Molecular Orbitals in Inorganic Chemistry

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Rm 110F (MSRH)

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

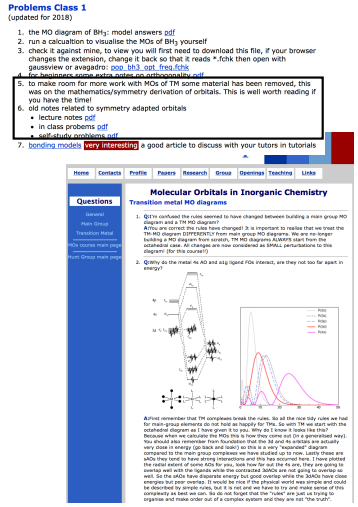
Your Feedback

- **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??** Mixed opinion!
  - go faster / go slower!
  - would have liked to cover mixing, harder examples

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

Feedback

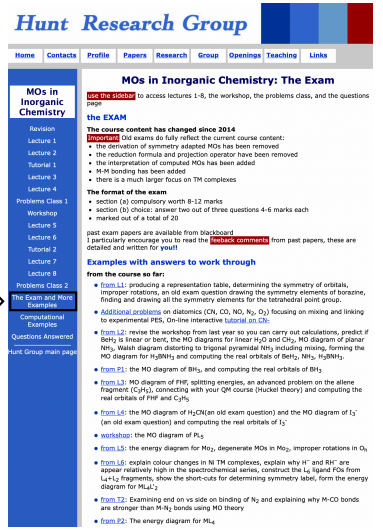
- **Symmetry adapted orbitals**
  - H_3 from problems class
  - Notes from an old lecture available on-line!
- **Check out "questions answered" page on the web**
  - more on FO energy levels and splitting
  - practice helps


Problems Class 1
(updated for 2018)

1. the MO diagram of BH_3: model answers pdf
2. run a calculation 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 gausview or avogadro: 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 problems pdf
   - self-study problems pdf
7. bonding models very interesting! a good article to discuss with your tutors in tutorials

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



Feedback

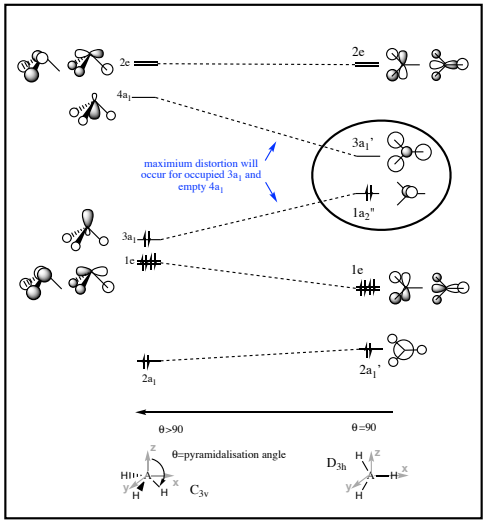
- **More Examples & Problems!**

all with extensive model answers!

  - 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 $H_3B{<}\text{-}NH_3$
  - 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



Feedback

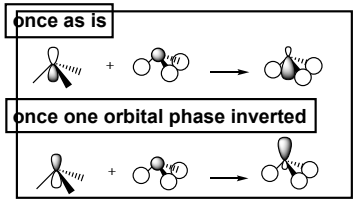
Mixing

use rules for mixing!

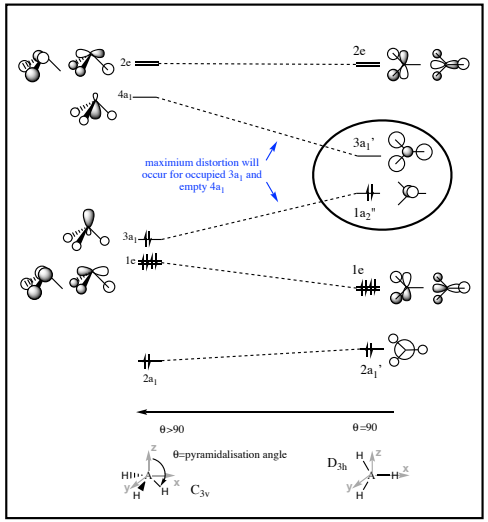
one occupied one unoccupied
HOMO-LUMO region
close in energy
same symmetry (NOT same pair)
overall stabilisation

"mix the orbitals"

once as is



once one orbital phase inverted



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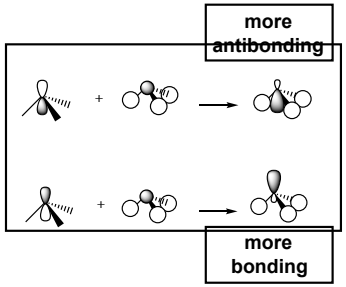
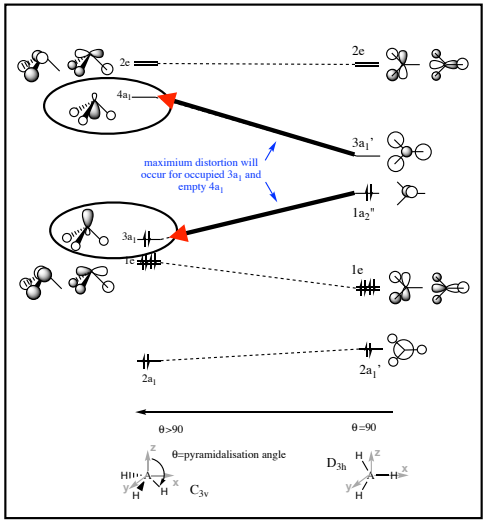
Feedback

Mixing

use rules for mixing!
"mix the orbitals"

identify which is stabilised and which is destabilised





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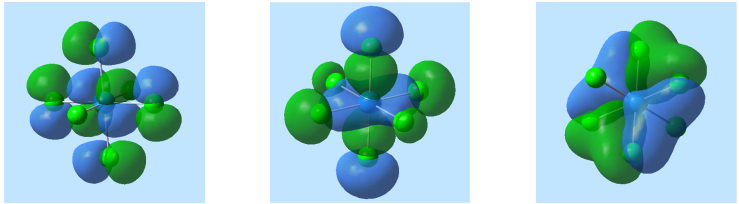
Real MOs

practice! $[WCl_6]$ draw the LCAOs that match these real MOs



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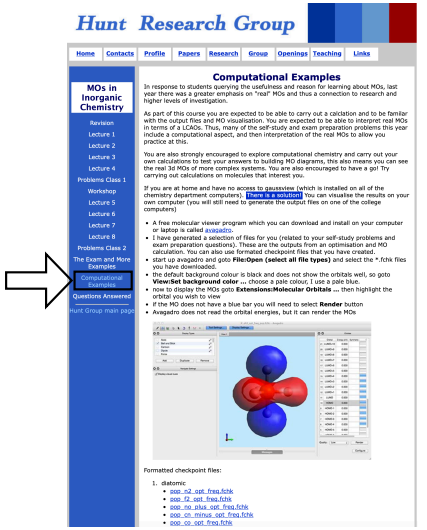
Feedback

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?



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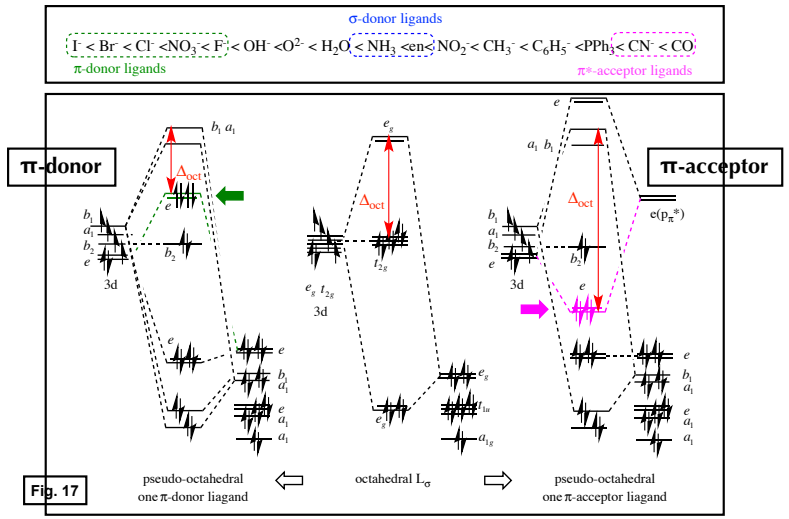
Lecture 8 Outline

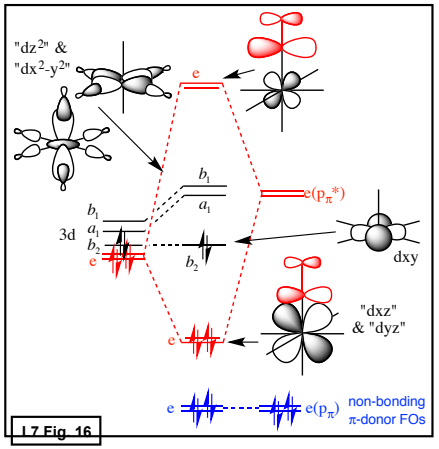
- your feedback!
- π-back-donation
- ML_6 molecular orbitals
- a real example!

Summary for Δ_{oct}



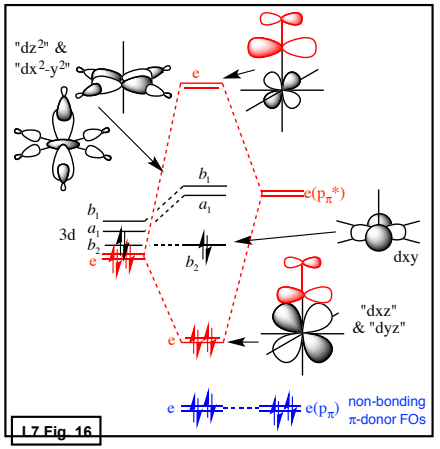
π-Acceptor Ligands

- **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



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



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!

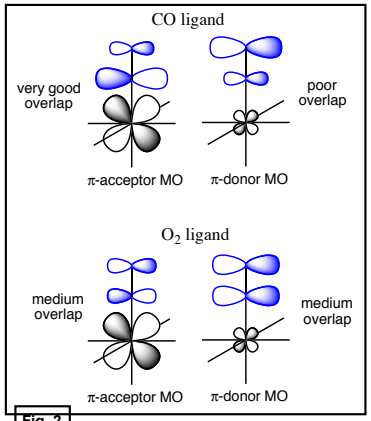


Fig. 2

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!

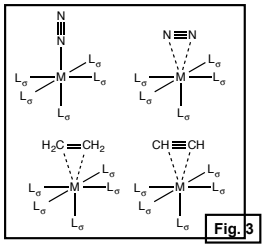


Fig. 3

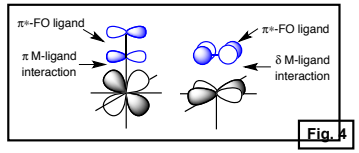


Fig. 4

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?

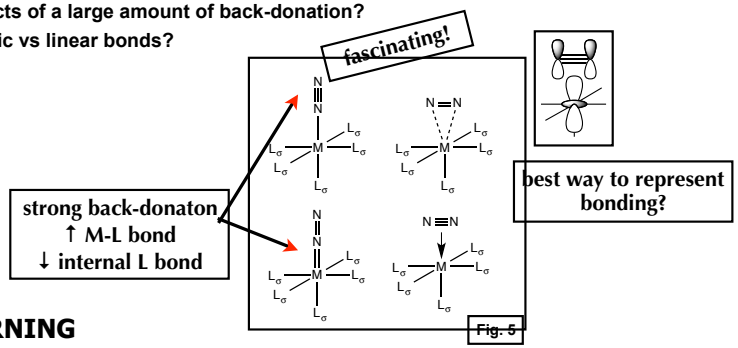
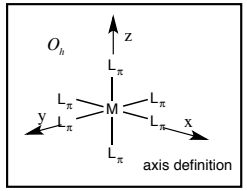


Fig. 5

- **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



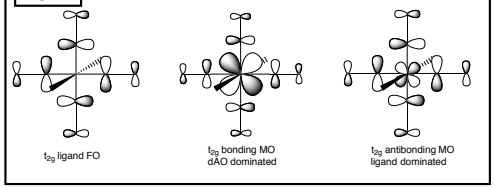
"one of each" T symmetry in O_h

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



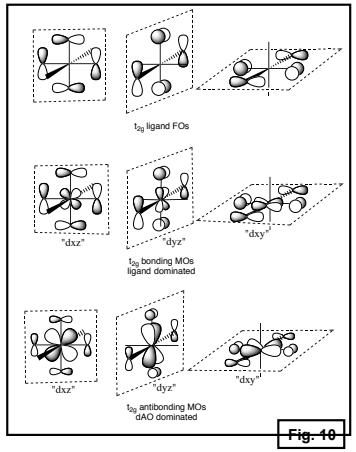


Fig. 10

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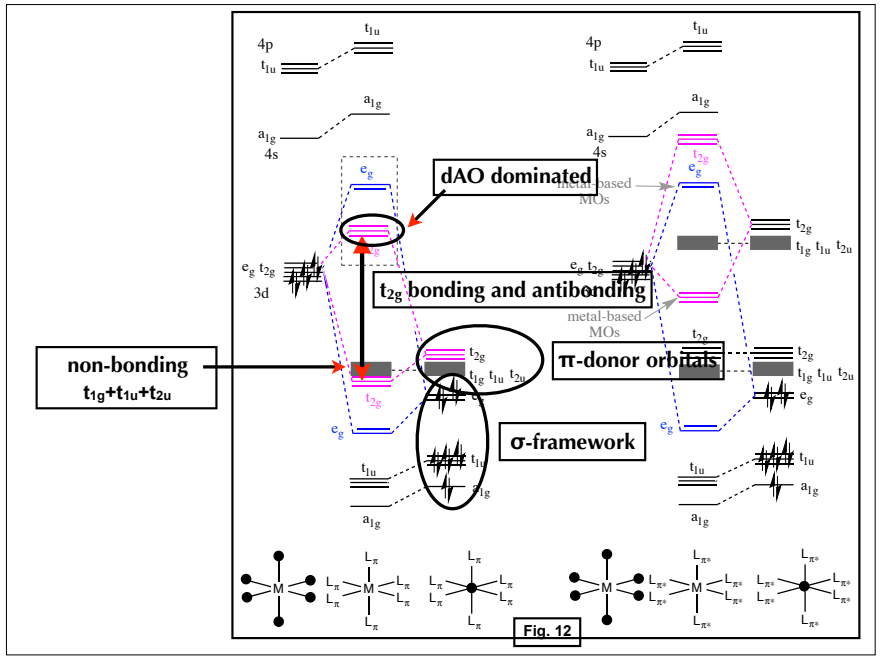

Fig. 12

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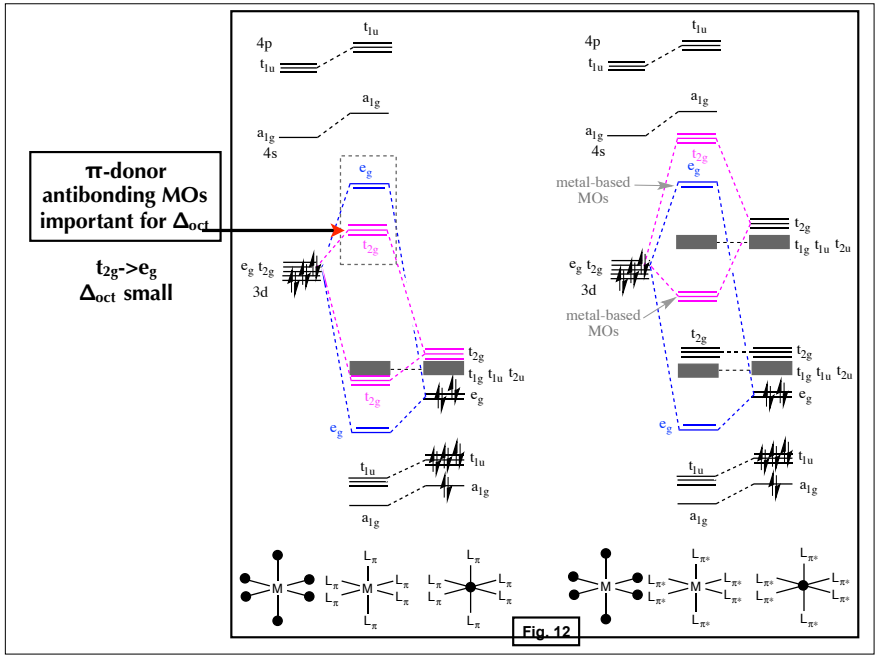

Fig. 12

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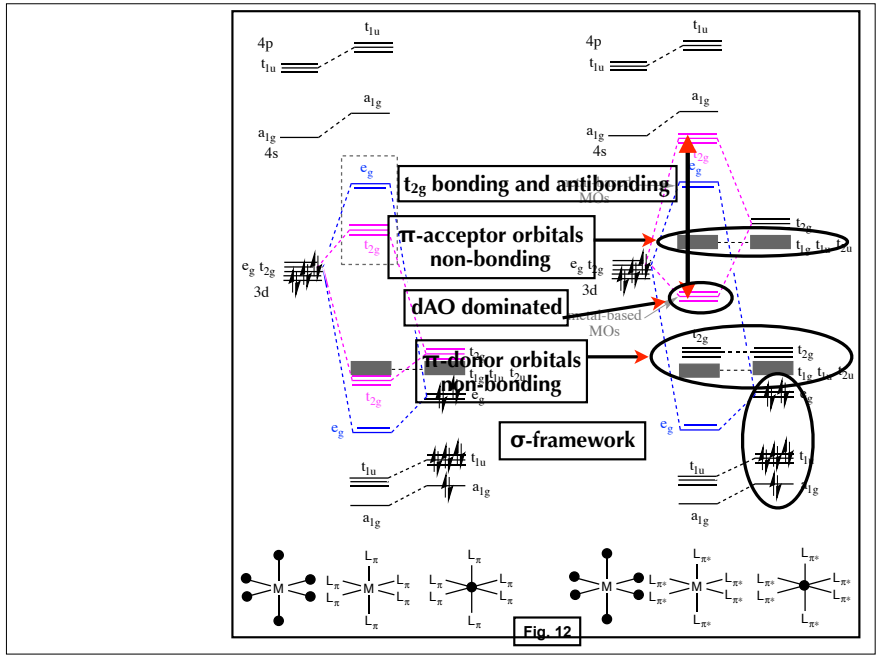

Fig. 12

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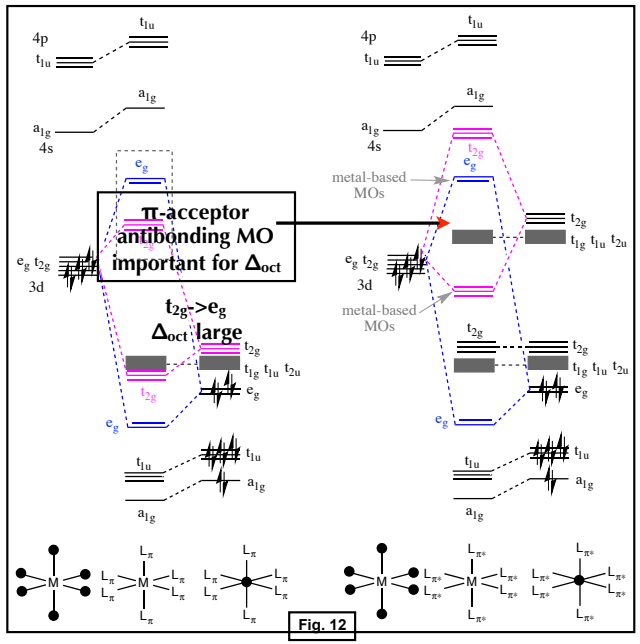

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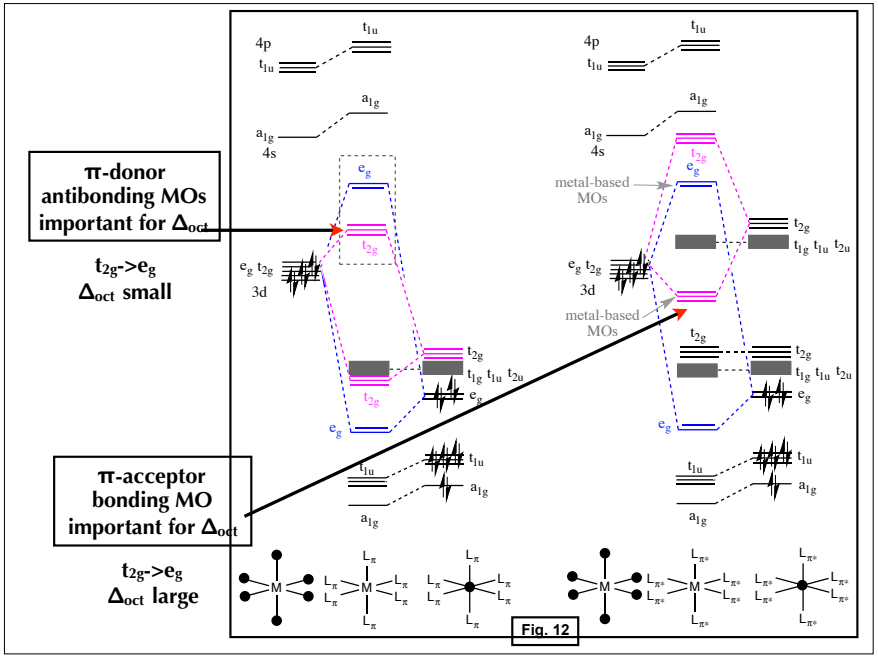

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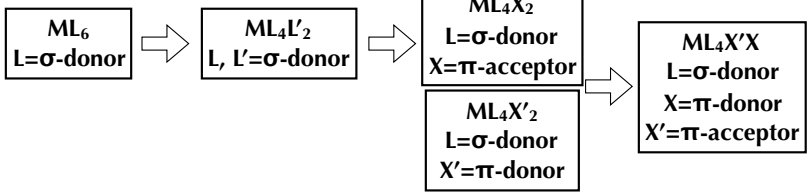
Two π-donor or π-acceptor Ligands



- 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

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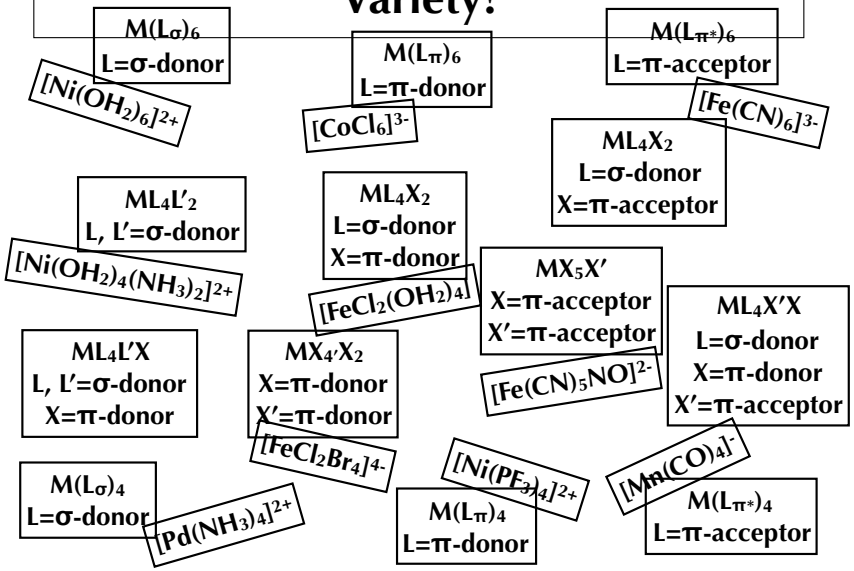
Variety!



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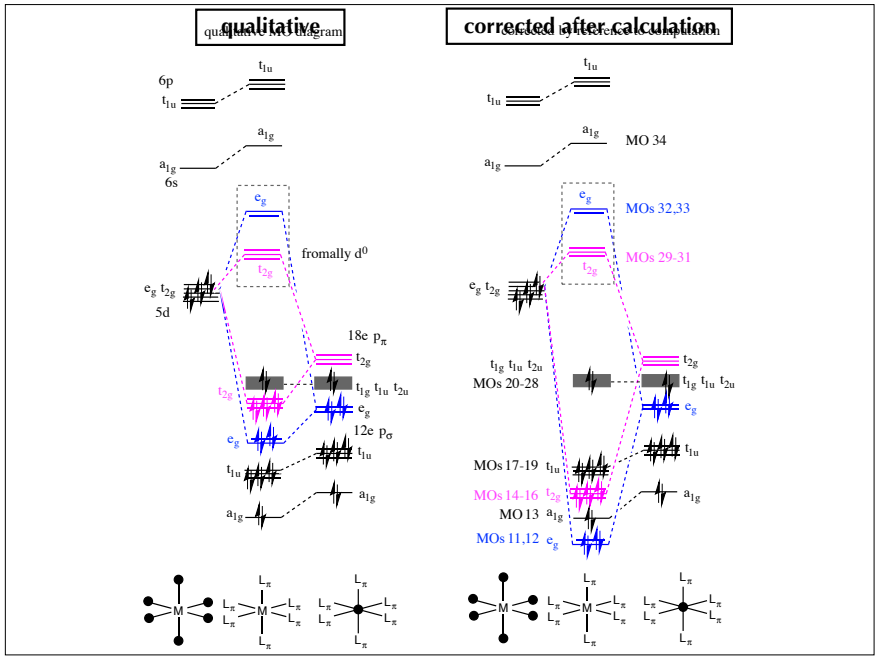
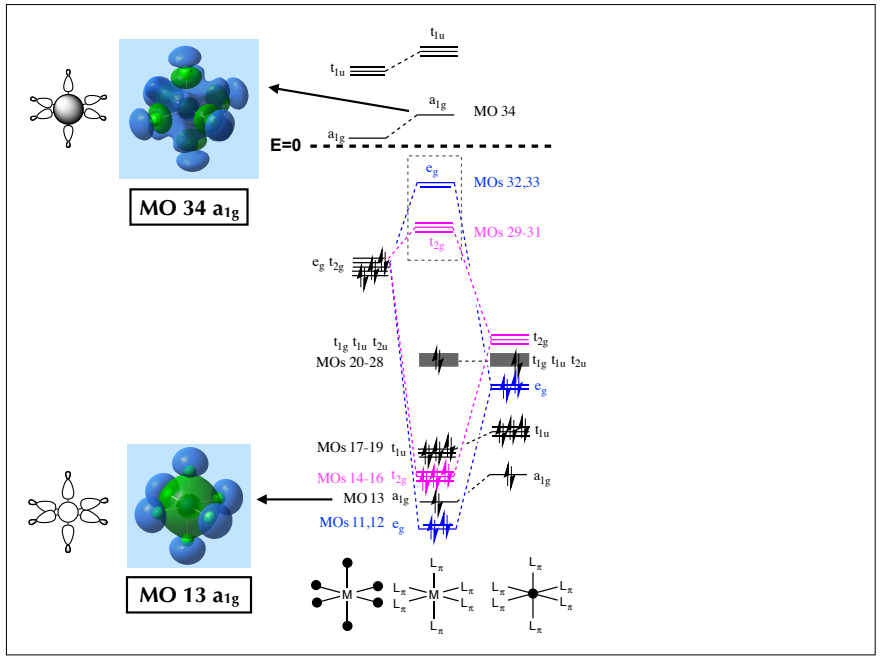
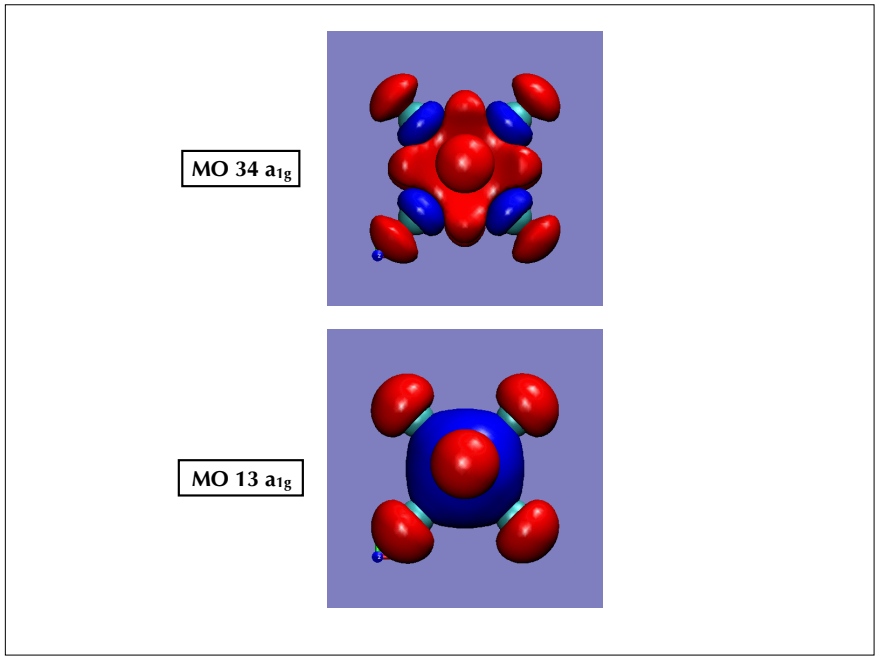

qualitative
qualitative MO diagram
corrected after calculation
corrected by reference to comparison
6p
t_{1u}
a_{1g}
6s
e_g
t_{2g}
fromally d^0
e_g t_{2g}
5d
18e p_π
t_{1g} t_{1u} t_{2u}
12e p_σ
MO 34
MOs 32,33
MOs 29-31
MOs 20-28
MOs 17-19
MOs 14-16
MO 13
MOs 11,12

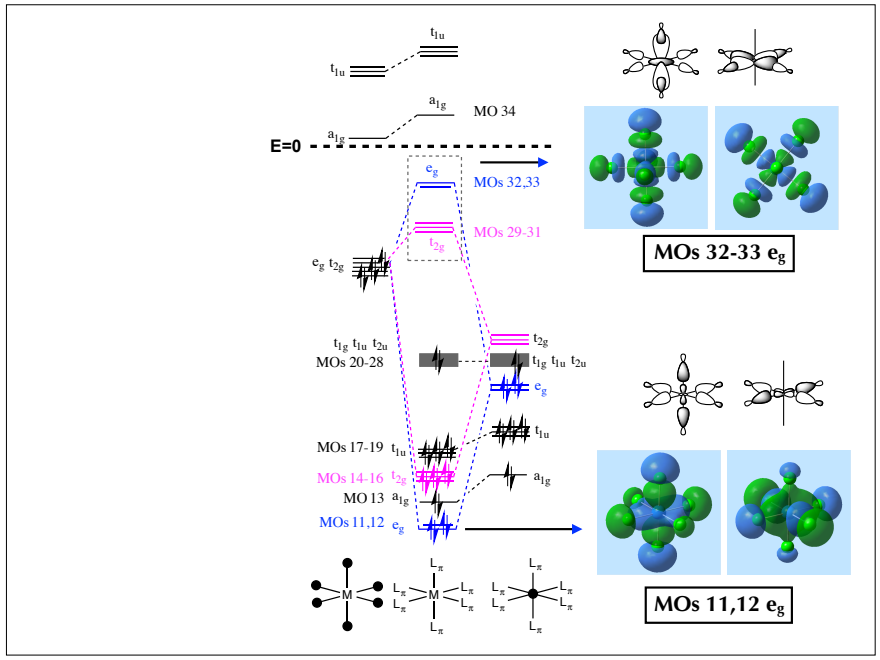
29


MO 34 a_{1g}
MO 13 a_{1g}
E=0
MO 34
MOs 32,33
MOs 29-31
MOs 20-28
MOs 17-19
MOs 14-16
MO 13
MOs 11,12

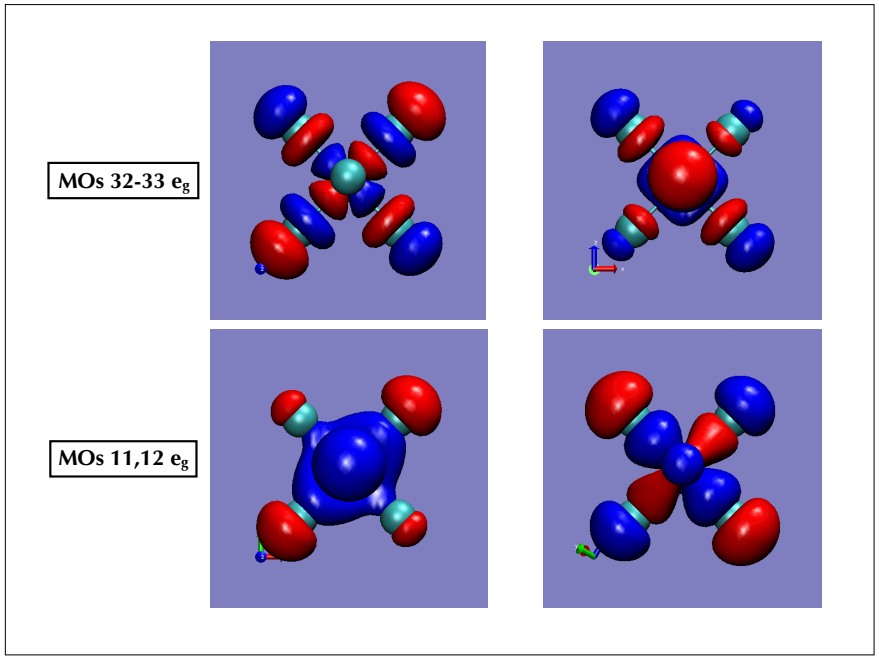
30


MO 34 a_{1g}
MO 13 a_{1g}

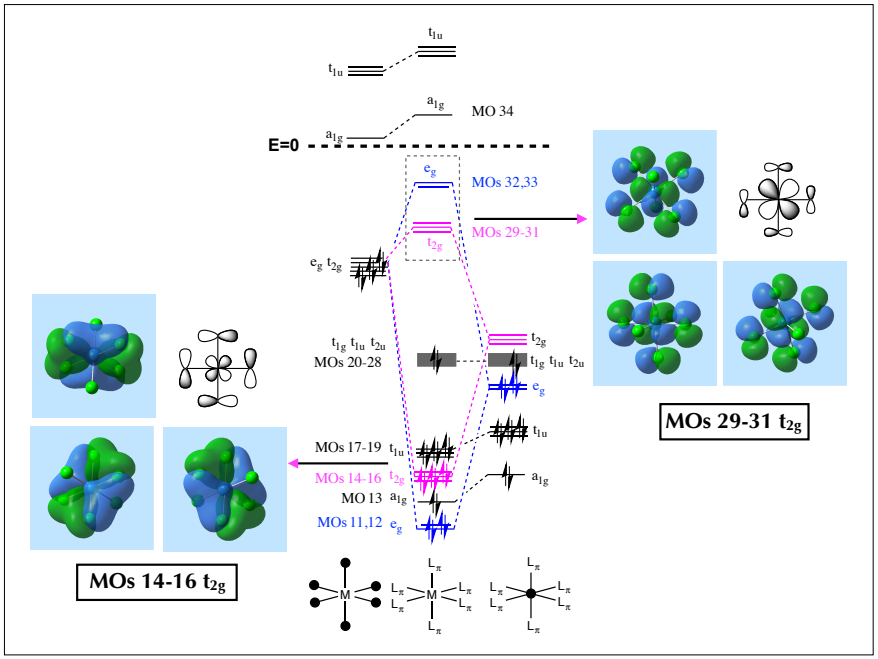
31


E=0
MO 34
MOs 32,33
MOs 29-31
MOs 20-28
MOs 17-19
MOs 14-16
MO 13
MOs 11,12
MOs 32-33 e_g
MOs 11,12 e_g

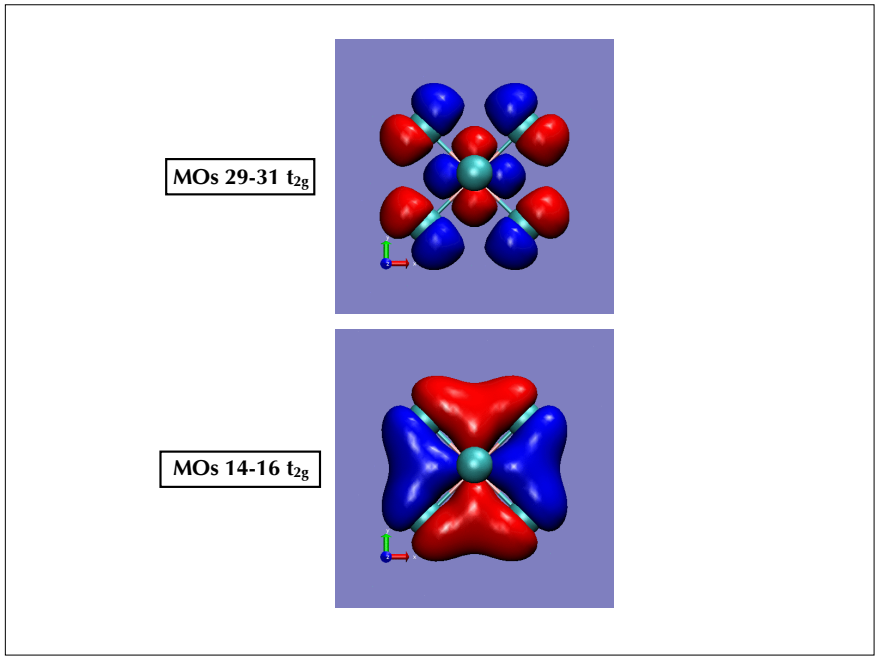
32


MOs 32-33 e_g
MOs 11,12 e_g

33


t_{1u}
t_{1u}
a_{1g}
MO 34
a_{1g}
E=0
e_g
MOs 32,33
t_{2g}
MOs 29-31
e_g t_{2g}
t_{1g} t_{1u} t_{2u}
MOs 20-28
t_{2g}
t_{1g} t_{1u} t_{2u}
e_g
t_{1u}
MOs 17-19 t_{1u}
MOs 14-16 t_{2g}
a_{1g}
MO 13 a_{1g}
MOs 11,12 e_g
MOs 29-31 t_{2g}
MOs 14-16 t_{2g}

34


MOs 29-31 t_{2g}
MOs 14-16 t_{2g}

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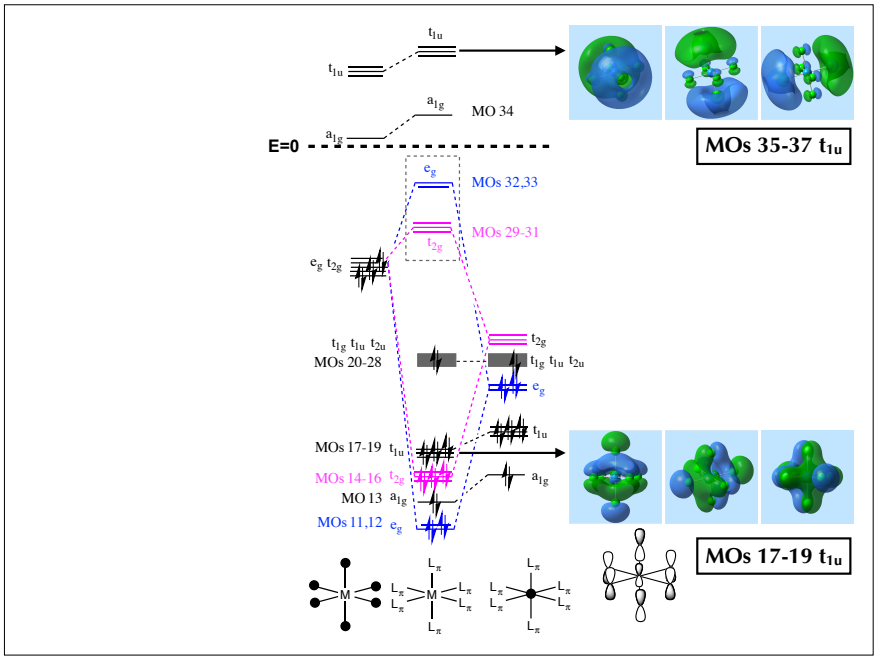
t_{1u}
t_{1u}
a_{1g}
MO 34
a_{1g}
E=0
e_g
MOs 32,33
t_{2g}
MOs 29-31
e_g t_{2g}
t_{1g} t_{1u} t_{2u}
MOs 20-28
t_{2g}
t_{1g} t_{1u} t_{2u}
e_g
t_{1u}
MOs 17-19 t_{1u}
MOs 14-16 t_{2g}
a_{1g}
MO 13 a_{1g}
MOs 11,12 e_g
MOs 35-37 t_{1u}
MOs 17-19 t_{1u}

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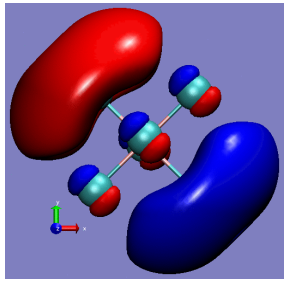
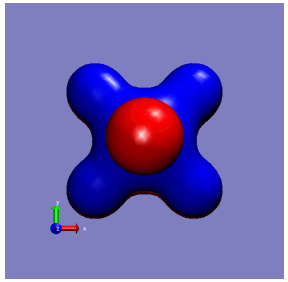
MOs 35-37 t_{1u}



MOs 17-19 t_{1u}



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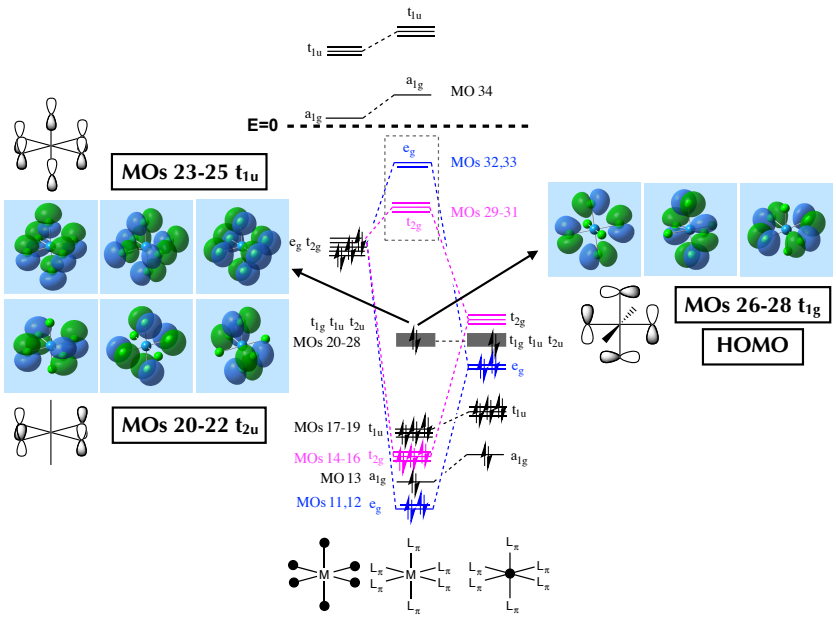

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Key Points

- 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}

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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/

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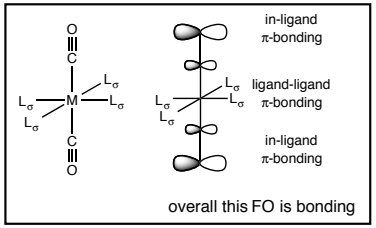
Extras

In-Class Activity

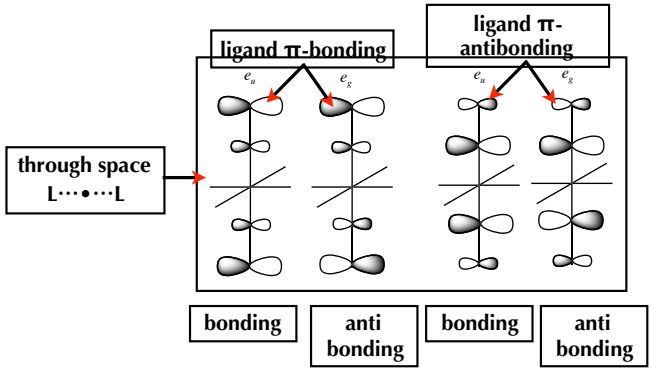
- **complexes can have more than one π-donor or π-acceptor ligand**

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



In-Class Activity

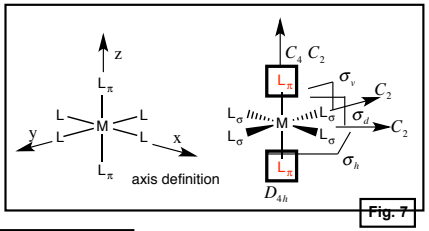
- **complexes can have more than one π-donor or π-acceptor ligand**

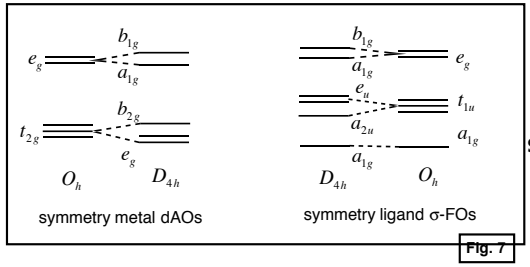


Two π-acceptor Ligands

- **same process!**

symmetry is reduced from O_h to D_{4h}
determine new symmetry of the FOs





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

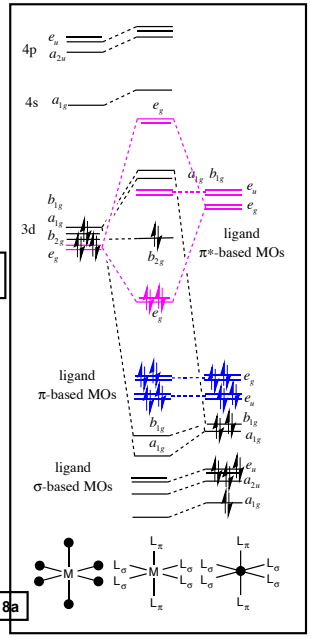


Fig. 8a

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

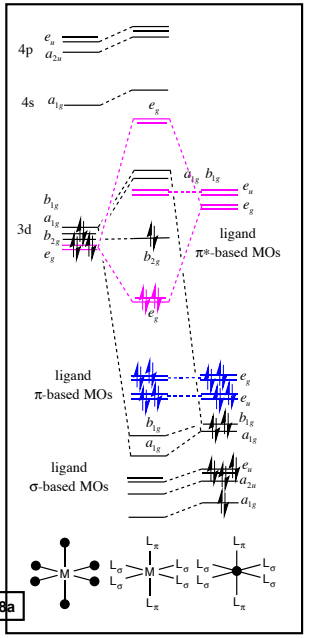


Fig. 8a

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

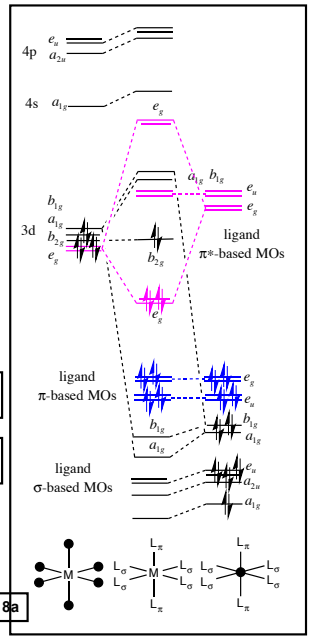


Fig. 8a

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!

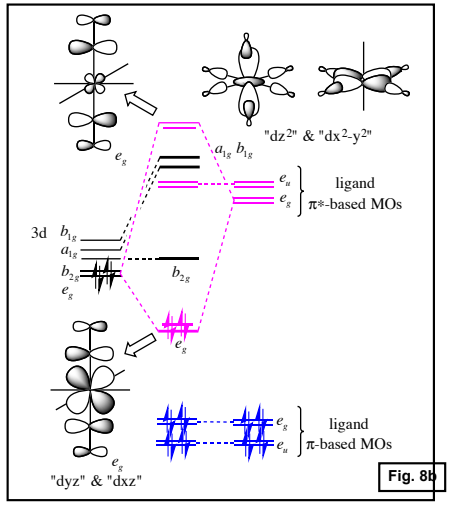


Fig. 8b

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

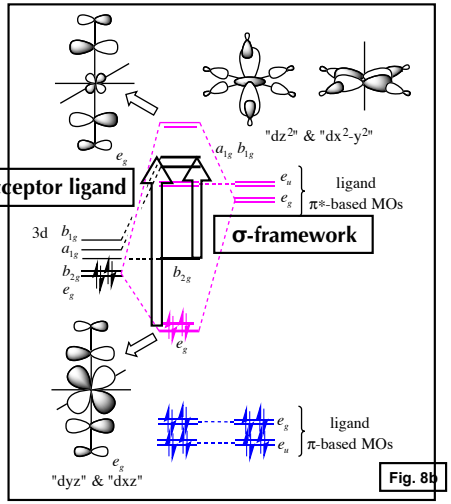
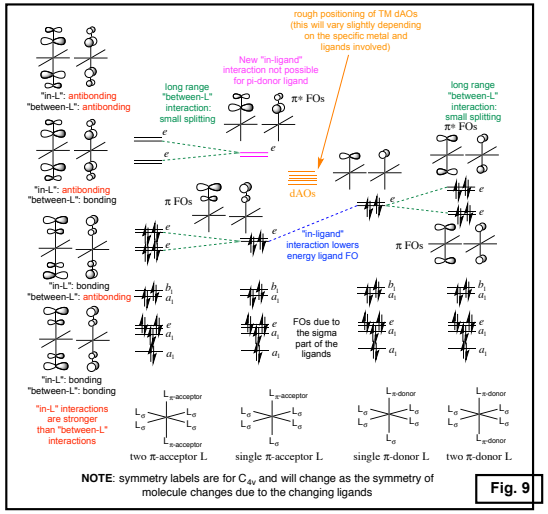


Fig. 8b

Summary Diagram

generated in response to student feedback 2014

use for revision



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

Fig. 9