Molecular Orbitals in Inorganic Chemistry

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Lecture 8 Outline

- your feedback!
- π-back-donation
- ML_6 molecular orbitals
- a real example!

almost finished!

Your Feedback

- 87% have seen the web-site Great!
- what have been the easiest parts of the course?
  - "stuff from last year"
  - symmetry, assigning symmetry elements, using character tables
  - MO diagram of diatomic, revision, water, first 2 lectures
- what have been the hardest parts of the course?
  - quantum mechanics part
  - Walsh diagrams, mixing
  - energies: FO energy levels, estimating splitting, relative MO energies
  - symmetry adapted orbitals
  - deciphering the LCAO from “real” MOs
  - assigning bonding/antibonding character
  - constructing full MO diagram
  - octahedral TM-MO diagram, complex MO diagrams with multiple fragments
  - last two lectures

Your Feedback

- did you find the problems classes useful?
  - 92% YES!
- what did you like?

Great!

I work hard and in my
own time to make good
resources for you.

  - perfect!
  - very clear explanation on each part of building the MO diagram
  - good to get the steps clear in my mind
  - liked we attempt the answer ourselves first, then you presented the answer
  - the immediate feedback was useful
  - able to discuss hard questions with peers
  - had a chance to ask questions
- how could they be improved??
  - go faster / go slower!

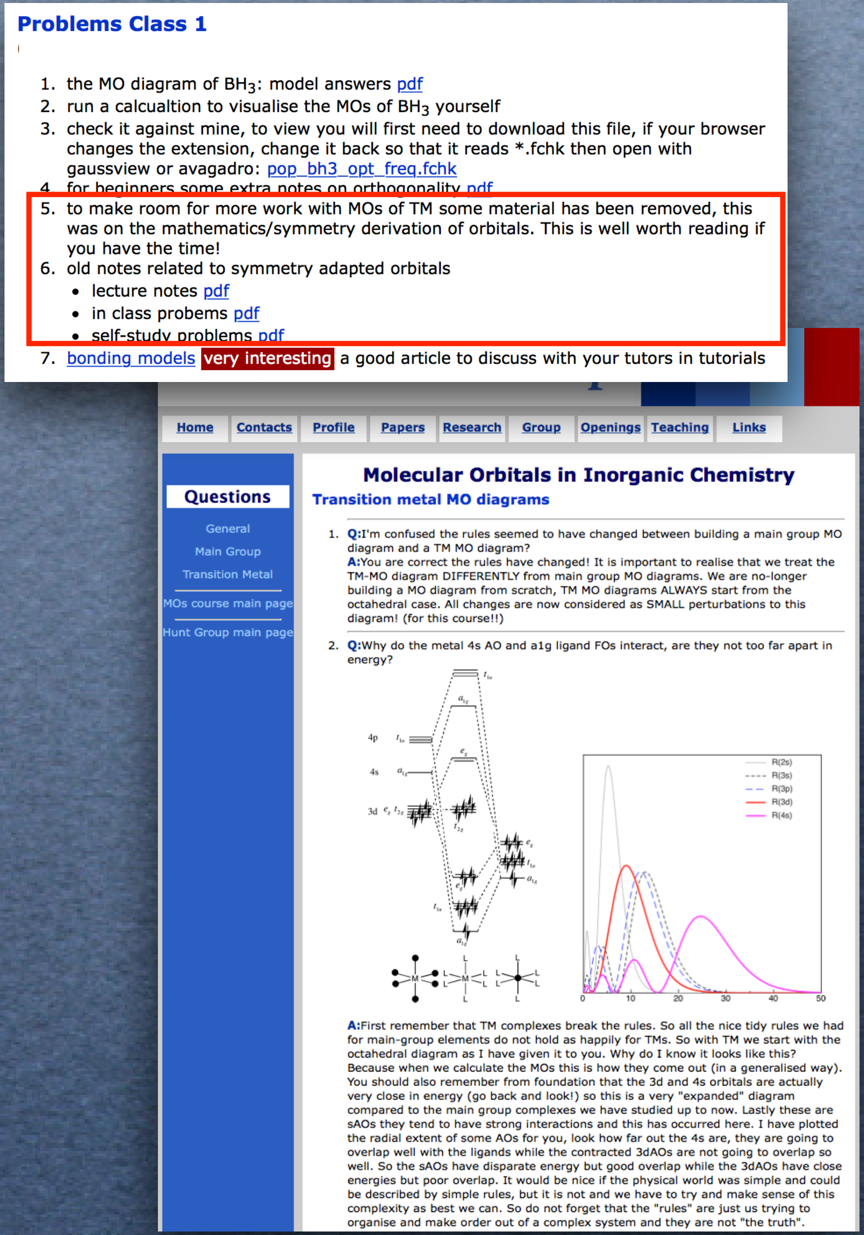
Mixed opinion!

  - would have liked to cover mixing, harder examples

focus on fundamentals → many harder problems with very good model answers

Feedback

- **Symmetry adapted orbitals**
  - H_3 from problems class
  - Notes from an old lecture available on-line!
- **Check out "questions answered" page on the web**
  - more on FO energy levels and splitting
  - practice helps



Problems Class 1

1. the MO diagram of BH_3: model answers pdf
2. run a calcualtion to visualise the MOs of BH_3 yourself
3. check it against mine, to view you will first need to download this file, if your browser changes the extension, change it back so that it reads *.fchk then open with gaussview or avagadro: pop_bh3_opt_freq.fchk
4. for beginners some extra notes on orthogonality pdf
5. to make room for more work with MOs of TM some material has been removed, this was on the mathematics/symmetry derivation of orbitals. This is well worth reading if you have the time!
6. old notes related to symmetry adapted orbitals
   - lecture notes pdf
   - in class probems pdf
   - self-study problems pdf
7. bonding models very interesting a good article to discuss with your tutors in tutorials

Molecular Orbitals in Inorganic Chemistry

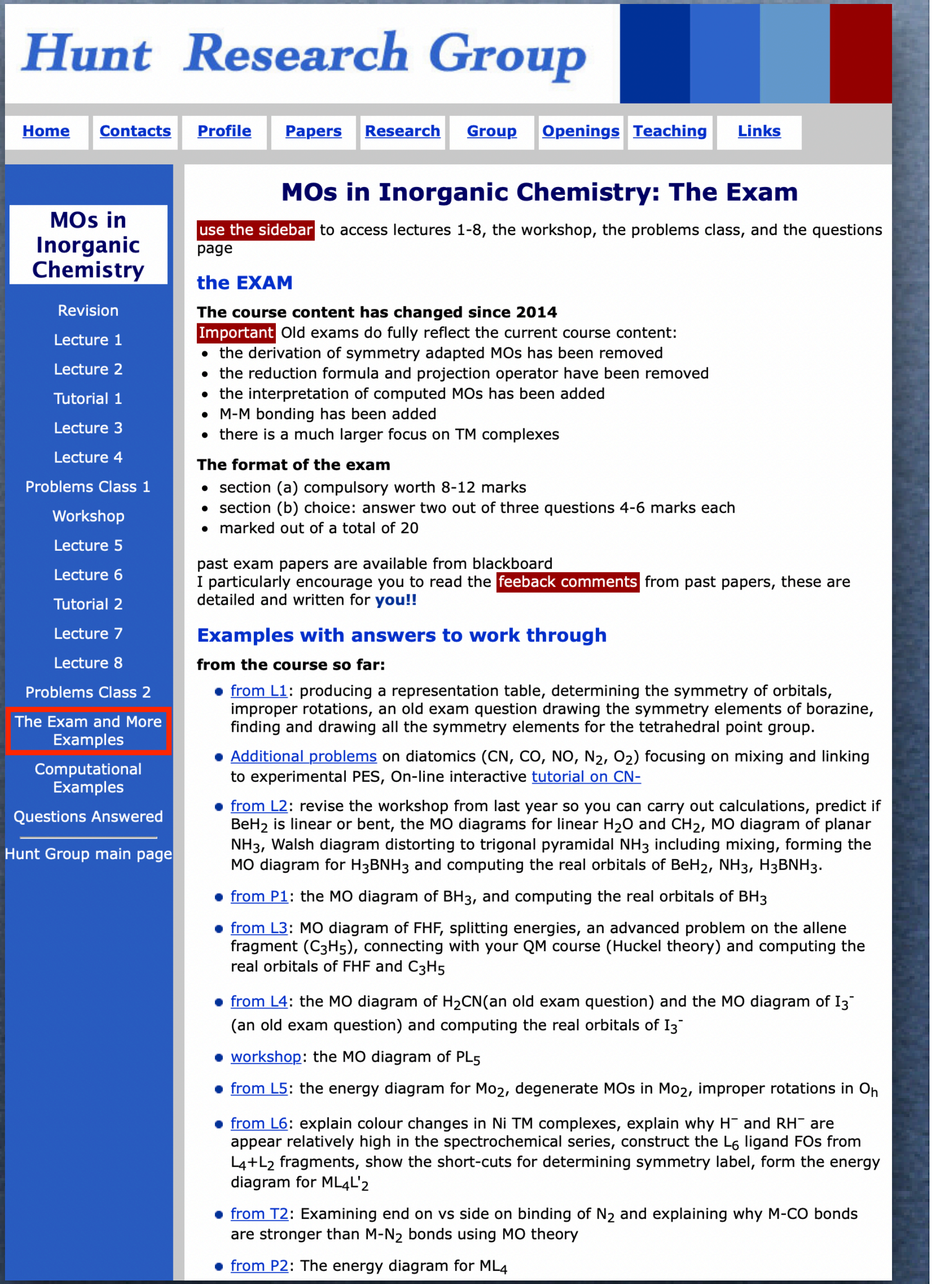
Transition metal MO diagrams

1. **Q:** I'm confused the rules seemed to have changed between building a main group MO diagram and a TM MO diagram?
   A: You are correct the rules have changed! It is important to realise that we treat the TM-MO diagram DIFFERENTLY from main group MO diagrams. We are no-longer building a MO diagram from scratch, TM MO diagrams ALWAYS start from the octahedral case. All changes are now considered as SMALL perturbations to this diagram! (for this course!!)
2. **Q:** Why do the metal 4s AO and a1g ligand FOs interact, are they not too far apart in energy?

A: First remember that TM complexes break the rules. So all the nice tidy rules we had for main-group elements do not hold as happily for TMs. So with TM we start with the octahedral diagram as I have given it to you. Why do I know it looks like this? Because when we calculate the MOs this is how they come out (in a generalised way). You should also remember from foundation that the 3d and 4s orbitals are actually very close in energy (go back and look!) so this is a very "expanded" diagram compared to the main group complexes we have studied up to now. Lastly these are sAOs they tend to have strong interactions and this has occurred here. I have plotted the radial extent of some AOs for you, look how far out the 4s are, they are going to overlap well with the ligands while the contracted 3dAOs are not going to overlap so well. So the sAOs have disparate energy but good overlap while the 3dAOs have close energies but poor overlap. It would be nice if the physical world was simple and could be described by simple rules, but it is not and we have to try and make sense of this complexity as best we can. So do not forget that the "rules" are just us trying to organise and make order out of a complex system and they are not "the truth".

Feedback

- Collected all problems together!
- Old exam questions with outline answers
  - ✦ all my old exams have extensive outline answers
  - ✦ written for you!
- Recommended texts contain additional problems
- If you are stuck, ask me
  - ✦ I prioritise student questions
  - ✦ p.hunt@imperial.ac.uk



MOs in Inorganic Chemistry: The Exam

use the sidebar to access lectures 1-8, the workshop, the problems class, and the questions page

the EXAM

The course content has changed since 2014

Important Old exams do fully reflect the current course content:

- the derivation of symmetry adapted MOs has been removed
- the reduction formula and projection operator have been removed
- the interpretation of computed MOs has been added
- M-M bonding has been added
- there is a much larger focus on TM complexes

The format of the exam

- section (a) compulsory worth 8-12 marks
- section (b) choice: answer two out of three questions 4-6 marks each
- marked out of a total of 20

past exam papers are available from blackboard
I particularly encourage you to read the feeback comments from past papers, these are detailed and written for **you!!**

Examples with answers to work through

from the course so far:

- from L1: producing a representation table, determining the symmetry of orbitals, improper rotations, an old exam question drawing the symmetry elements of borazine, finding and drawing all the symmetry elements for the tetrahedral point group.
- Additional problems on diatomics (CN, CO, NO, N_2, O_2) focusing on mixing and linking to experimental PES, On-line interactive tutorial on CN-
- from L2: revise the workshop from last year so you can carry out calculations, predict if BeH_2 is linear or bent, the MO diagrams for linear H_2O and CH_2, MO diagram of planar NH_3, Walsh diagram distorting to trigonal pyramidal NH_3 including mixing, forming the MO diagram for H_3BNH_3 and computing the real orbitals of BeH_2, NH_3, H_3BNH_3.
- from P1: the MO diagram of BH_3, and computing the real orbitals of BH_3
- from L3: MO diagram of FHF, splitting energies, an advanced problem on the allene fragment (C_3H_5), connecting with your QM course (Huckel theory) and computing the real orbitals of FHF and C_3H_5
- from L4: the MO diagram of H_2CN(an old exam question) and the MO diagram of I_3^- (an old exam question) and computing the real orbitals of I_3^-
- workshop: the MO diagram of PL_5
- from L5: the energy diagram for Mo_2, degenerate MOs in Mo_2, improper rotations in O_h
- from L6: explain colour changes in Ni TM complexes, explain why H^- and RH^- are appear relatively high in the spectrochemical series, construct the L_6 ligand FOs from L_4+L_2 fragments, show the short-cuts for determining symmetry label, form the energy diagram for $ML_4L'_2$
- from T2: Examining end on vs side on binding of N_2 and explaining why M-CO bonds are stronger than M-N_2 bonds using MO theory
- from P2: The energy diagram for ML_4

Feedback

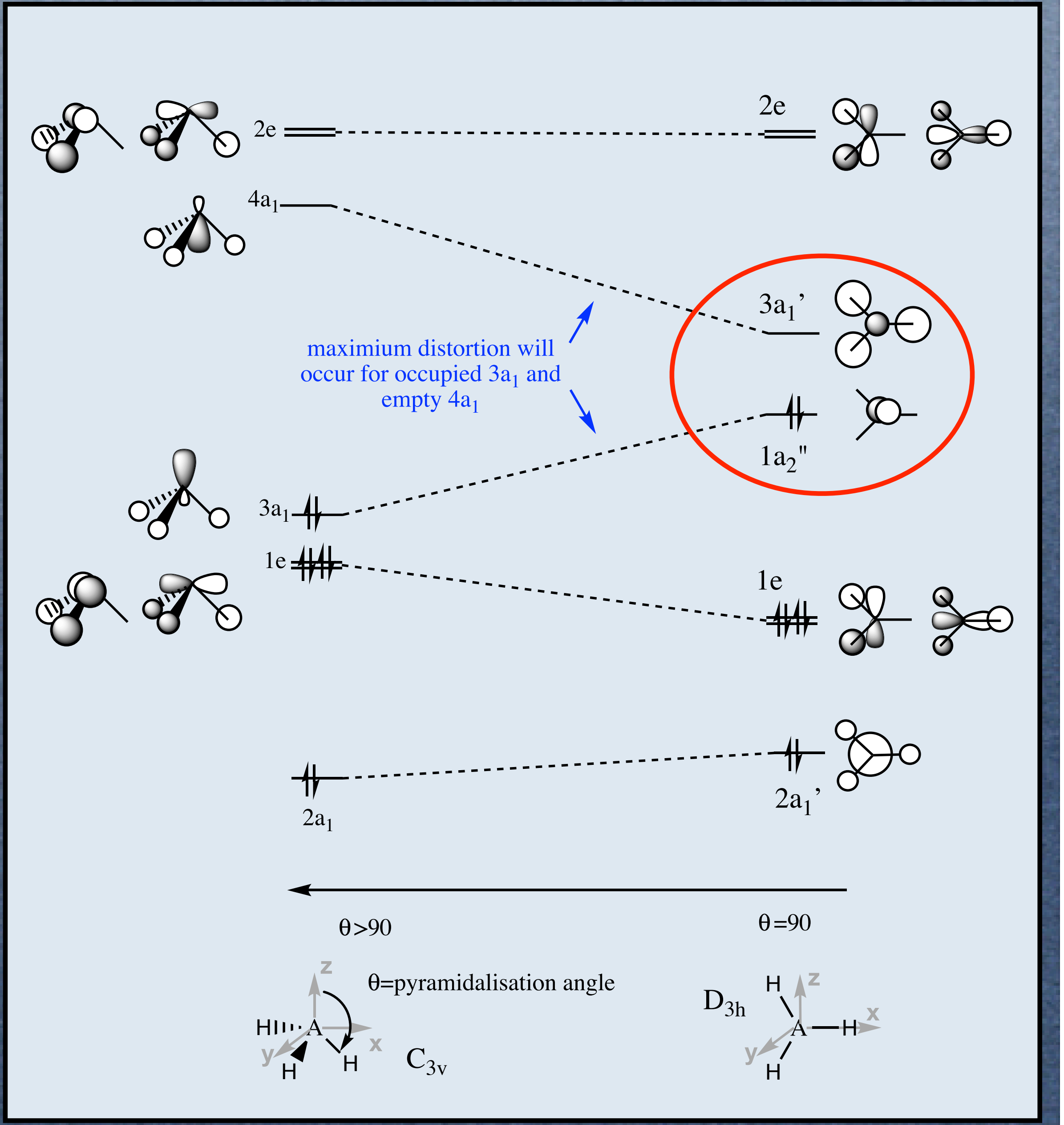
all with extensive model answers!

More Examples & Problems!

- ✦Lecture 1: improper rotations, borazine, AH_4 molecule
- ✦Lecture 2: BeH_2, linear OH_2, CH_2,
- ✦Problems class: BH_3, D_{3h} NH_3, Walsh diagram/mixing and C_{3v} NH_3 adduct $H_3B{<}{-}NH_3$
- ✦Lecture 3: HFH^-, working with QM equations, Huckel allene anion $(C_3H_5)^-$
- ✦L3 Additional: advanced diatomics CN^-, CO, N_2
- ✦Lecture 4: old exam questions H_2CN^-, I_3^-
- ✦Lecture 5: Mo_2, degeneracy dxz/dyz MOs, S_4 rotations O_h, S_6 rotations O_h
- ✦Lecture 6: colour Ni complexes, H- & R- as ligands in TM complexes, generate L_6, C_{4v} TM-MO diagram, descent in symmetry D_6->C_{3v}, cis-$ML_2(L')_4$ TM-MO diagram
- ✦Lecture 7: interpreting Δ_{oct}, the O^{2-} ligand in TM-complexes, dAO interactions O_2 end on and O_2 side, full MO diagrams O_2 end on and side on, H_2O as ligand, cis and trans $[CoCl_2(NH_3)_4]^+$ colour changes and MO-diarams, ML_4X_2 X=pi-donor ligand MO-diagram
- ✦Tutorial 2: dAO interactions N_2 end on & side on, comparison with CO
- ✦Problems class1: BH_3 MOs
- ✦Problems class2: square planar TM-complex MO
- ✦New problems! given on "The Exam and More Examples" page: $MgCl_2$, H_2CO, PH_3Cl_2, H_4

Feedback

- **Mixing!!**
  - example in L2 problems
  - start with NH_3 trigonal planar
  - H to fold down to form C_{3v} trigonal pyramidal NH_3
  - change in point group, so change in symmetry labels
  - use C_{3v} character table
  - ➡ $1a_2''$ p_z-like -> a_1
  - ➡ $3a_1'$ -> a_1



maximium distortion will occur for occupied $3a_1$ and empty $4a_1$

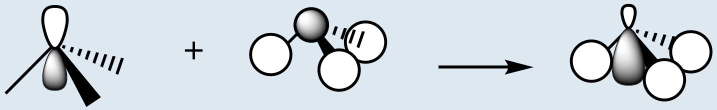
θ=pyramidalisation angle

Feedback

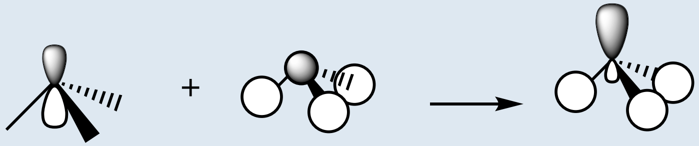
Mixing

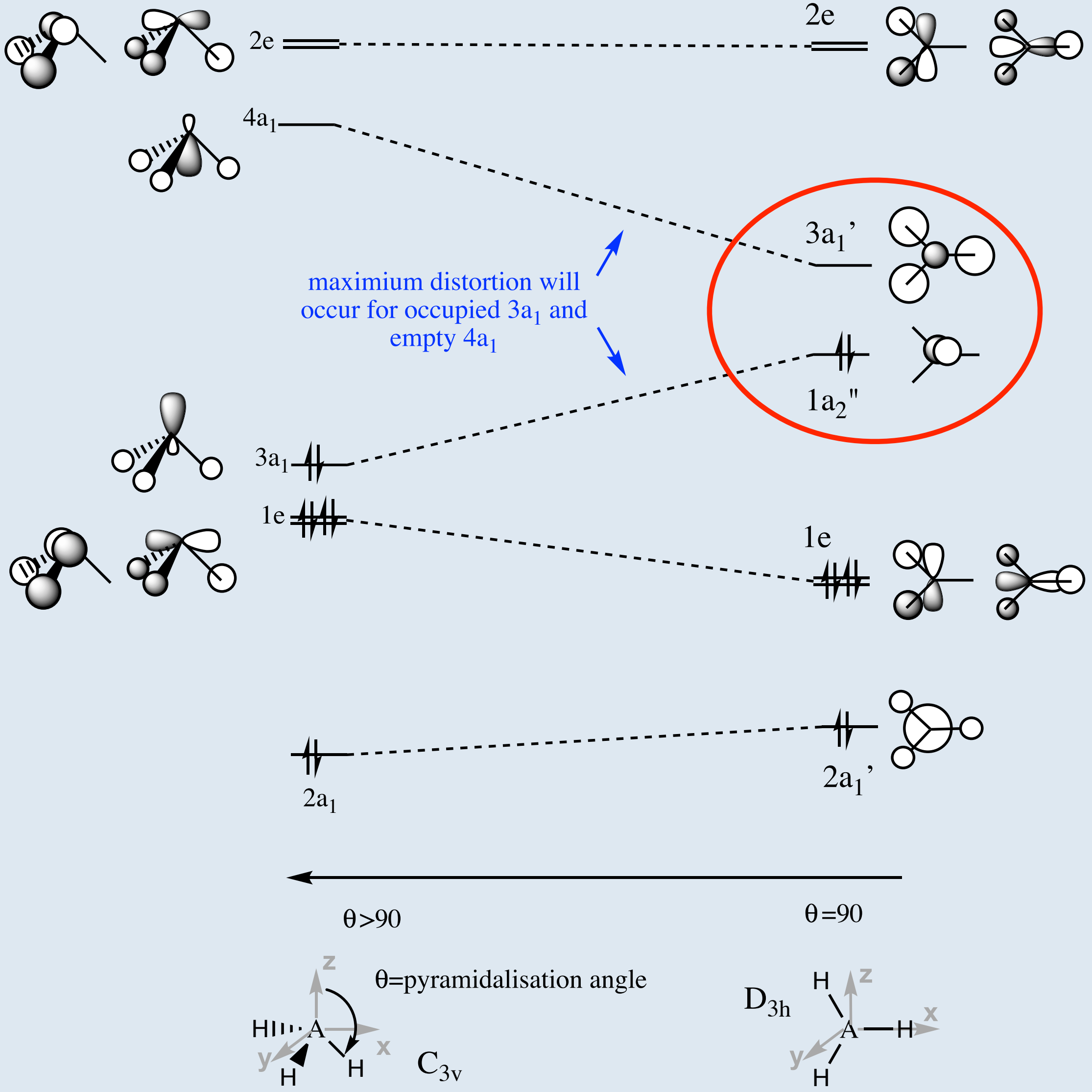
- use rules for mixing!
  - ➡ one occupied one unoccupied
  - ➡ HOMO-LUMO region
  - ➡ close in energy
  - ➡ same symmetry (NOT same pair)
  - ➡ overall stabilisation
- "mix the orbitals"

once as is



once one orbital phase inverted

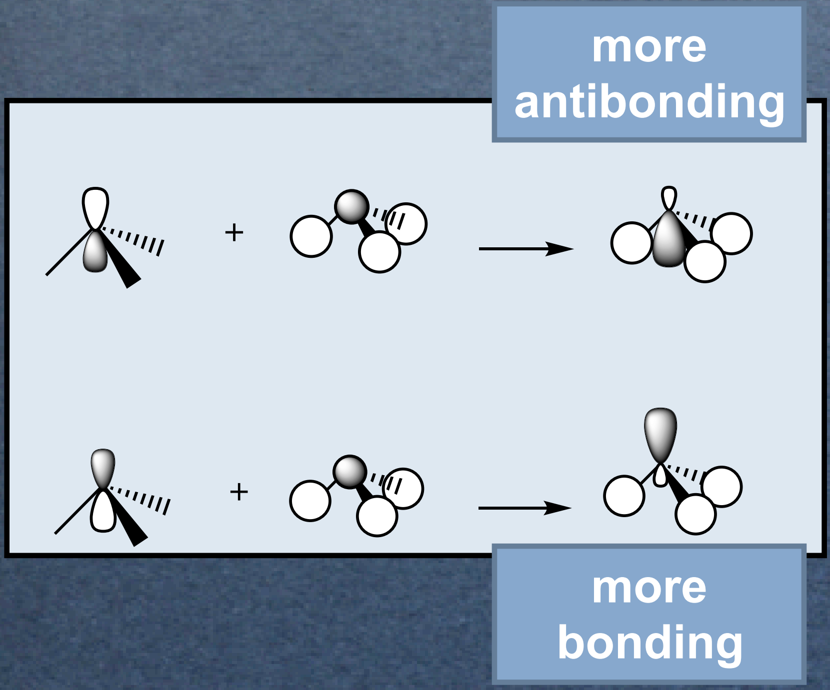




Feedback

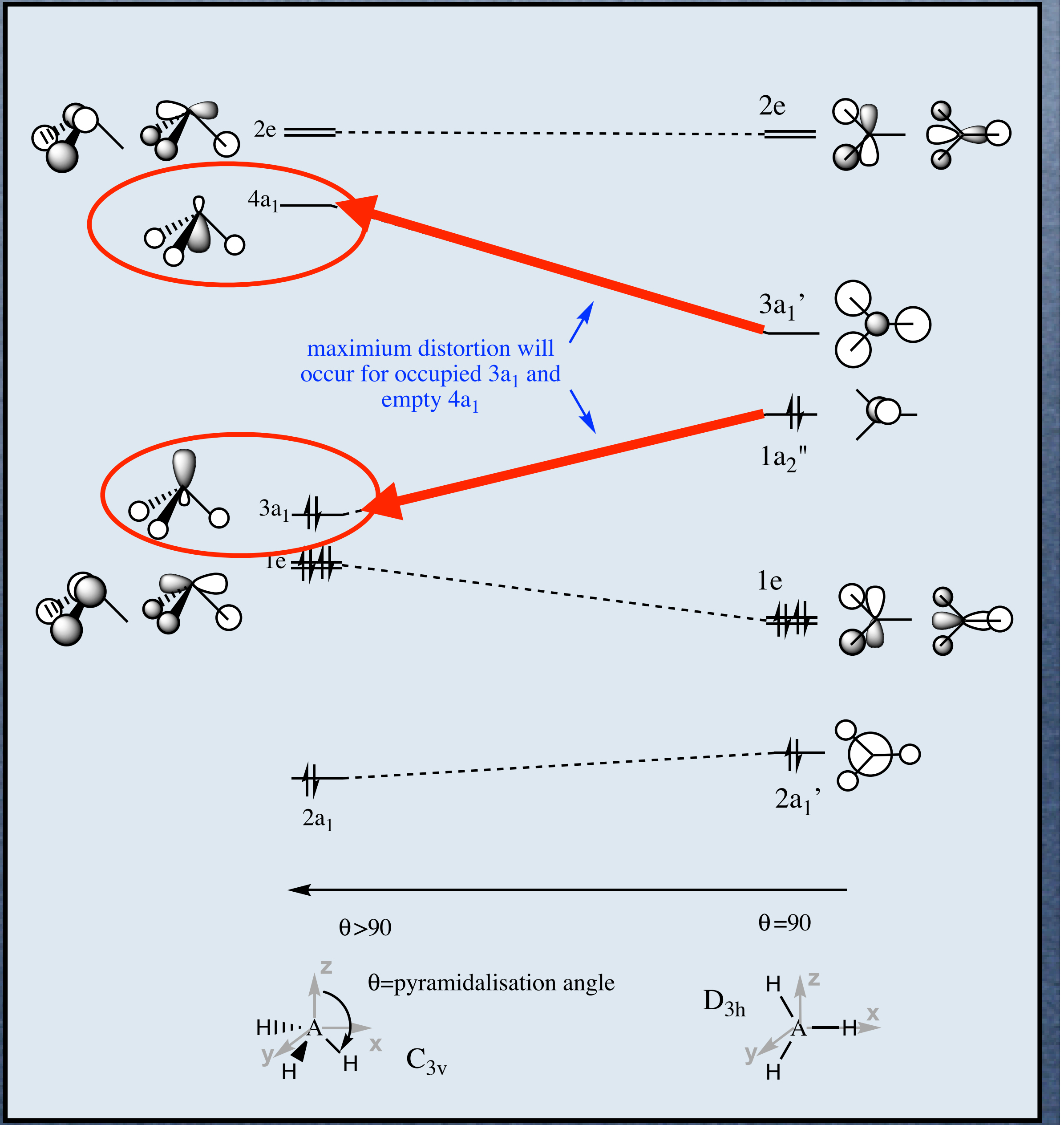
Mixing

- use rules for mixing!
- "mix the orbitals"
- identify which is stabilised and which is destabilised



more antibonding

more bonding



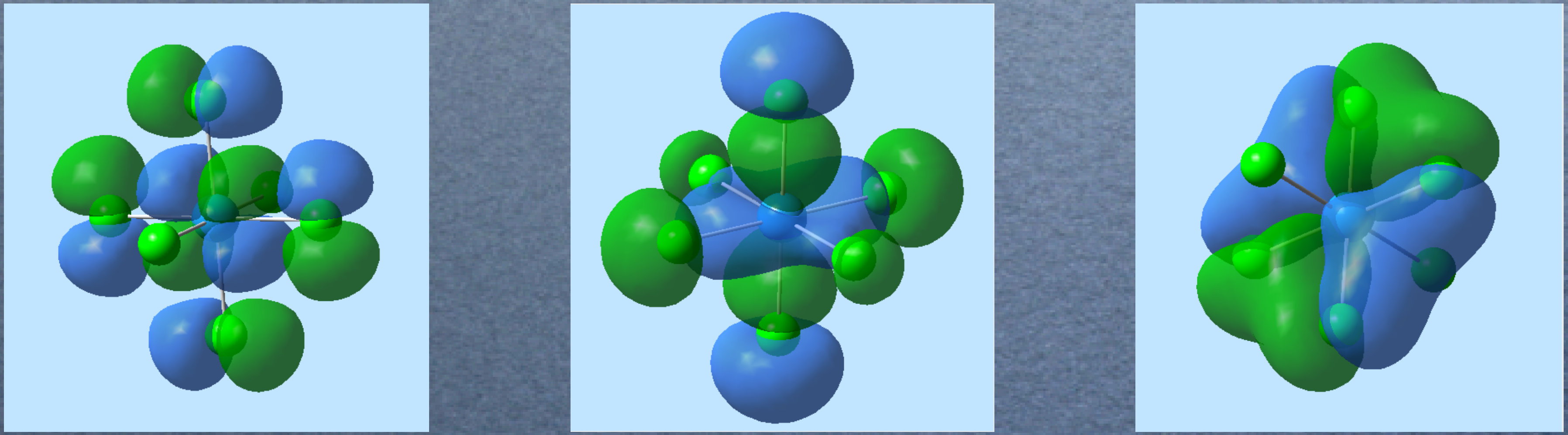
maximium distortion will occur for occupied $3a_1$ and empty $4a_1$

Real MOs

- **practice!**

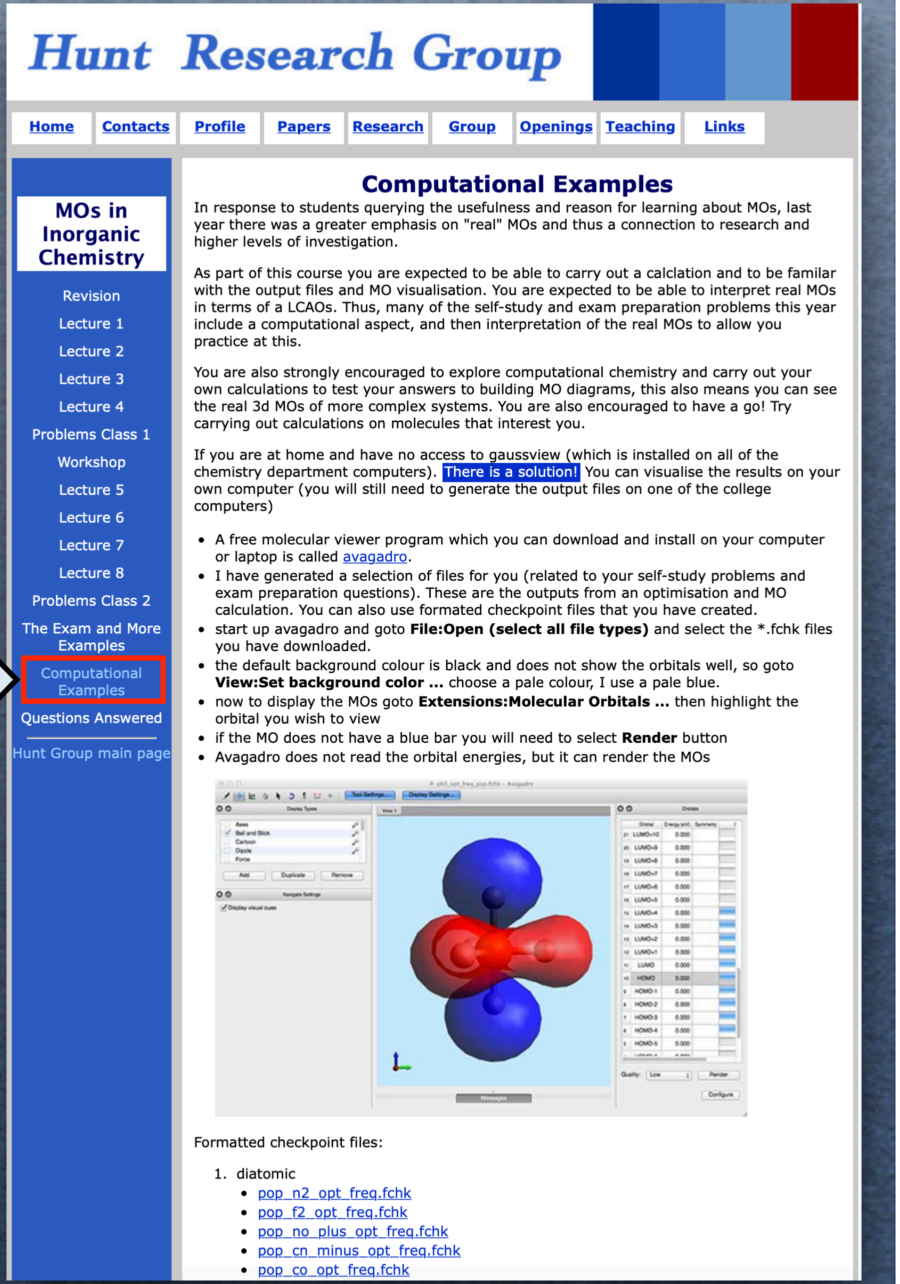
$[WCl_6]$

draw the LCAOs that match these real MOs



Feedback

- Try some of the molecules in the “computational examples” on the web
- Make your own questions!
  - ✦ pick a simple molecule, create a MO diagram
  - ✦ do a calculation, does it match your MO diagram?



Computational Examples

In response to students querying the usefulness and reason for learning about MOs, last year there was a greater emphasis on "real" MOs and thus a connection to research and higher levels of investigation.

As part of this course you are expected to be able to carry out a calclation and to be familar with the output files and MO visualisation. You are expected to be able to interpret real MOs in terms of a LCAOs. Thus, many of the self-study and exam preparation problems this year include a computational aspect, and then interpretation of the real MOs to allow you practice at this.

You are also strongly encouraged to explore computational chemistry and carry out your own calculations to test your answers to building MO diagrams, this also means you can see the real 3d MOs of more complex systems. You are also encouraged to have a go! Try carrying out calculations on molecules that interest you.

If you are at home and have no access to gaussview (which is installed on all of the chemistry department computers). There is a solution! You can visualise the results on your own computer (you will still need to generate the output files on one of the college computers)

- A free molecular viewer program which you can download and install on your computer or laptop is called avagadro.
- I have generated a selection of files for you (related to your self-study problems and exam preparation questions). These are the outputs from an optimisation and MO calculation. You can also use formatted checkpoint files that you have created.
- start up avagadro and goto **File:Open (select all file types)** and select the *.fchk files you have downloaded.
- the default background colour is black and does not show the orbitals well, so goto **View:Set background color ...** choose a pale colour, I use a pale blue.
- now to display the MOs goto **Extensions:Molecular Orbitals ...** then highlight the orbital you wish to view
- if the MO does not have a blue bar you will need to select **Render** button
- Avagadro does not read the orbital energies, but it can render the MOs

Formatted checkpoint files:

1. diatomic
   - pop_n2_opt_freq.fchk
   - pop_f2_opt_freq.fchk
   - pop_no_plus_opt_freq.fchk
   - pop_cn_minus_opt_freq.fchk
   - pop_co_opt_freq.fchk

Lecture 8 Outline

- your feedback!
- π-back-donation
- ML_6 molecular orbitals
- a real example!

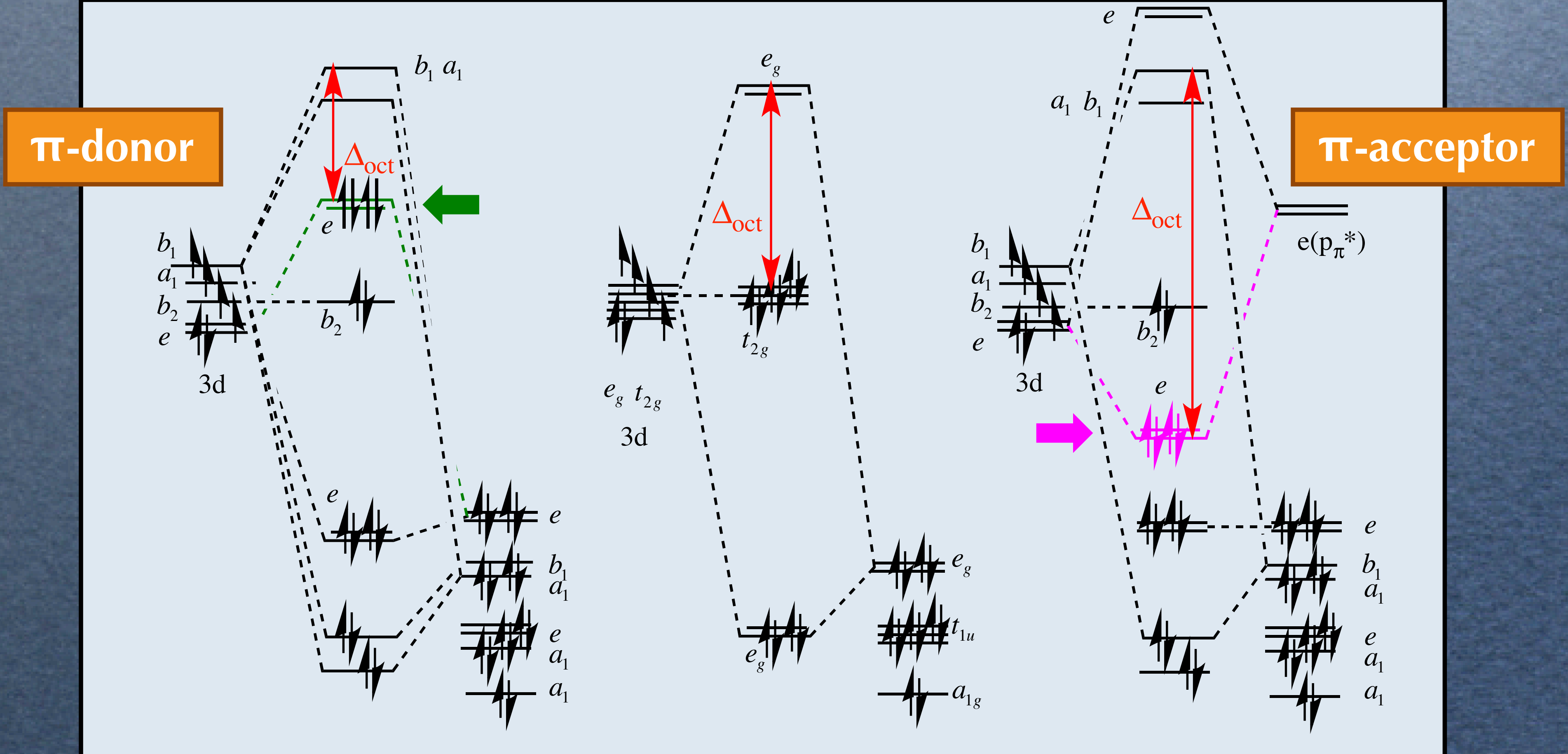
Summary for Δ_{oct}

σ-donor ligands

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < O^{2-} < H_2O < NH_3 < en < NO_2^- < CH_3^- < C_6H_5^- < PPh_3 < CN^- < CO$

π-donor ligands

π*-acceptor ligands



pseudo-octahedral
one π-donor liagand

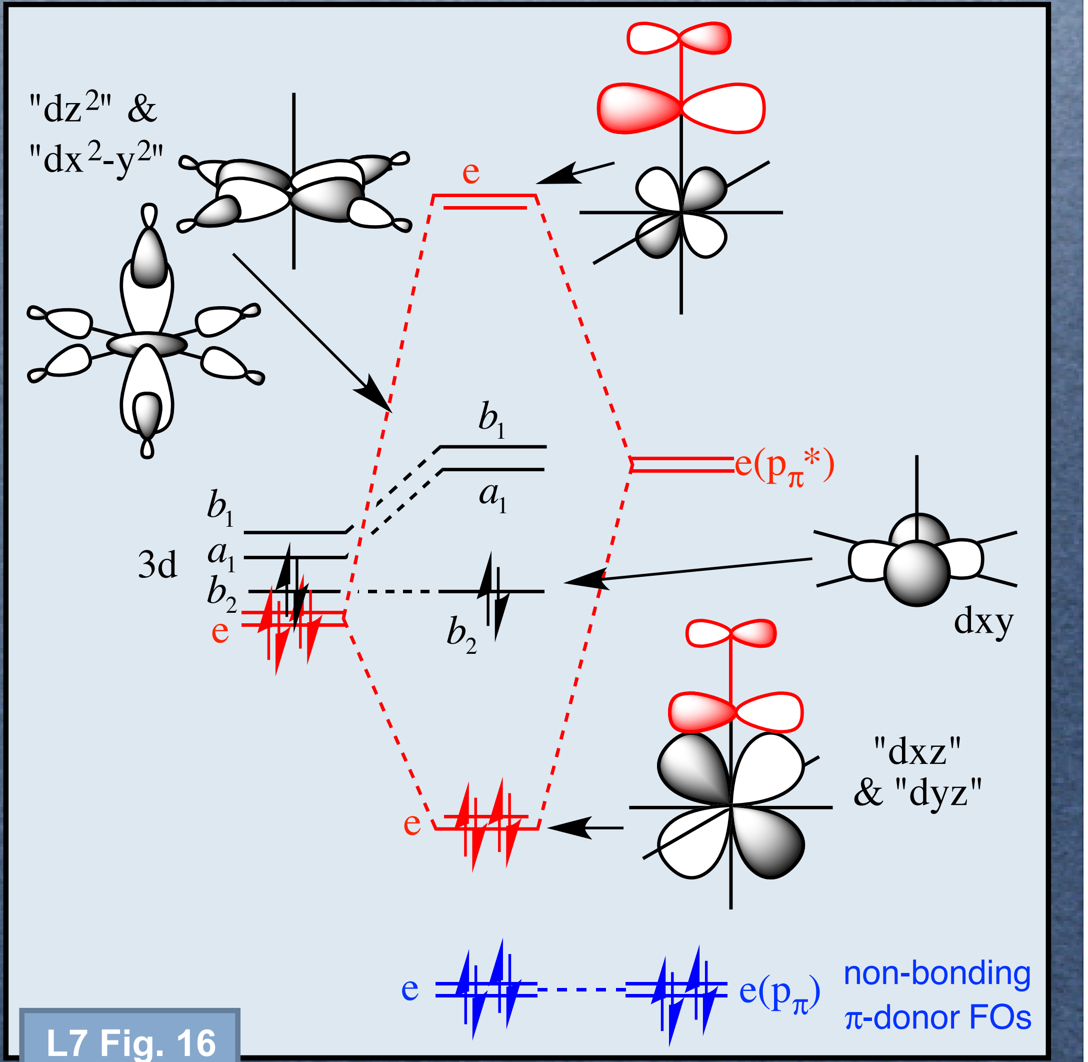
octahedral L_σ

pseudo-octahedral
one π-acceptor liagand

Fig. 17

π-Acceptor Ligands

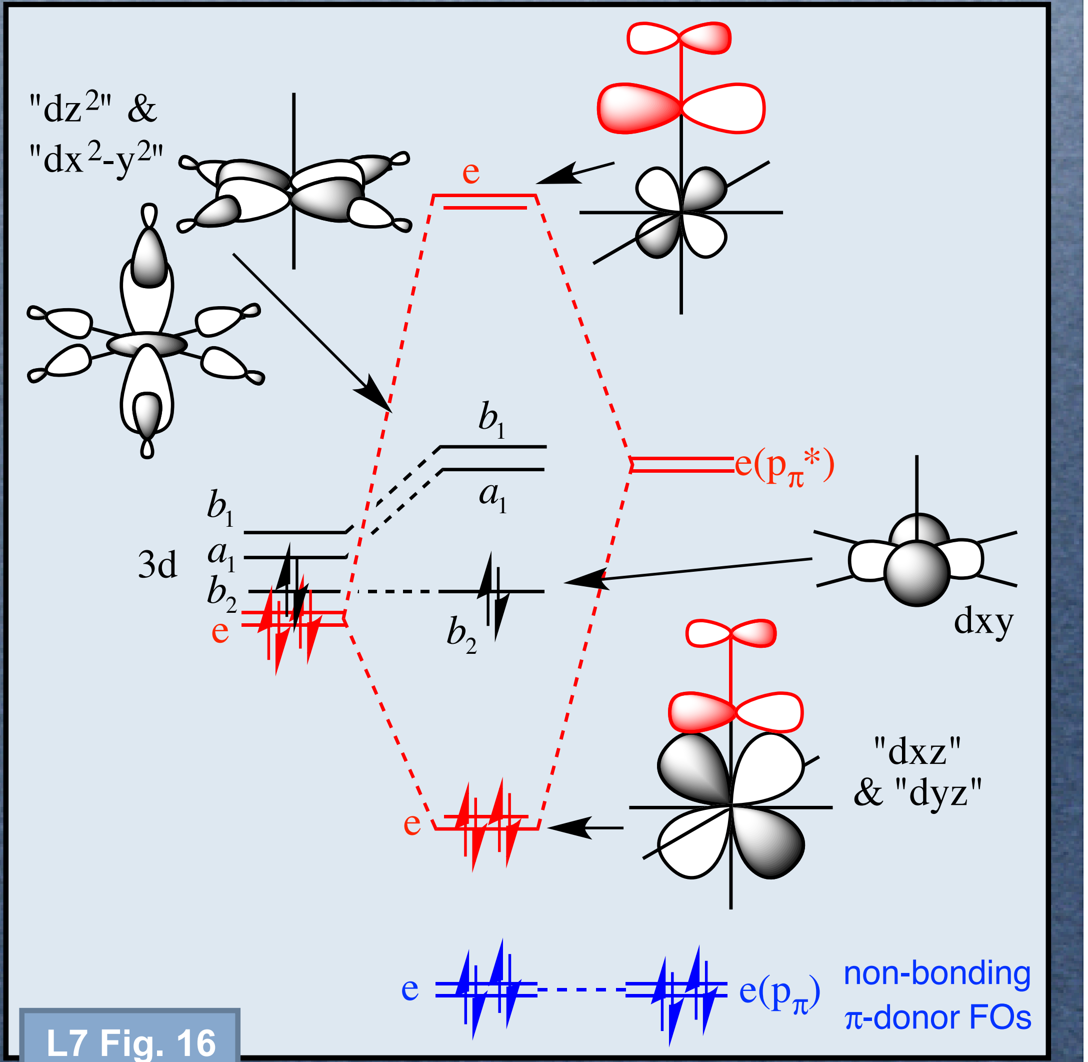
- **backdonation**
  - formally e are in the dAO of M
  - when the MO is formed they are shared with π*-orbitals of L
  - e are “back-donated” into L



L7 Fig. 16

π-Acceptor Ligands

- **backdonation**
  - formally e are in the dAO of M
  - when the MO is formed they are shared with π*-orbitals of L
  - e are “back-donated” into L
- **stretching vibration of CO is sensitive to the amount of backdonation**
  - other good donor L means M has a greater ability to backdonate
  - increased occupation L π*-orbitals
  - reduced bond order in L
  - increased bond order M-L bond!
  - reduction in C-O stretch frequency
  - gives measure of σ-donor and π-acceptor ability of other L



L7 Fig. 16

π-Acceptor Ligands

- **for a strong interaction**
  - small Δε
  - large S_{ij}
  - large H_{ij}
- **consider overlap for different π-acceptor ligands**
  - CO large contribution on C atom for π-acceptor FOs => strong M-L interaction
  - N_2 and O_2 homonuclear so FO contributions are the same size => weaker M-L interaction

Important!

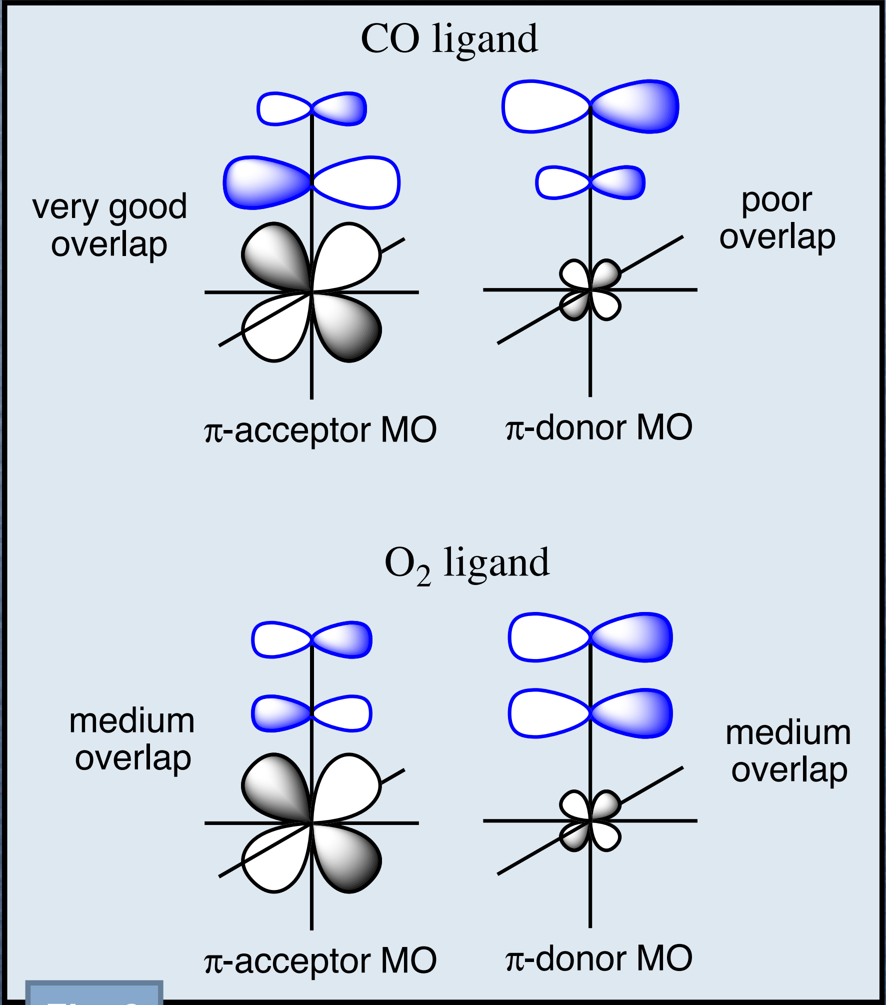


Fig. 2

π-Acceptor Ligands

- **ligands of the form E_2**
  - can bind end-on or side-on
  - end-on generally favoured
- **multiple bonds**
  - alkenes and alkynes
  - have to bind side-on
  - use π and π* FOs (see L7)
- **careful**
  - distinguish between internal ligand bonding and M-L bond
  - remember “σ- π- δ-“ are not strict but refer to rotation about the local bond

Important!

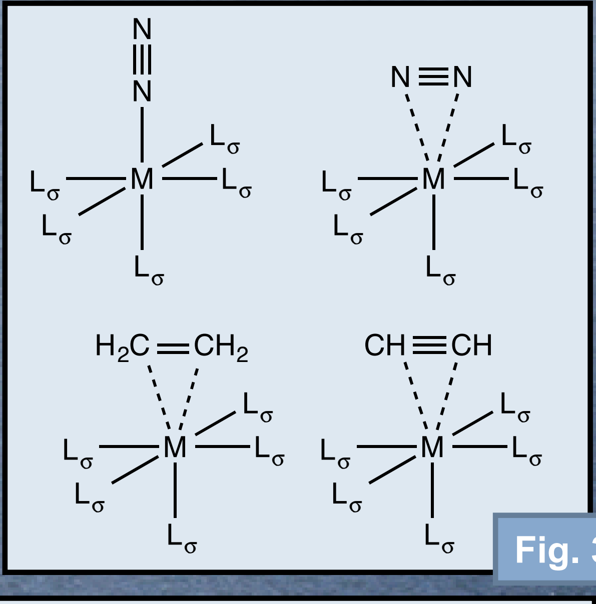


Fig. 3

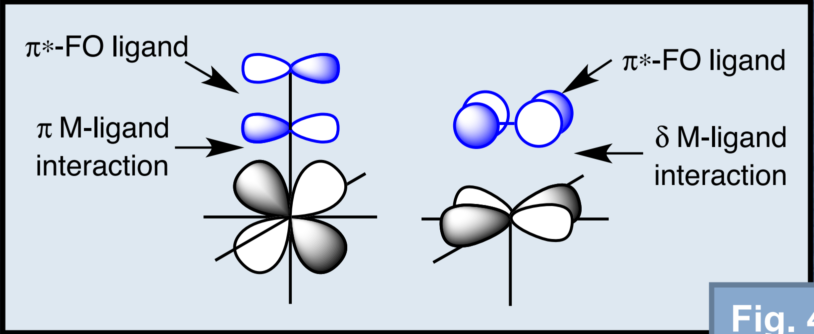


Fig. 4

π-Acceptor Ligands

how to describe the bonding?

- traditional oxidation state ideas break down!
- effects of a large amount of back-donation?
- cyclic vs linear bonds?

fascinating!

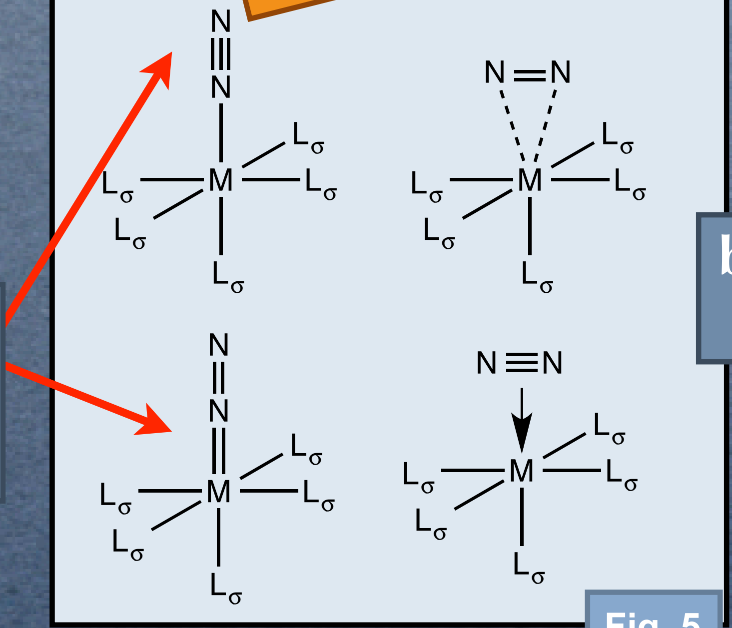
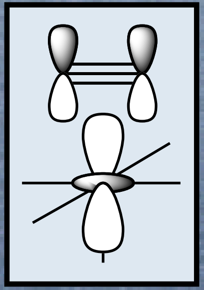


Fig. 5

strong back-donaton
↑ M-L bond
↓ internal L bond

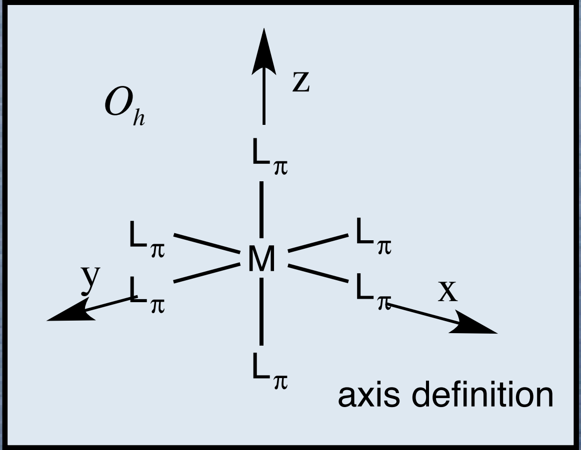


best way to represent bonding?

WARNING

- bonding is complex
- MOs are only part of the story!!
- “quantum” contributions such as Pauli repulsion

Six π-donor or π-acceptor Ligands



- **octahedral**
- **same process!**
  - symmetry is O_h
  - start from σ-framework
  - NO new symmetry
- **new orbitals**
  - π-donor: “new” FOs: 6 ligands 2π each = total 12 FOs
  - π-acceptor: 12 additional FOs
  - π-donor: a set $t_{1g}+t_{1u}+t_{2g}+t_{2u}$
  - π-acceptor: a second set $t_{1g}+t_{1u}+t_{2g}+t_{2u}$
  - ONLY t_{2g} can interact $t_{1g}+t_{1u}+t_{2u}$ remain non-bonding
  - pictures of active t_{2g} FOs next slide

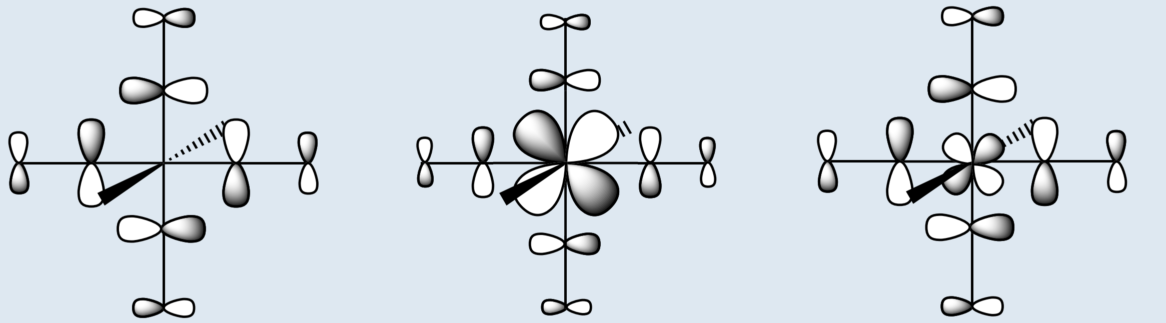
“one of each” T symmetry in O_h

Six π-donor or π-acceptor Ligands

- **what do the MOs look like?**

you don't need to be able to reproduce these for the exam!

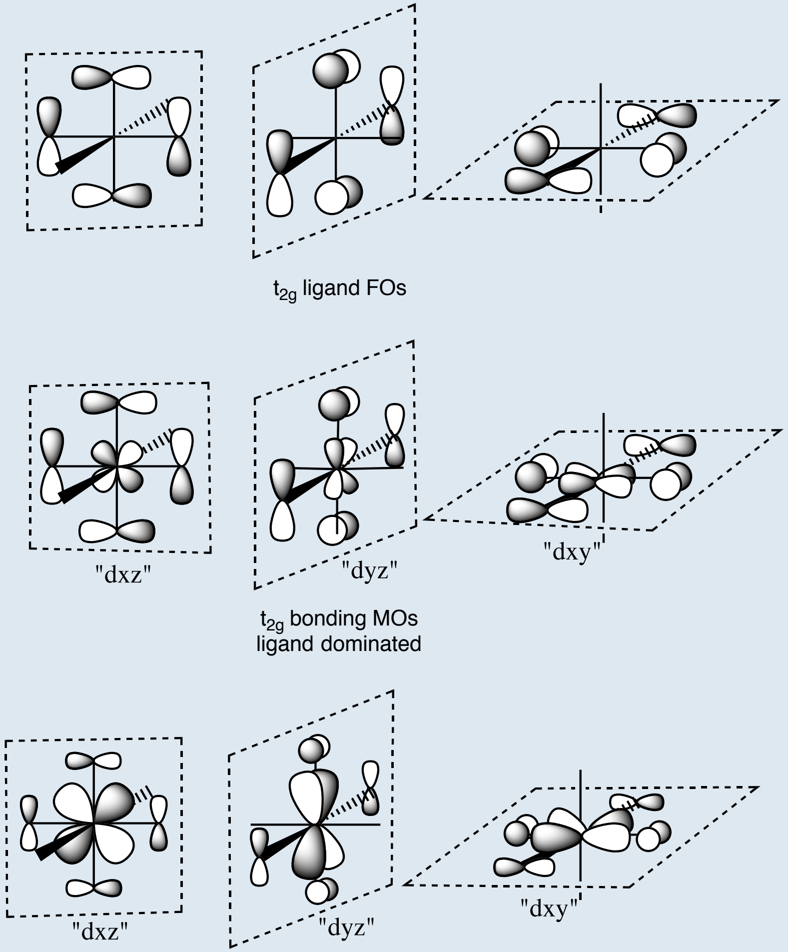
Fig. 11



t_{2g} ligand FO

t_{2g} bonding MO
dAO dominated

t_{2g} antibonding MO
ligand dominated

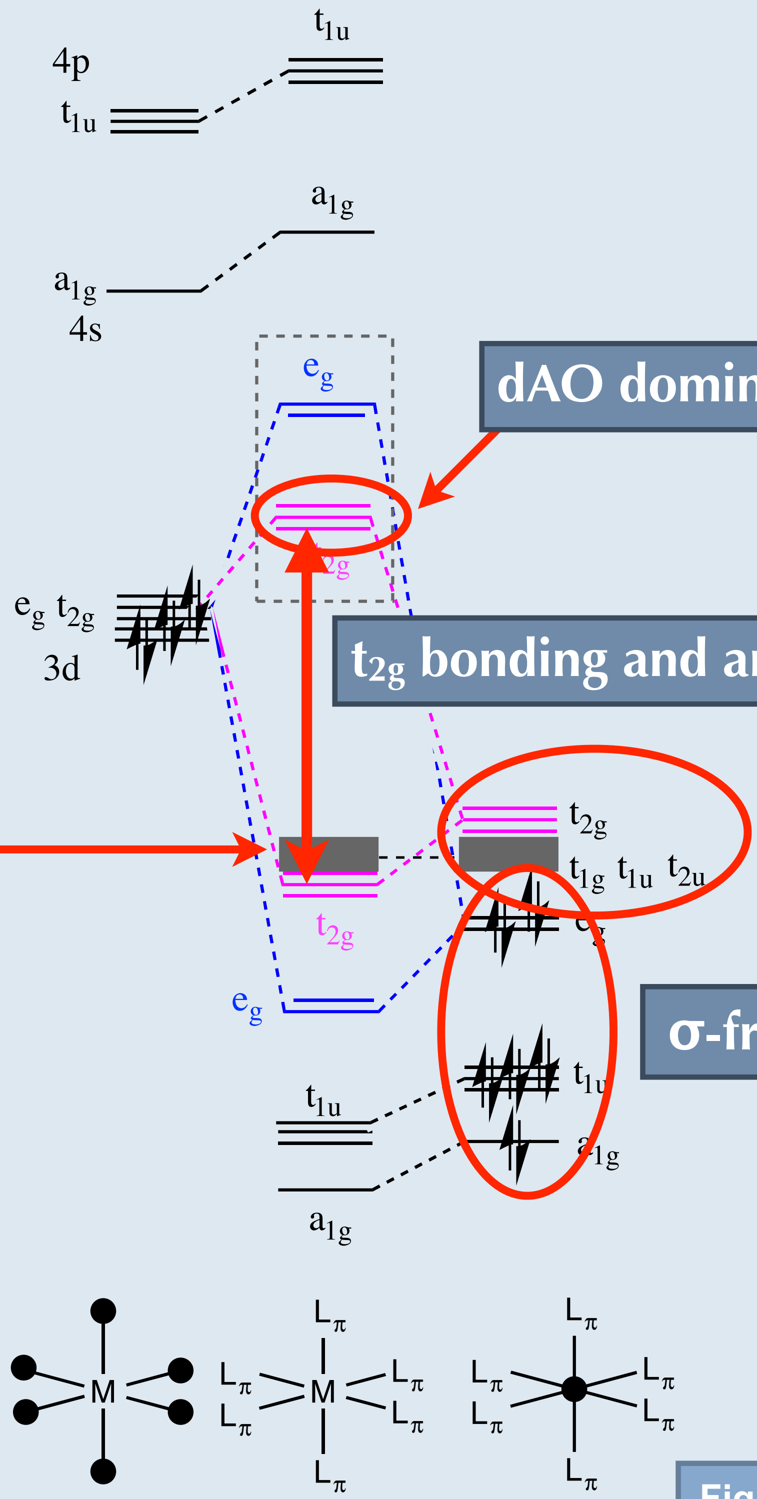


t_{2g} ligand FOs

t_{2g} bonding MOs
ligand dominated

t_{2g} antibonding MOs
dAO dominated

Fig. 10



dAO dominated

t_{2g} bonding and antibonding

π-donor orbitals

σ-framework

non-bonding
$t_{1g}+t_{1u}+t_{2u}$

Fig. 12

π-donor antibonding MOs important for Δ_{oct}

t_{2g}->e_g
Δ_{oct} small

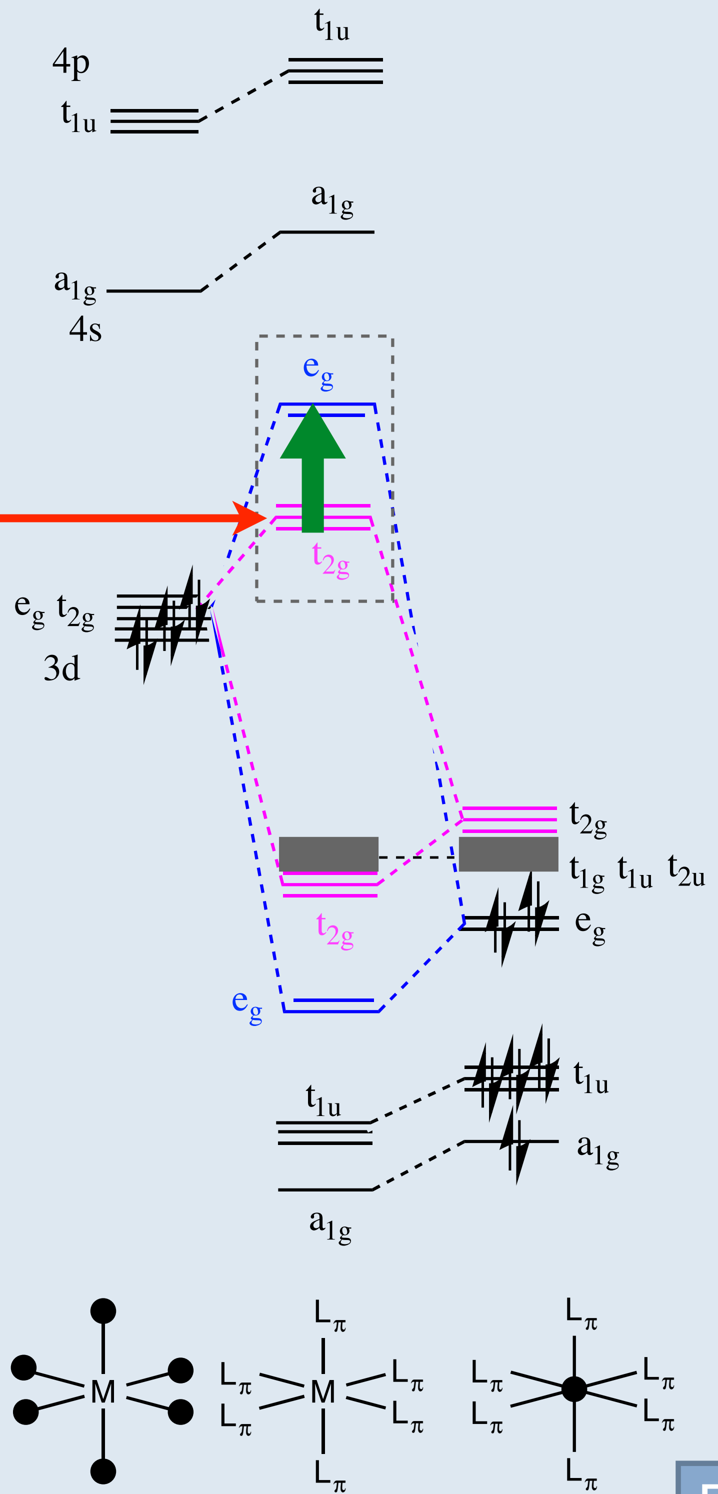
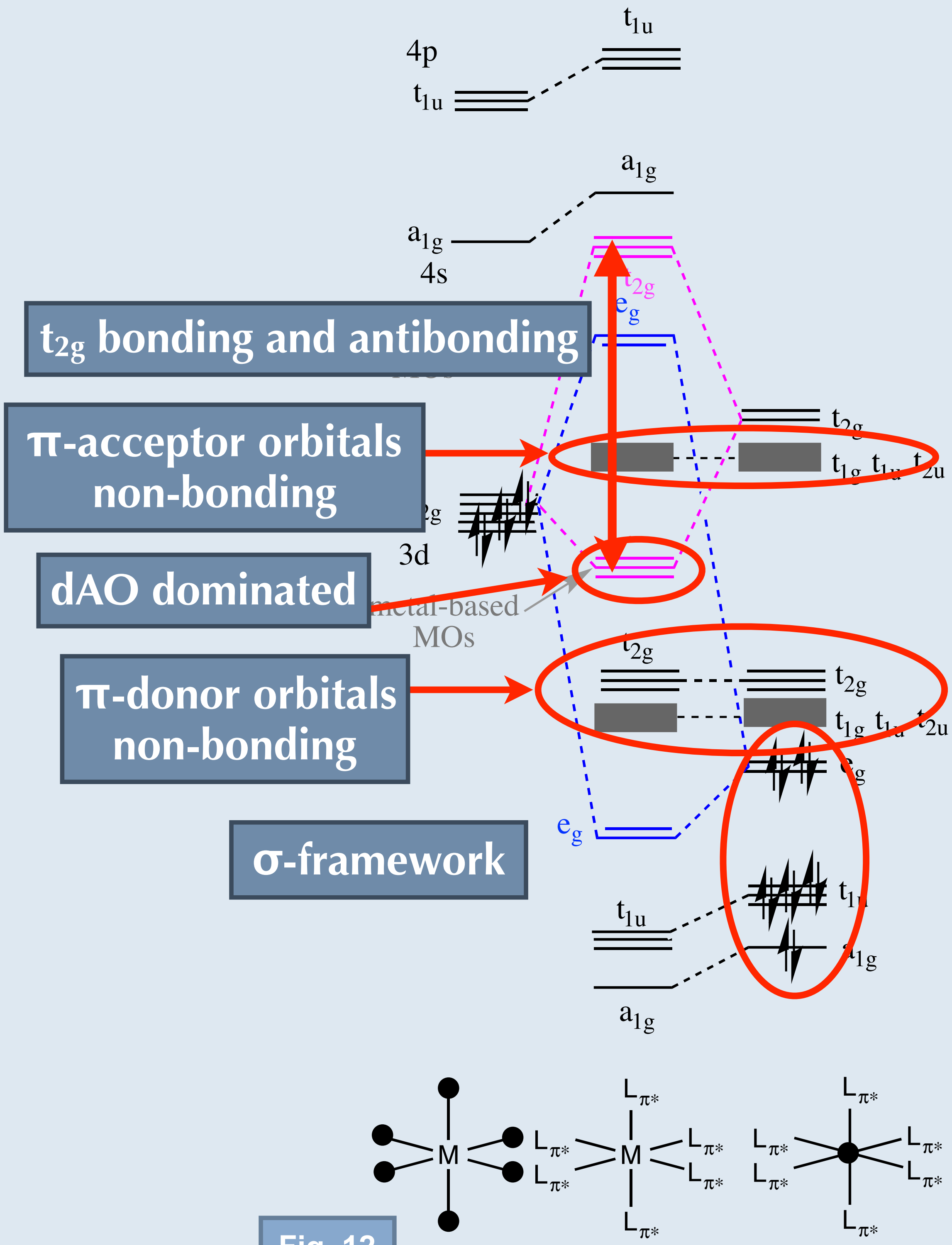


Fig. 12



t$_{2g}$ bonding and antibonding

π-acceptor orbitals non-bonding

dAO dominated

π-donor orbitals non-bonding

σ-framework

Fig. 12

π-acceptor antibonding MO important for Δ_{oct}

t_{2g}->e_g
Δ_{oct} large

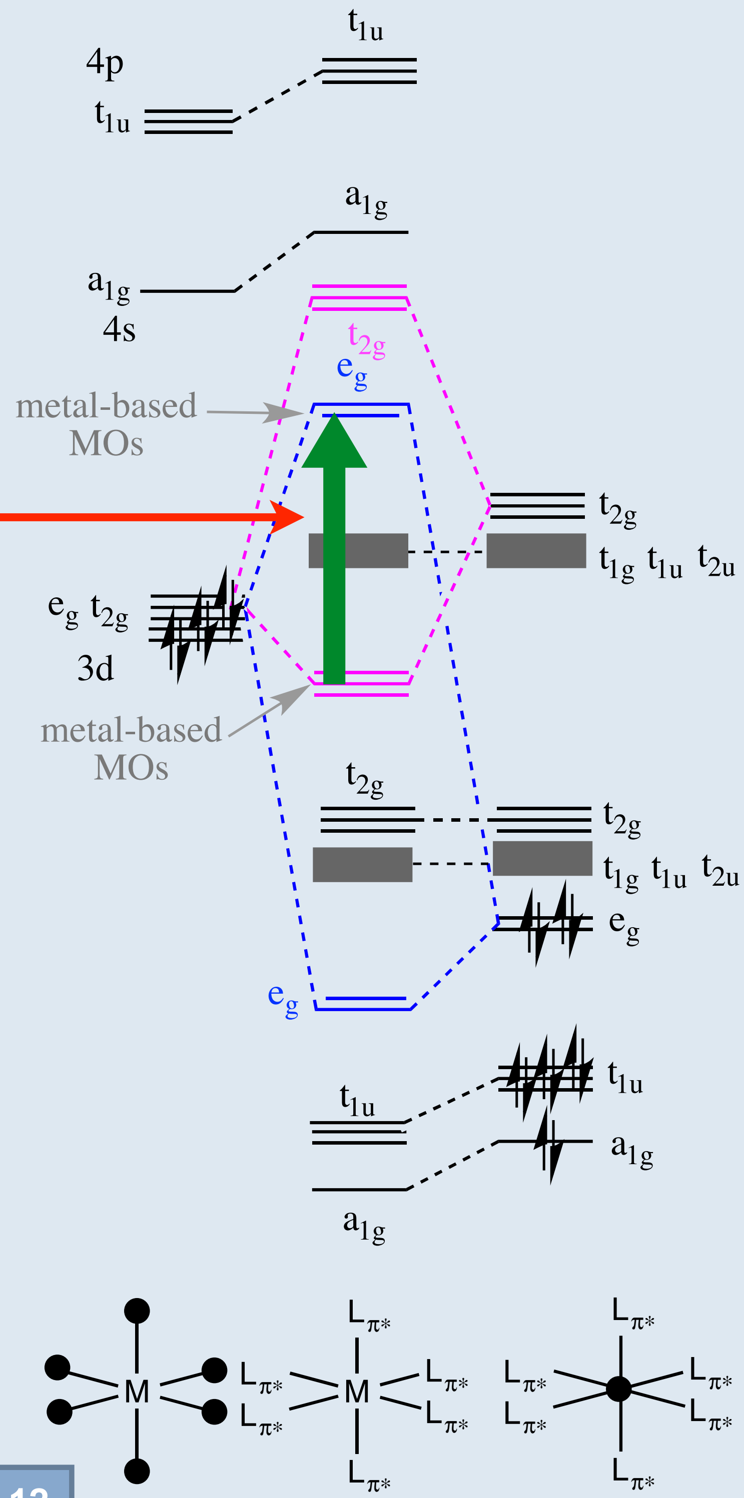
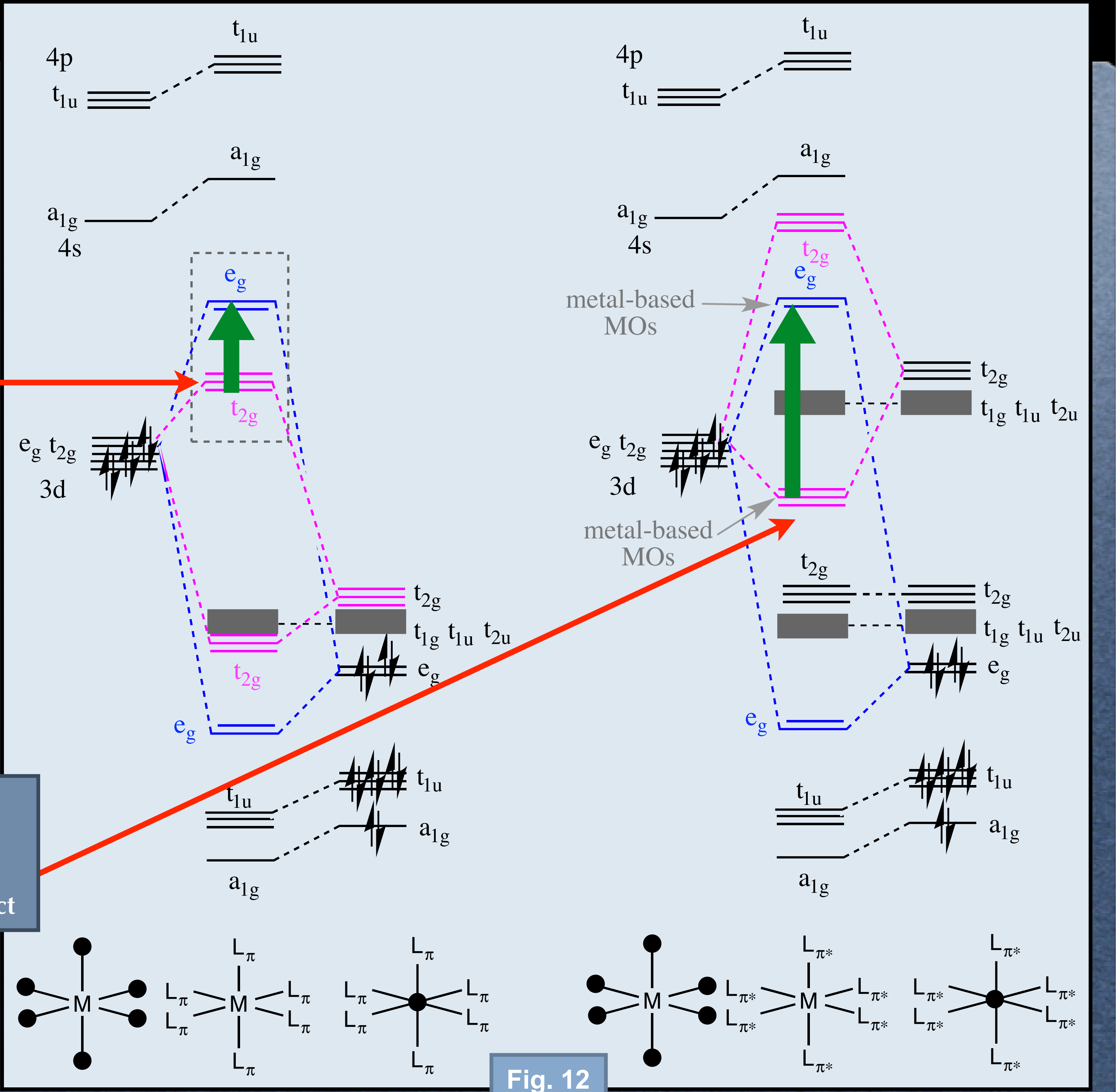


Fig. 12



π-donor antibonding MOs important for Δ_{oct}

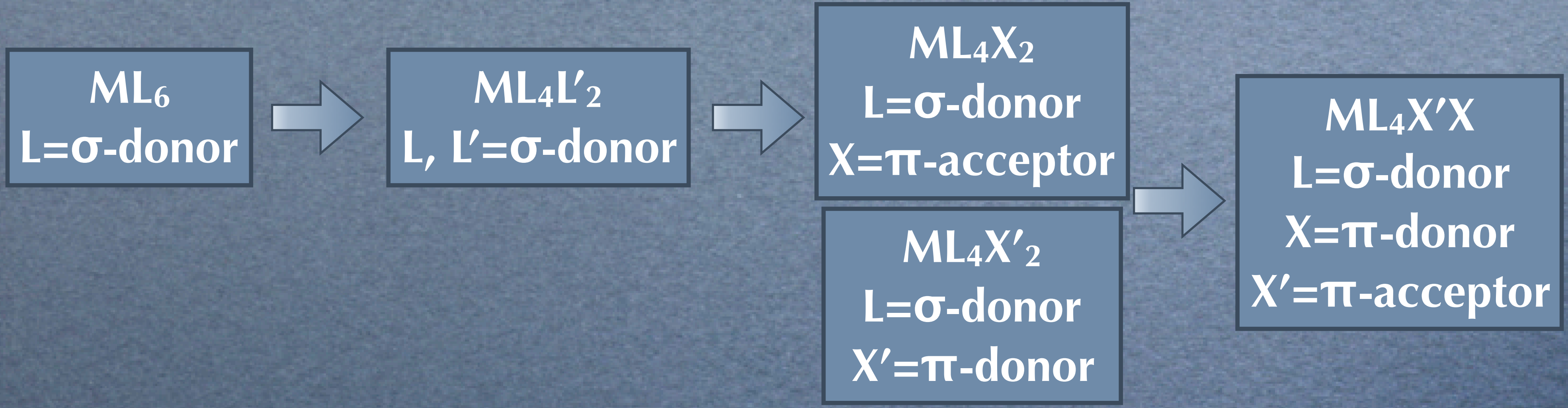
t_{2g}->e_g
Δ_{oct} small

π-acceptor bonding MO important for Δ_{oct}

t_{2g}->e_g
Δ_{oct} large

Fig. 12

Two π-donor or π-acceptor Ligands



ML_6
L=σ-donor

$ML_4L'_2$
L, L′=σ-donor

ML_4X_2
L=σ-donor
X=π-acceptor

$ML_4X'_2$
L=σ-donor
X′=π-donor

$ML_4X'X$
L=σ-donor
X=π-donor
X′=π-acceptor

- **large number of complexes can be modelled with knowledge of few key ligand types**
- **same process for all!**
    - start from σ-framework
    - work out reduced symmetry labels from O_h
    - add the“new” FOs
    - complex diagrams, make a rough diagram first

Variety!

$M(L_\sigma)_6$
L=σ-donor

$[Ni(OH_2)_6]^{2+}$

$M(L_\pi)_6$
L=π-donor

$[CoCl_6]^{3-}$

$M(L_{\pi^*})_6$
L=π-acceptor

$[Fe(CN)_6]^{3-}$

ML_4X_2
L=σ-donor
X=π-acceptor

$ML_4L'_2$
L, L′=σ-donor

$[Ni(OH_2)_4(NH_3)_2]^{2+}$

ML_4X_2
L=σ-donor
X=π-donor

$[FeCl_2(OH_2)_4]$

MX_5X'
X=π-acceptor
X′=π-acceptor

$[Fe(CN)_5NO]^{2-}$

$ML_4X'X$
L=σ-donor
X=π-donor
X′=π-acceptor

$ML_4L'X$
L, L′=σ-donor
X=π-donor

$MX_{4'}X_2$
X=π-donor
X′=π-donor

$[FeCl_2Br_4]^{4-}$

$M(L_\sigma)_4$
L=σ-donor

$[Pd(NH_3)_4]^{2+}$

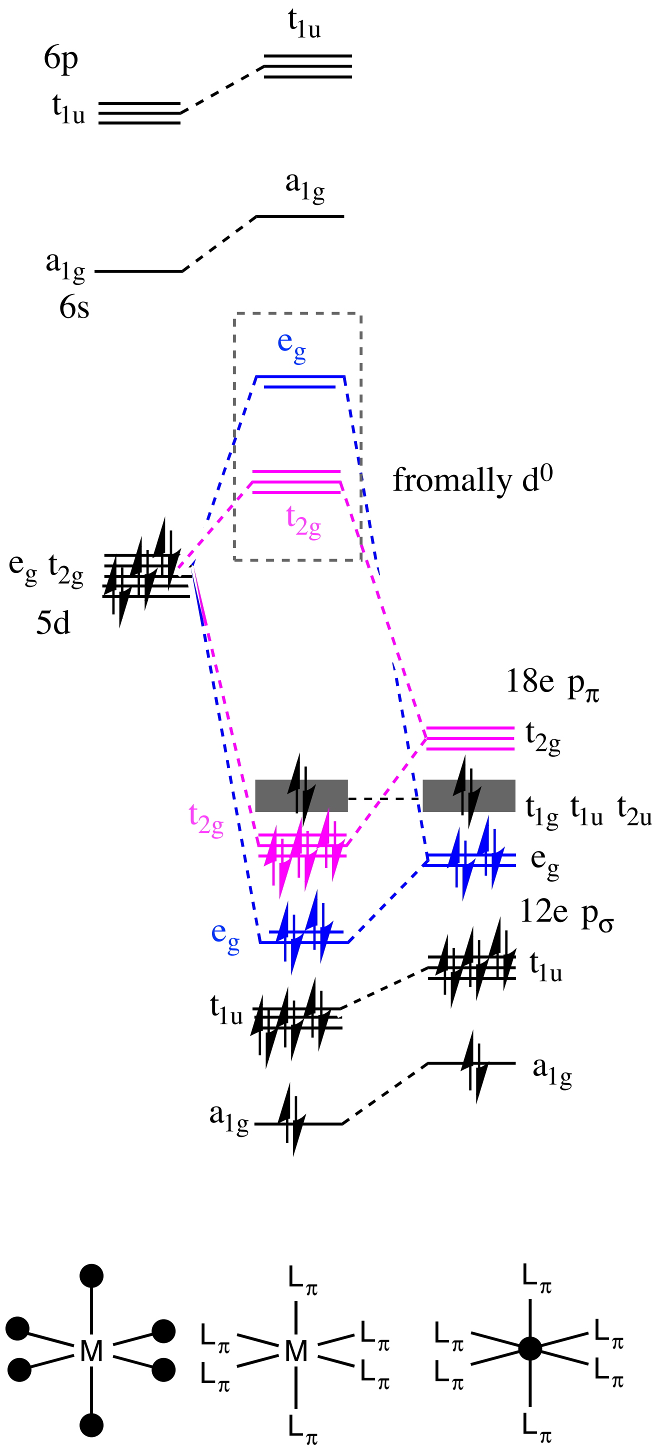
$M(L_\pi)_4$
L=π-donor

$[Ni(PF_3)_4]^{2+}$

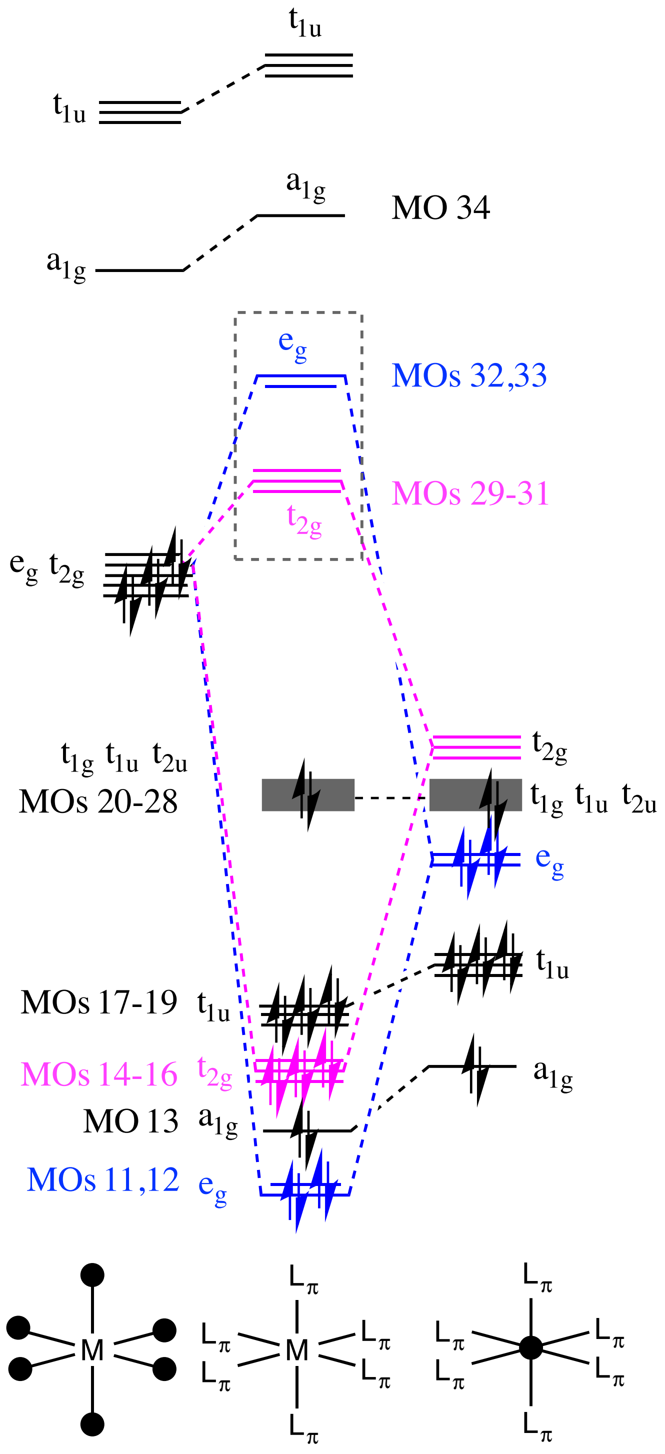
$[Mn(CO)_4]^-$

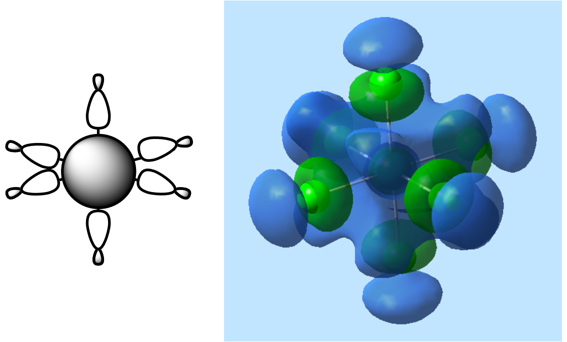
$M(L_{\pi^*})_4$
L=π-acceptor

qualitative

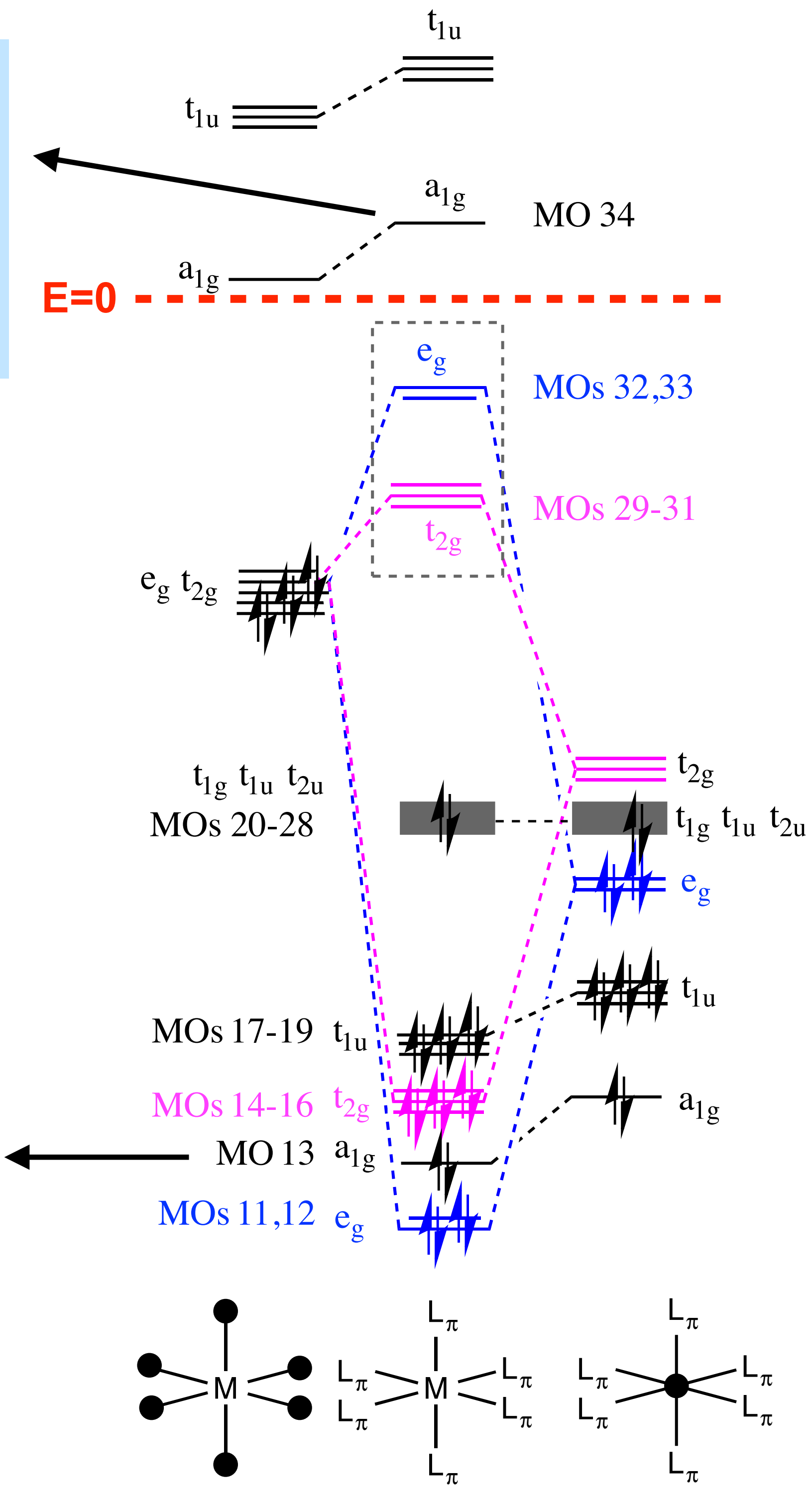


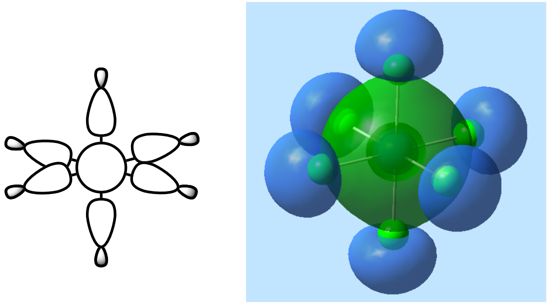
corrected after calculation





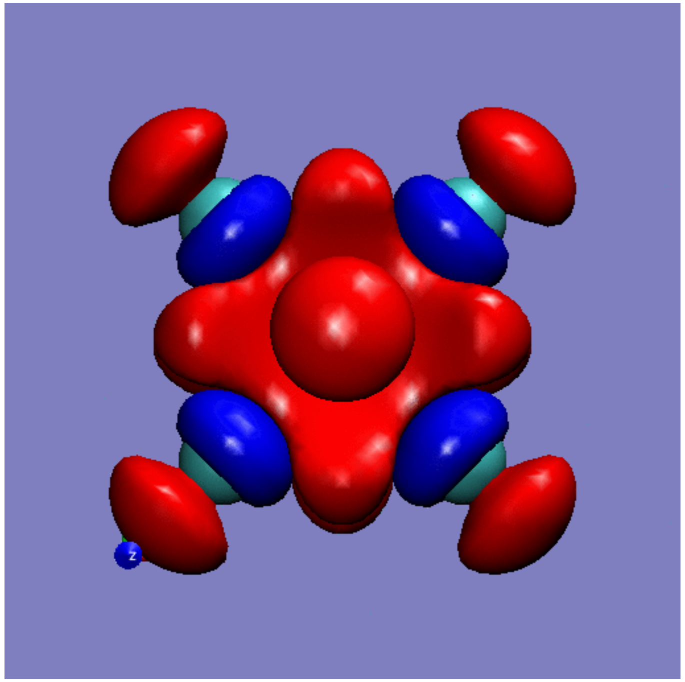
MO 34 a_{1g}



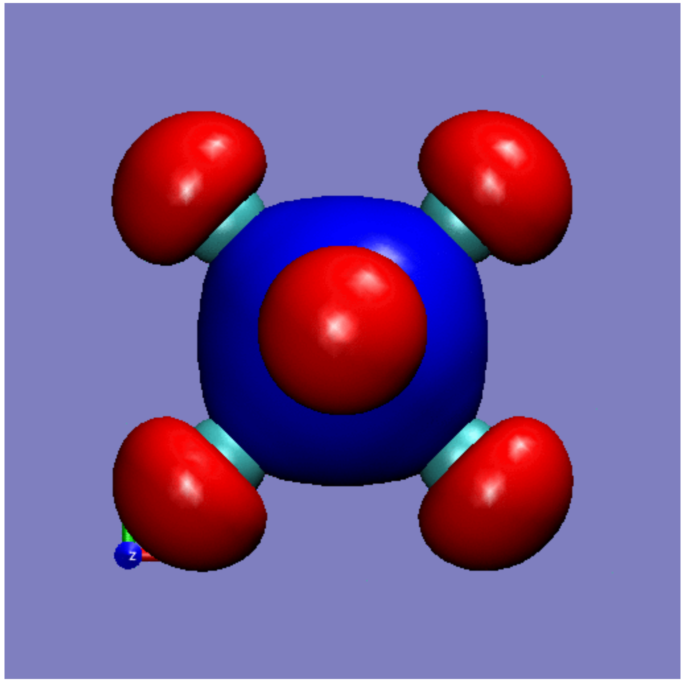


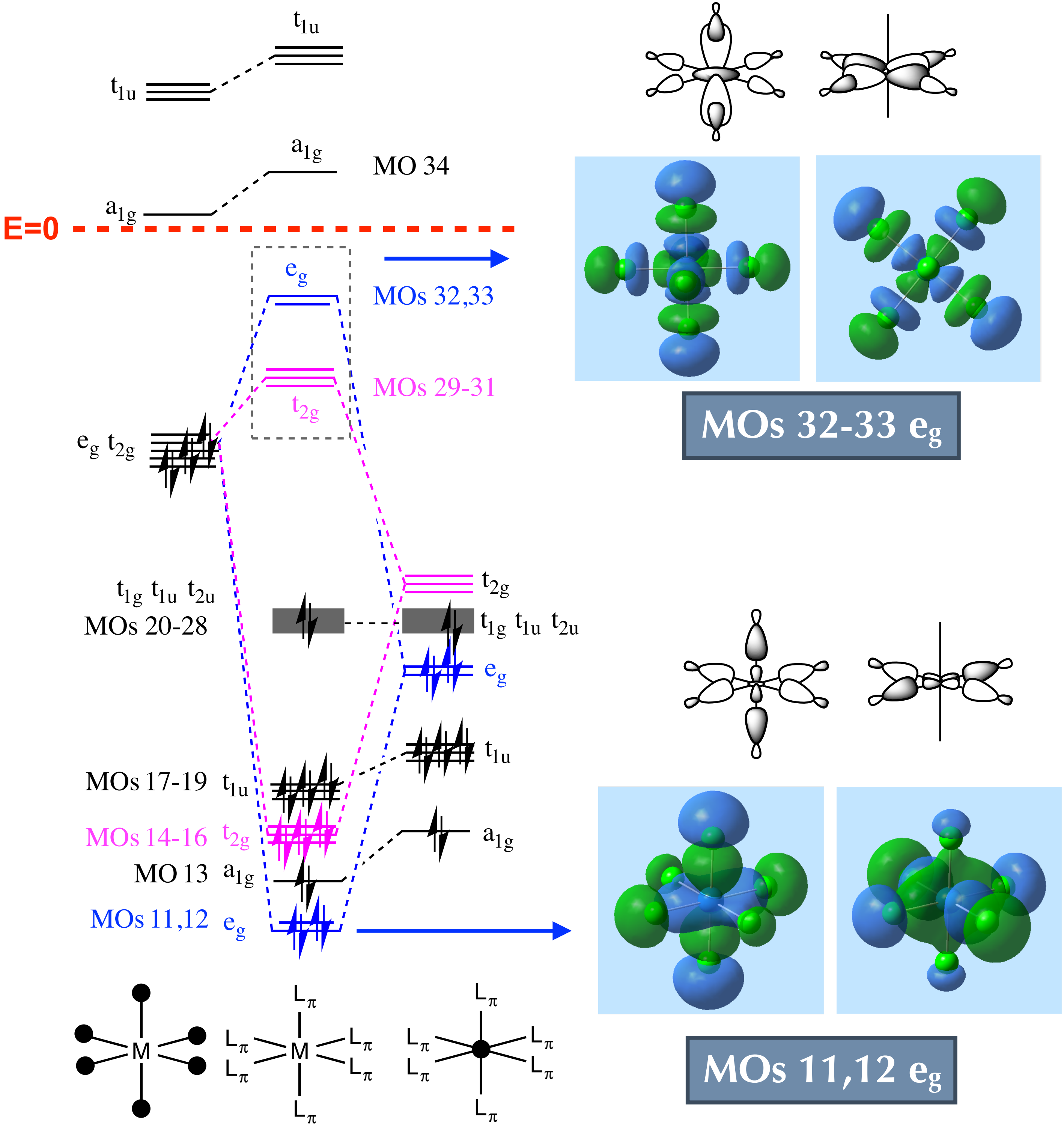
MO 13 a_{1g}

MO 34 a_{1g}



MO 13 a_{1g}

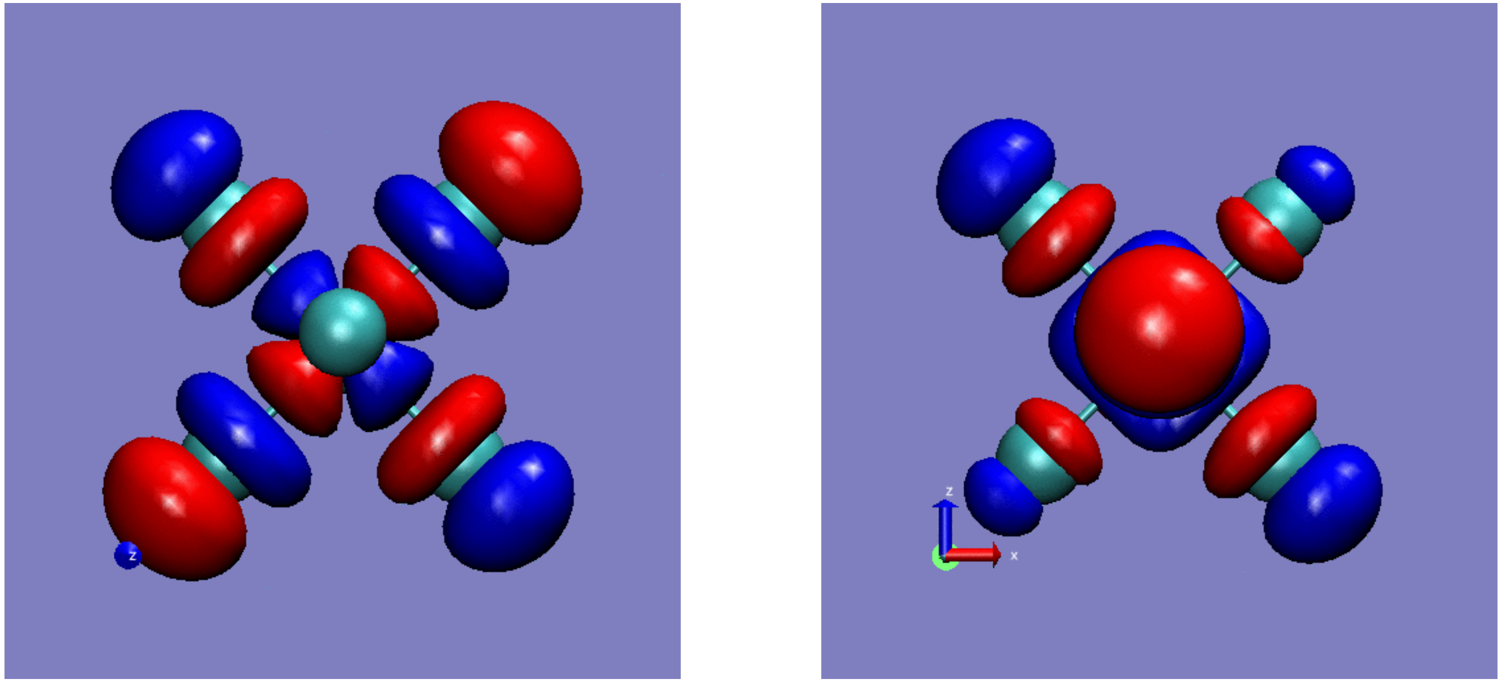




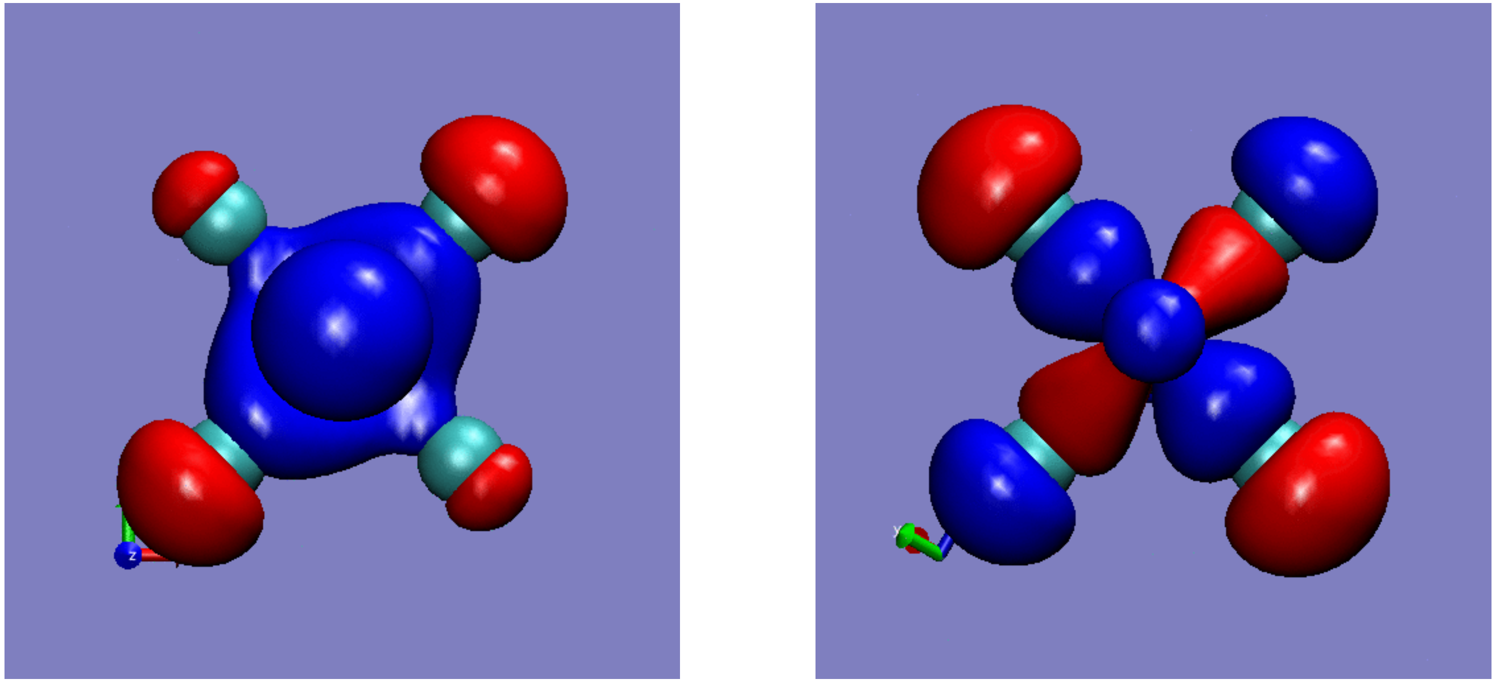
MOs 32-33 e_g

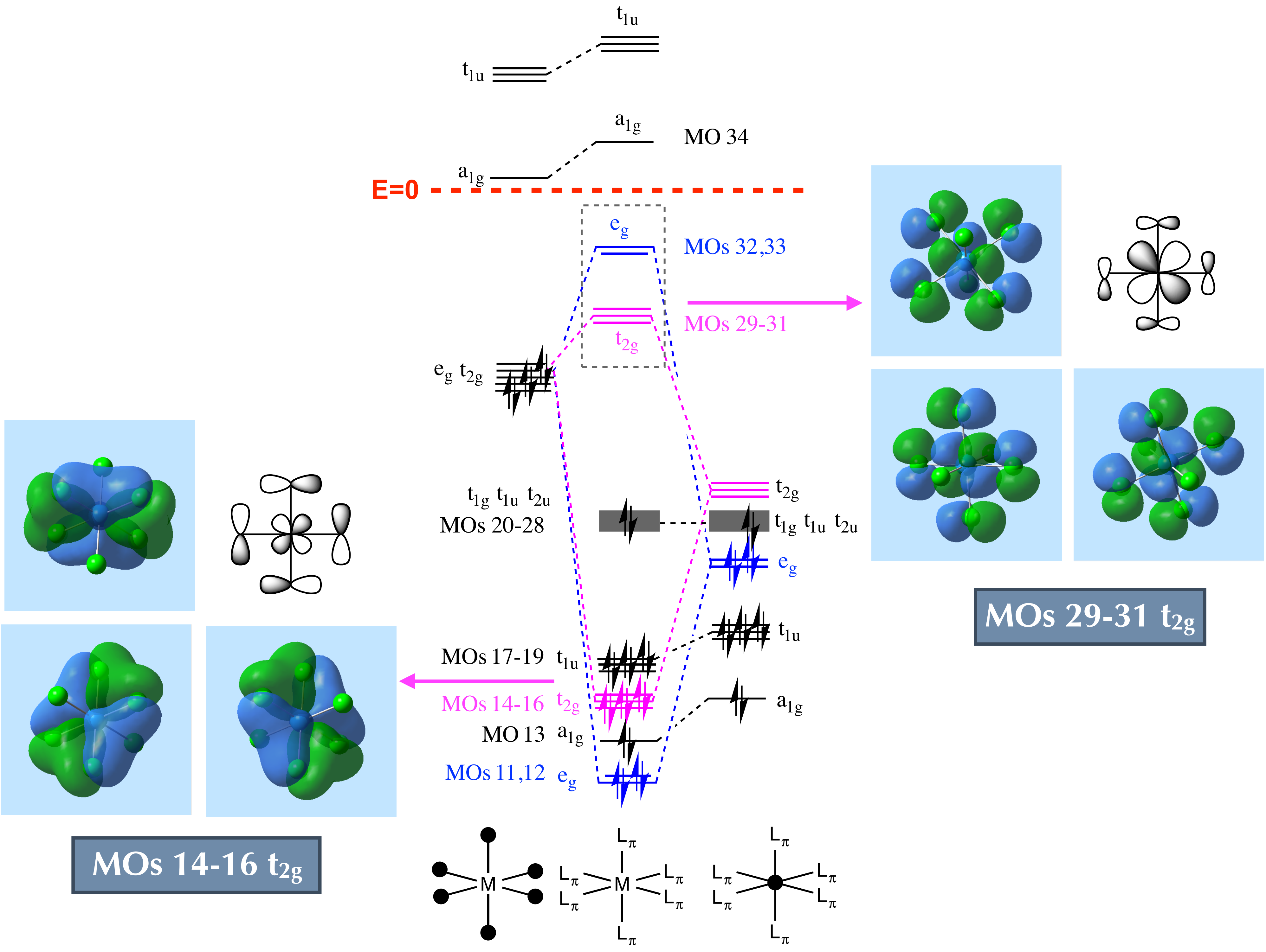
MOs 11,12 e_g

MOs 32-33 e_g



MOs 11,12 e_g

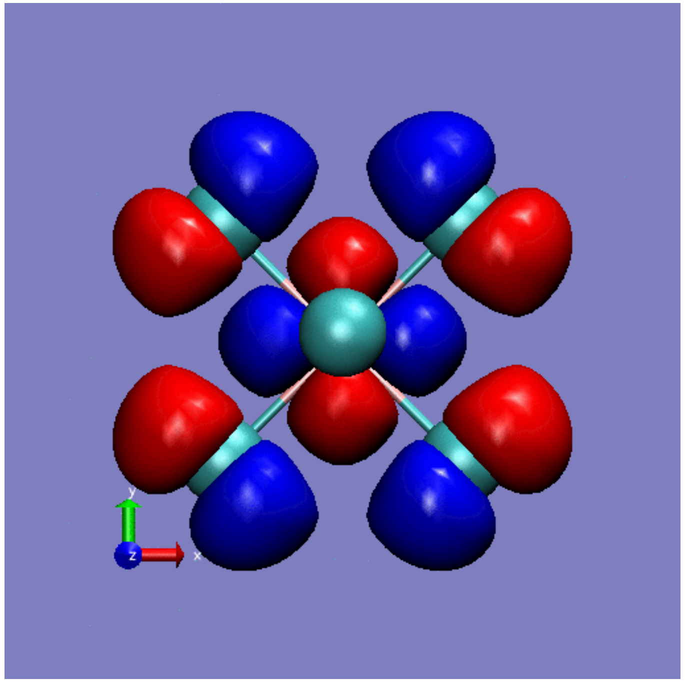




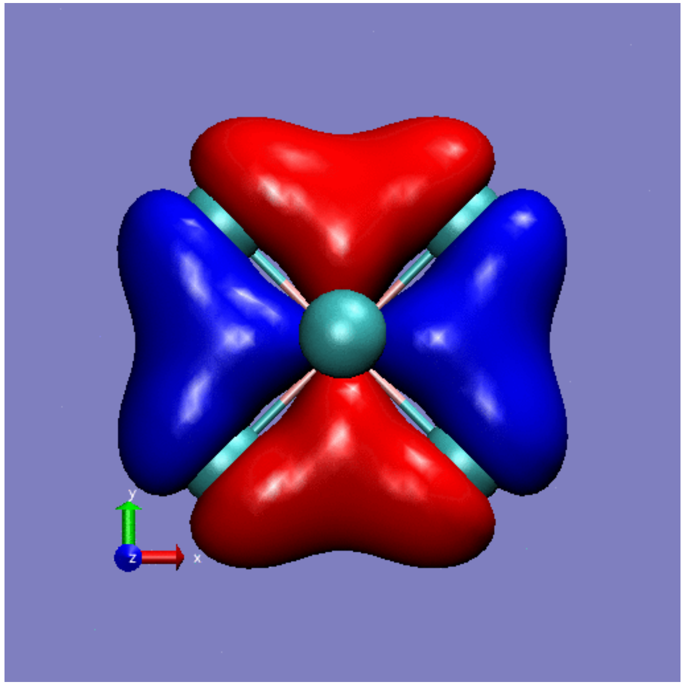
MOs 29-31 t_{2g}

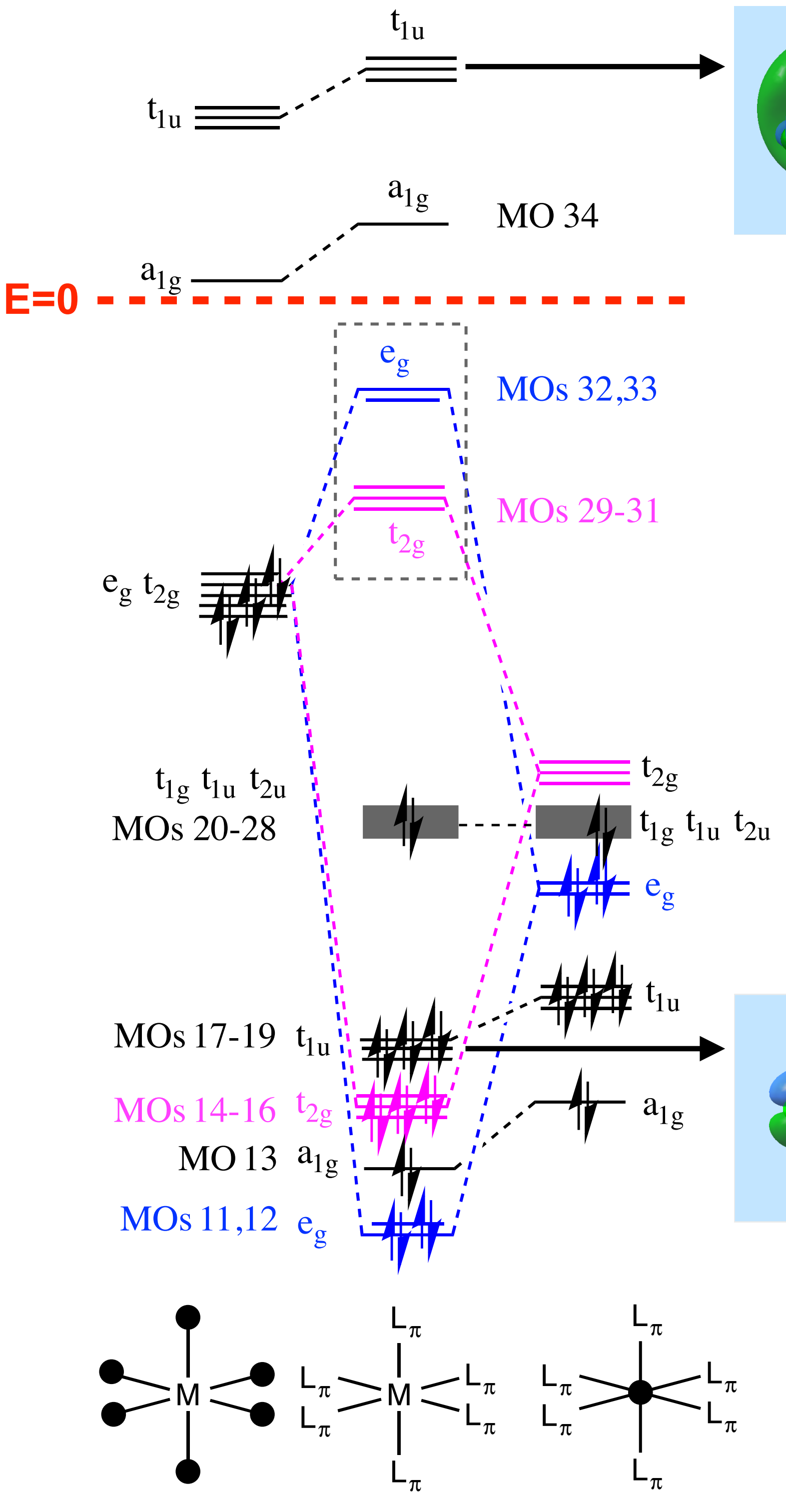
MOs 14-16 t_{2g}

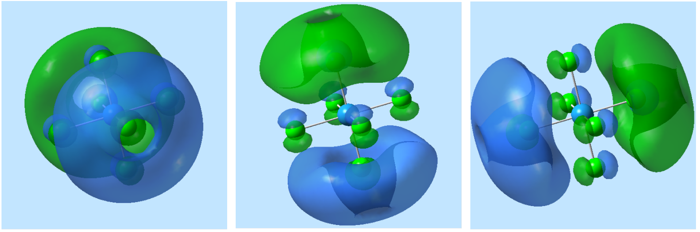
MOs 29-31 t_{2g}



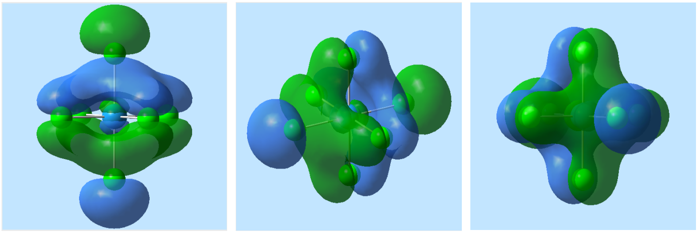
MOs 14-16 t_{2g}

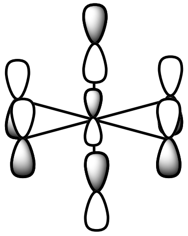






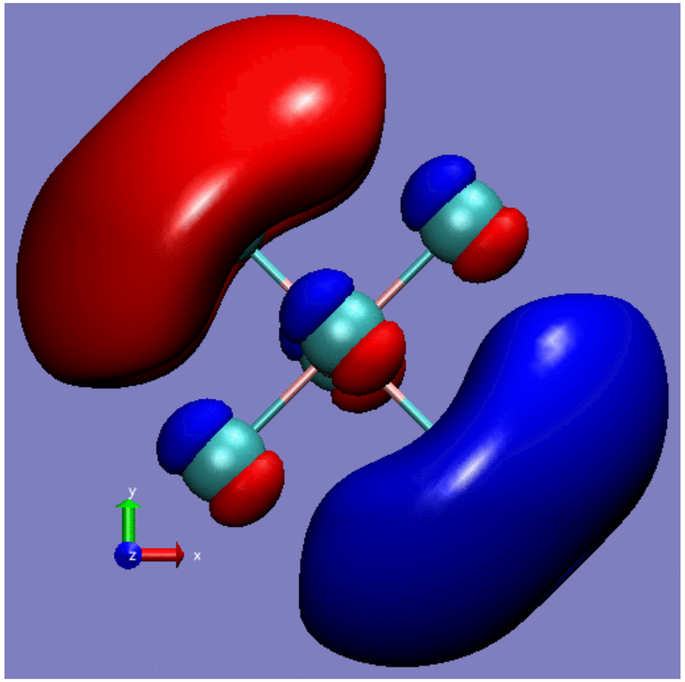
MOs 35-37 t_{1u}



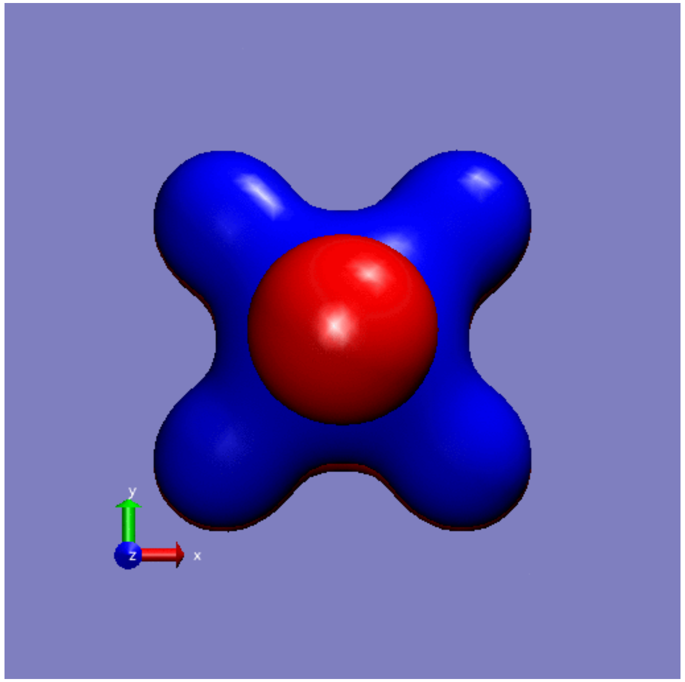


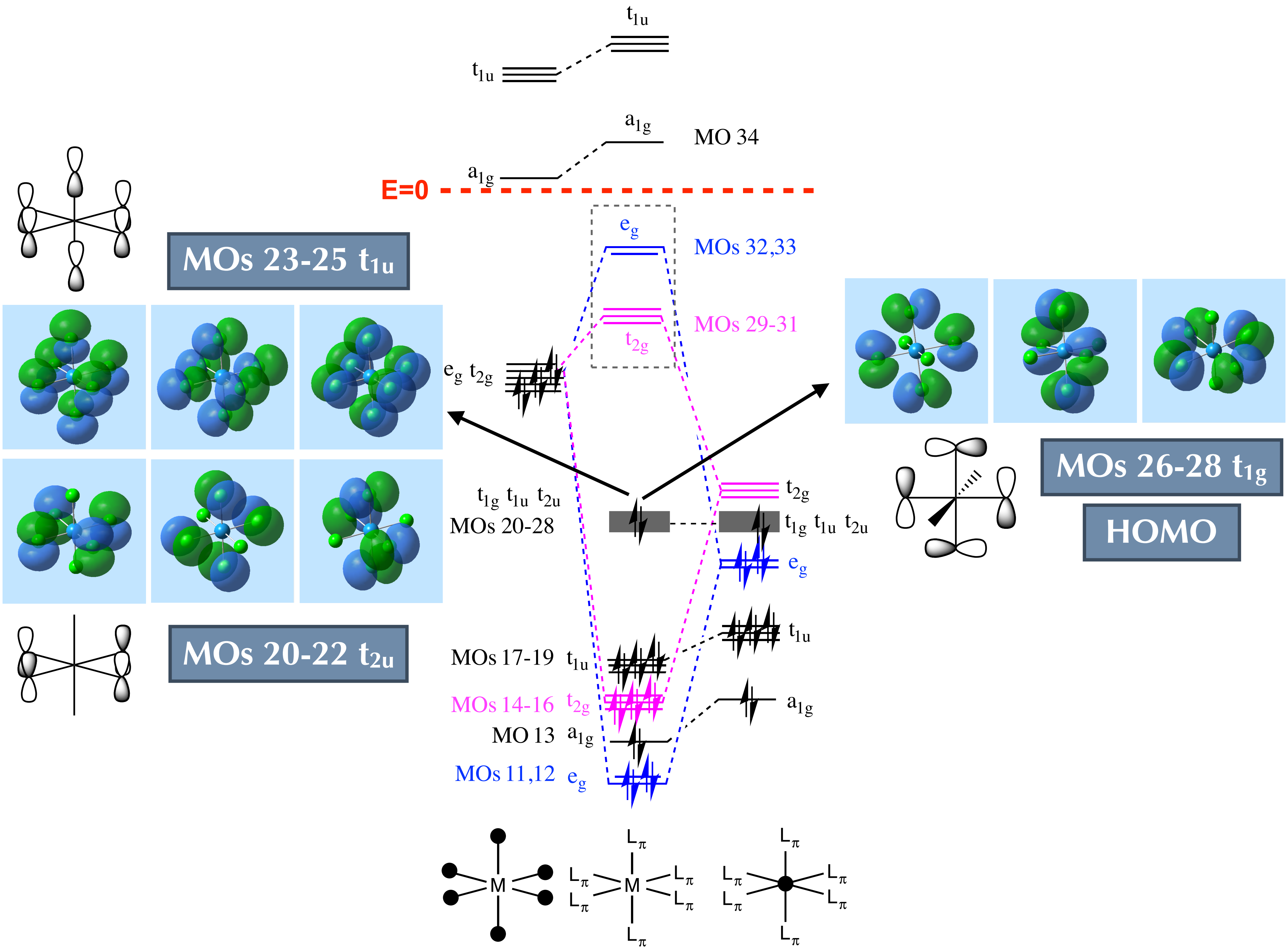
MOs 17-19 t_{1u}

MOs 35-37 t_{1u}



MOs 17-19 t_{1u}




t$_{1u}$
t$_{1u}$
a$_{1g}$
MO 34
a$_{1g}$
E=0
e$_g$
MOs 32,33
MOs 29-31
t$_{2g}$
MOs 23-25 t$_{1u}$
e$_g$ t$_{2g}$
MOs 26-28 t$_{1g}$
HOMO
t$_{1g}$ t$_{1u}$ t$_{2u}$
MOs 20-28
t$_{2g}$
t$_{1g}$ t$_{1u}$ t$_{2u}$
e$_g$
t$_{1u}$
MOs 20-22 t$_{2u}$
MOs 17-19 t$_{1u}$
MOs 14-16 t$_{2g}$
MO 13 a$_{1g}$
a$_{1g}$
MOs 11,12 e$_g$
M
L$_\pi$
M

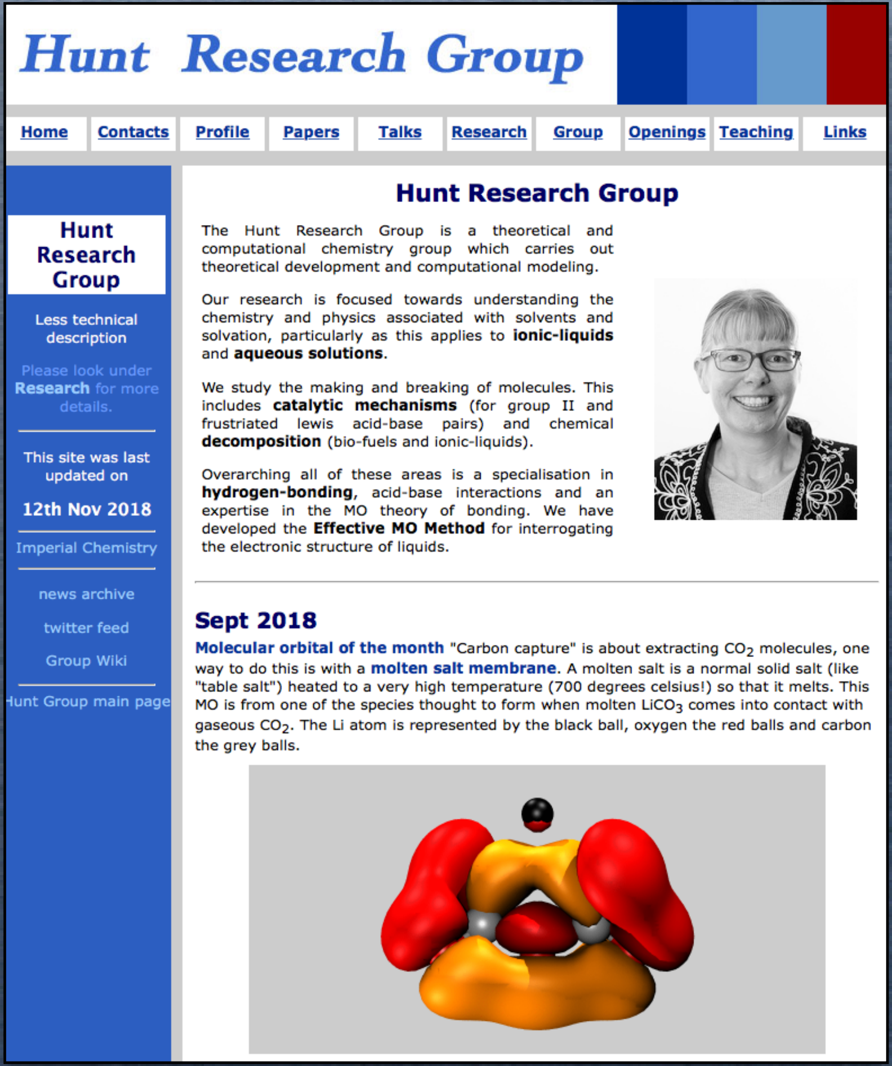
Key Points

- be able to discuss back-bonding and ligand orientation in relation to orbital overlap and energy match of FOs
- be able to draw energy level diagrams TM complex with one or two π-donor and π-acceptor (trans) ligands
- be able to draw and describe the important MOs
- be able to draw energy level diagrams for octahedral and square planar complexes with all π-bonding ligands
- be able to discuss key features of these diagrams, especially relating to character of MOs and Δ_{oct}

Finally

- **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!!

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



Hunt Research Group

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Hunt Research Group

Less technical description

Please look under **Research** for more details.

This site was last updated on

12th Nov 2018

Imperial Chemistry

news archive

twitter feed

Group Wiki

Hunt Group main page

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 **aqueous solutions**.

We study the making and breaking of molecules. This includes **catalytic mechanisms** (for group II and frustrated lewis acid-base pairs) and chemical **decomposition** (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.

Sept 2018

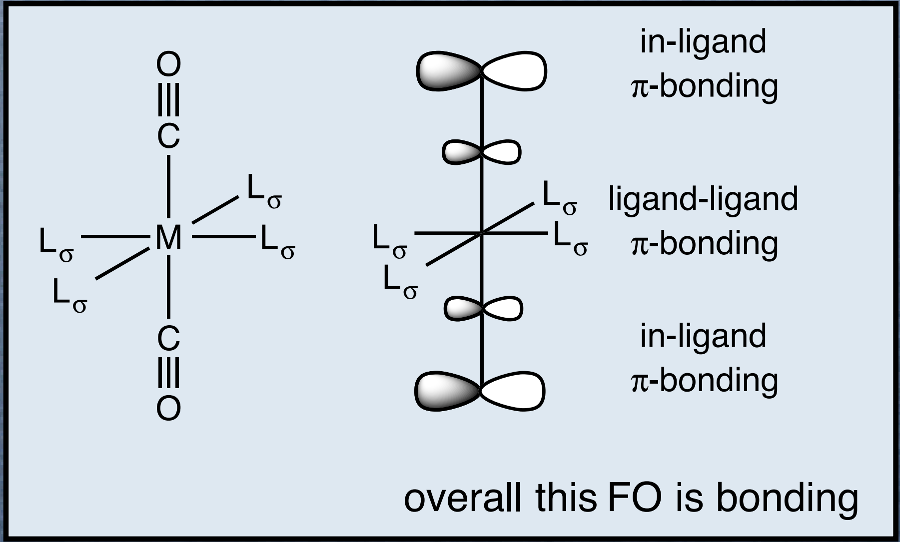
Molecular orbital of the month "Carbon capture" is about extracting CO_2 molecules, one way to do this is with a **molten salt membrane**. A molten salt is a normal solid salt (like "table salt") heated to a very high temperature (700 degrees celsius!) so that it melts. This MO is from one of the species thought to form when molten $LiCO_3$ comes into contact with gaseous CO_2. The Li atom is represented by the black ball, oxygen the red balls and carbon the grey balls.

Extras

In-Class Activity

- **complexes can have more than one π-donor or π-acceptor ligand**

draw the bonding and antibonding combinations of the π and π* ligand FOs



in-ligand π-bonding

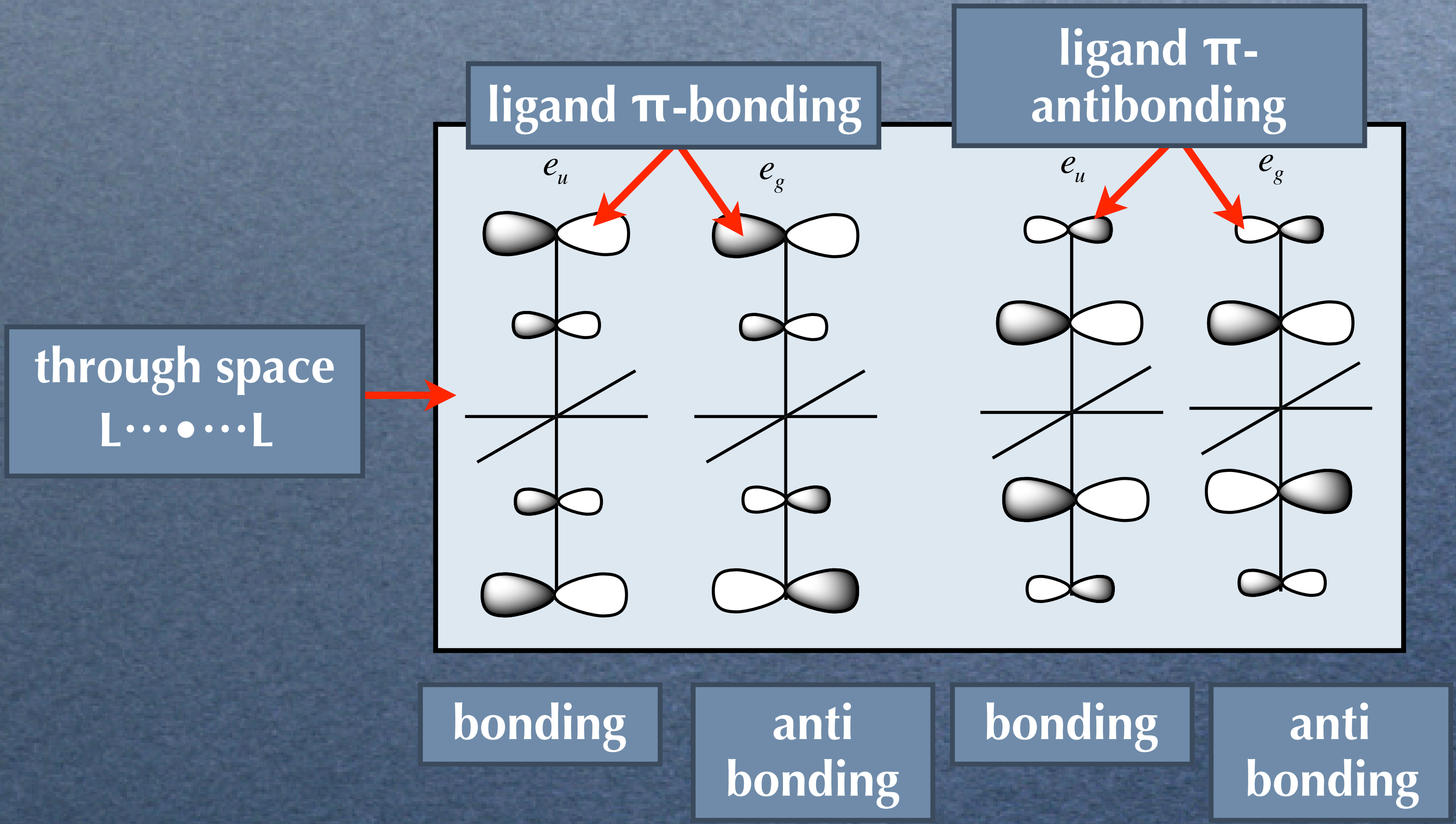
ligand-ligand π-bonding

in-ligand π-bonding

overall this FO is bonding

In-Class Activity

- complexes can have more than one π-donor or π-acceptor ligand



through space
L···●···L

ligand π-bonding

ligand π-antibonding

bonding

anti bonding

bonding

anti bonding

Two π-acceptor Ligands

- **same process!**
  - symmetry is reduced from O_h to D_{4h}
  - determine new symmetry of the FOs

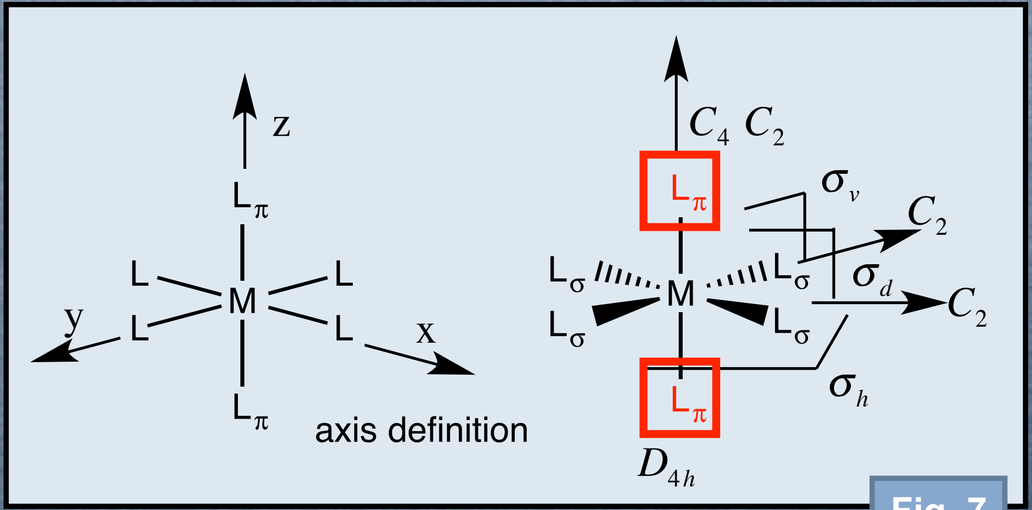
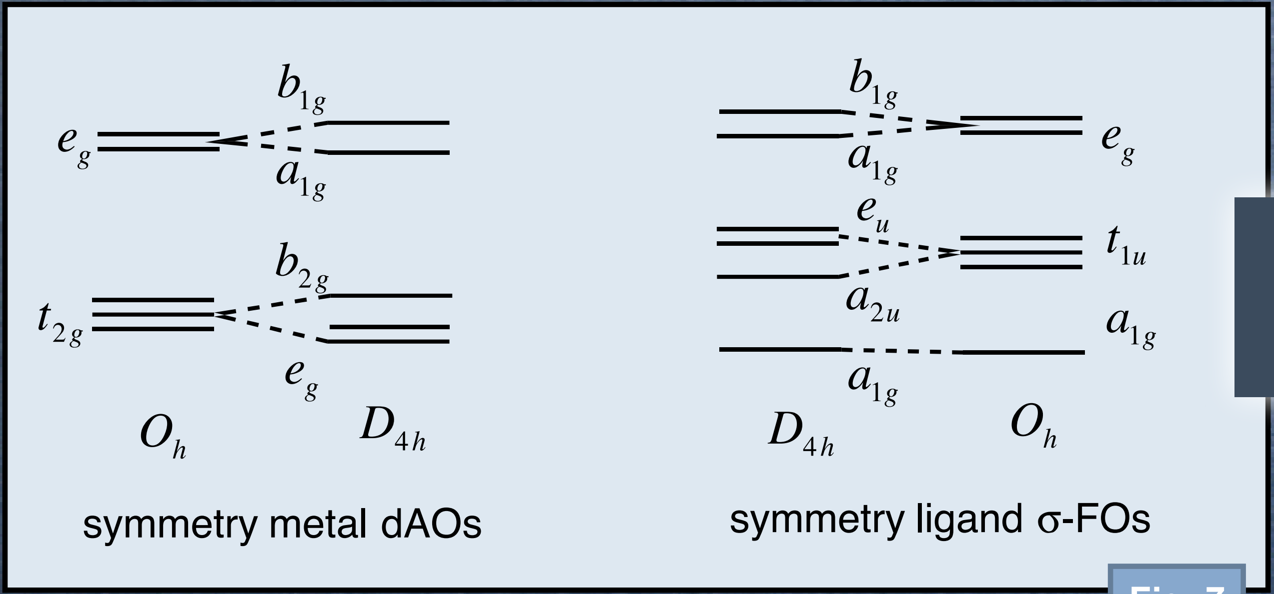


Fig. 7



symmetry metal dAOs

symmetry ligand σ-FOs

Fig. 7

use the short-cuts!

Two π-acceptor Ligands

- **same process!**
  - symmetry is reduced from O_h to D_{4h}
  - determine new symmetry of the FOs
  - add “new” FOs

draw in σ-framework → **black**

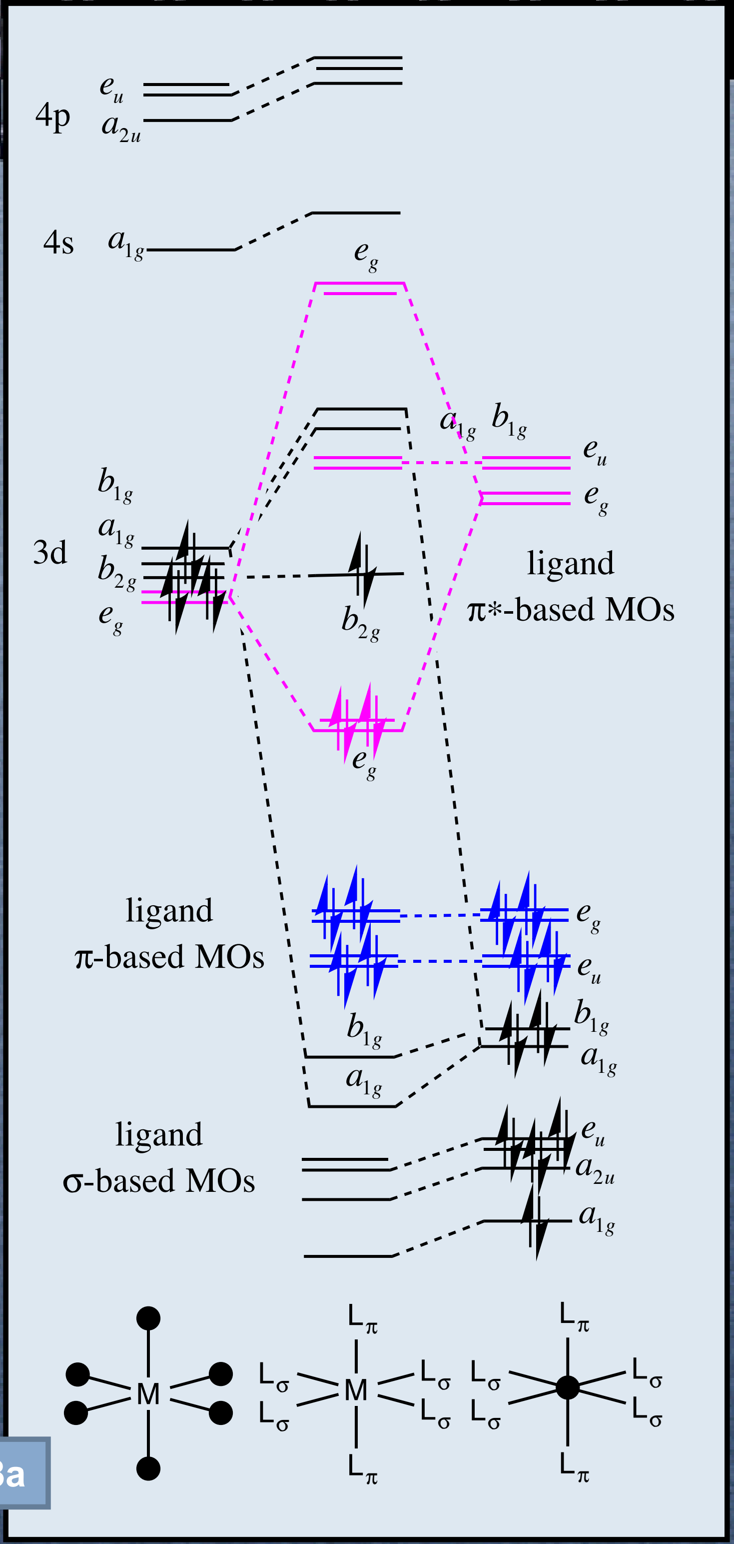


Fig. 8a

Two π-acceptor Ligands

- **same process!**
  - symmetry is reduced from O_h to D_{4h}
  - determine new symmetry of the FOs
  - add “new” FOs

Add in the “new” orbitals

π -bonding remain non-bonding → **blue**

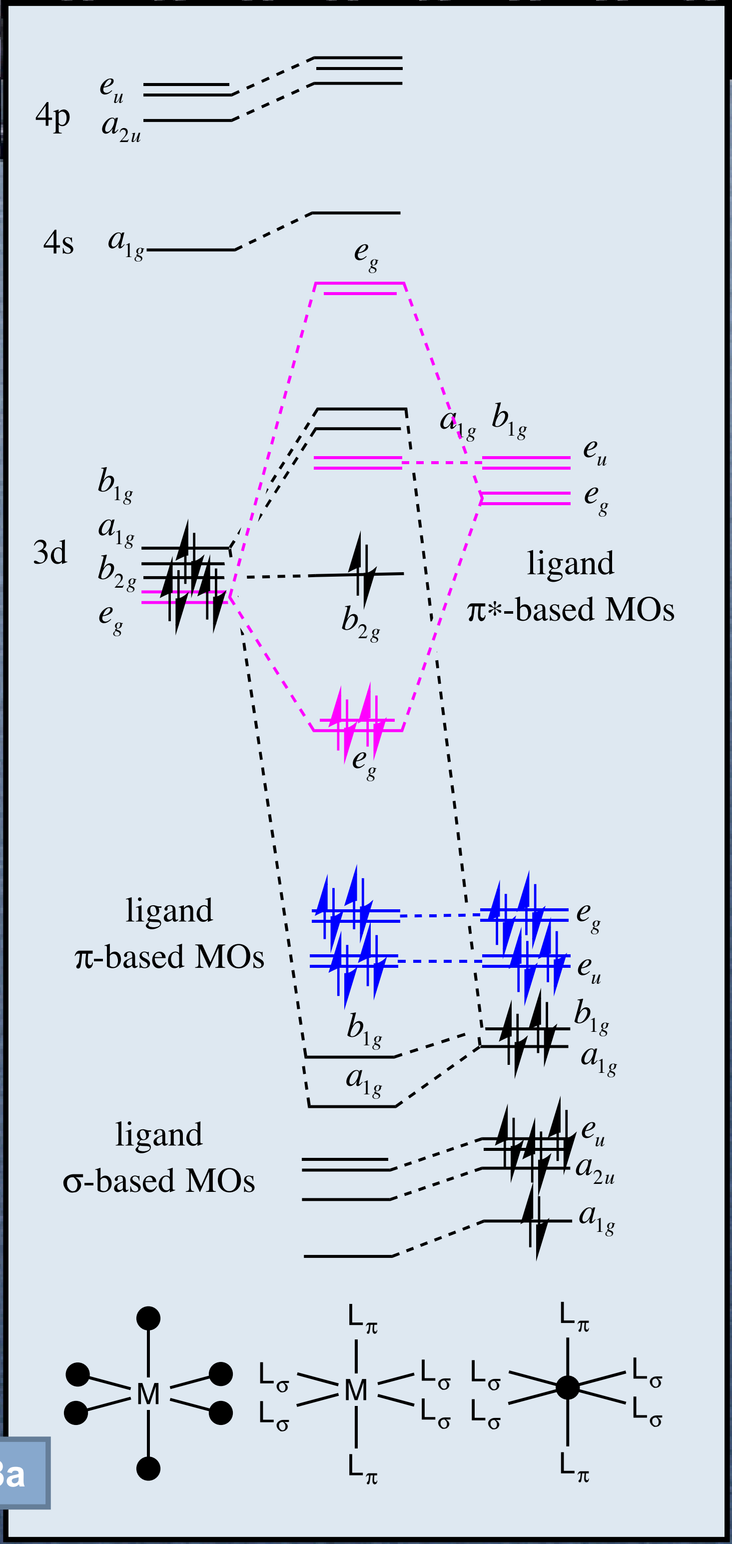


Fig. 8a

Two π-acceptor Ligands

- **same process!**
  - symmetry is reduced from O_h to D_{4h}
  - determine new symmetry of the FOs
  - add "new" FOs

Add in the "new" orbitals

π -bonding remain non-bonding → blue

π*-antibonding above the TM dAOs (as with single CO ligand) → pink

work out the interactions

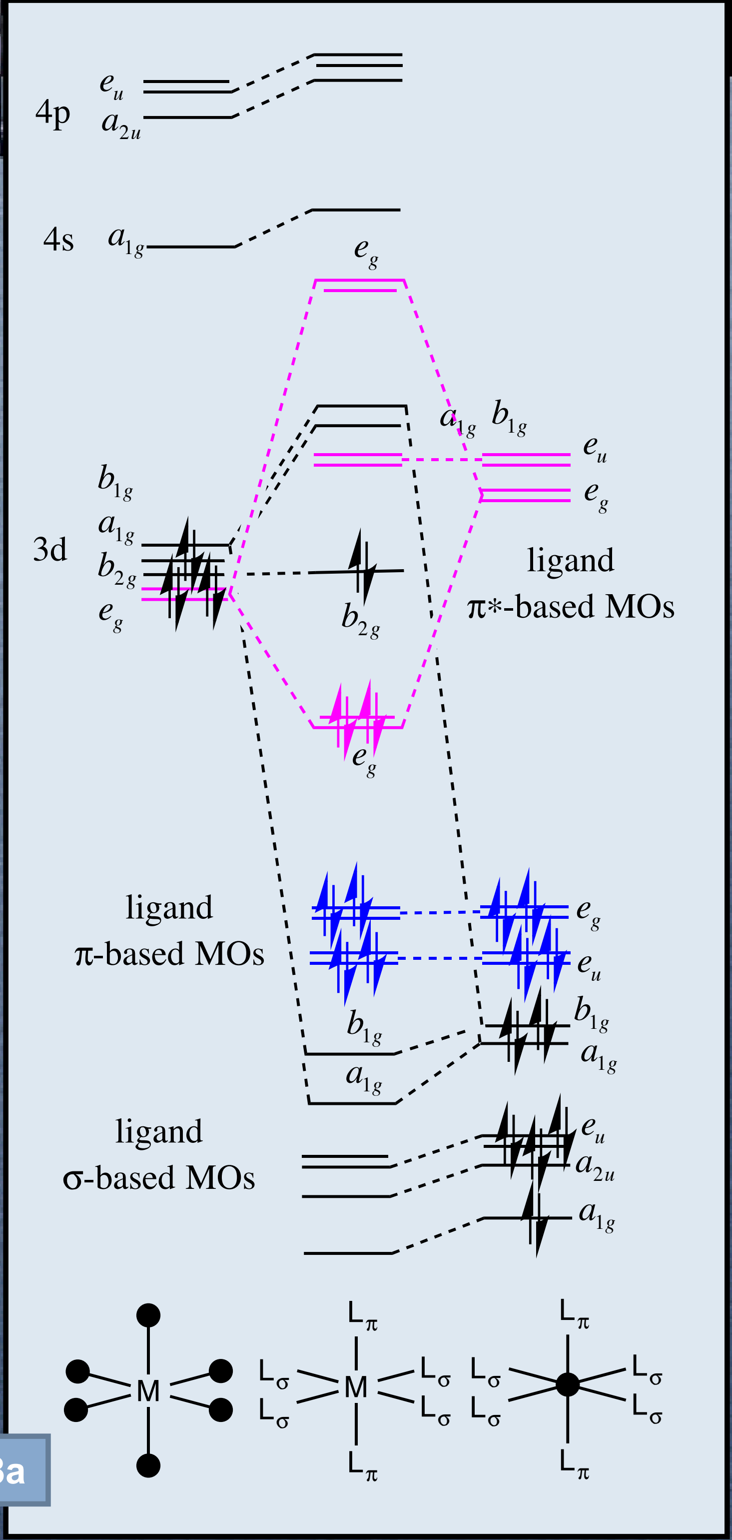


Fig. 8a

Two π-acceptor Ligands

- **focus on the important MOs**
  - those of the d manifold
  - include antibonding “e_g” MOs
  - add the “t_{2g}” MOs
  - size of FO contributions matters!

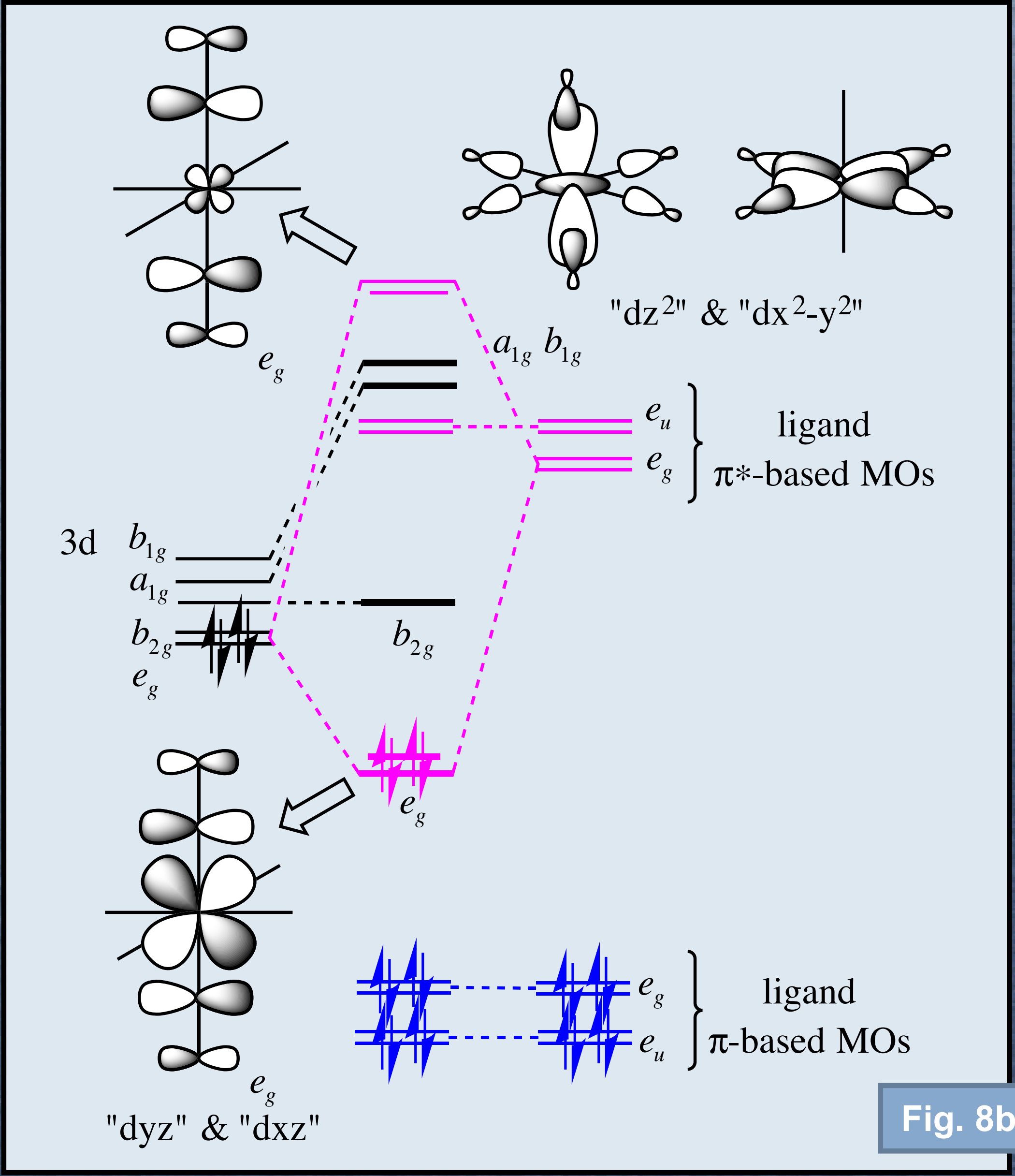


Fig. 8b

Two π-acceptor Ligands

- **focus on the important MOs**
  - those of the d manifold
  - include antibonding "e_g" MOs
  - add the "t_{2g}" MOs
  - size matters!
- **consider Δ_{oct}**
  - σ-framework
  - π-ligands
  - Δ_{oct} two π-acceptors is very similar to single π-acceptor ligand

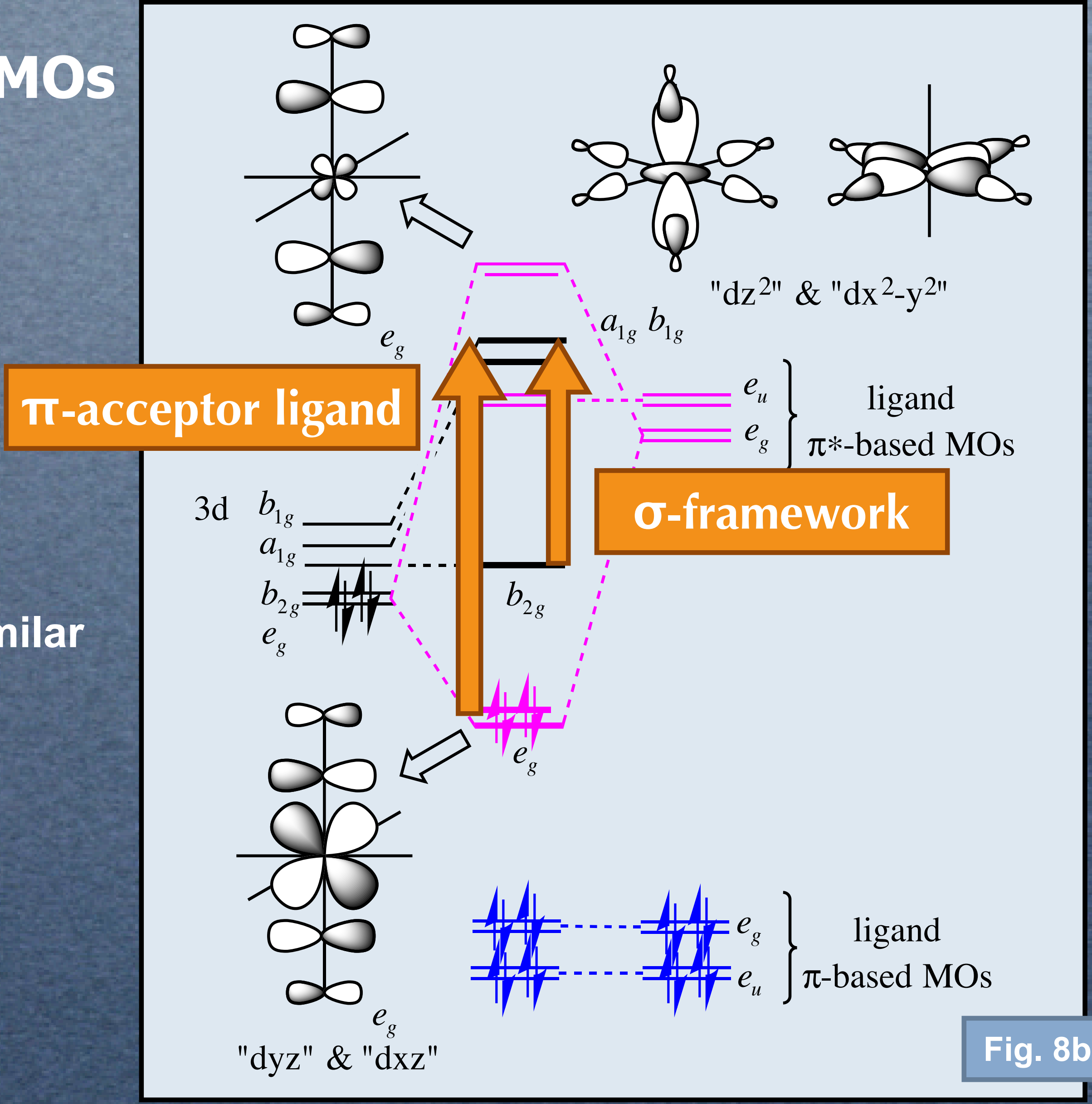
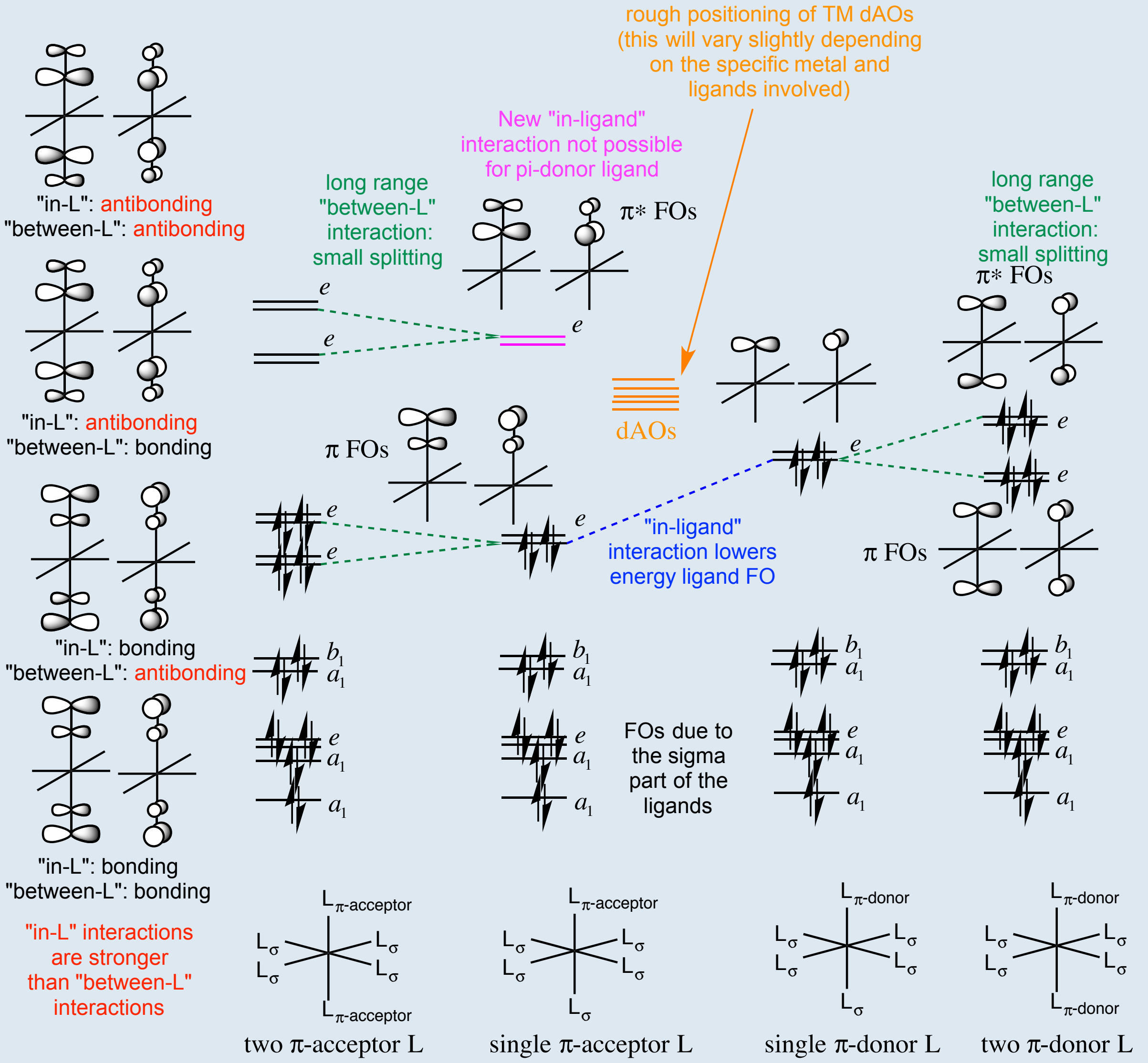


Fig. 8b

Summary Diagram

generated in response to student feedback 2014

use for revision



"in-L": antibonding
"between-L": antibonding

"in-L": antibonding
"between-L": bonding

"in-L": bonding
"between-L": antibonding

"in-L": bonding
"between-L": bonding

"in-L" interactions are stronger than "between-L" interactions

long range "between-L" interaction: small splitting

New "in-ligand" interaction not possible for pi-donor ligand

rough positioning of TM dAOs (this will vary slightly depending on the specific metal and ligands involved)

long range "between-L" interaction: small splitting

"in-ligand" interaction lowers energy ligand FO

FOs due to the sigma part of the ligands

two π-acceptor L

single π-acceptor L

single π-donor L

two π-donor L

NOTE: symmetry labels are for C_{4v} and will change as the symmetry of molecule changes due to the changing ligands

Fig. 9