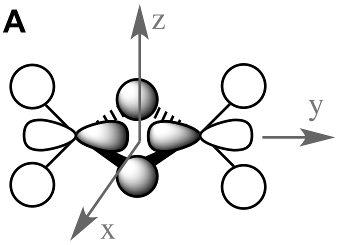
Self-Study Problems / Exam Preparation Questions

- Construct the symmetry adapted octahedral L_6 ligand FOs from an L_4 and L_2 fragment.
- Annotate a diagram of MO **A** below, identify and explain the features that are important in evaluating the overall bonding or antibonding character of this MO

A



- The axial alignment of a transition metal (M) complex MX_2L_4 (where X and L are σ-bonding ligands, is shown in **B** below, the point group of MX_2L_4 is D_{4h}. The ligand fragment orbitals are given, in no particular order, in **C** below.

    i) Identify the symmetry labels of the metal orbitals, and the ligand fragment orbitals **C(1)** through to **C(6)**

(3 marks)

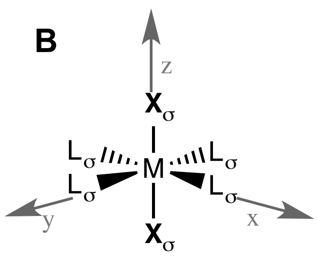
    ii) Draw an **energy level** diagram for MX_2L_4.

(6 marks)

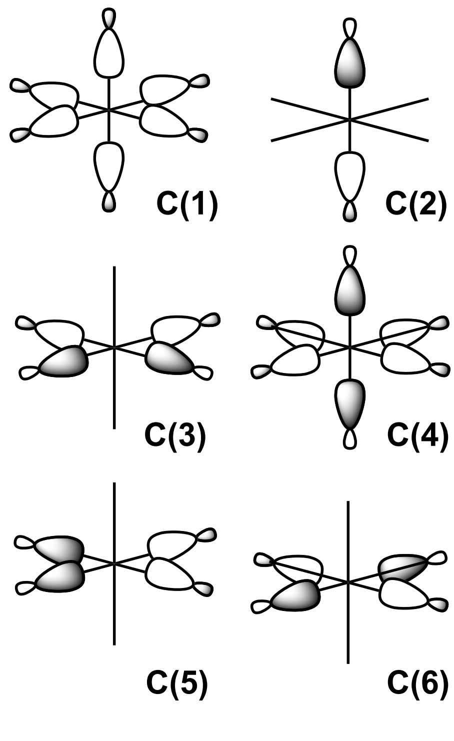
    iii) Identify Δ_{oct} on your diagram.

(1 mark)

B



C



Self-Study Problems / Exam Preparation Answers

- Construct the symmetry adapted octahedral L_6 ligand FOs from an L_4 and L_2 fragment.
  - the L_4 and L_2 fragments are assumed known
  - because these fragments are not identical we need to determine their symmetry under the O_h point group
  - L_2 fragments originally belong to the $D_{\infty h}$ point group:
    - bonding L_2 FO is totally symmetric in $D_{\infty h}$ this is σ_g^+ in O_h this is a_{1g}
    - antibonding L_2 FO is p_z like in $D_{\infty h}$ this is σ_u^+ in O_h this is one of a degenerate set t_{1u}
  - L_4 fragments originally belong to the D_{4h} point group:
    - totally bonding L_4 FO is totally symmetric in D_{4h} this is a_{1g} and in O_h this is a_{1g}
    - 2 degenerate L_4 FO are p_x and p_y like in D_{4h} this is e_u in O_h and is one of a degenerate set t_{1u}
    - antibonding L_4 FO is dx^2-y^2 like in D_{4h} this is b_{1g} in O_h and is one of a degenerate set e_g
  - combining FOs of the same symmetry, that is the a_{1g} MOs we form a bonding antibonding pair, then we need to determine the symmetry of the formed MO under the O_h point group
    - bonding MO for L_6 is totally symmetric a_{1g}
    - antibonding MO for L_6 is dz^2 like which is one of a degenerate set e_g
  - we then need to decide where they sit in terms of energy
    - determine a reference line for a single sigma L orbital
    - the fragment bonding orbitals will lie below this line
    - in L_2 the FO splitting will not be large because the orbitals are two bonds apart
    - in L_4 only the totally bonding FO will lie below the reference
    - the p type combination will lie just above the reference, there are only two orbitals interacting and they are far apart
    - the 4 and 5 component fragments are more antibonding due to the closer through space interactions

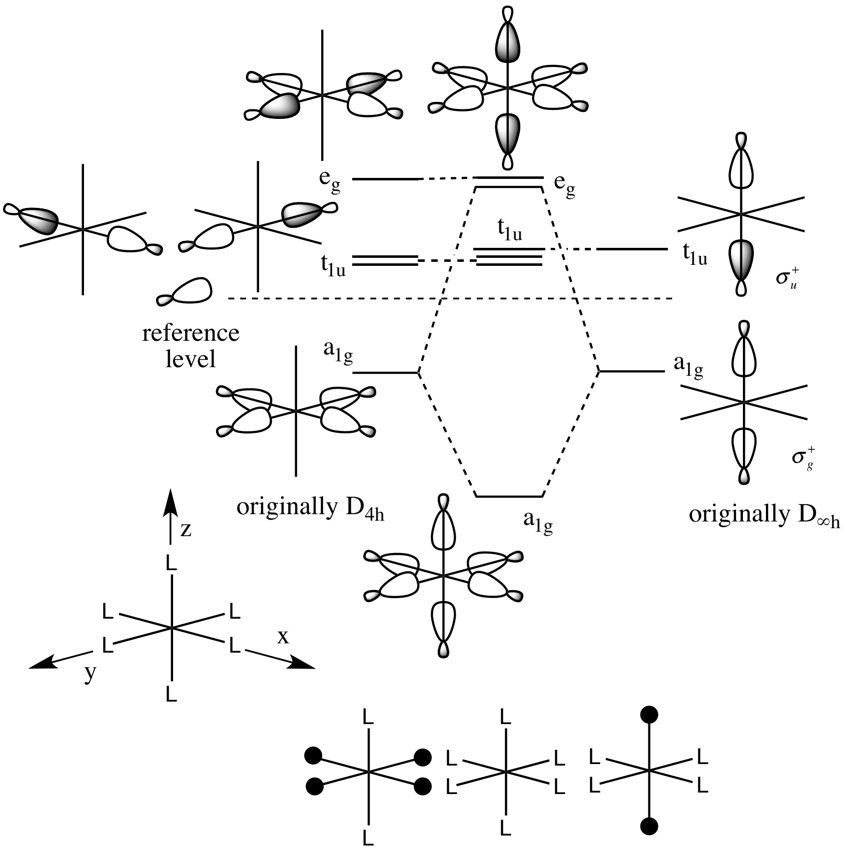
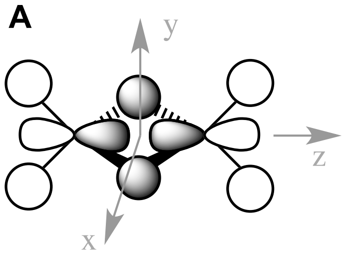


Figure 1FOs for L_6

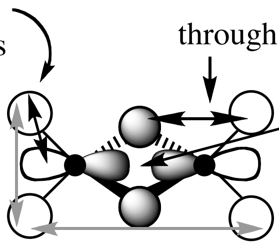
- Annotate a diagram of MO **A** below, identify and explain the features that are important in evaluating the overall bonding or antibonding character of this MO



strong bonding due to strong s-p overlap and a short "bonded" distance between AOs

through space weak antibonding

weak through space bonding



directional p-p overlap is strongly bonding, overlap with bridging H s-p is also strongly bonding, all orbitals are close leading to strong interactions

overall a strongly bonding MO both terminal and bridging H's exhibit primarily bonding interactions

very weak through space bonding

2-nodal planes, but nodes at atomic centers are not as important as nodes in the internuclear region

- **1 mark** identify type of interaction s-s, s-p etc as important to bonding strength
- **1 mark** identify distance as important to bonding strength
- **1 mark** for including all types interaction, eg through space interactions
- **1 mark** for commenting on the nodes
- **1 mark** for specific interactions as shown on diagram
- **1 mark** overall bonding character

Generally very well answered, however some comments:
1. an over concentration on through bond vs through space arguments, it is primarily the distance that is important. A bond represents a build up of total electron density, an individual MO contributes only a small part to the total density. The MO is able to represent a much larger range of interactions than old 2c-2e "bonding", these two should be treated as separate theories and not conflated.
2. the interaction in the center is not pi, this is a symmetry label that refers to a phase change on cylindrical rotation, this is a sigma type interaction. It is very strong and bonding.
3. a number of people forgot to mention the nodes!

- The axial alignment of a transition metal (M) complex MX_2L_4 (where X and L are σ-bonding ligands, is shown in **B** below, the point group of MX_2L_4 is D_{4h}. The ligand fragment orbitals are given, in no particular order, in **C** below.
  - i) Identify the symmetry labels of the metal orbitals, and the ligand fragment orbitals **C(1)** through to **C(6)**

(3 marks)

  - ii) Draw an **energy level** diagram for MX_2L_4.

(6 marks)

  - iii) Identify Δ_{oct} on your diagram.

(1 mark)

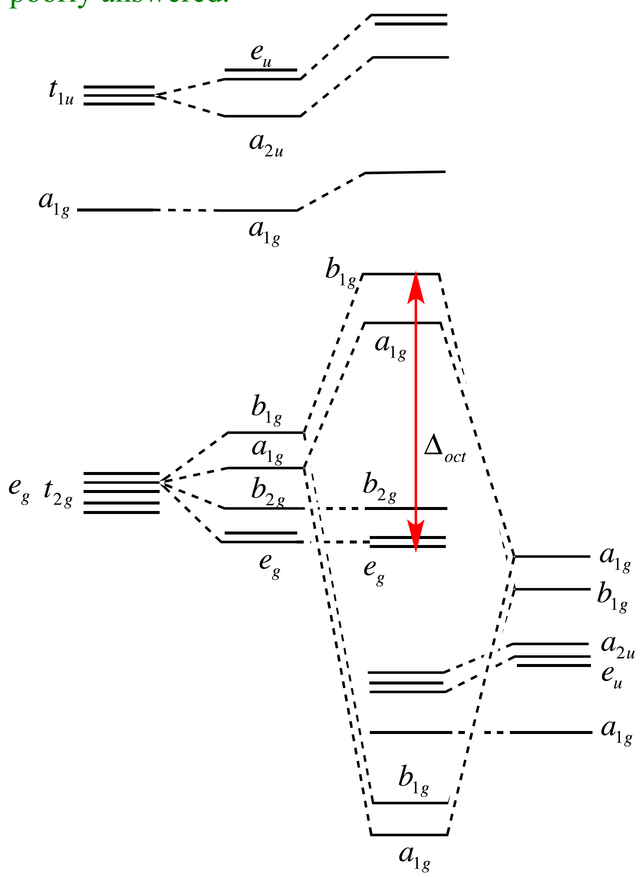
for the metal this will be b_{1g} (dx^2-y^2) a_{1g} (dz^2) b_{2g} (dxy) and e_g (dxz & dyz) for the dAOs, and a_{1g} (s) and e_g (px & py) and a_{2u} (pz) for the p orbitals.
for the ligand FOs C(1) a_{1g}, C(2) a_{2u}, C(3) e_u,, C(4) a_{1g}, C(5) e_u, C(6) b_{1g}
1 mark for the metal orbitals and **2** marks for listing the ligand orbital symmetries

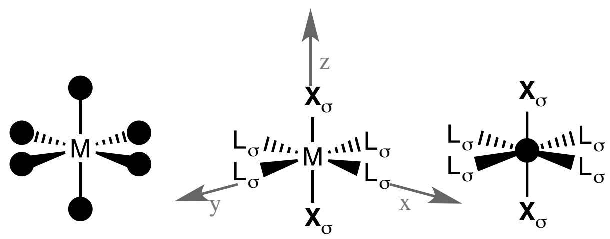
Generally very well answered

ii) Draw an **energy level** diagram for MX_2L_4 (pictures of orbitals are not required).

(6 marks)

Generally very poorly answered.





marks:
1 fragments and molecule on diagram
1 all metal FOs with energies roughly correct
2 energy ordering of ligand FOs correct (symmetry labels required)
2 MO energies roughly right
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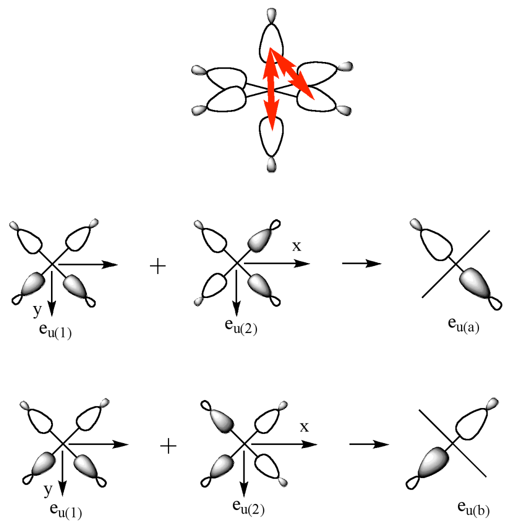
6 total

1. we assume that the change in ligands has really only effected the symmetry labels and the orbital patterns (both shape and energy ordering) remain similar
2. the FOs shown are the "other" possible combination for degenerate L_4 ligands, we can see how these are generated below:



3. even if these ligand patterns were confusing you could still determine the symmetry and energy ordering of the ligand FOs just by looking at them (using short-cuts) and considering the strength of the through space interactions
4. The pre- "splitting" of the metal d and pAOs is only for ease of analysis, these orbitals are all formally degenerate
5. the extent of interaction between a_{1g} and b_{1g} can be difficult to guess so no emphasis was placed on the depth of the bonding MOs, but the anti-bonding ones must lie below the metal sAO (a_{1g})

ii) Identify Δ_{oct} on your diagram.

(1 mark)

Δ_{oct} goes from non-bonding dAOs (e_g) up to the highest orbital dominated by dAO character, this will be the highest of of the a_{1g}/ b_{1g} MOs (**1 mark**)