

Molecular Orbital Diagrams for Diatomic Molecules

- part of your revision was to re-visit the MO diagram of a homonuclear diatomic molecule, now that you have a much better idea of how to produce a good MO diagram practice by attempting the following problem sets
- supporting materials, some online and some follow this introduction
 - follow the online tutorial for CN^-
 - complete the MO problem for CO
 - complete the MO problem for N_2
- MO problem 1: follow the online tutorial for CN^-
 - Draw the MO diagram for the heteronuclear diatomic CN^- .
 - The 2s orbital energy for C is -19.43 eV and for N is -25.56 eV, while the energy for the 2p orbitals of C are -10.66 eV and for N are -13.18 eV.
- MO problem 2: CO
 - The dipole moment of CO is ≈ 0.1 D with the negative end of the dipole on the carbon atom.
 - However, the Mulliken electronegativity of C=2.67 and that of O=3.22.
 - Use MO theory to explain this apparent contradiction (MO mixing in CO is particularly large).
 - The average orbital ionization energy (in kJmol^{-1}) for the C 2s AO is 1888 and 2p AO is 1029 and the average orbital ionization energy for the O 2s AO is 3122 and 2p AO is 1531 eV.
 - How many valence electrons does CO have and what is the electronic configuration?
 - What molecules are isoelectronic with CO and what are their electronic configurations?
 - What differences will there be in the MO diagrams of these molecules?
 - Use your diagram to explain why CO is a good π -acceptor ligand in organometallic chemistry. Would you expect CO to be a good π -donor ligand?
- MO problem 3: N_2
 - Below is a photoelectron spectrum of N_2 , **Figure 1**, the y-axis is count rate and the x-axis is the ionization potential in eV. The fine structure of the $1\pi_u$ peak is due to vibrational excitation.

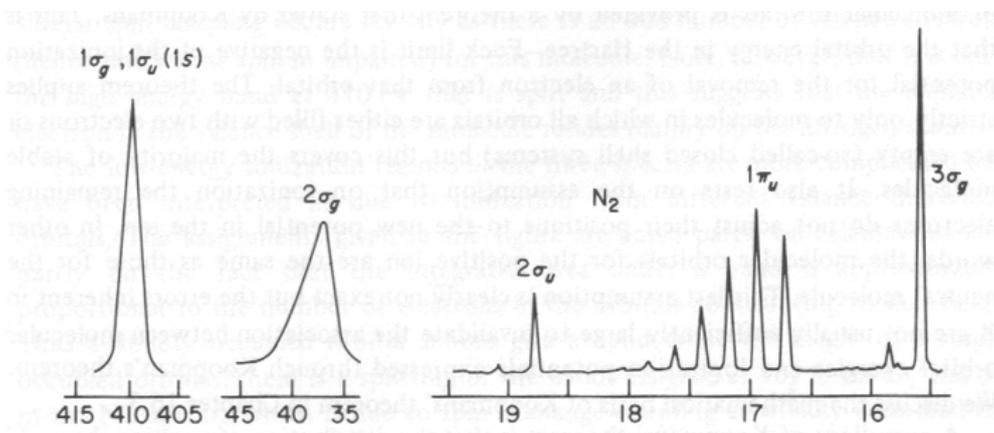


Figure 1 PES of N_2

- Draw a MO diagram for N_2 and use it to discuss and explain key features of the photoelectric spectrum of N_2 .

- Draw a partial MO diagram for the interaction of the antibonding π^* orbitals and the HOMO of N_2 with transition metal dAOs (still in $D_{\infty h}$ point group), the dAOs will lie between the π^* and σ MOs.
- Consider replacing N_2 with CO and evaluate the effect this change will have on the FOs and hence on the metal-ligand bonding. The relevant MO of CO (5σ) is complex to derive and is given here: 

- MO problem 4: NO

- Below is a photoelectron spectrum of NO, **Figure 2**, the y-axis is count rate and the x-axis is the ionization potential in eV. The fine structure of the $1\pi_u$ peak is due to vibrational excitation.

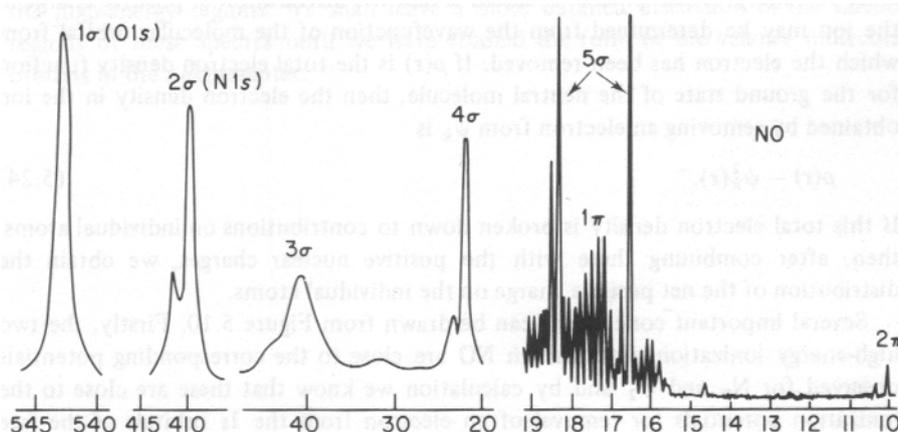
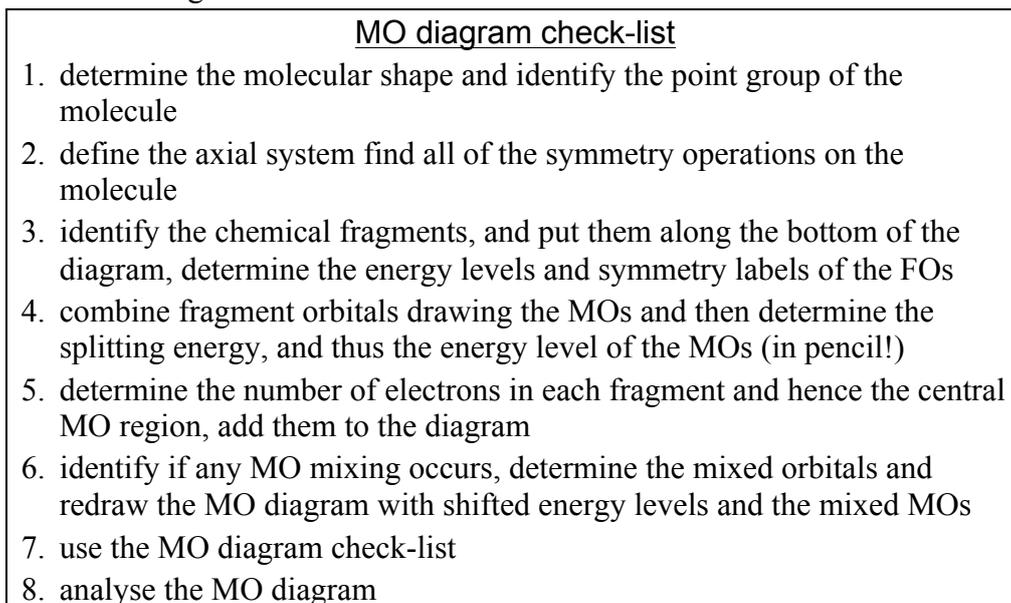


Figure 2 PES of NO

- Draw a MO diagram for NO and use it to discuss and explain key features of the photoelectric spectrum of NO.
- MO problem 5: O_2
 - Draw the Lewis structure for O_2 , explain why we expect this structure to be diamagnetic
 - Draw the MO diagram for O_2 , explain why we expect this structure to be paramagnetic
 - What is the experimental evidence is there for the electronic structure of O_2 ?
 - Discuss the O-O bond distances for the following molecules O_2^+ (dioxygenyl), O_2 (dioxygen), O_2^- (superoxide), O_2^{2-} (peroxide)

MO problem 2: CO

- Start with the MO diagram check-list



- determine the symmetry point group of the molecule

- is the molecule linear? YES
- is there a center of inversion? NO

the molecule is $C_{\infty v}$

- define the axial system find all of the symmetry operations on the molecule, **Figure 3**
- identify the chemical fragments, and put them along the bottom of the diagram, **Figure 3**
- determine the energy levels, **Figure 4**

- first O is much more electronegative than C so the O orbitals will lie deeper in energy
 - C and O are separated in the PT and thus we can expect their sAOs not to interact, the 2s orbital energy for C is -19.43 eV and for O is -32.38 eV, while the energy for the 2p orbitals of C are -10.66 eV and for O are -15.85 eV.
 - if the 2s AOs are not interacting we have to consider the option that the C 2s AO will interact with the O 2p AOs. The C 2s AO has an energy -19.43 eV while the O 2p has an energy -15.85 eV, these are sufficiently close to interact!
- determine the symmetry labels of the fragment orbitals, **Figure 4**
 - go and look at the character tables for $C_{\infty v}$ and $D_{\infty h}$, this is important because a surprising number of students label the FOs and MOs incorrectly in exams

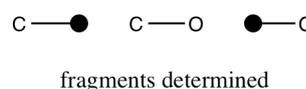
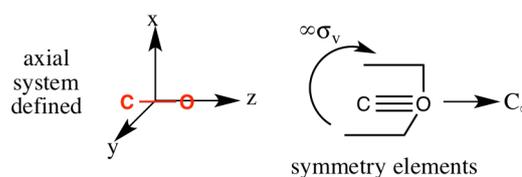


Figure 3 symmetry of, axis for and fragments for CO

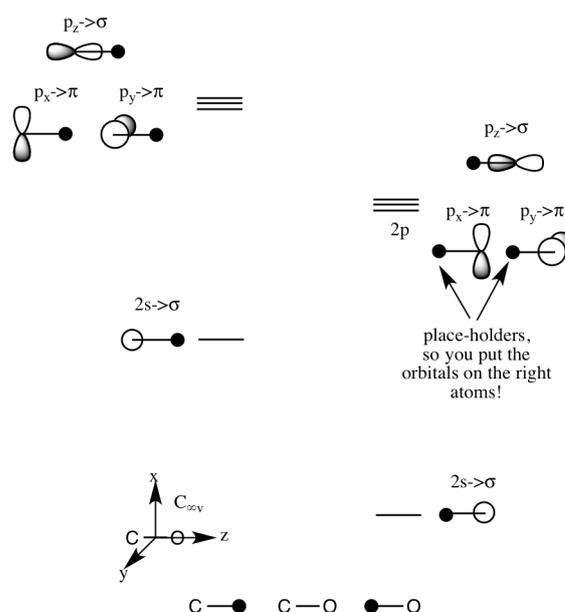


Figure 4 CO setting up the MO diagram

- these are the only character tables where we use the **LOWER CASE Greek** symbols to label the FOs and MOs
- so rather than labelling a level as Σ_g^+ we label it σ_g^+ and so on
- we never use the A and E labels for the $D_{\infty h}$ point group
- if you don't know the Greek alphabet you should revise it now!
- however, we don't actually need to use the character table to determine the symmetry of the orbitals (since this character table is quite difficult)
- orbitals which are symmetrical around the C_{∞} axis are σ -orbitals, orbitals which do not map onto themselves around the C_{∞} axis are π -orbitals. If this is not obvious to you, go back and look at the revision document for the homonuclear diatomic where this is explained in detail with diagrams
- alternatively just use the T_x , T_y and T_z labels in the character table to identify the symmetry labels
- since this is a heterodiatomic there is no center of inversion and the gerade and ungerade labels of the $D_{\infty h}$ point group are not present.
- combine fragment orbitals drawing the MOs and then determine the splitting energy, and thus the energy level of the MOs
 - the π -MOs form standard combination, don't forget that size matters, and to adjust the MO contributions for the relative energy of the contributing FOs, **Figure 5**
 - the orbitals with a lower energy contribute more to the bonding MO, the orbitals with the higher energy contribute more to the antibonding MO
 - anti-bonding orbitals rise in energy more than bonding orbitals are stabilised, π orbital splitting is less than σ orbital splitting, however how close in energy the FO are is also important, **Figure 6**
 - annotate the diagram as you go explaining relevant features

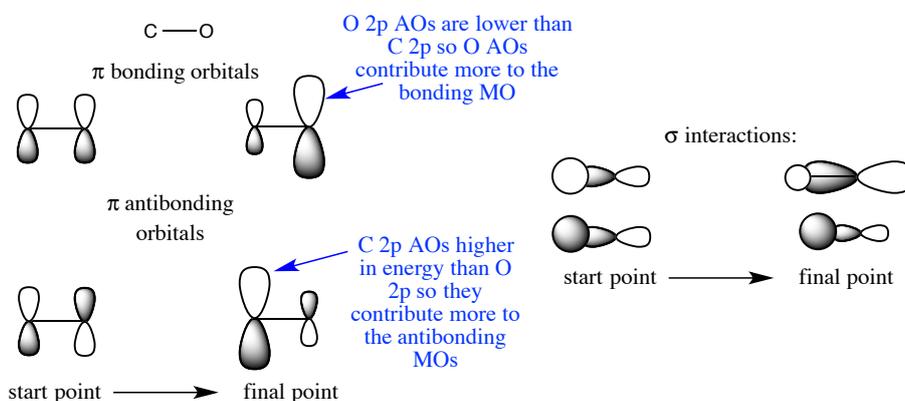


Figure 5 CO determining the form of the MOs

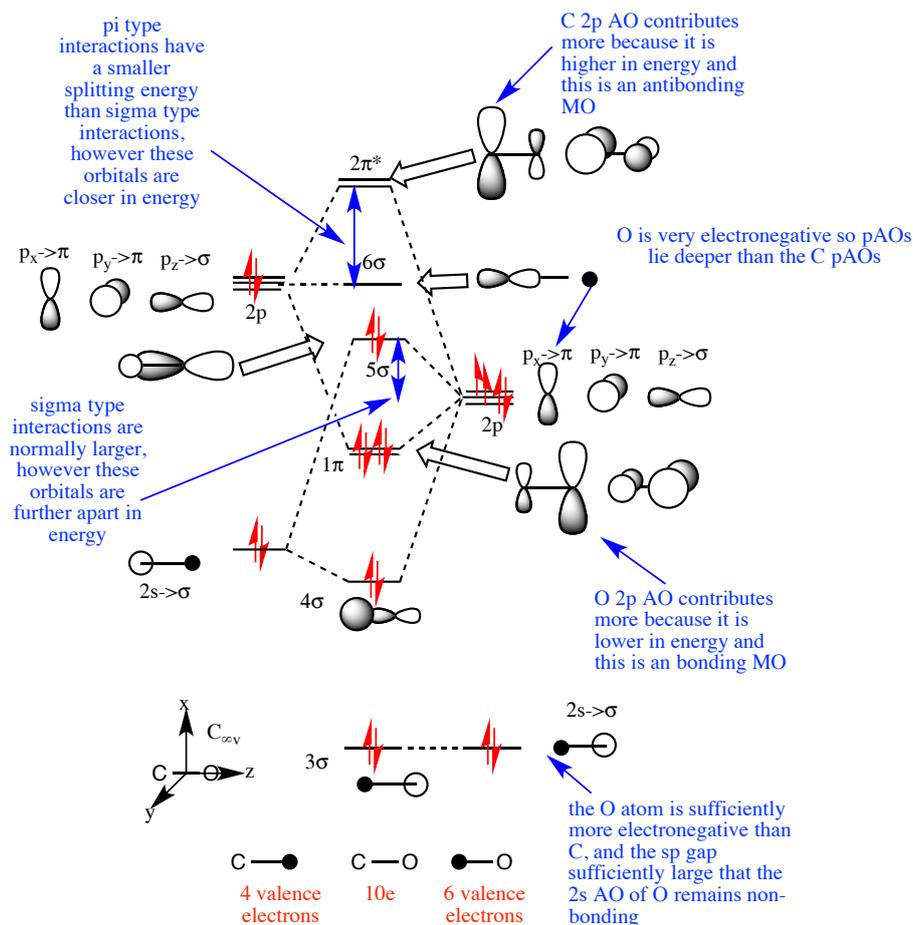


Figure 6 First stage MO diagram

- determine the number of electrons in each fragment and hence the central MO region, add them to the diagram work out if any mixing occurs
 - there are many σ -type orbitals, generally only those closest in energy will interact, in this case it will be the 5σ and 6σ
 - in addition the 5σ is occupied and the 6σ is unoccupied, and one of them is non-bonding.
 - thus these MOs fulfil the requirements for extensive mixing and stabilisation of the lower energy MO to occur.
 - work out the effect on the MOs of mixing, **Figure 7** and determine which of the new MOs is the most bonding, ie that with the largest overlap of two lobes in-phase.
 - add the mixed MOs to the diagram, shifting the antibonding MO up and the bonding MO down, determining exactly how far the 5σ is stabilised is not possible using qualitative MO theory, however calculations and experimental evidence tell us that it lies below the 1π MOs which are the HOMO for CO.

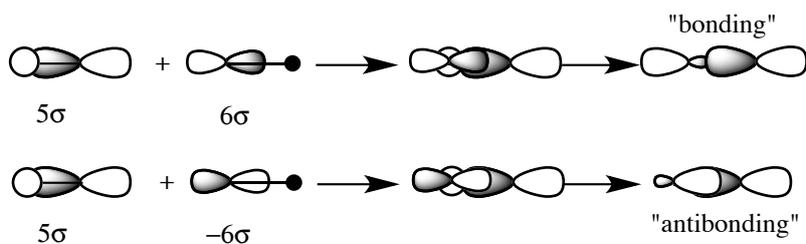


Figure 7 perturbations due to mixing

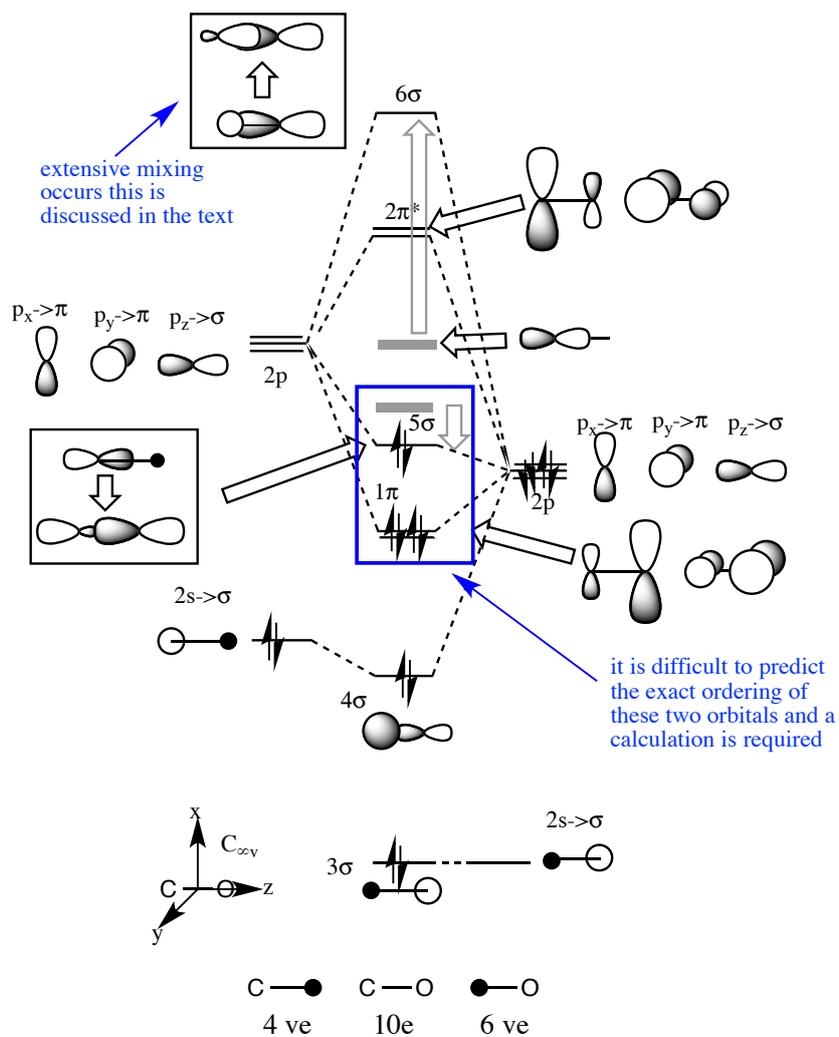


Figure 8 final MO diagram after mixing

- calculations carried out at the B3LYP/6-311G(d,p) level

	C_2	O_2		CO
$3\sigma_u^*$	+0.26617	+0.31182	6σ	+0.21625
$1\pi_g^*$	+0.00031	-0.31182	2π	-1.02915
$1\pi_u$	-0.3259	-0.56872	1π	-0.38074
$3\sigma_g$	-0.26443	-0.55315	5σ	-0.43155
$2\sigma_u^*$	-0.41104	-0.83920	4σ	-0.57948
$2\sigma_g$	-0.79189	-1.31486	3σ	-1.17202

Table 1 MO energies in au.

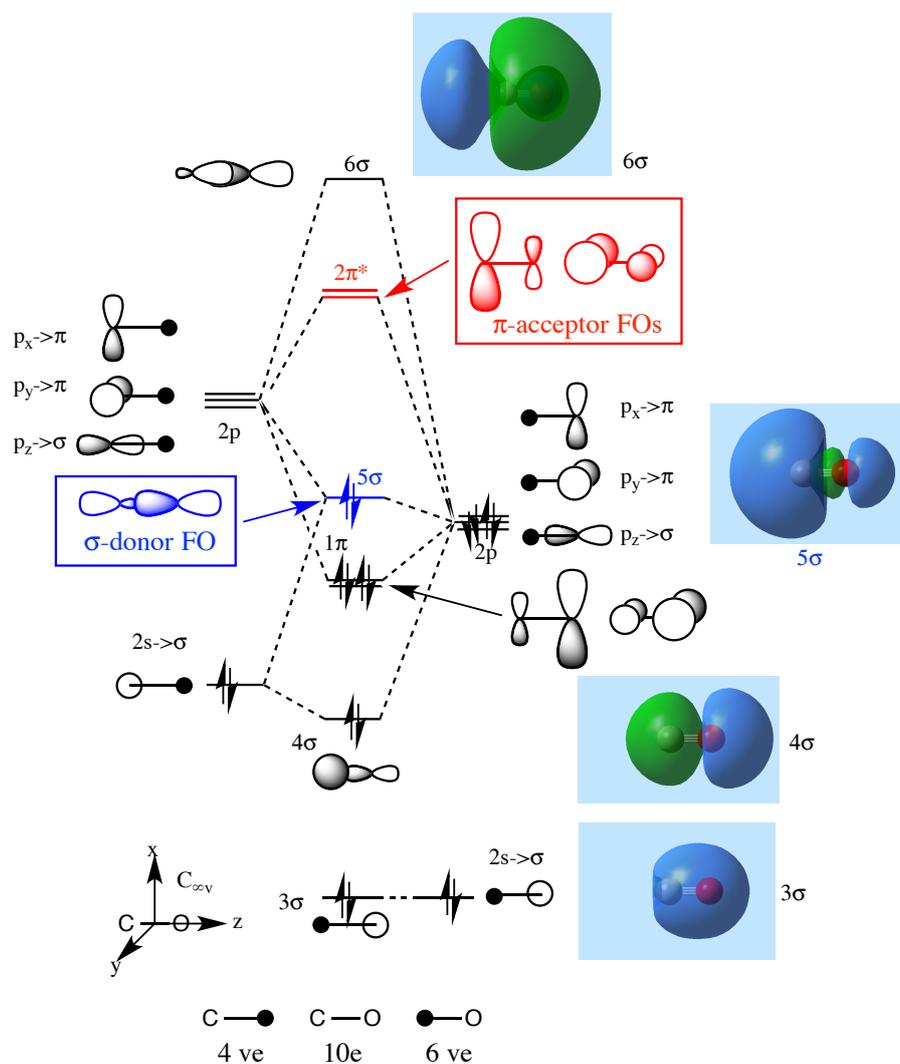


Figure 9 important MOs

- analyse the MO diagram
 - the real computed MOs are shown in **Figure 9** and the energies are listed in **Table 1**. The estimated MOs are a good approximation to the computed MOs. However, typically in the context of research we “decompose” the computed MOs in order to understand the bonding.
 - the molecular dipole on CO is very small for a molecule with atoms of very different electronegativity, and it is aligned contrary to that expected on the basis of the electronegativity of these atoms. However the dipole moment $\mu = \sum_i q_i r_i$ is the sum of all the contributions of charge times the distance of the charge from a defined zero point, normally taken as the center of mass of the molecule. In this case we can relate the reversal in the dipole moment to the polarisation of the 5σ MO, which moves electron density toward the C atom and into a lobe pointing out and away from the C (like a lone pair orbital).
 - the experimentally determined reversal of the dipole moment indicates that this effect is significant, and a good representation of this orbital might place more emphasis on the C “lp” like character of this MO.



- note that there is a difference between the charge on an atom and the dipole. The charge on the C atom is +0.458 and on the O atom is -0.458 (NBO). Actually the charge has to be of the same magnitude and opposite in sign for these two atoms because the molecule is neutral overall. The charge is nuclear charge and the electron density divided up between the two

atoms, how this is carried out is complex and is a matter of current intense research! The “charges” calculated using the NBO method are in this case, not sophisticated enough to be able to recover the strong anisotropy of the electronic distribution.

- How many valence electrons does CO have and what is the electronic configuration?
 - CO has ten valence electrons and the electronic configuration is CO: $(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$
- What molecules are isoelectronic with CN^- and what are their electronic configurations?
 - Isoelectronic molecules have the same number of electrons.
 - NO^+ : $(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4$
 - CN^- : $(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$
 - N_2 : $(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$
 - CN^- and CO both have configurations with a 5σ HOMO (ie above the 1π) while in NO^+ the larger $2s$ - $2p$ gap means that mixing is insufficient to lift the 5σ above the 1π HOMO.
- What differences will there be in the MO diagrams of these molecules?
 - differences due to different relative electronegativities, and the changing size of the s - p gap will move the final MO energy levels relative to each other
 - differences due to the higher symmetry of N_2 meaning that different MOs mix
 - different HOMO and LUMO orbitals
- Use your diagram to explain why CO is a good π -acceptor ligand in organometallic chemistry. Would you expect CO to be a good π -donor ligand?
 - the 5σ MO is important as this is the σ -bonding FO of the CO ligand, also very important are the antibonding 2π MOs which are the π -accepting FO of the CO ligand, these FOs dominate much of the importance of the CO ligand in organometallic and TM chemistry, **Figure 10** CO as a ligand **Figure 10**

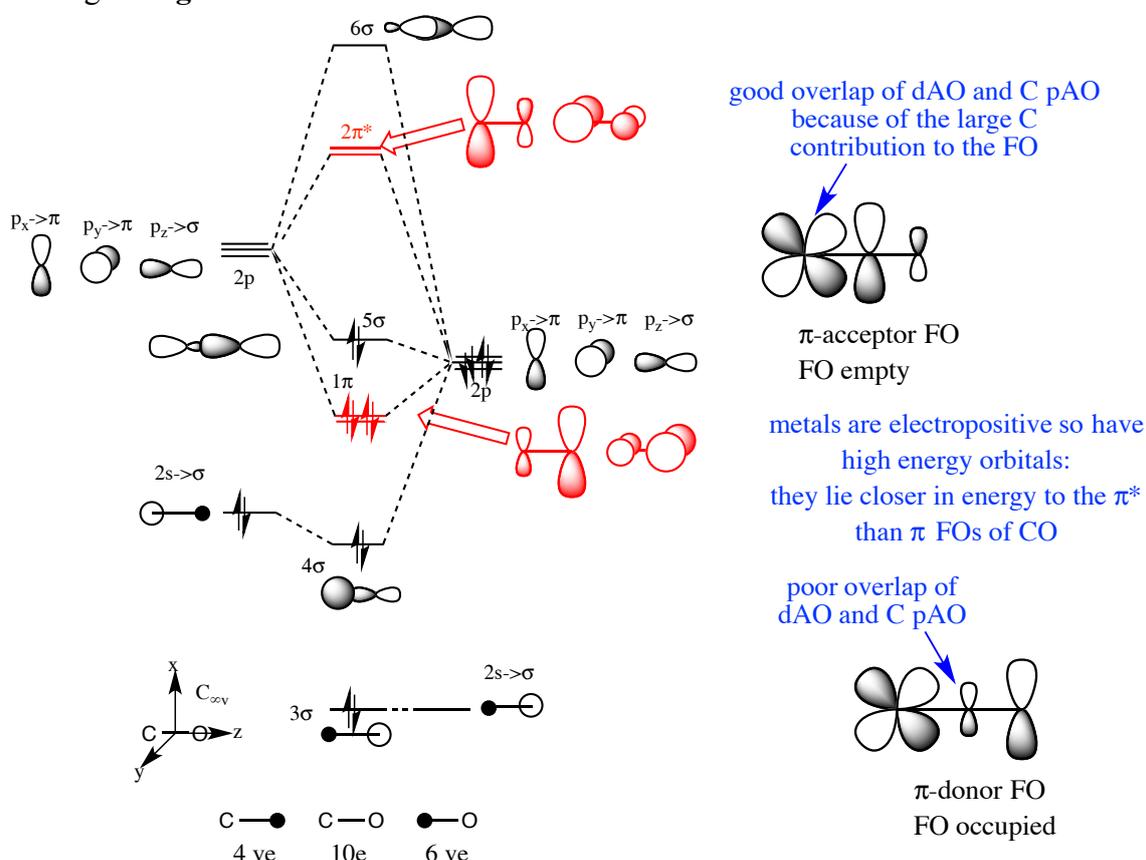


Figure 10 CO as a ligand

- MO problem 3: N₂
 - Below is a photoelectron spectrum of N₂, **Figure 1**, the y-axis is count rate and the x-axis is the ionization potential in eV. The fine structure of the 1π_u peak is due to vibrational excitation.

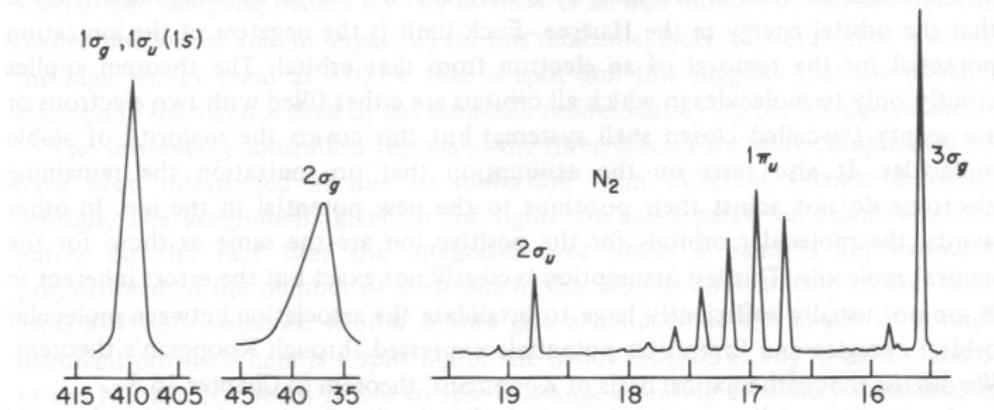


Figure 1 PES of N₂

- Draw a MO diagram for N₂ and use it to discuss and explain key features of the photoelectric spectrum of N₂.
- Draw a partial MO diagram for the interaction of the antibonding π* orbitals and the HOMO of N₂ with transition metal dAOs (still in D_{∞h} point group), the dAOs will lie between the π* and σ MOs.
- Consider replacing N₂ with CO and evaluate the effect this change will have on the FOs and hence on the metal-ligand bonding. The relevant MO of CO (5σ) is complex to derive and is given here:

- Start with the MO diagram check-list

MO diagram check-list
9. determine the molecular shape and identify the point group of the molecule
10. define the axial system find all of the symmetry operations on the molecule
11. identify the chemical fragments, and put them along the bottom of the diagram, determine the energy levels and symmetry labels of the FOs
12. combine fragment orbitals drawing the MOs and then determine the splitting energy, and thus the energy level of the MOs (in pencil!)
13. determine the number of electrons in each fragment and hence the central MO region, add them to the diagram
14. identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
15. use the MO diagram check-list
16. analyse the MO diagram

- shape has been given, point group is D_{∞h}
- axial system has been defined, symmetry operations identified, **Figure 11**
- MO diagram shown below, **Figure 12**

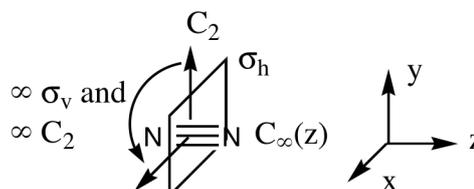
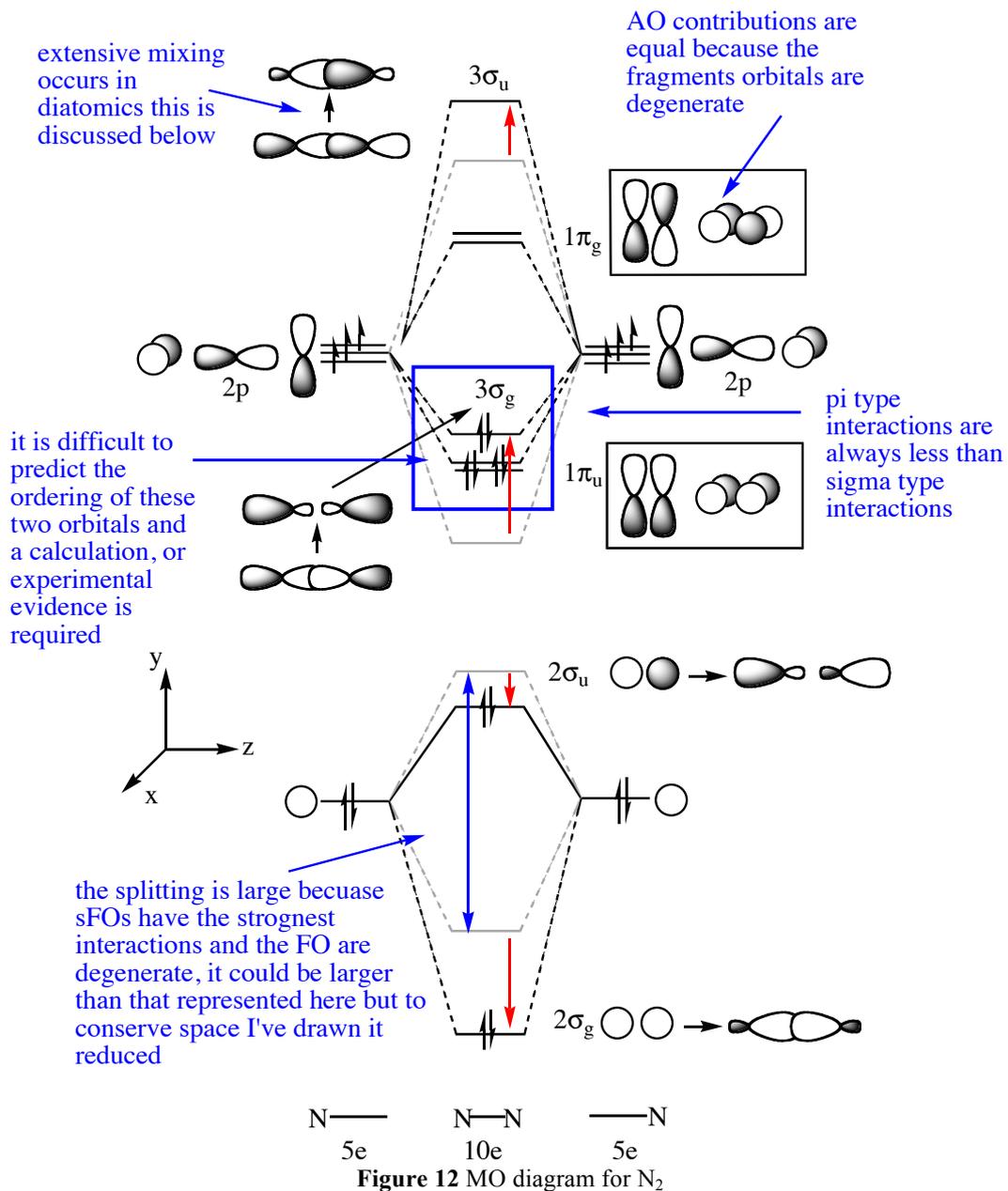
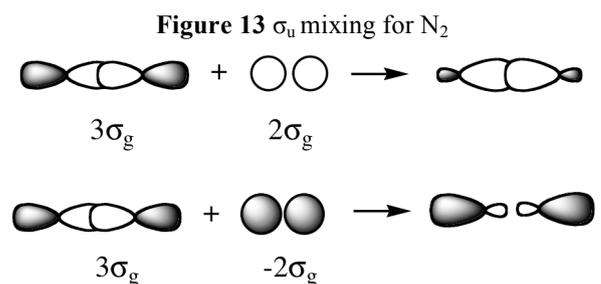
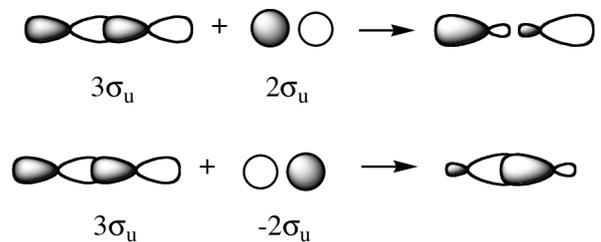


Figure 11 symmetry of, axis for and fragments for N₂



- Mixing occurs and is important for N₂.
 - MO mixing is large in diatomics with a small sp gap and this includes N.
 - Mixing is normally greatest between MOs that are close in energy, when one is non-bonding and when one is occupied and the other is unoccupied.
 - However, the final arbiter of whether mixing occurs or not, is if the molecule as a whole is stabilised, and in 1st year we were told this is the case for homonuclear diatomics to the left of O₂.
 - This knowledge is obtained from calculations and experimental data, and is shown in this PES for N₂.



- In N_2 the $2\sigma_u$ is occupied and the $3\sigma_u$ is unoccupied, these MOs are not particularly close in energy, but they can mix as is shown in **Figure 13**.
- In N_2 the $2\sigma_g$ and the $3\sigma_g$ MOs are both occupied and not particularly close in energy, however we also know that these orbitals mix, and by a sufficient amount to raise the energy of the $3\sigma_g$ MO above the $1\pi_u$ MO, see the spectrum! The effects of mixing are shown in **Figure 14**.
- The final MO diagram is consistent with the photo-electron spectrum (PES). The PES shows the energy required to eject an electron from a particular MO. Koopman's theorem states that the orbital energy is the negative of the ionisation potential required to remove an electron from that orbital. Thus the peaks on this diagram represent the energy levels of the real MOs.
- It is clear from this diagram that the core N 1sAOs lie very deep in energy and do not interact (hence a single degenerate peak is observed). The $2\sigma_g$ and $2\sigma_u$ bonding and antibonding pair are then observed. Above this lies the $1\pi_u$ MO, and this gives us explicit experimental evidence that mixing pushes the $3\sigma_g$ orbital above the $1\pi_u$ MO. The PES cannot measure the energy level of unoccupied orbitals and so the virtual orbitals of the MO diagram are not represented in the spectrum.
- A partial MO diagram for the interaction of the antibonding π^* orbitals and the HOMO of N_2 with a transition metal dAOs is shown in **Figure 15**. The metal has been given 4d electrons.

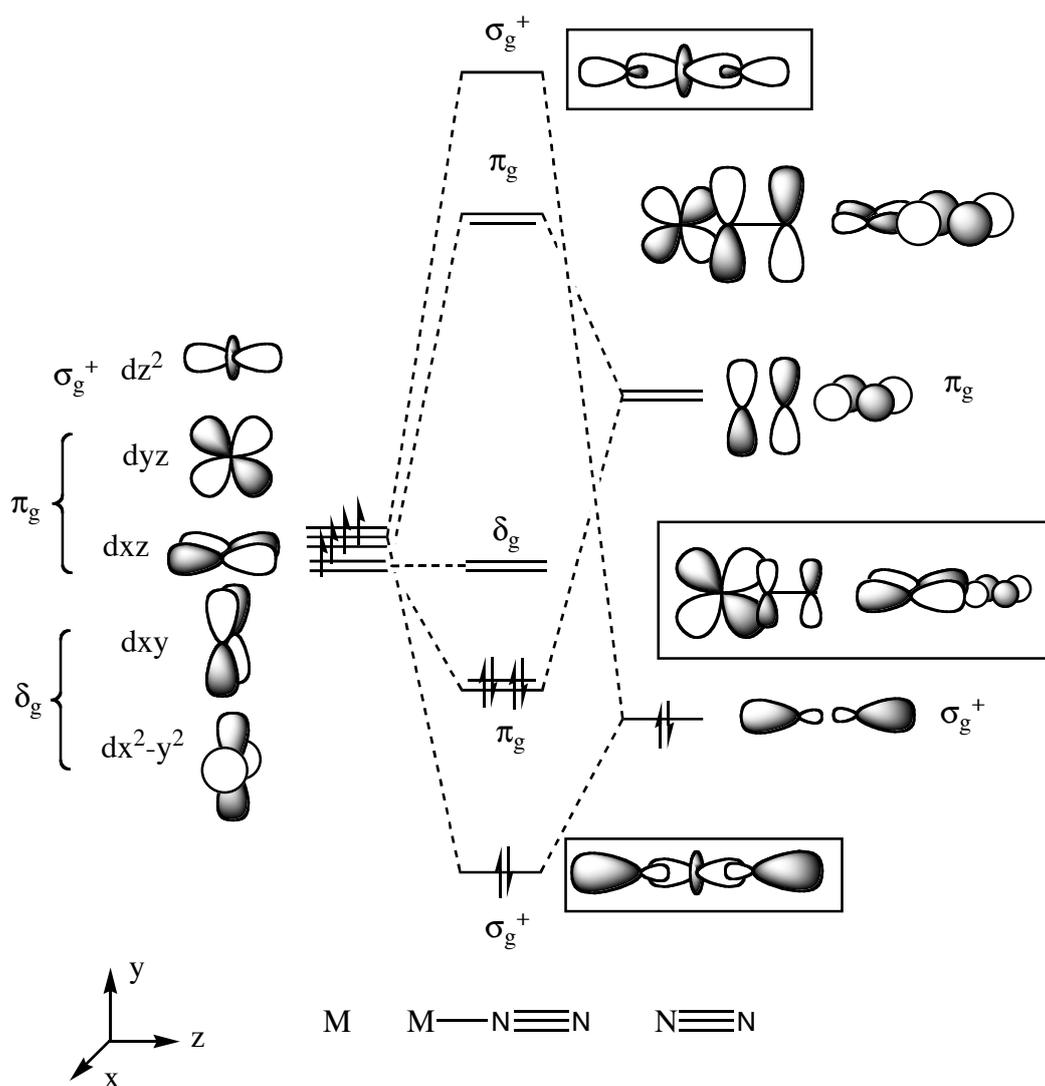


Figure 15 MO diagram for a TM interacting with N_2

- Consider replacing N_2 with CO and evaluate the effect this change will have on the FOs and hence the metal-ligand bonding. Carbon is less electronegative than oxygen and so will dominate the antibonding π^* MOs of CO as shown in **Figure 16**. This has the effect of enhancing overlap and interaction with the dAOs of the metal. While the σ orbital of N_2 has an equal contribution from each N, the equivalent MO in CO is dominated by a lone-pair or sp type hybrid on the C atom, this again enhances the overlap between the metal and ligand. Both of these effects will serve to enhance the metal-ligand bond (and decrease the C-O bond relative to the N-N bond).

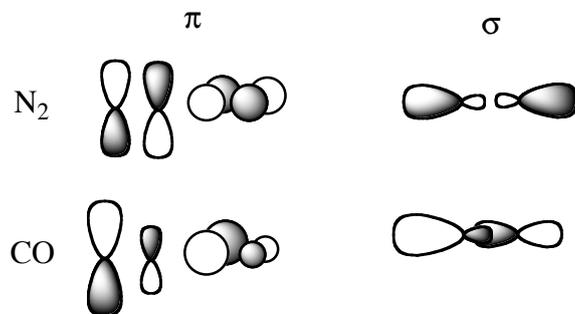


Figure 16 Orbital interactions of CO vs N_2