In-Class Problems / Self-study Problems / Test Preparation: Lecture 4

- **In-Class P1** your turn, you try mixing of the σ_u MOs, **Figure 1**

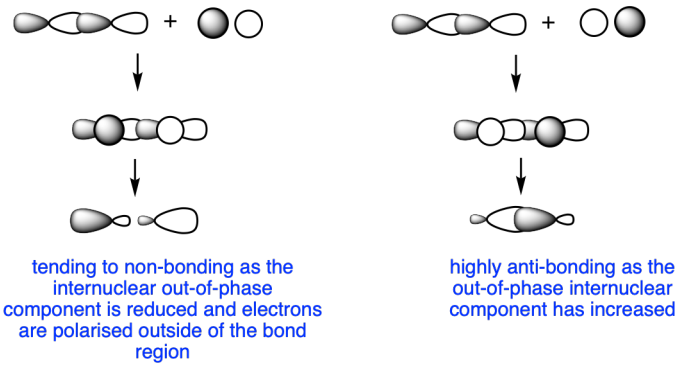

Figure 1 Combining AOs to form MOs

- **In-Class P2** , Do the 2sAOs of NO interact? Do the 2sAOs of CO interact?
  - N and O are adjacent on the PT, yes the 2sAOs will interact
  - C and O are not adjacent on the PT, no the 2sAOs will not interact

- **In-Class P3 a)** draw the MO diagram for N_2
  - follow the same procedure as shown in the notes for a MO diagram with mixing
  - now add in the electrons N has 5 valence electrons and N_2 10 electrons in the MO diagram

- **In-Class P3 b)** use your MO diagram to explain why N_2 is so stable
  - in the pAO manifold all of the bonding MOs are occupied while none of the antibonding MOs are occupied
  - in terms of MO mixing even though the occupied $3\sigma_g^+$ is destabilised, overall the stabilisation in the $2\sigma_u^-$ and $2\sigma_g^+$ must more than compensate for this.

- **In-Class P3 c)** use your MO diagram to help you rank N_2, $[N_2]^-$, $[N_2]^+$ and $[N_2]^{2+}$ in order of stability.
  - N_2 will be the most stable
  - $[N_2]^-$ will have an extra electron in the antibonding $1\pi_g$ degenerate set of MOs
  - $[N_2]^+$ will have lost an electron from the bonding $3\sigma_g$ MO, the π_u MOs will still be bonding, the stability with respect to $[N_2]^-$ will depend on the relative destabilisation energy of the π_u MOs vs the relative stabilisation energy of the $3\sigma_g$ MO, the stability of these molecular ions will be approximately the same
  - $[N_2]^{2+}$ will have lost two electrons from the bonding $3\sigma_g$ MO and be less stable than $[N_2]^+$
  - N_2, > $[N_2]^- \approx [N_2]^+ > [N_2]^{2+}$

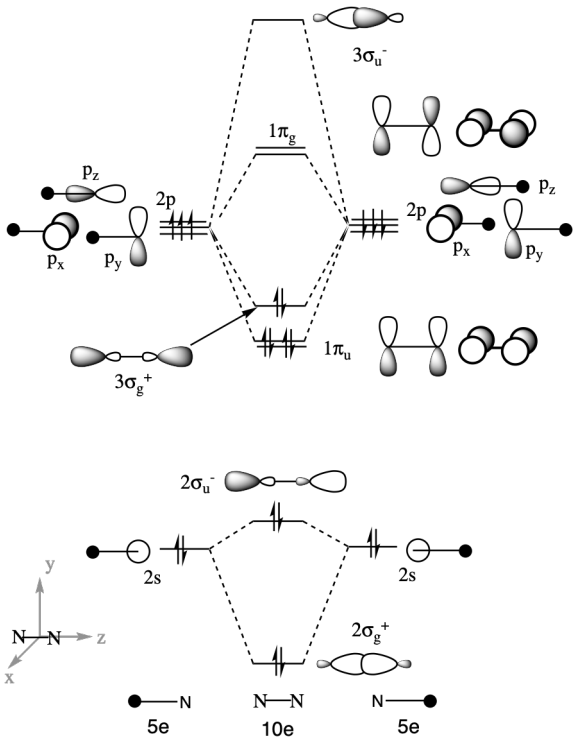

Figure 2 MO diagram for N_2

- **Q1** produce a "sketch" diagram such as that shown in **Figure 12** of the notes for CO, showing the relative energy of the FOs, include annotations to explain your reasoning
- **Q2 Follow the on-line tutorial** and draw the MO diagram for the heternucler 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.

http://www.huntresearchgroup.org.uk/patch/patch_CN_intro.html

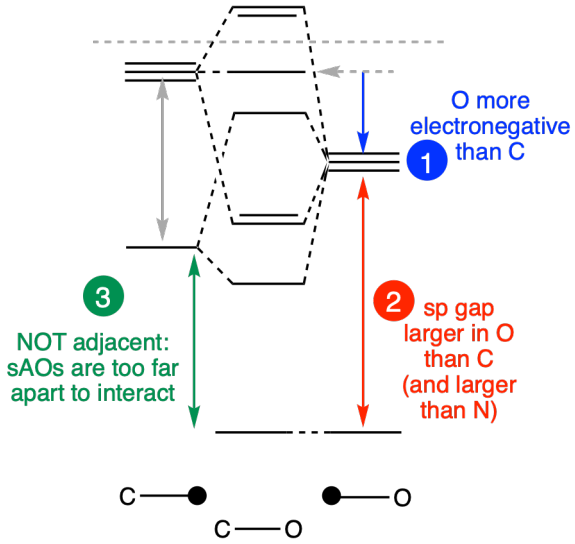

Figure 3 sketch for setting up the FO energy levels for the diagram of CO

- **Q3** draw a MO diagram for CO include annotations to explain your reasoning, give the electronic configuration of CO
  - determine the symmetry point group of the molecule: $\mathbf{C_{\infty v}}$
  - define the axial system find all of the symmetry operations, see **Lecture 2**
  - identify the chemical fragments, and put them along the bottom of the diagram and determine the FO 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
  - 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**
  - make sure you use the lower case Greek letters
  - orbitals which are symmetrical around the C∞ axis are □-orbitals, orbitals which do not map onto themselves around the C∞ axis are □-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 Tx, Ty and Tz 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∞h point group are not present.

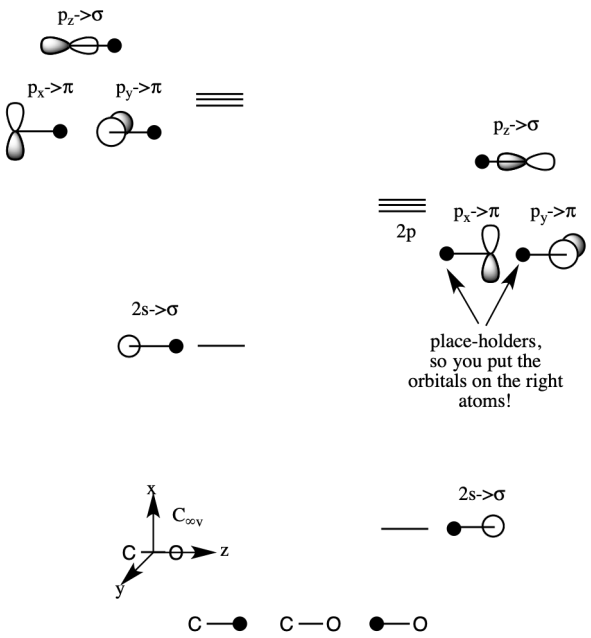

Figure 4 CO setting up the MO diagram

- combine fragment orbitals drawing the MOs and then determine the splitting energy, and thus the energy level of the MOs
  - the π-MOs form a 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

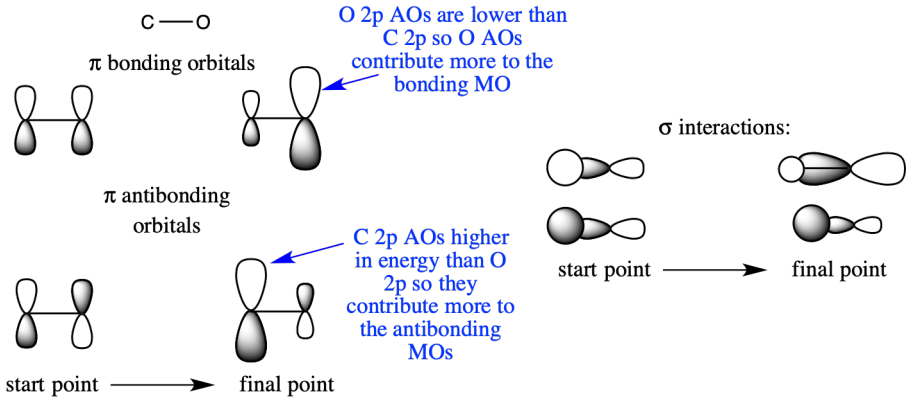

Figure 5 CO determining the form of the MOs

  - 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
  - add the orbital levels and MOs onto your diagram, **Figure 6Error! Reference source not found.**
  - annotate the diagram as you go explaining relevant features

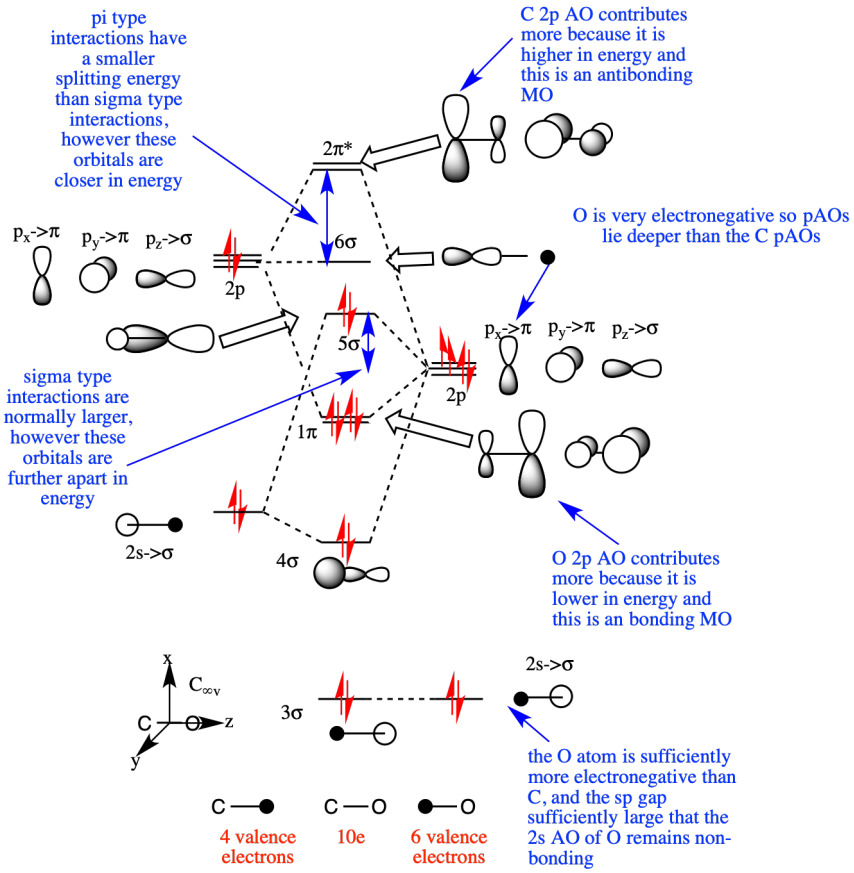

Figure 6 Stage 1 MO diagram for CO

- determine the number of electrons in each fragment and hence the central MO region, add them to the diagram
- now 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 a**nd determine which of the new MOs is the most bonding, ie that with the largest overlap of two lobes in-phase.

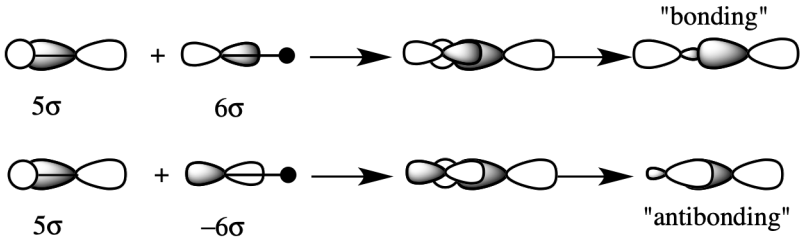

Figure 7 perturbations due to mixing

- 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.

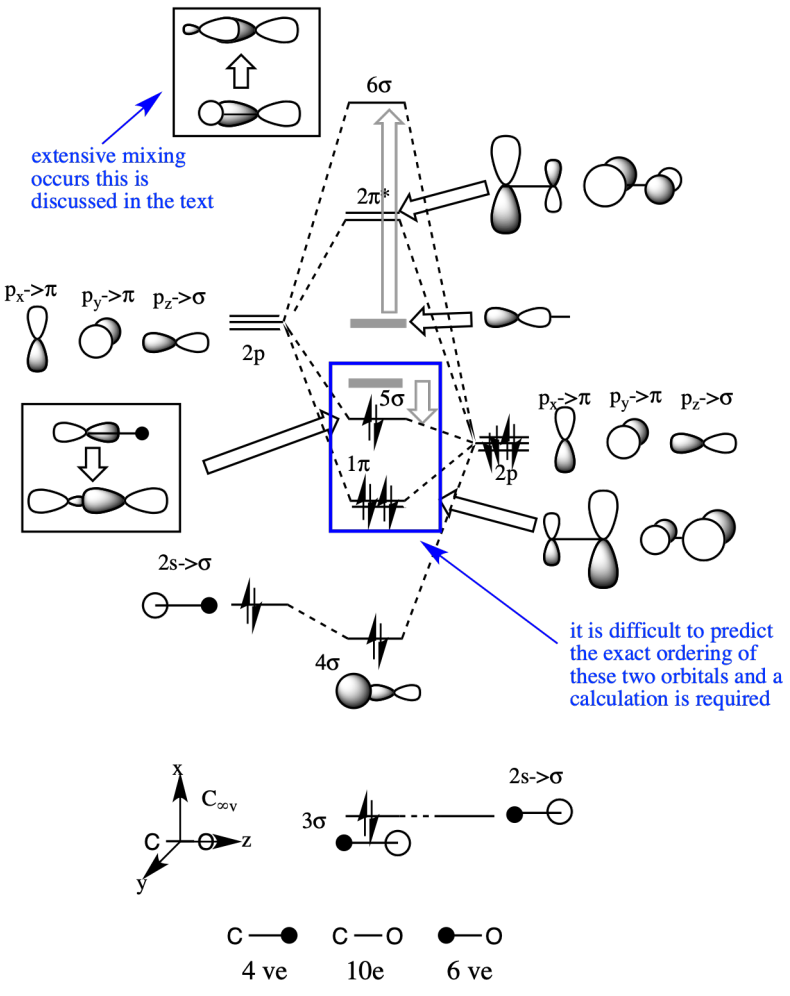

Figure 8 Final MO diagram for CO including mixing

- 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.

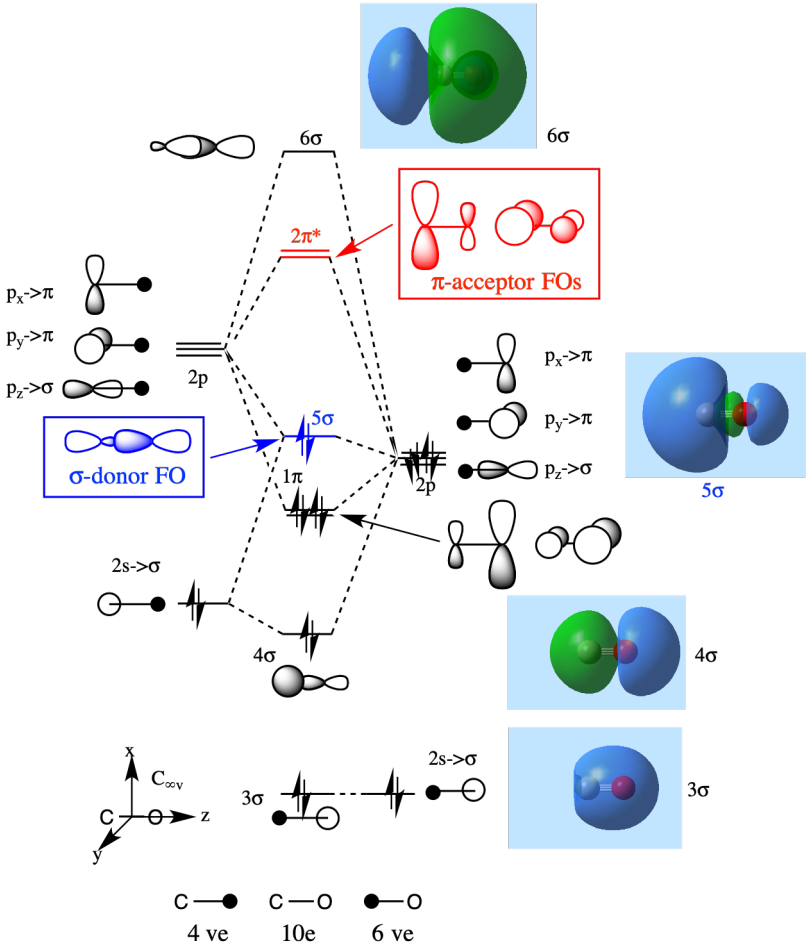

Figure 9 Important MOs

- **Q4** Use your MO diagram of CO to explain why CO is a good π-acceptor ligand in organometallic chemistry. Would you expect CO to be a good π-donor ligand? (*advanced!*)
  - CO has ten valence electrons and the electronic configuration is CO: $(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$
  - the 5σ MO is important as this is the σ-bonding FO of the CO ligand
  - there are also 2 sets of π MOs, the antibonding 2π are more important for CO acting as a π-acceptor ligand in organometallic and TM chemistry, see the discussion on **Figure 10**

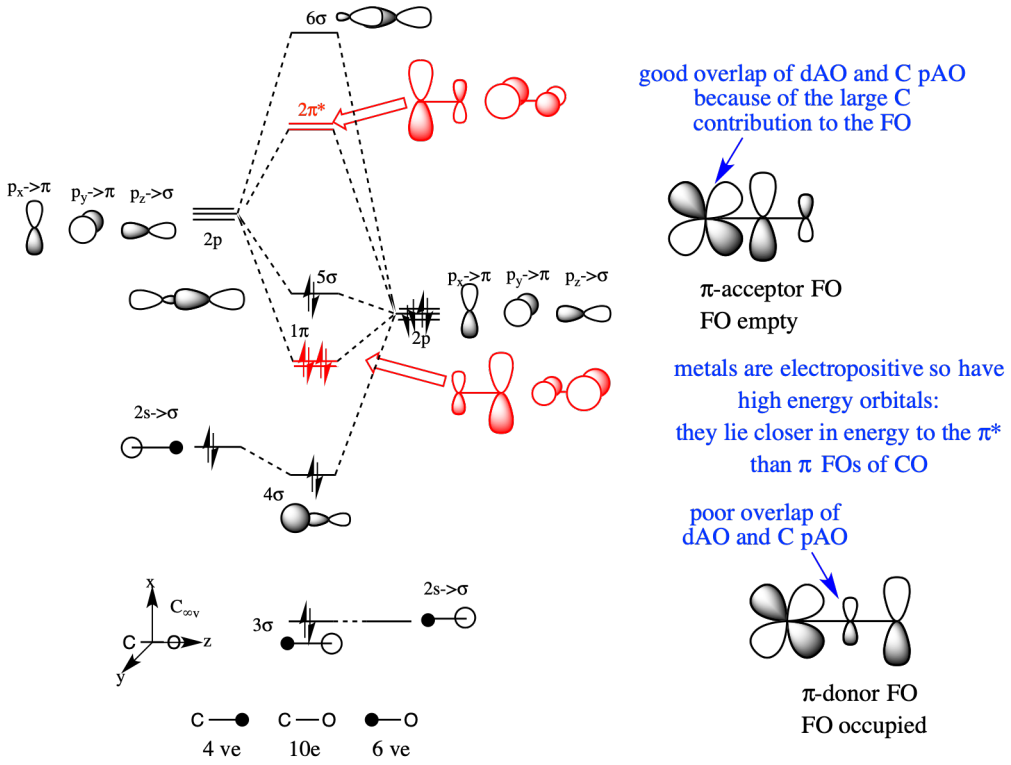

Figure 10 CO as a ligand

- **Q5** Below is a photoelectron spectrum of N_2, **Figure 11**, 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.

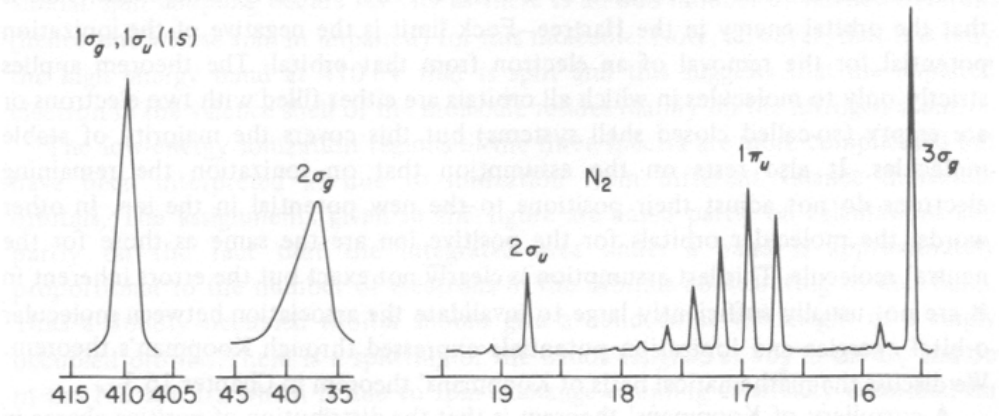

Figure 11 PES of N_2

- The final N_2 MO diagram **Figure 2** 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 and 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 ≈410 eV 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 at ≈38 and 19 eV. Above these lies the $1\pi_u$ MO, 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.