Self-Study Problems / Exam Preparation

- Use MO diagrams and specific examples to explain how a very large Δ_{oct} could be obtained
  - Δ_{oct} depends on the splitting of the e_g and t_{2g} MOs in O_h (or their related lower symmetry analogues), a strong π-acceptor stabilises the t_{2g} increasing Δ_{oct} and good σ-donor destablises the e_g increasing Δ_{oct} , Figure 1
  - the best ligand will be a good σ-donor and π-acceptor, however good π-acceptors are often poor σ-donors (eg NO^+) or good σ-donors are poor π-acceptors (eg CN^-) because if the energy alignment is good for one set of FOs it is poor for the other. However, CO provides a good balance and has a very large Δ_{oct}. An alternative way to generate a large Δ_{oct} would be to have a mixed ligand complex with a mix of good σ-donors and some good π-acceptor ligands.

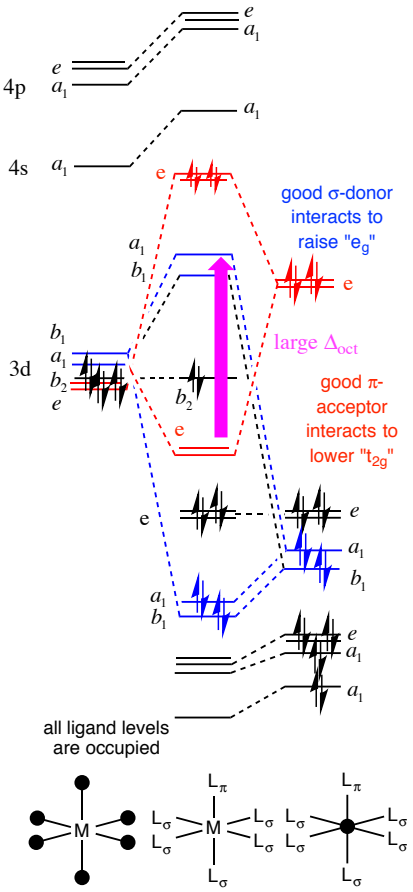

Figure 1 maximising Δ_{oct}

- Explain (employing an energy diagram including key MOs) why NH_3 generates a larger Δ_{oct} than H_2O in the following complexes; $[Cr(NH_3)_6]^{2+}$ $\Delta_{oct} \approx 21{,}600$ cm^{-1} and $[Cr(OH_2)_6]^{2+}$ $\Delta_{oct} \approx$ 17,400 cm^{-1}
  - both complexes have the same charge and the metal is in the same oxidation state, thus the difference in Δ_{oct} must be due to the ligands
  - work out the d electron count and oxidation state of the metal: Cr is in group 6 which means d^6 as neutral metal, the NH_3/H_2O are 0 acceptors, and there is a positive charge removing 2e thus this is Cr(II) and the complex is d^4.
  - H_2O is in the middle of the spectrochemical series while NH_3 is a stronger field ligand, this means that NH_3 generates a larger Δ_{oct}
  - NH_3 is a pure σ-donor ligand and generates the standard O_h e_g above t_{2g} pattern where the e_g orbitals are antibonding dx^2-y^2 and dz^2 with the ligand d-donor orbitals, **Figure 2**

- H_2O is a strong σ-donor and weak π-donor ligand, the $1b_2$ (HOMO) of water is a non-bonding pAO and is a π-donor orbital, a symmetry combination of these orbitals has the correct final symmetry to interact with the t_{2g} dAOs, creating antibonding MOs which are occupied by the metal d electrons, **Figure 2**
- π-donor ligands reduce Δ_{oct} relative to σ-donor ligands by raising the energy of the t_{2g} MOs from the non-bonding to antibonding by interaction with the π-donor FOs, this has the effect of reducing Δ_{oct} which is measured as an excitation wavelength from the t_{2g} to the e_g MOs

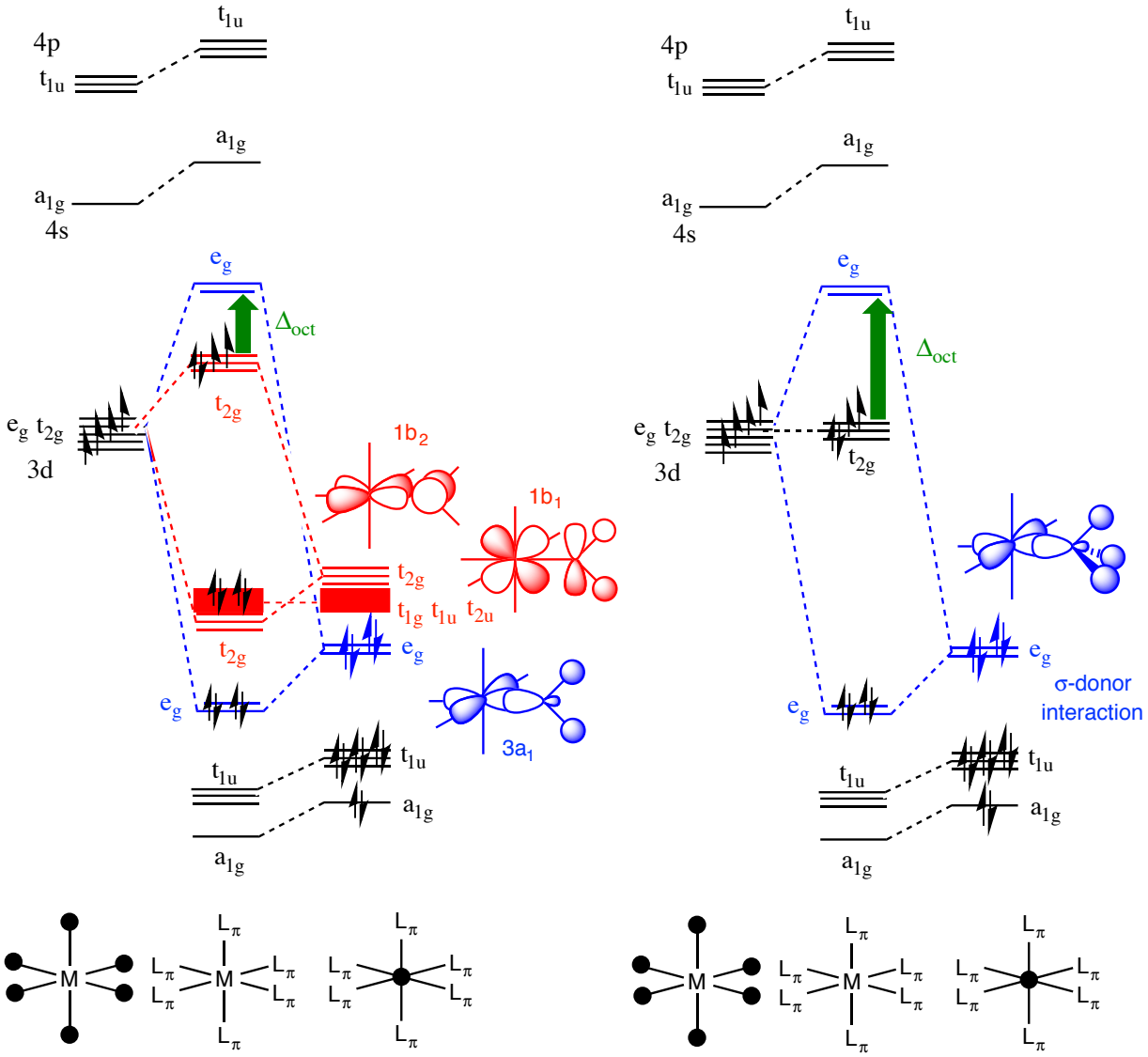

Figure 2 σ-donor vs π-acceptor Δ_{oct} and energy diagram

- N_2 can interact either side-on or end-on, however end on coordination is almost exclusively found, rationalise why N_2 prefers to coordinate end-on based on the π*-FO interactions with a TM
  - N_2 can interact either side-on or end-on, the preferred conformation is end-on, for example, $IrCl(CO)(PPh_3)_2$ and $IrCl(N_2)(PPh_3)_2$ are analogous compounds.
  - the MOs for side-on coordinated N_2 are similar to those of ethyne
  - the MOs for end-on coordinated N_2 are similar to those of CO but without the size difference found within the CO FOs
  - when bound side on N_2 the σ-donor and π-acceptor overlap is not as good, end on coordination allows for strong π-donor and twice as much π-acceptor overlap
  - alkenes and alkynes cannot overlap end-on and thus bind side-on.

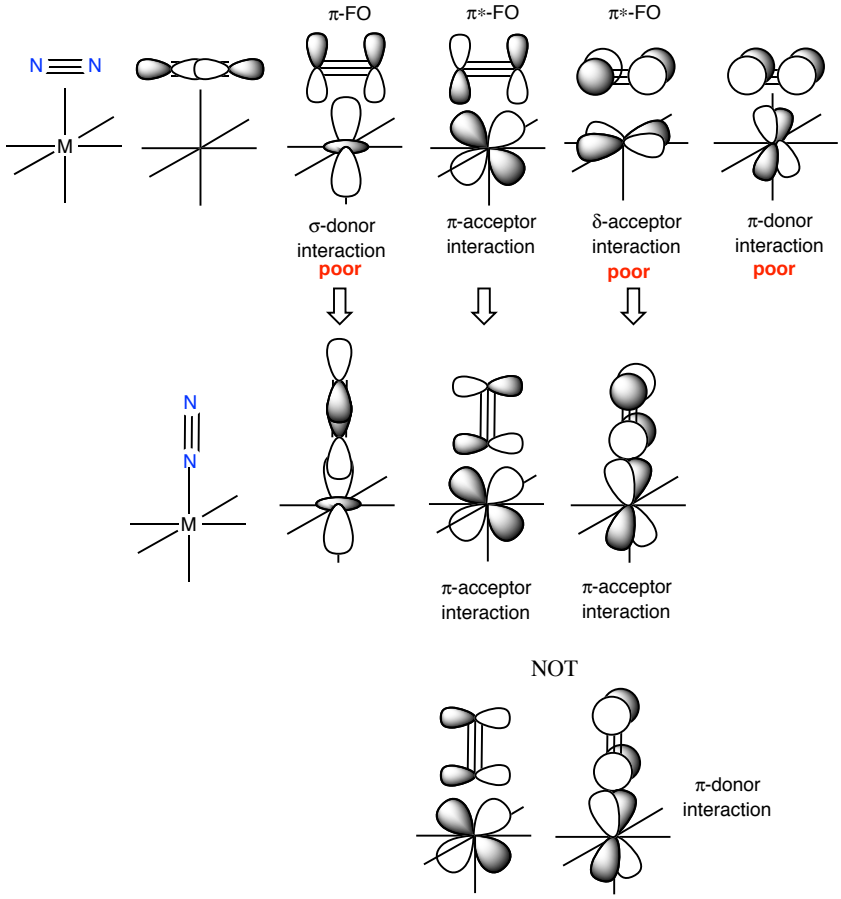

Figure 3 side-on and end-on bonding modes for N_2

- Construct the MO diagram for M_2L_{10} where L are σ-donor ligands, ensure you consider the the formation of a quadruple M-M bond
  - M_2L_{10} has D_{4h} symmetry, the axis is shown in, **Figure 4**, the symmetry elements are not reproduced here
  - identify the chemical fragments put them on the bottom of the diagram, the chemical fragments are two ML_5 fragments because these are degenerate and the orbitals will be easier to combine

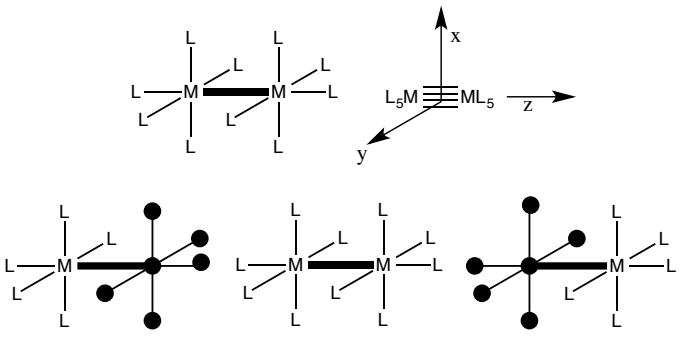

Figure 4 structure, axis and fragments for M_2L_{10}

- determine the energy levels and symmetry labels of the fragment orbitals. The ligand FOs for the ML_5 fragment are generated from the octahedral symmetry adapted ligand FOs by removing one of the ligands along the z-axis, **Figure 5**.

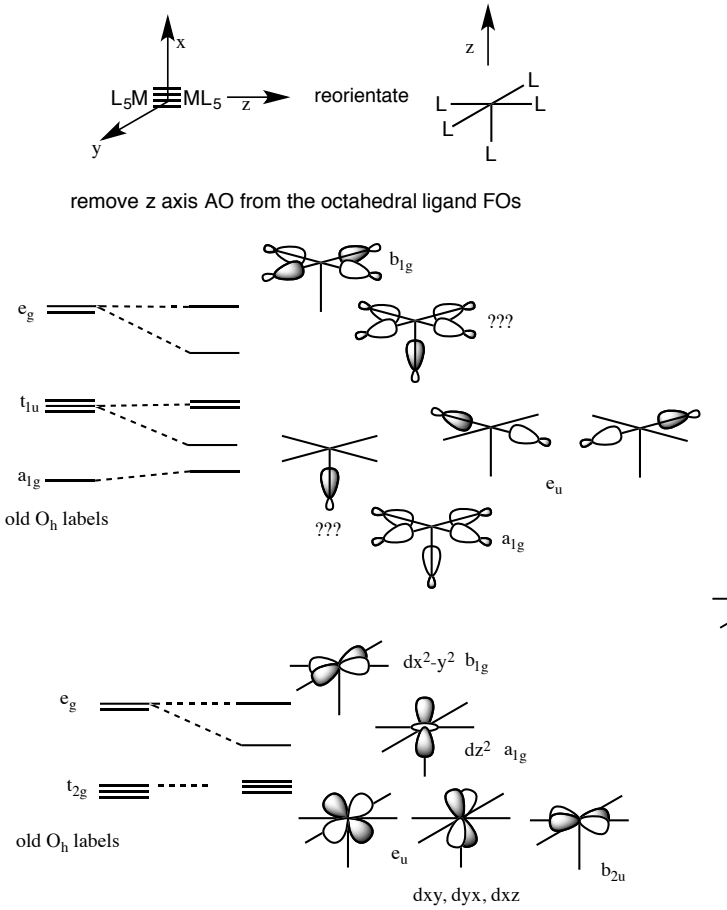

Figure 5 ML_5 ligand and dAO FOs

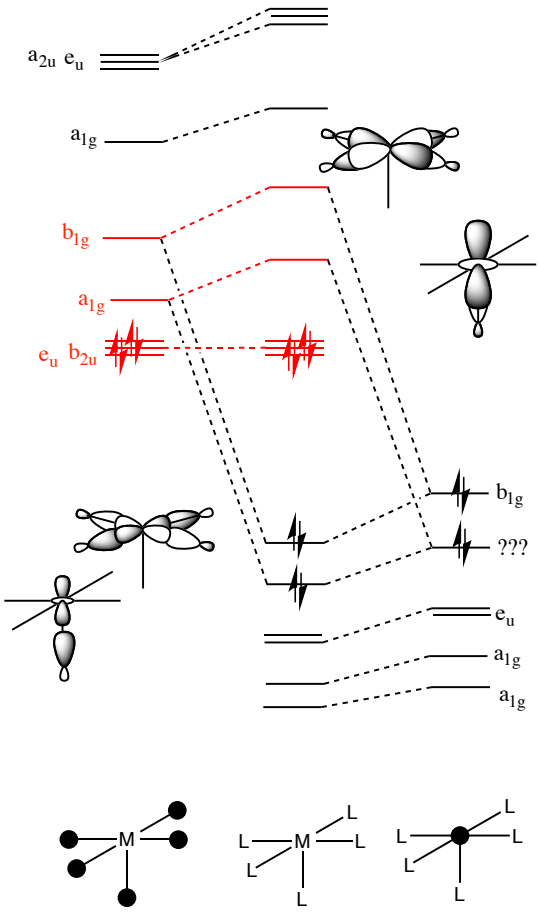

Figure 6 ML_5 intermediate diagram

- combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs. This fragment is not straight forward, however you can guess the orbitals that will associate, **Figure 5** and **Figure 6**
  - the b_{1g} (dx^2-y^2) metal dAO is high in energy due to antibonding interactions with the ligands which lie along the x and y axis.
  - the a_{1g} dz^2 based FO is only slightly destabilised due to a small antibonding interaction with a single ligand
  - the e_u and b_{2u} dAOs are non-bonding and remain degenerate and non-interacting
- combine the intermediate fragment energy diagrams, in forming the M-M bond we are interested in the dAO based MOs only, the new diagram focuses only on these FOs, **Figure 7**
  - the b_{1g} (dx^2-y^2) FOs are too high in energy to be occupied moreover the splitting is of a δ type and so is very small.
  - the a_{1g} dz^2 based splitting is much harder to determine, the dz^2 overlap is directional and strong (compared to the other d based MO interactions), however these FOs are higher in energy than the degenerate e_u and b_{2u} dAOs
  - the splitting of the non-bonding dAOs is easy to determine there will be a larger π and smaller δ splitting.
- determine the number of electrons in each fragment and hence the central MO region; add them to the diagram. Typically to get a large M-M bond order we need 4, 5 or 6 dAO electrons, in this diagram I have put 4 dAOe
  - identify if any MO mixing occurs, in this case there are no orbitals of the right symmetry or type to mix

- this MO diagram provides a more realistic interpretation than simply combining the bare dAOs as we did in **Lecture 6**
- however we are not quite all the way there, a famous complex with a quadruple bond is $[Re_2Cl_8(OH_2)_2]]^{2-}$ which has π-donor ligands! For example the single Re-Re bond length in $[Re_2(CO)_{10}]$ is 3.04Å while the quadruple Re-Re bond length in $[Re_2Cl_8(OH_2)_2]]^{2-}$ is 2.22Å

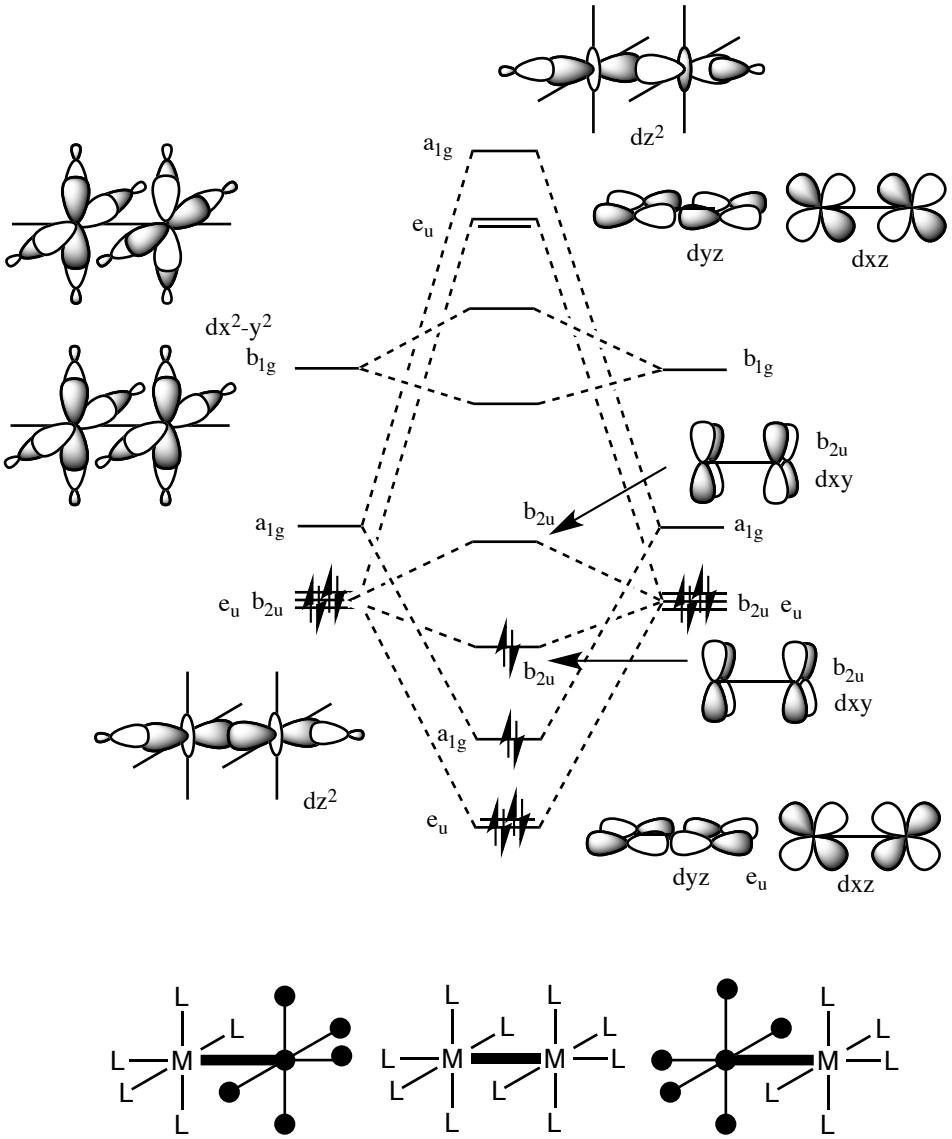

Figure 7 M_2L_{10} MO diagram