The Diatomic MO Diagram: Part 2

Introduction

- today I will introduce LCAO theory (Linear Combination of AOs)
- I am going to introduce MO mixing, and spend some time on this aspect as I know students find this particularly difficult
- we will finish today by introducing heteronuclear diatomic MO diagrams

Linear Combination of Atomic Orbitals (LCAO)

- qualitatively MOs are formed by combining or "adding" fragment orbitals (FOs) once "as is" and once with the phase of all components reversed
- the cartoon represents an equation: the MO wavefunction, **Figure 1**

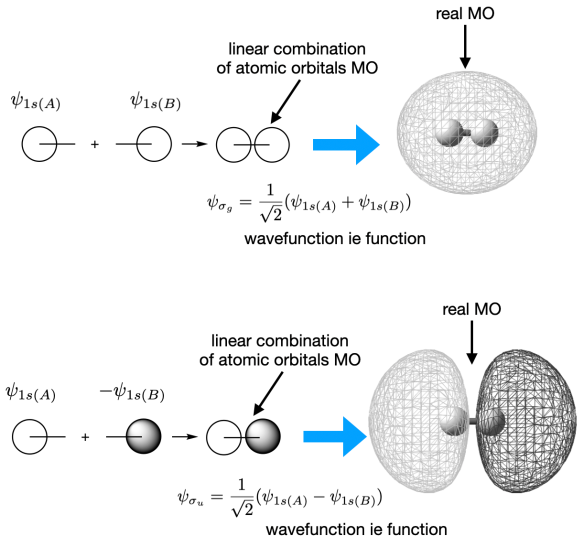

Figure 1 "cartoon" and "real" MOs of H_2

- the MOs we draw are representations of the "real" orbitals (far right of **Figure 1** which are obtained from solving the Schrödinger equation
    - you have already seen this effect in your year 1 chemical bonding course, but in a slightly different representation, **Figure 2**

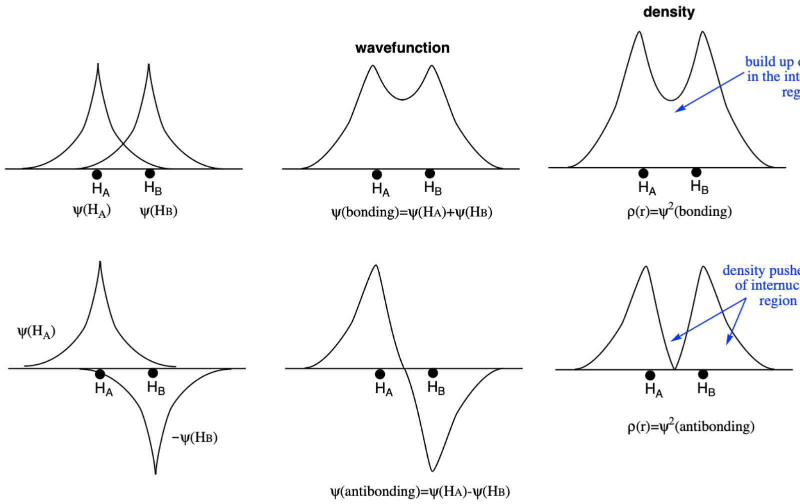

Figure 2 Images from your chemical bonding 114 course

- mathematically a MO is a **l**inear **c**ombination of **a**tomic **o**rbitals or LCAO
- The general formula is:

$$\psi_\Gamma = N(c_1\psi_1 + c_2\psi_2 + \cdots c_n\psi_n) = N\sum c_i\psi_i$$

  - Γ=symmetry label of the MO and N =normalisation factor
  - the c's (are numbers) that determine the *magnitude of the contribution* of each atomic orbital relative to the others
  - i is an index that runs over all the contributing atomic orbitals
  - *linear* means the AO functions are *only added or subtracted* (there are no exponents e^x or powers x^2 or other functional forms involved)
- when a calculation is carried out *the code is optimising the c's* for the molecular system, outputs of the calculation are the MOs and MO energies
  - however as you have seen we can estimate the c's and the energy very effectively qualitatively!
  - this allows us to avoid the complex mathematics involved in quantitatively solving the Schrödinger equation

important

- in this course we do not combine the AOs on different centres when drawing the MO diagrams,
  - we want to show the individual AO components because these tell us about the bonding within a molecule, **Figure 3**

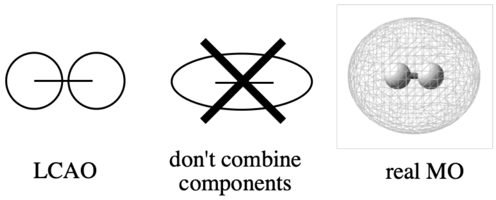
LCAO
don't combine components
real MO

Figure 3 leave AO components separate

  - in research we mostly *work backwards*, from the final MOs and energies to understand the overlap and interaction of fragment orbitals and thus obtain insight into the bonding within a molecule (more on this in a later lecture)

Molecular Orbital Mixing and the MO diagrams of C_2 and N_2

- The MO diagram we drew yesterday is an appropriate MO diagram for atoms with a large s-p gap such as O_2 and F_2 but not for the other second row diatomic molecules, C_2 or N_2 which exhibit **MO mixing**
- MO mixing occurs when certain MOs are allowed to interact to form a new bonding/antibonding pair

important

- **necessary** conditions for MO mixing to occur:
  - only MOs of the *same symmetry* can mix
  - MOs *cannot be from the same bonding-antibonding pair*
  - mixing *must stabilise the total energy of the molecule*
- mixing tends to be **large** or important when:
  - MOs are *close in energy*
  - *one* of the MOs is *non-bonding or unoccupied*
  - MOs are *in the HOMO-LUMO region*
- MOs that mix form a new bonding/antibonding pair.
- the *closer in energy* the stronger mixing between MOs
- MO mixing in a homonuclear diatomic
  - the MO pairs $2\sigma_g^+$ & $3\sigma_g^+$ and $2\sigma_u^-$ & $3\sigma_u^-$ have the same symmetry, and are not from the same bonding -antibonding pair, **Figure 4**
  - however these MO pairs are not close in energy and so mixing is weak.

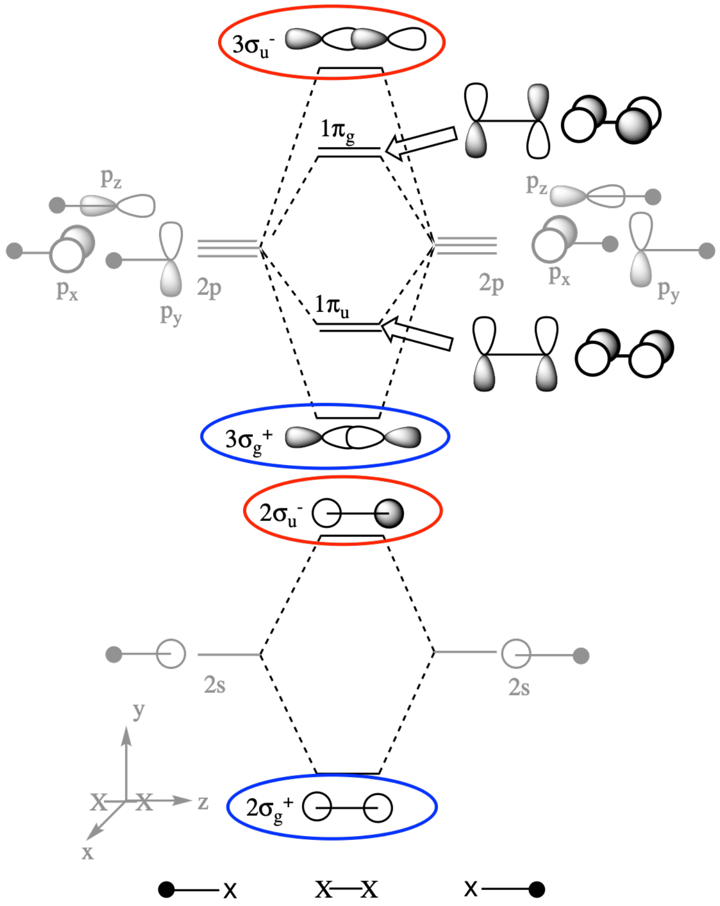

Figure 4 MO diagram showing the MOs that mix

- to mix MOs take them once "as is" and once with phase of one MO inverted
- lets start with the two σ_g orbitals and work out the effects of mixing
  - first draw the orbitals one on top of the other, then "add" the orbitals on a single atomic centre, **Figure 5**
  - remember that the shaded part of the orbital means the function describing the orbital is negative and the non-shaded (white) part of the orbital means the function describing the orbital is positive
  - combining (adding) positive parts “increases” the function (ie x+x=2x), combining the negative parts makes the function more negative (ie -x + -x = -2x), combining negative and positive parts cancels out (-x + x =0)

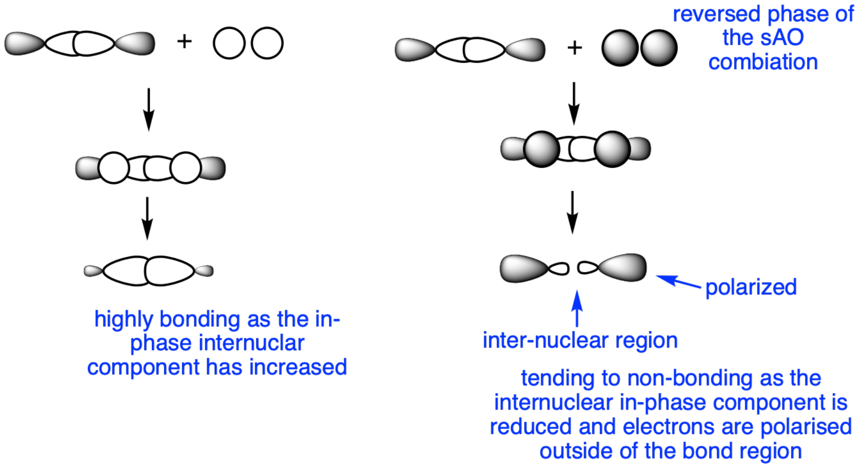

Figure 5 positive and negative combination of σ_g MOs

  - some of the resultant orbitals look very much like an "sp" hybrid orbitals because they are made from an s and p components
- next take the "negative" of one of the MOs, by taking the phase inverted MO and do the same again, **Figure 5**
  - the negative combination has decreased bonding character because there is less overlap of in-phase orbitals in the inter-nuclear region and a polarisation of orbital density out of the bonding region.
  - because we don't have a strong antibonding overlap in the inter-nuclear region, this is not a strongly antibonding orbital, this orbital is more *non-bonding* than antibonding.
  - the net effect of mixing has been to stabilise one mixed-MO while destabilising the other mixed-MO, MO mixing only occurs if the *overall electronic structure is stabilised*
- in **Figure 6** plots show how the "real" computed MOs look while the cartoons show the qualitative MOs

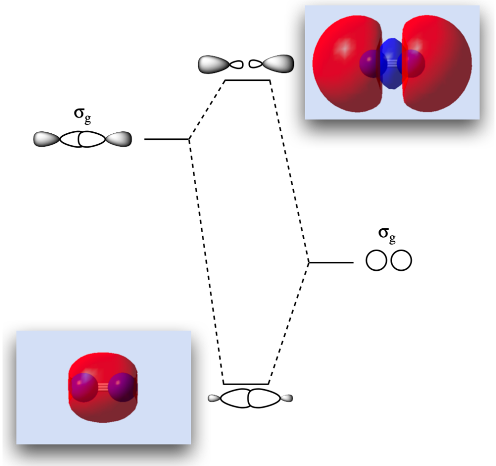

Figure 6 Mixing the σ_g orbitals

In-Class Activity P1

- your turn, you try mixing of the σ_u MOs, **Figure 7**

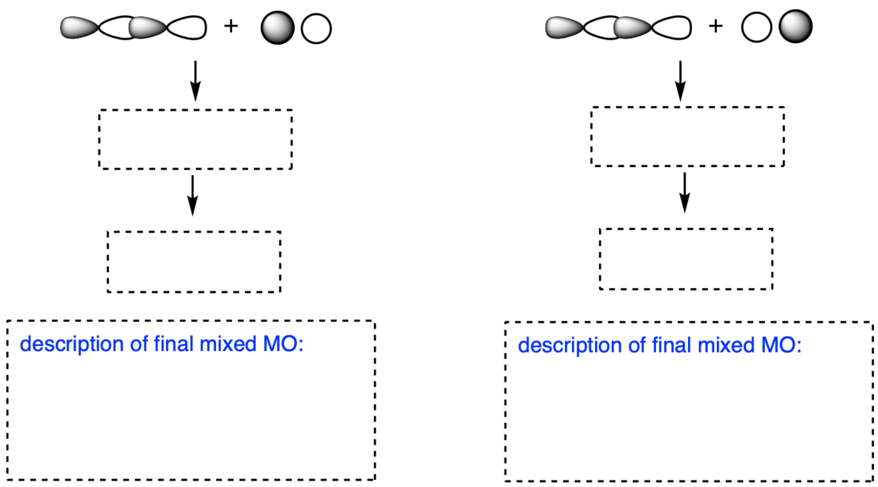

Figure 7 Mixing the σ_u orbitals

- now we need to consider the energy level shifts which orbital is the high energy one and which is the low energy one? This is shown in **Figure 8**
    - one orbital has gone from very antibonding to much less antibonding, this MO is now essentially non-bonding!
    - one orbital has strong antibonding interactions and is unoccupied, it has gone up in energy
    - here our predicted MO does not match the real MO particularly well, this can happen for very high energy MOs, other considerations besides overlap and interaction energy become important

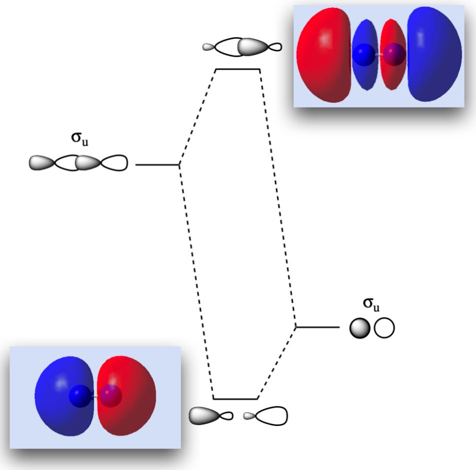

Figure 8 Mixing the σ_u orbitals

- the final qualitative MO diagram is shown in **Figure 9**
    - σ_g mixing MOs are shown in blue, σ_u mixing MOs are shown in red

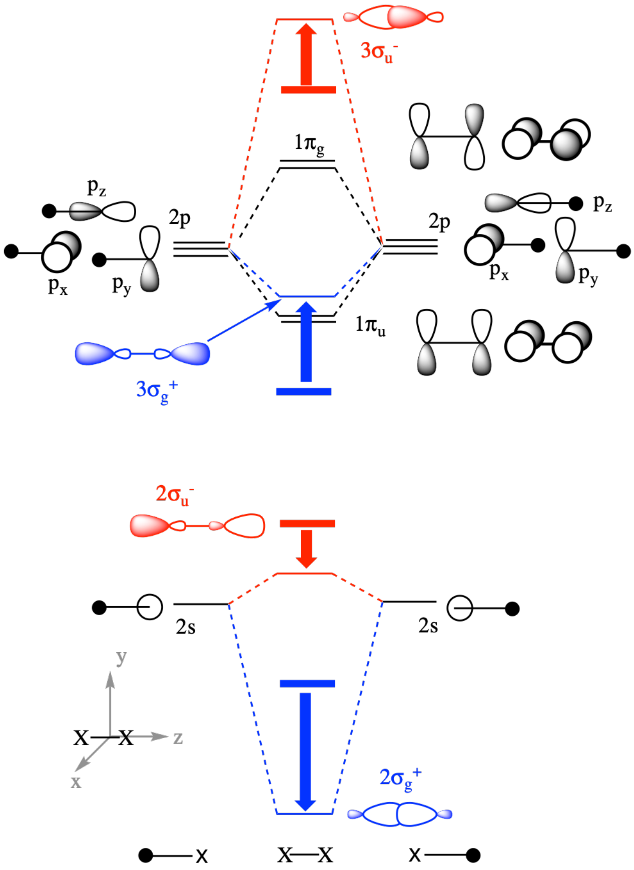

Figure 9 MO mixing diagram for homonuclear diatomic molecules

Periodic Trends for X_2 MO Diagrams

- molecules with the same type of valence orbitals have similar MO diagrams.
- thus a single MO diagram can provide qualitative information about the stability of related compounds
- differences do occur in terms of occupation and mixing
- for diatomic molecules the 2s-2p energy gap is very important, this "switches" mixing on/off, **Figure 10**
    - the sp-gap increases across the periodic table
    - in C_2 and N_2 the sp-gap is small enough for mixing
    - in O and F the sp-gap is too large for mixing to be significant
    - the "cross-over" of the $3\sigma_g$ and $1\pi_u$ occurs between O_2 and N_2 and this affects the valence electronic configuration of O_2 and N_2!

O_2 (12 valence electrons)	$(2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^2$
N_2 (10 valence electrons)	$(2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4 (3\sigma_g)^2$

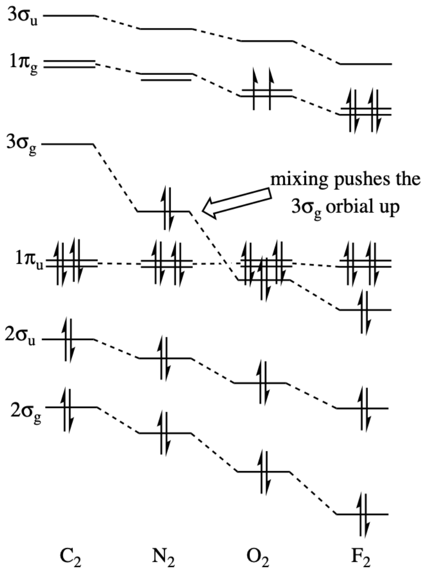

Figure 10 Variation in MO energies

Heteronuclear Diatomic Molecules

- heteronuclear diatomic molecules such as CO, $[CN]^-$ and NO have similar MO diagrams to homonuclear diatomic molecules
    - BUT the symmetry is reduced to $C_{\infty v}$ because the following symmetry operations/elements are gone: σ_h, i, ∞C_2 and S_∞^ϕ
    - due to the changing symmetry of MOs the MOs that mix also changes
    - BUT the FO energy levels are no-longer the same (degenerate)
    - the contributions of each FO to the MO also change

Fragment Orbital Energy Positioning

- placing energy levels is easier when you have an internal reference, for main group elements a *H 1sAO reference* is a good choice
- for atomic orbitals the *highest occupied AO energy* depends roughly on the electronegativity
    - the more electronegative the atom the lower (more negative) the orbital energies
    - electronegativity increases across a row of the periodic table, you are expected to know *ordering* of electronegativity shown in **Table 1**
    - an estimate for the energy levels for the highest occupied 2p AOs of the 2nd row elements, relative to the H 1sAO reference is made in **Figure 11**

important

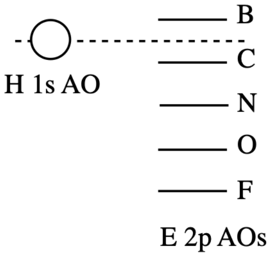

Figure 11 AO energy ordering

H	Li	Be	B	C	N	O	F
2.20	0.98	1.57	2.04	2.55	3.04	3.44	3.98
	Na	Mg	Al	Si	P	S	Cl
	0.93	1.31	1.61	1.90	2.19	2.58	3.16

Table 1 Pauling electronegativity of the first row elements

- other properties such as the ionization energy can be used to predict the relative position of AOs, these will be given to you if you need them.
- to determine the position of the 2sAOs we need to combine information from the relative energy of the 2pAOs with the size of the 2s-2p energy gap (which we already know increases substantially along the row)
  - this tends to mean that the 2s AOs will interact only if the atoms are *directly adjacent to each other* in the periodic table
- the 2pAOs always interact
- for example consider $[CN]^-$, **Figure 12**
  - first set-up one side of the MO diagram, place your H 1sAO reference
  - evaluate C first: the C is more electronegative than H, so the C2p is lower than the H 1sAO
  - C has a relatively small sp-gap,
  - then evaluate the position of the other fragments using the C orbital energies as a guide
  - N is more electronegative than C so the N2p lies below the C2p
  - N has a larger sp-gap than C
  - then evaluate if the 2s AOs will interact, C and N are adjacent on the periodic table so their 2s AOs will interact

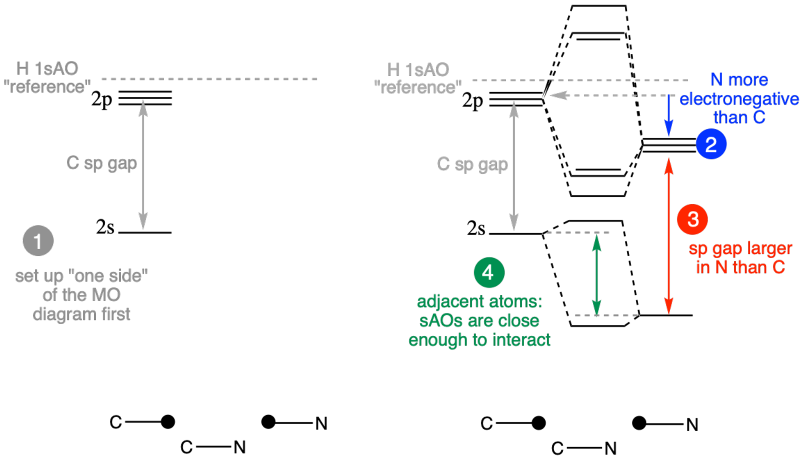

Figure 12 Effects of relative electronegativity and increasing sp gap

In-Class Activity P2

- Do the 2sAOs of NO interact?
- Do the 2sAOs of CO interact?

Orbital Size in a MO diagram

important

- so far we have seen degenerate FOs where each FO contributes the same amount to a MO
- when the contributing FO energy levels are different, **Figure 13**
  - the more stable (lower energy) FO makes a larger contribution to the bonding MO
  - the less stable (higher energy) FO makes a larger contribution to the antibonding MO
- this makes sense, the more stable FO will stabilise the MO more, and vice versa for the least stable FO

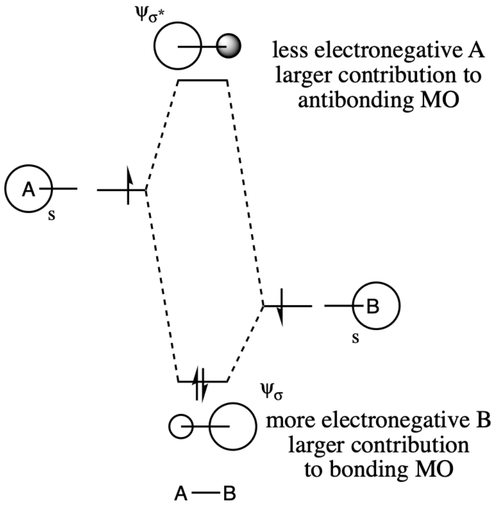

Figure 13 different AO contributions

In Class Problem P2

- **P2a** draw the MO diagram for N_2
- **P2b** use your MO diagram to explain why N_2 is so stable
- **P2c** use your MO diagram to help you rank N_2, $[N_2]^-$, $[N_2]^+$ and $[N_2]^{2+}$ in order of stability.

Key Points

- be able to explain the acronym LCAO, give the general equation, describe each of the components and illustrate the process on a diagram
- be able to describe and illustrate MO mixing
- be able to draw MO diagrams for diatomic molecules that exhibit mixing
- be able to use the MO diagram to interpret or discuss the electronic structure and bonding in a diatomic molecule
- be able to rationalise the relative position of fragment orbital energy levels
- be able to draw a MO diagram for a heteronuclear diatomic XX'
- be able to explain and predict the relative size of AO contributions to MOs

Self-study Problems / Test Preparation

- **Q1** produce a "sketch" diagram such as that shown in **Figure 12** 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.
- **Q3** draw a MO diagram for CO include annotations to explain your reasoning, give the electronic configuration of CO
- **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!*)
- **Q5** Below is a photoelectron spectrum of N_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. Use your MO diagram for N_2 to discuss and explain key features of the photoelectric spectrum of N_2.

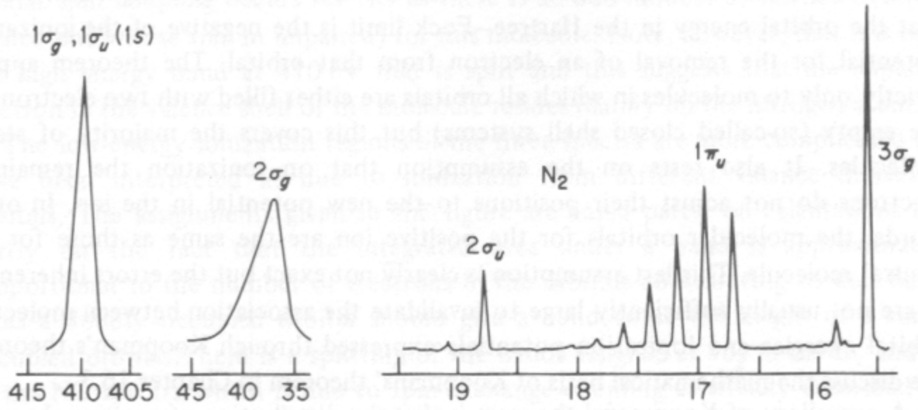

Figure 14 PES of N_2