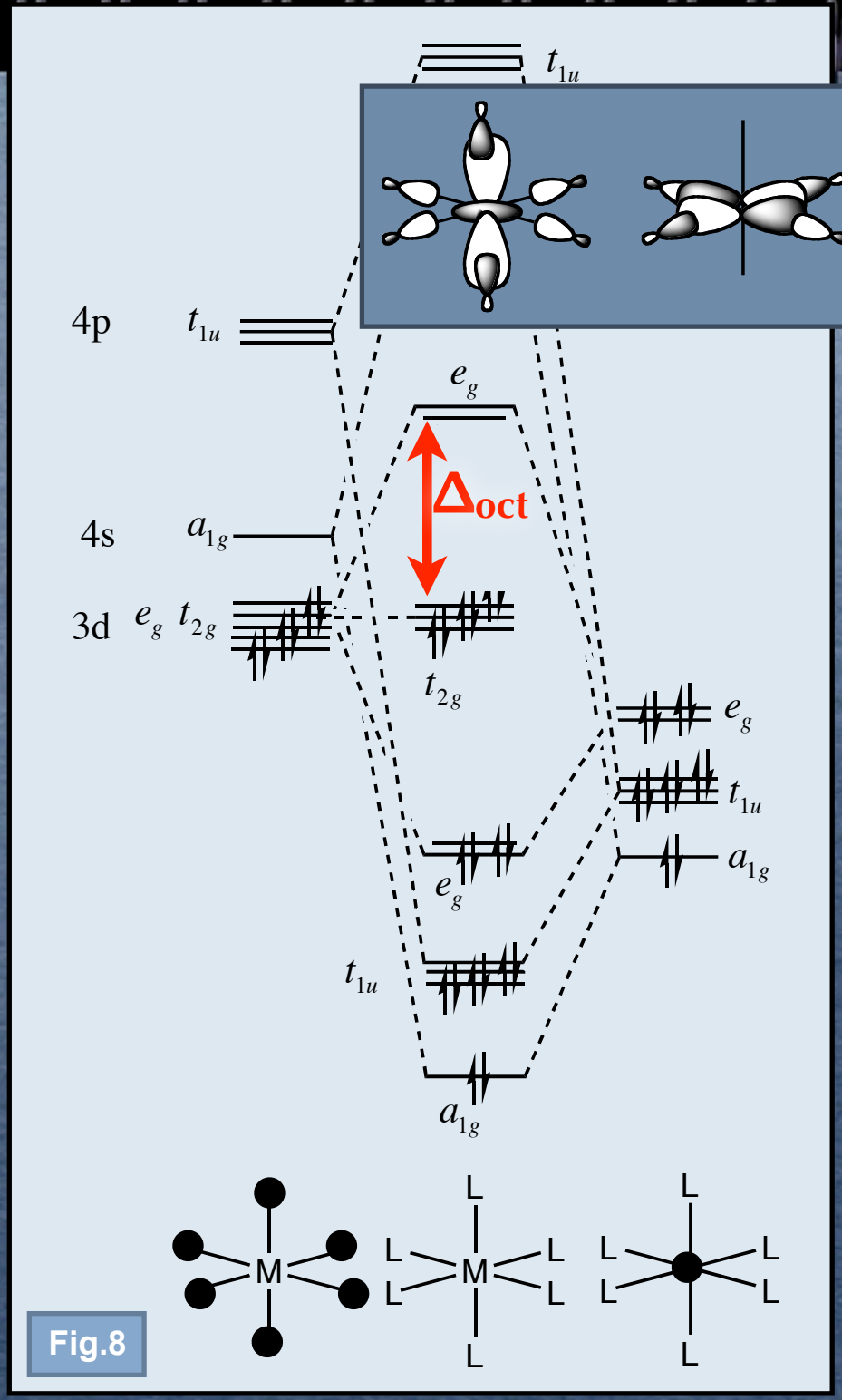


Fig.8

Δ_{oct} parameter

- higher in energy the ligand FOs the better the interaction

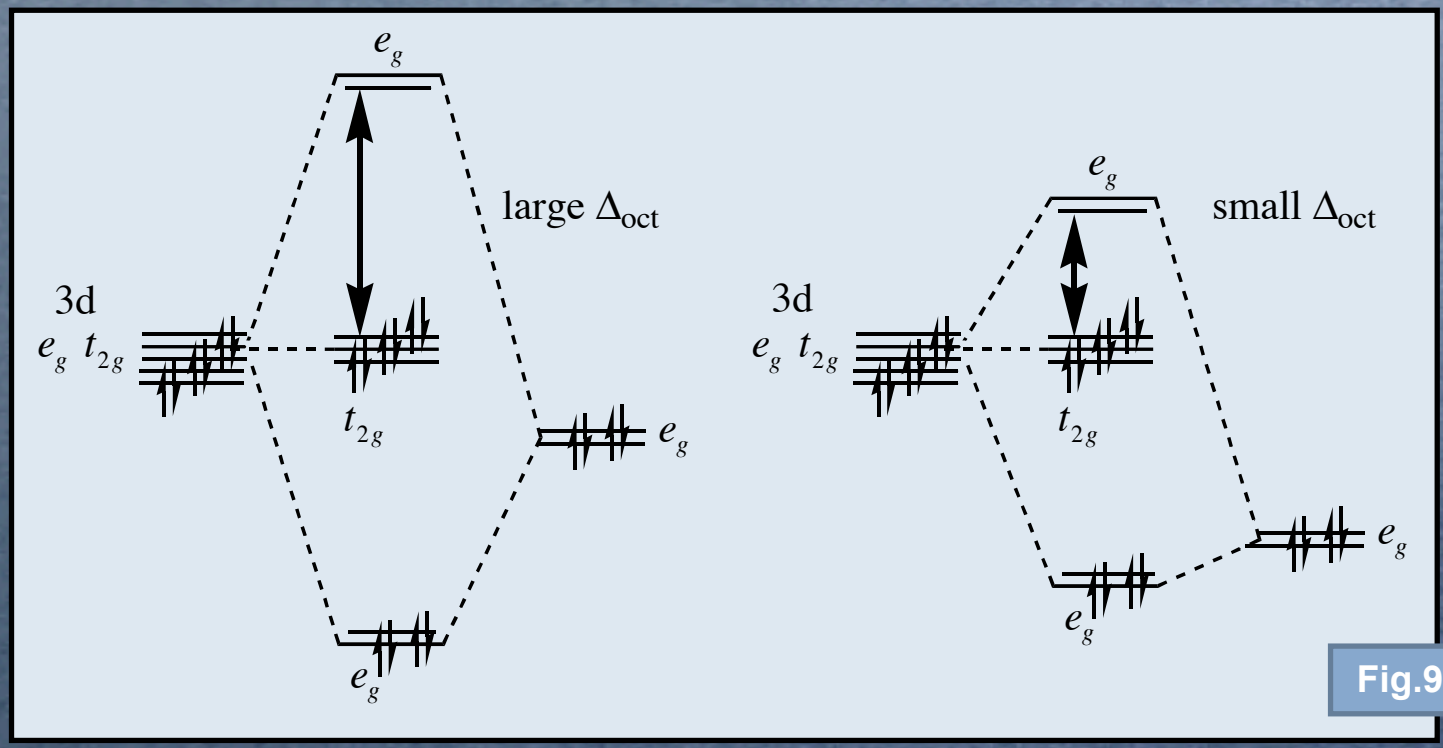


Fig.9

=> 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
- $[Ti(OH_2)_6]^{3+}$ absorbs in yellow/ green and appears red/violet

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Fig.10

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Fig.13

Colour and d-d Transitions

reminder

Selection Rules

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

d->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)

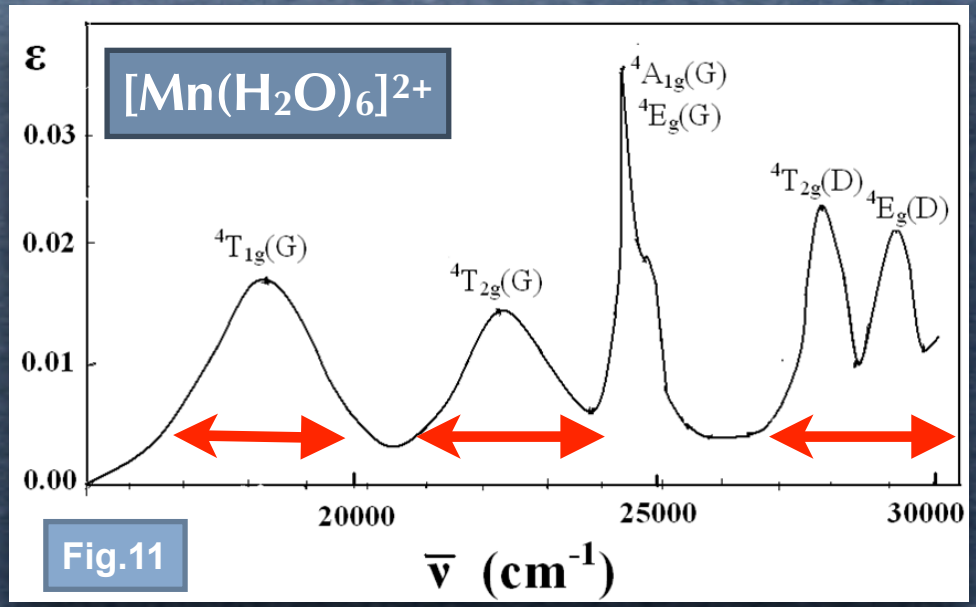


Fig.11

Absorption spectrum of $[Mn(H_2O)_6]^{2+}$, downloaded from http://en.wikipedia.org/wiki/Tanabe–Sugano_diagram, Dec 8 2014

Colour and d-d Transitions

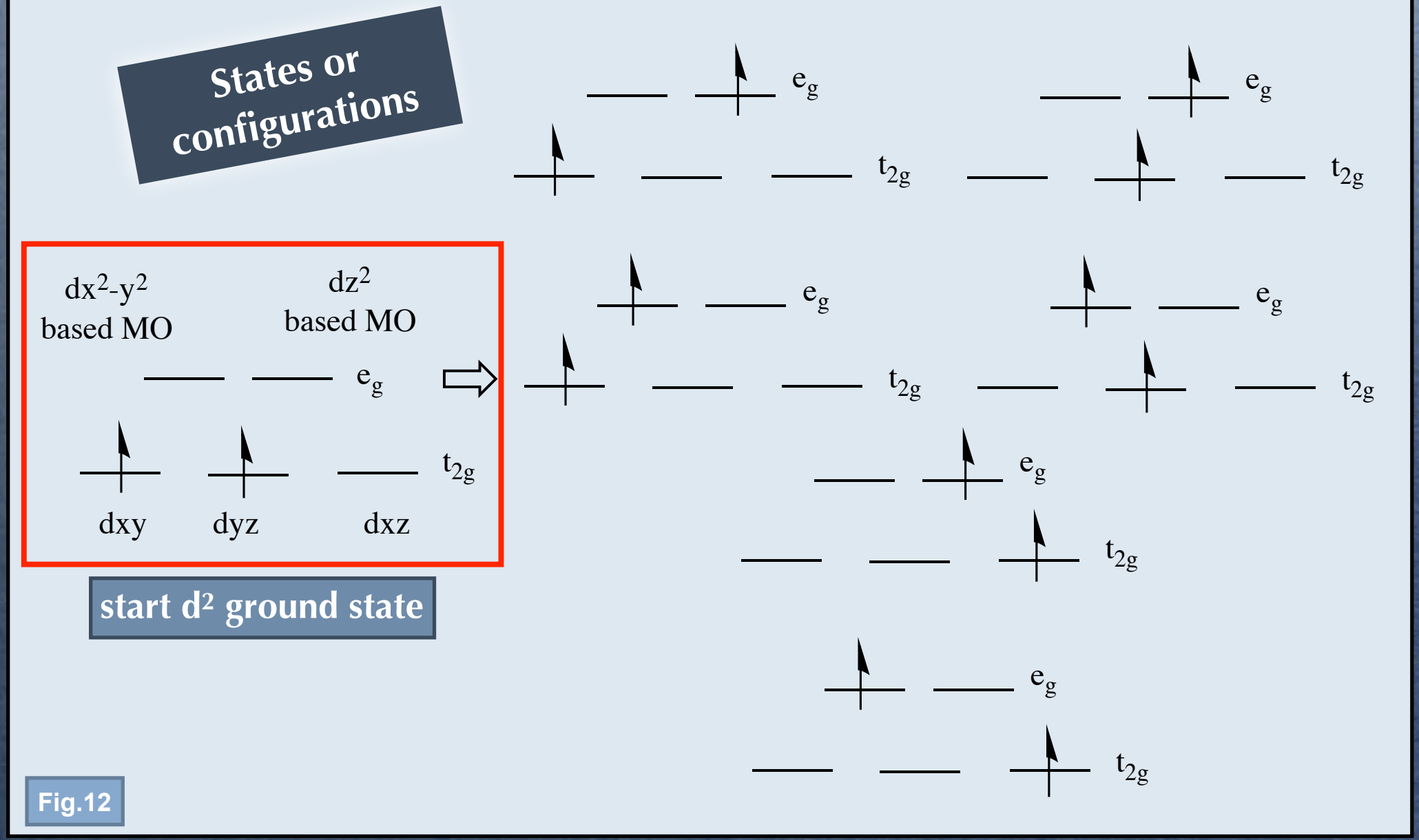
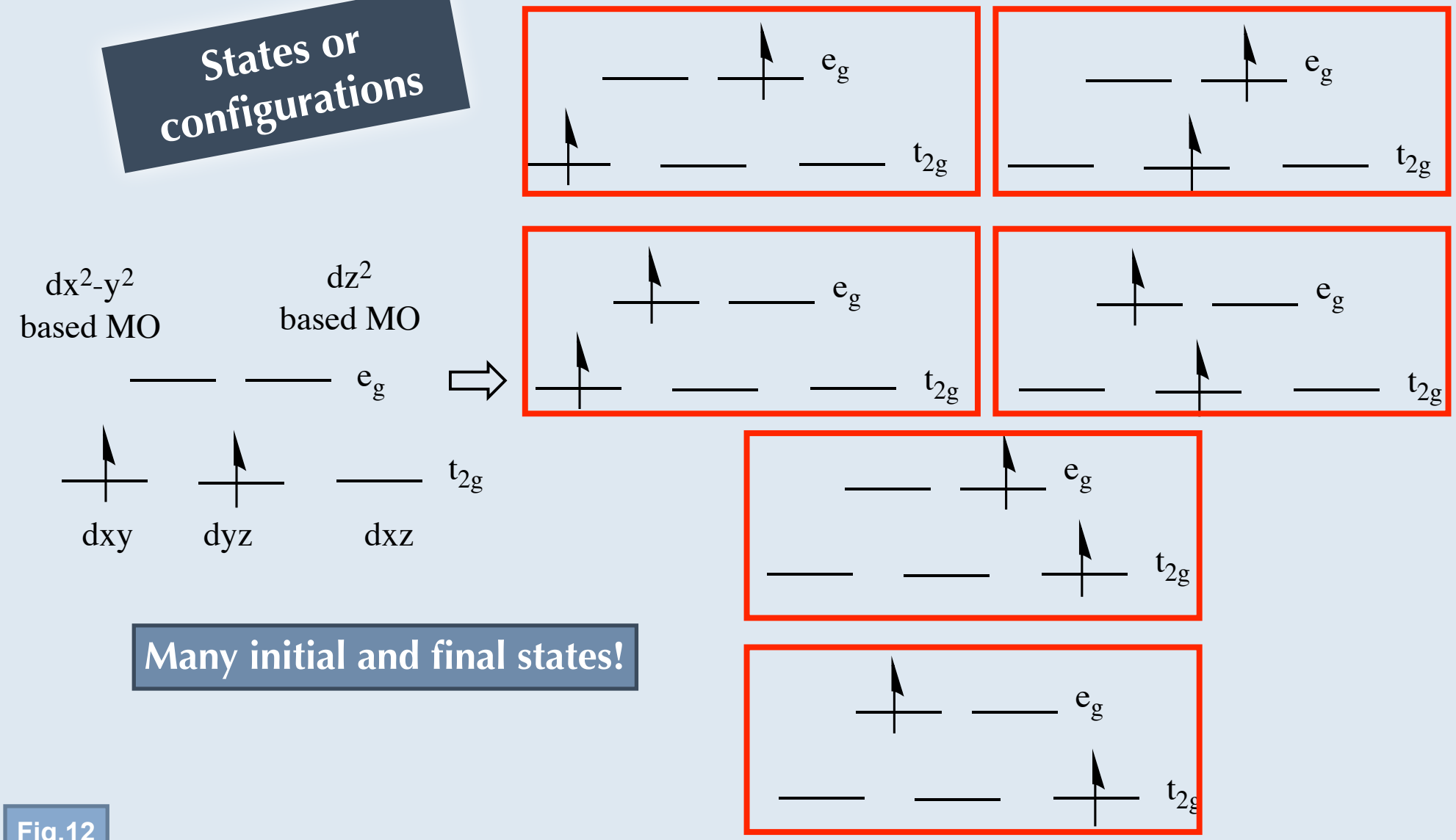


Fig.12

Colour and d-d Transitions

States or configurations



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!

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$[Mn(H_2O)_6]^{2+}$

Fig.12

Absorption spectrum of $[Mn(H_2O)_6]^{2+}$, downloaded from http://en.wikipedia.org/wiki/Tanabe–Sugano_diagram, Dec 8 2014

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

$I^- < Br^- < Cl^- < F^- <$

$OH^- < O^{2-} < H_2O <$

$py < NR_3 < NH_3 < en < NO_2^-$

$< CH_3^- < C_6H_5^- <$

$CN^- < CO < NO^+$

strong field

Spectrochemical Series

- example!
- replace NiL_6 ligands from stronger field to weaker field change Δ_{oct} and the colour
  - ✦ $[Ni(H_2O)_6]^{2+}$ has low energy, small Δ_{oct}
  - ✦ absorbs in the red and is green

Spectrochemical series

$I^- < Br^- < Cl^- < F^-$

$< OH^- < O^{2-} < H_2O$

$< NH_3 < en < NO_2^- < CH_3^-$

$< C_6H_5^- < CN^- < CO$

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

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Fig.13

$[Ni(NH_3)_6]^{2+}$, $[Ni(en)_3]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(H_2O)_6]^{2+}$

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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, 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}

reminder

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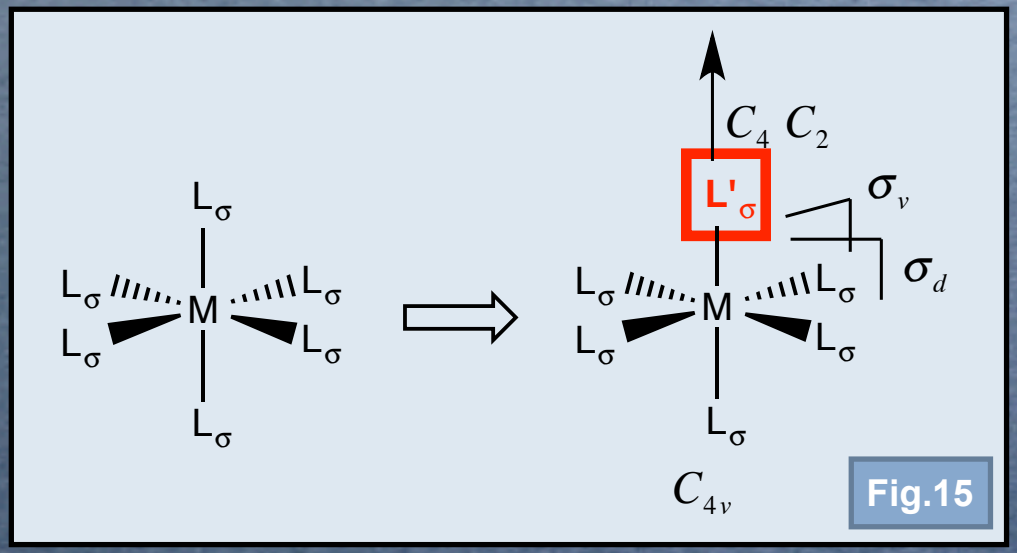
Fig.14

Reduce the Symmetry

- replace 1 ligand with a different σ-ligand
- loss of symmetry O_h -> 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

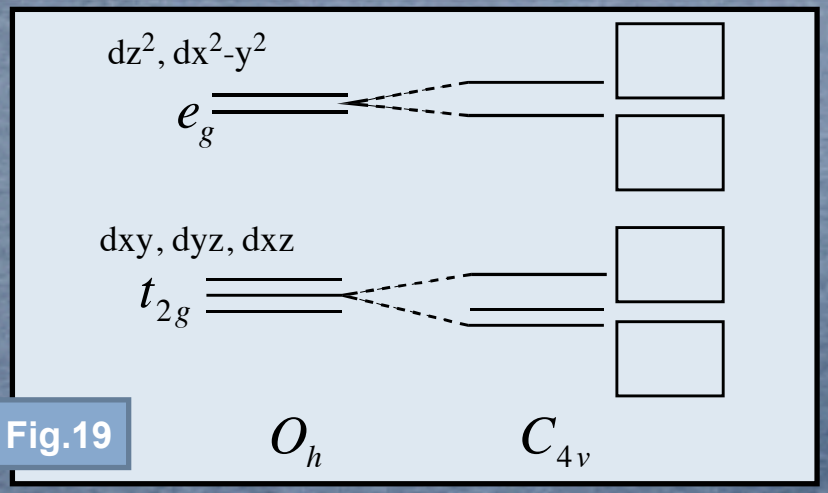


Fig.19

VERY Important!

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

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

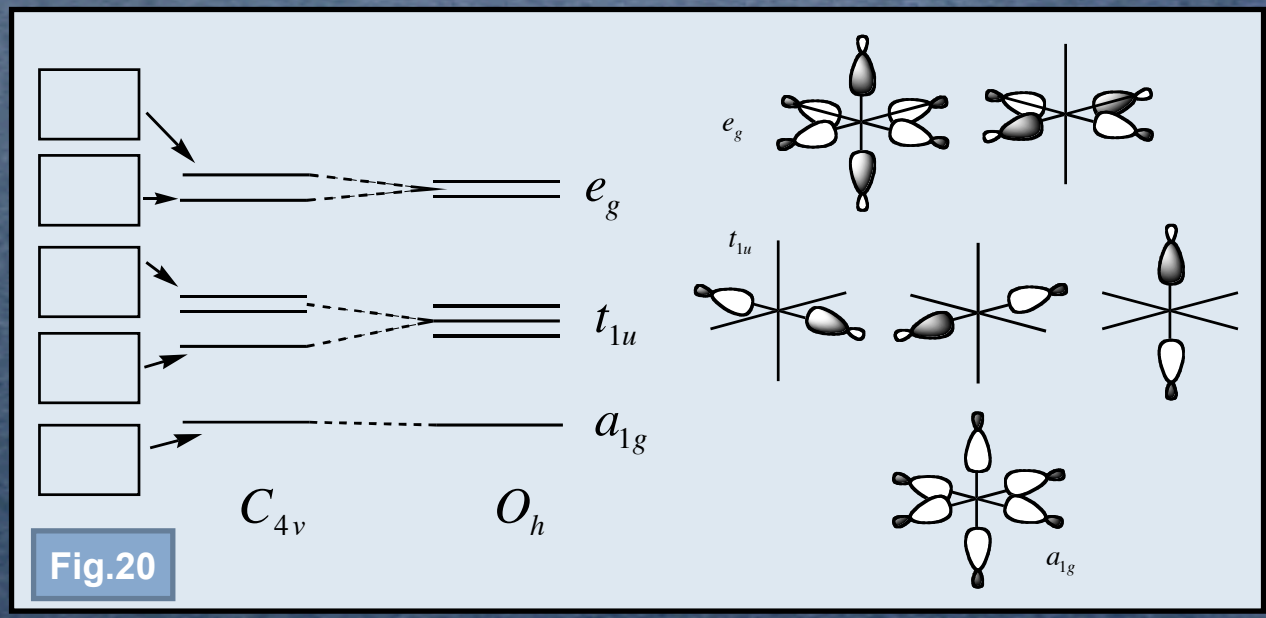


Fig.20

In-Class Activity

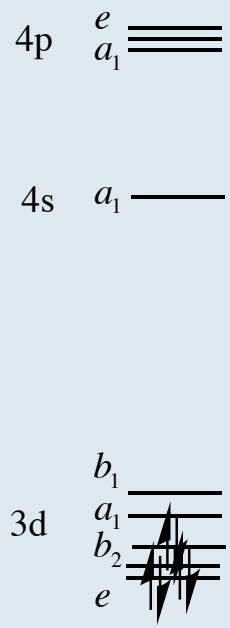
- now combine the TM dAOs and the ligand FO to form the energy level diagram for a C_{4v} TM complex

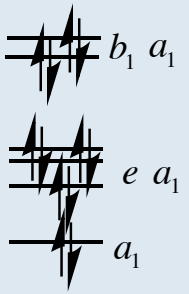
Fig.18, page 10 of your notes

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





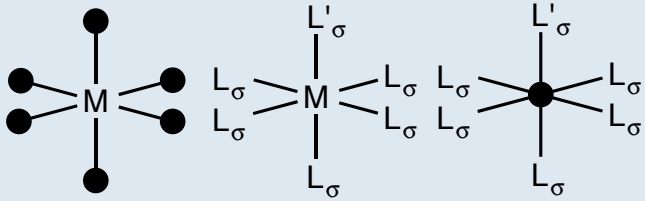
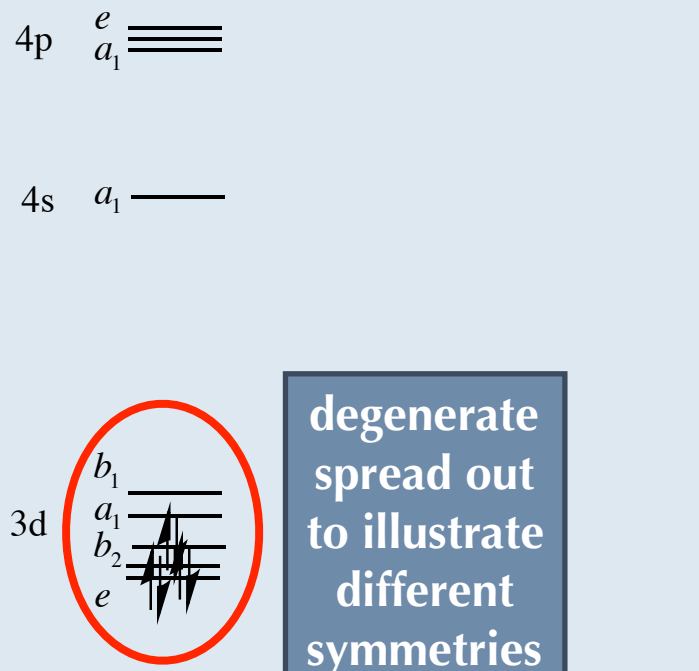
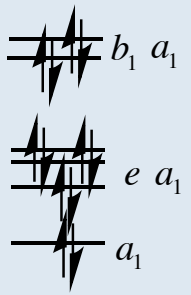


Fig.19

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





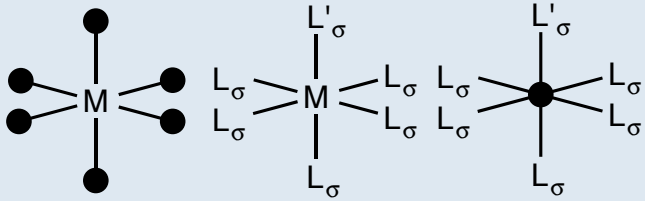


Fig.19

C_{4v} Diagram

- completed!

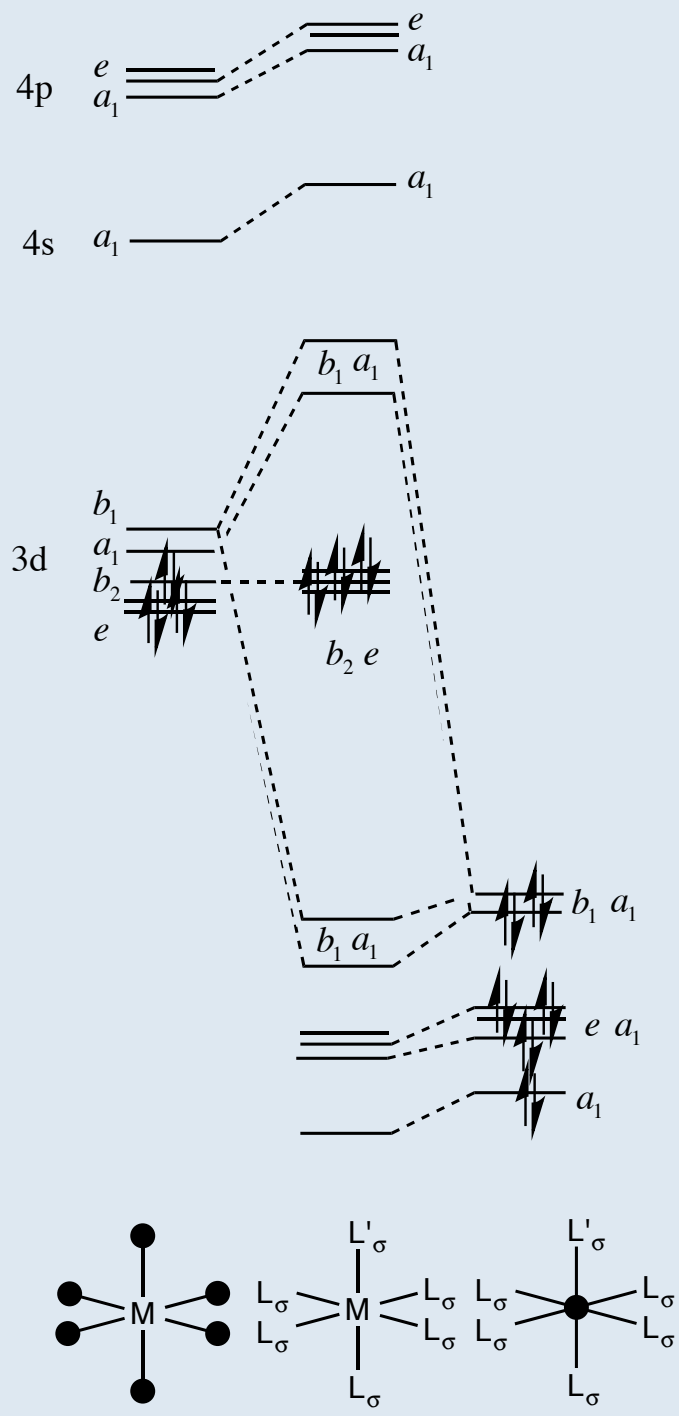


Fig.19

C_{4v} Diagram

- completed!

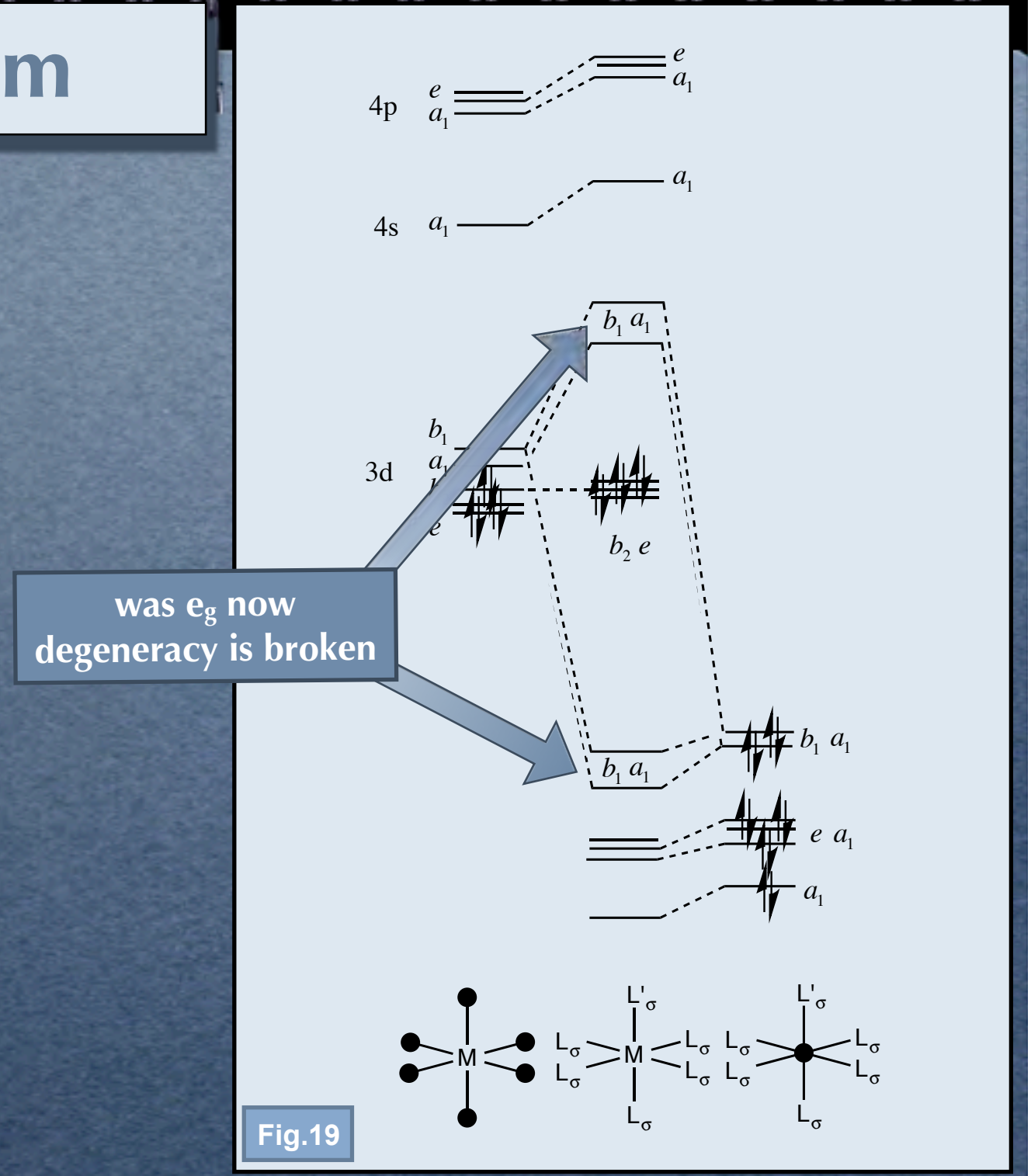
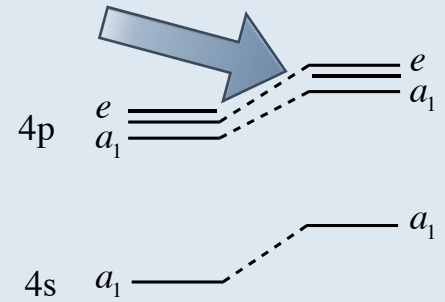
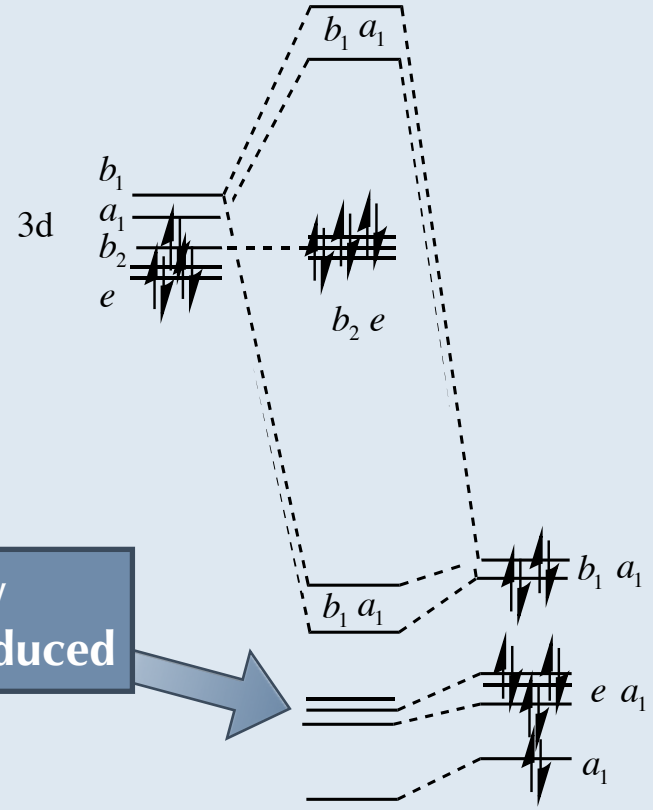


Fig.19

C_{4v} Diagram

- completed!





was t_{1u} now degeneracy is reduced

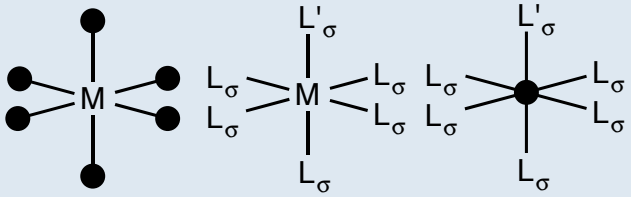


Fig.19

C_{4v} Diagram

- completed!

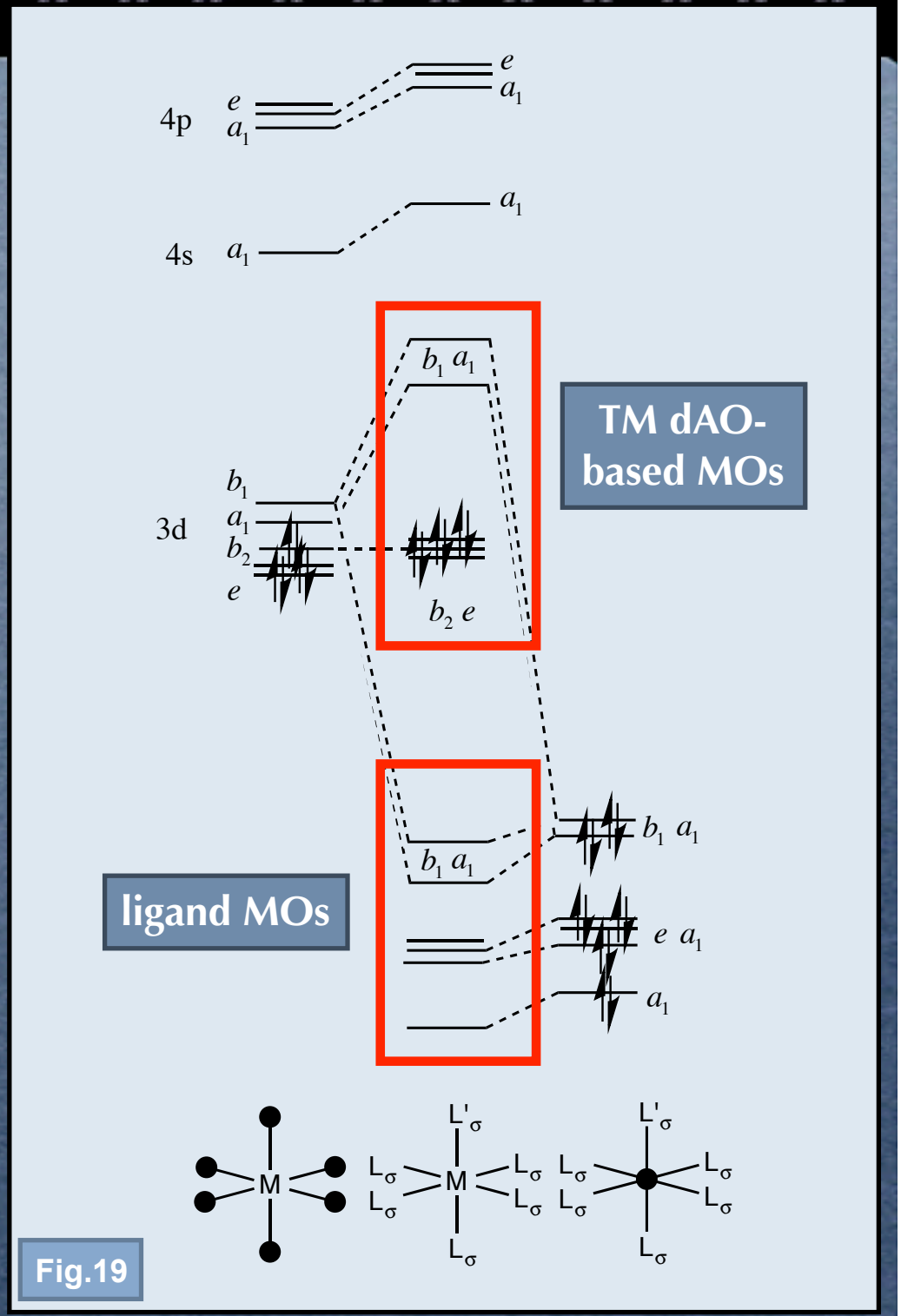


Fig.19

C_{4v} TM Diagram

- primary effect of the reduction in symmetry => 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!)

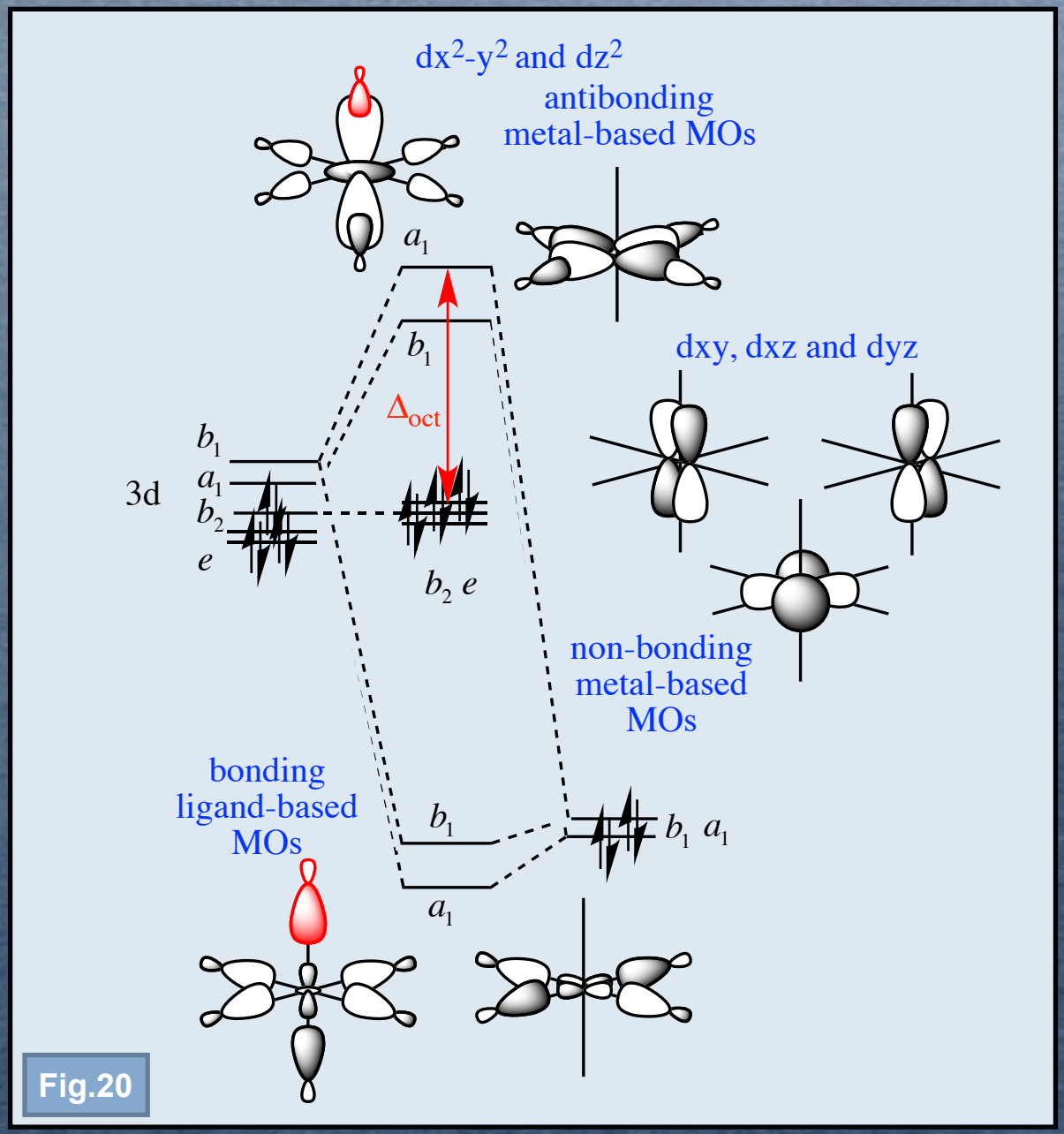


Fig.20

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!!