The Diatomic MO Diagram: Part1

Introduction

- Molecular Orbital (MO) theory supersedes valence bond theory (main group elements), crystal field theory (transition metal and organometallic chemistry) and ad-hoc bonding models. MO theory is one way to think about bonding in solids.
- in this lecture we will go through forming the MO diagram for a homonuclear diatomic molecule together.
- in later lectures I will come back and explain individual steps in more detail
- we are also going to look into how accurate MO theory actually is by comparing our O_2 MO diagram to calculations and experimental data
- I will outline PES photo-electron spectroscopy and how the MO diagram relates to a PES spectrum

What is a Molecular Orbital (MO) Diagram?

- a MO diagram shows how the atomic orbitals of component atoms interact to form the bonding/antibonding MOs of a molecule, **Figure 1**.
- individual MOs describe the "bonding" between different atoms (or groups) within a molecule.
- the MOs together form the basis of the electronic structure of a molecule.
- today we are going to build the MO diagram shown in **Figure 1**

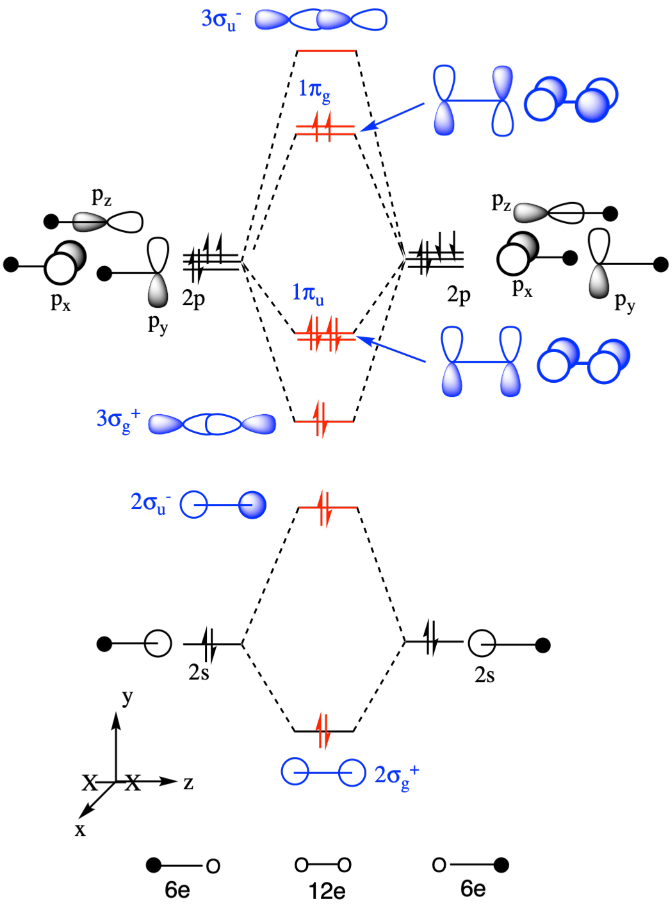

Figure 1 MO diagram for a O_2

MO Diagram Components

- **Figure 1** is an example of a MO diagram
    - the vertical "axis" of the whole diagram is **energy** the short horizontal lines represent relative **energy levels**
    - the horizontal axis contains the molecular **fragments** on the sides. In the case of a simple diatomic the fragments are atoms, the fragments combine to form the molecule in the centre
    - black= **fragment orbitals (FOs)** and fragment energy levels
    - blue= **molecular orbitals (MOs)** with symmetry labels
    - red= MO **energy levels** and **electrons** (small up-down arrows)
    - thus the energy part of the diagram is just a more complex version of the filling of atomic energy levels for atoms

- we use MO diagrams to understand bonding, for even the simplest of molecules!
    - For example the VSEPR picture of O_2 has no unpaired electrons, yet experimentally (liquid) O_2 is found to be paramagnetic **Figure 2** indicating that there are unpaired electrons!
    - MO theory naturally and easily explains why liquid oxygen is paramagnetic, we have unpaired electrons in a degenerate orbital set.

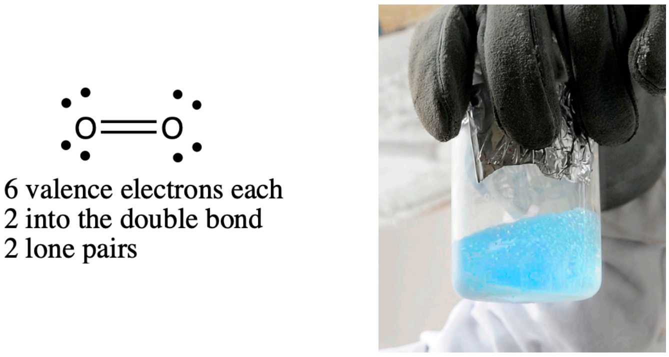
6 valence electrons each
2 into the double bond
2 lone pairs

Figure 2 VSEPR for O_2 and liquid oxygen[1]

important

MO diagram check list

- over the years I've developed a MO diagram checklist to help students with making MO diagrams
- this is important because the focus of this course is to understand and be able to carry out the process of forming MO diagrams, not in memorising MO diagrams for a few specific examples.
- this has an advantage that when faced with a new challenging molecule, you know the process to be applied.

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[1] U.S. Air Force photo/Staff Sgt. Jim Araos, image in the public domain.

- **The MO diagram checklist**
  1. determine the molecular shape and identify the point group
  2. define the axial system identify the symmetry operations
  3. identify the chemical fragments; put them on the bottom of the diagram
  4. determine the energy levels and symmetry labels of the fragment orbitals (use H1s AO as a reference level)
  5. combine fragment orbitals of the same symmetry, sketch out the MOs and analyse the bonding/antibonding character
  6. estimate the splitting energy for each MO pair, draw in the MO energy levels and MOs (in pencil!)
  7. determine the number of electrons in each fragment and hence the central MO region; add them to the diagram
  8. identify if any MO mixing occurs, determine the mixed orbitals, redraw the mixed MOs with shifted energy levels
  9. annotate the MO diagram
  10. use your MO diagram to understand the structure, bonding and chemistry of the molecule

Setting up a MO diagram

- determine the molecular shape and identify the point group
  - this is already done for us today!
  - our molecule is linear and the point group is $D_{\infty h}$
- define the axial system find all of the symmetry operations

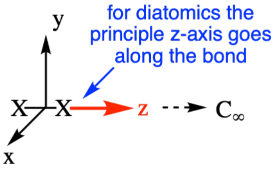


Figure 3 Diatomic axis orientation

important

  - *always add an axial system diagram to an MO diagram*
  - the highest rotation axis, this is the z-axis, $D_{\infty h}$ this will be the C_∞ axis
  - for diatomic molecules always put the z-axis along the bond, **Figure 3**
  - we identified all the symetry elements for linear molecules last lecture
- now we need to add the fragments along the bottom, **Figure 4**
  - draw the structure of the whole molecule on each side, explicitly write in the fragment atoms and leave **place holders** for the other atoms
  - put the molecule in the center bottom

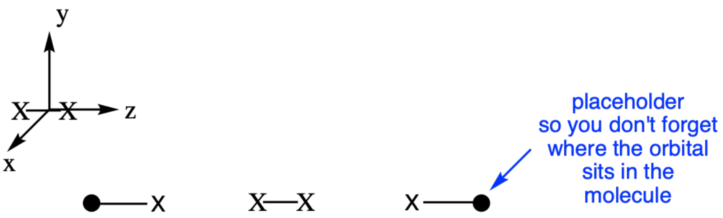


Figure 4 Starting the MO diagram

Positioning of the Fragment Orbital Energy Levels

- put in the energy levels for the fragments on each side of the diagram, in the case of a diatomic molecule these are the AOs
- MO diagrams, are "valence" MO diagrams
  - we leave off the core 1s AOs
  - for second row diatomic molecules this leaves the 2s and 2p AOs
- how large do we make the gap between the s and p AOs?
  - *the s-p energy gap increases substantially along the row*, **Figure 5**
  - in C the 2s-2p energy gap is small, this is why C forms sp hybrids
  - for *all the other elements* to the right of C the 2s-2p energy gap is large
  - for this diagram lets assume X= N, O or F

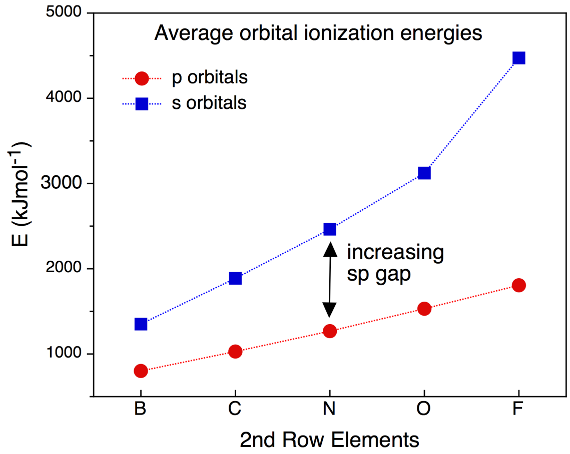
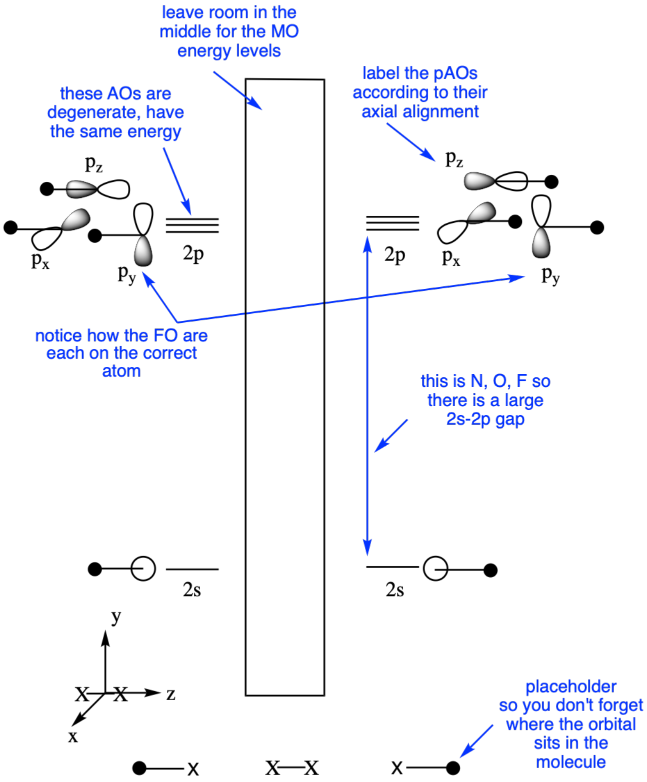


Figure 5 sp-gap across the second row

- in an atom the $2p_x$, $2p_y$ and $2p_z$ AOs are *degenerate*, this is represented by putting the energy lines for each AO very close together
- because the atoms in the X_2 diatomic are the same the energy levels for each fragment will be the same
- place the fragment (atomic) energy levels and the orbitals, add the symmetry labels for the orbitals, **Figure 6**



leave room in the middle for the MO energy levels

these AOs are degenerate, have the same energy

label the pAOs according to their axial alignment

notice how the FO are each on the correct atom

this is N, O, F so there is a large 2s-2p gap

placeholder so you don't forget where the orbital sits in the molecule

Figure 6 Starting the MO diagram

important

Form the Molecular Orbitals 1

- **first work out the MOs** from this we will assess their interactions to determine the energy splitting for the final MO energy levels
- make sketches of the MOs **in a separate place**
  - do not try putting these directly onto the diagram, I have discovered that students make too many mistakes! First work out the orbitals as described in the following.
- a couple of "rules"
  - we allow orbitals of the same symmetry and close in energy to interact (more details on this in a later lecture)
  - FOs (atomic orbitals in this case) interact only once
- form a bonding/antibonding pair for the FOs that interact
  - take orbitals of one fragment and "add" them to the orbitals of the other fragment, do this once "as is", and once with the phase of all components of one fragment reversed
  - inverting the phase is that same as adding the negative of the orbital
  - **bonding** is when two orbitals have the *same phase in their overlap region* (are in-phase)
  - **antibonding** is when the overlapping orbitals have *opposite phase* (are out-of-phase)
  - this process is shown for the sAOs in **Figure 8**

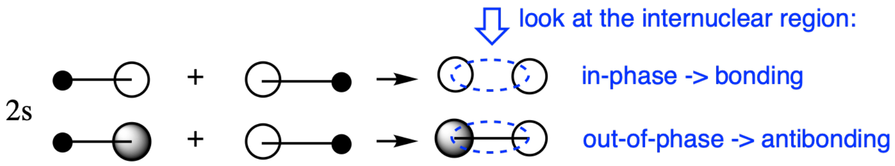


Figure 7 Combining AOs to form MOs

In-Class Activity P1

- complete the diagrams showing how the p_z AOs “along the bond” combine in a bonding and antibonding pair
- label the internuclear region for the in-phase bonding and out-of-phase antibonding MOs

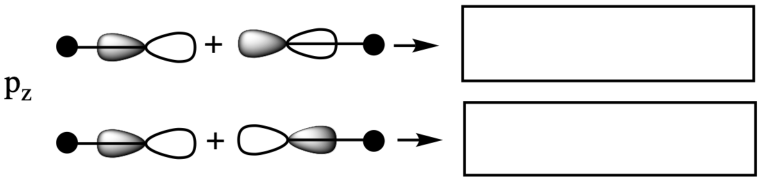


Figure 8 Combining AOs to form MOs

Form the Molecular Orbitals 2

- the p_x and p_y AOs are "perpendicular to the bond"
    - these orbitals also combine in bonding and antibonding pairs (two p_x orbitals and then $2p_y$ orbitals)
    - the overlap for side-by-side orbitals is weaker and often we don't show the overlap explicitly, but it is assumed!
    - this feature underlies the "rule" from organic chemistry that π bonds are weaker than σ bonds
- the formation of the MOs based on the p_y AOs is shown in **Figure 9**
- p_x and p_y based MOs remain degenerate, they have the same energy

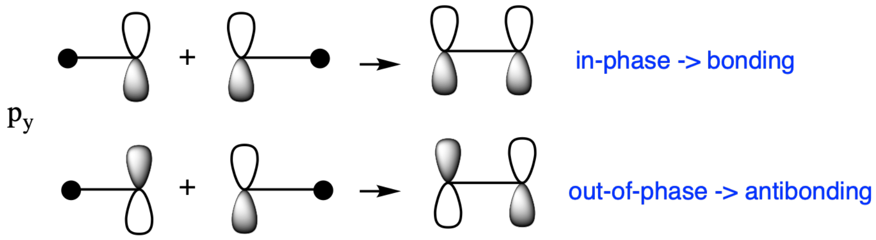


Figure 9 Combining AOs to form MOs

- the p_x AOs are more difficult to draw, especially if your art skills are not strong, because they come out of the plane of the page
    - it is possible to draw the p_x AOs slightly rotated, but a better representation is shown in **Figure 10**

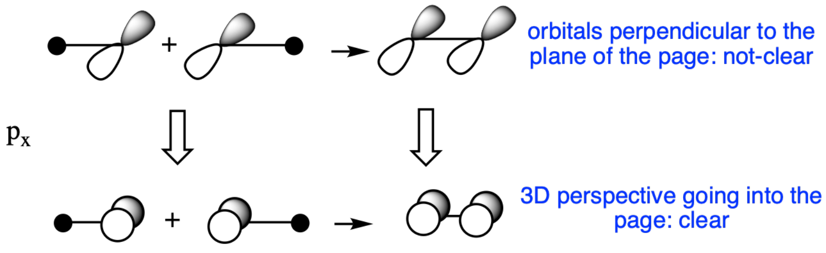


Figure 10 Drawing pAOs that go into the page

- the p_x AOs then combine as shown in **Figure 11**

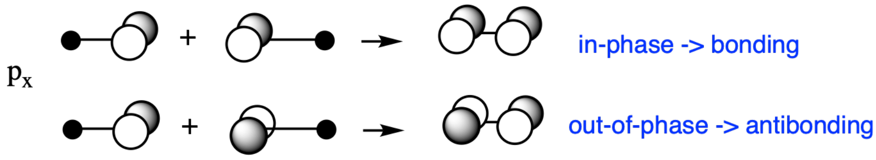


Figure 11 Combining AOs to form MOs

Determine the Splitting Energy of the MOs

- next we determine the size of the splitting energy (ΔE) between the bonding and antibonding MOs
- we will cover this in more detail in a later lecture, however to get us started there are some general rules of thumb for evaluating the splitting energy
    - sAOs have a large to moderate splitting energy
    - pAOs have strong direct end on overlap and a large splitting
    - pAOs with weak side-on overlap have only a small splitting

important

important

- antibonding orbitals are always destabilised more than bonding orbitals are stablised
- now we are ready to add the MOs to the MO diagram! **Figure 12**
  - decide on the 2sAO based MO splitting then use this as a *reference*
  - the 2s AOs combine in a bonding and antibonding pair with a *moderate splitting*, the 2s AOs are so deep in energy that the bonding and antibonding pair still lie below the p AOs orbitals
  - the $2p_z$ AOs have combined, and have strong (end on) overlap so they have a *very large splitting*, they form they σ MOs
  - the $2p_x$ and $2p_y$ AOs have poor side-on overlap and so they have significantly *smaller splitting*, they form the π MOs
  - the $2p_x$ and $2p_y$ AOs are very similar, they have the same kind of symmetry (π) and remain degenerate when they form MOs

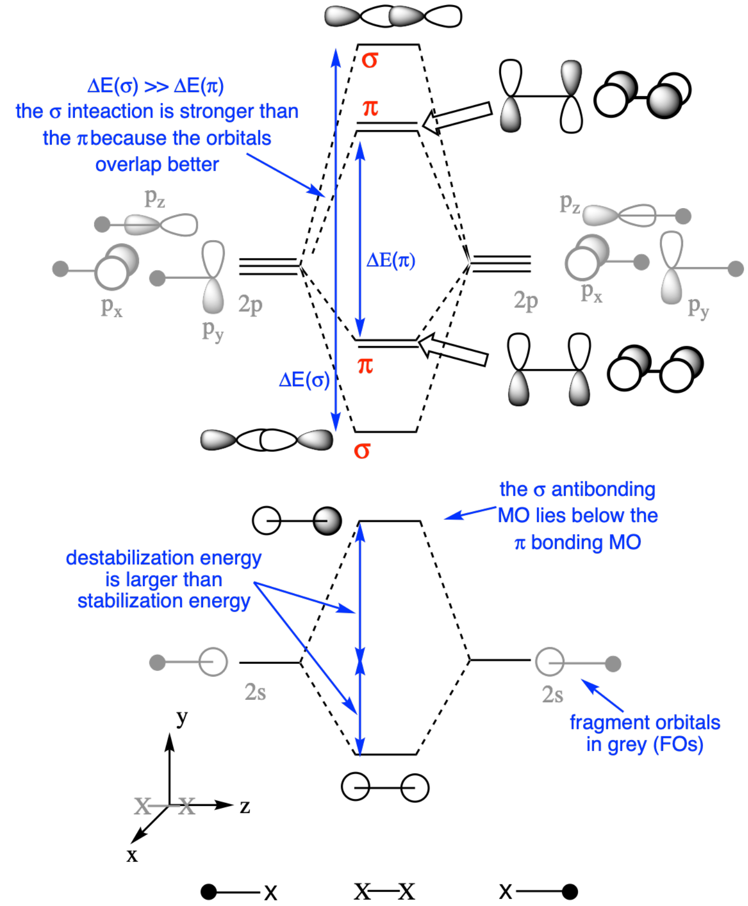


Figure 12 Adding MOs to the diagram

Determine the Symmetry of the MOs

- next we need to label the symmetry of the orbitals
  - there are no atoms on the CoM so we cannot use the direct AO way of assigning the symmetry,
  - we need to use the "pattern" method or resort to the representation table
  - we can also use our general knowledge of symmetry
- first distinguish between σ and π
  - orbitals symmetric around the C_∞ axis are σ-orbitals, **Figure 13**
  - any rotation of a σ-orbital around the bond axis must map onto itself
  - π-orbitals have a phase change on a 180° rotation around the bond axis

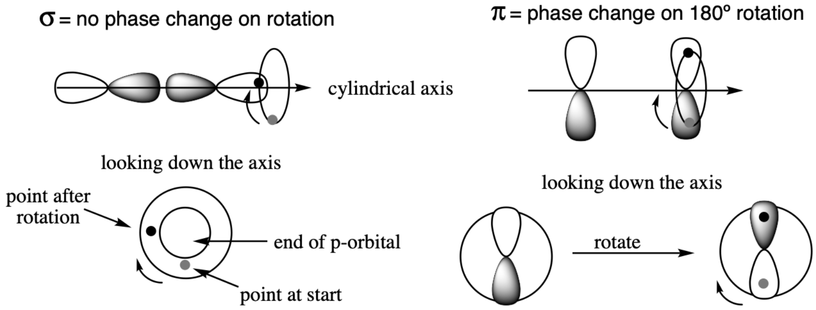


Figure 13 σ and π symmetry

- determine the "u" and "g" **Figure 14**
  - g=gerade orbitals, same phase on inversion
  - u=ungerade orbitals change phase on inversion

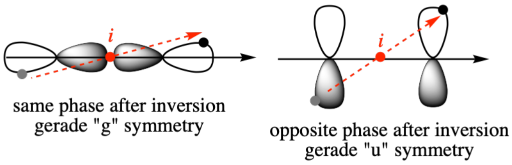


Figure 14 inversion symmetry

- MOs can also be "+" or "-" **Figure 15**
  - this relates to the change in phase under a C_2 axis perpendicular to C_∞
  - \+ orbitals have the same phase on rotation
  - \- orbitals change phase on rotation

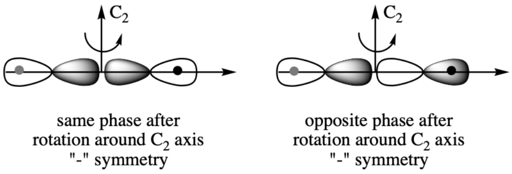
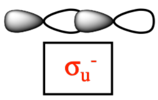


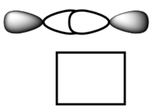
Figure 15 C_2 rotation symmetry

In-Class Activity P2

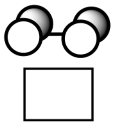
- determine the full symmetry label for the following MOs, I have done the first example for you.



symmetry
C_∞ rotation: σ
inversion: u
C_2 rotation: -



symmetry
C_∞ rotation:
inversion:
C_2 rotation:

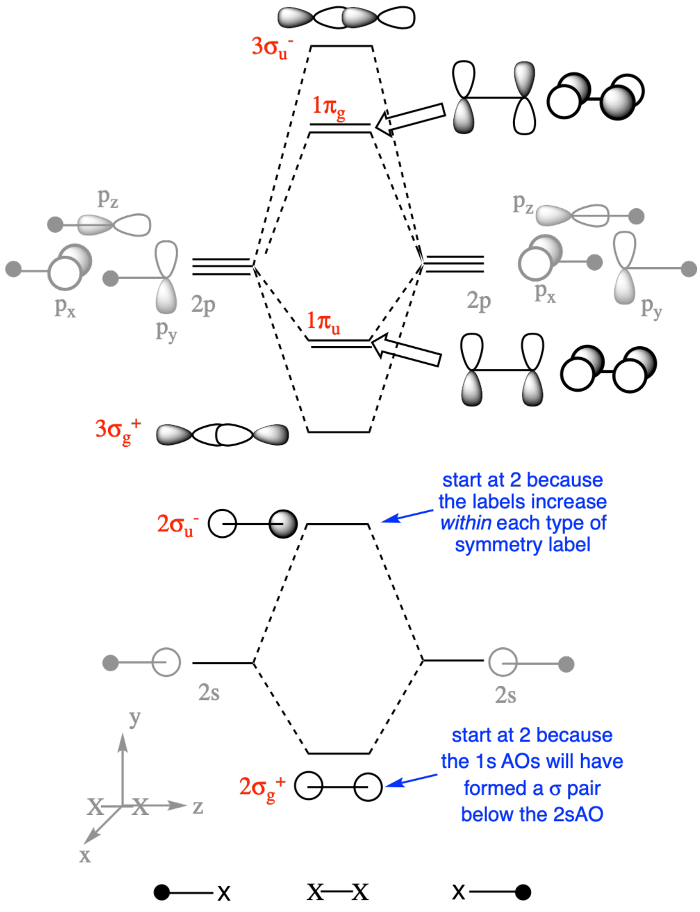


symmetry
C_∞ rotation:
inversion:
C_2 rotation:

Figure 16 Combining AOs to form MOs

Labelling the MOs

- now the symmetry of all the MOs can be labelled, **Figure 17**
  - to distinguish individual orbitals of the same symmetry, *within each symmetry type*, each orbital is labelled incrementally eg 1, 2, 3 …
  - the 1s AOs not shown on the diagram form the $1\sigma_g$ and $1\sigma_u$ pair, thus the first orbital is labelled $2\sigma_g^+$ and the first σ_u MO is labelled $2\sigma_u^-$
  - sometimes in text books orbitals will have a "star" eg σ* or π* which indicates an antibonding orbital, the * technically *only* applies to diatomic molecules, *do not use the * notation* (you will see why in a future lecture!)



start at 2 because the labels increase *within* each type of symmetry label

start at 2 because the 1s AOs will have formed a σ pair below the 2sAO

Figure 17 Labelling the MOs

important

Add the Electrons

- now we add in the electrons depending on the exact X, this MO diagram is suitable for X= O, F and as a starting point for X=C, N
- one of the advantages of MO diagrams is that they can be used (with small adjustments) for multiple molecules
- lets assume that X=O and this is oxygen gas O_2 **Figure 18**
- fill in the electrons for the fragments: O has an electronic configuration $1s^2 2s^2 2p^4$, and as this is a valence MO diagram we add 6e each side
- then fill up the central MOs we have 12e overall for the whole MO diagram
- the filling of the energy levels (on both fragments and central molecule) follows both the Pauli exclusion principal and Hund's rule.

- each AO/MO is filled from the lowest energy up and holds only ever a maximum of two electrons of opposite spin.
- if orbitals are degenerate fill them with parallel spin electrons until they are half-fill, and then start pairing the electrons.

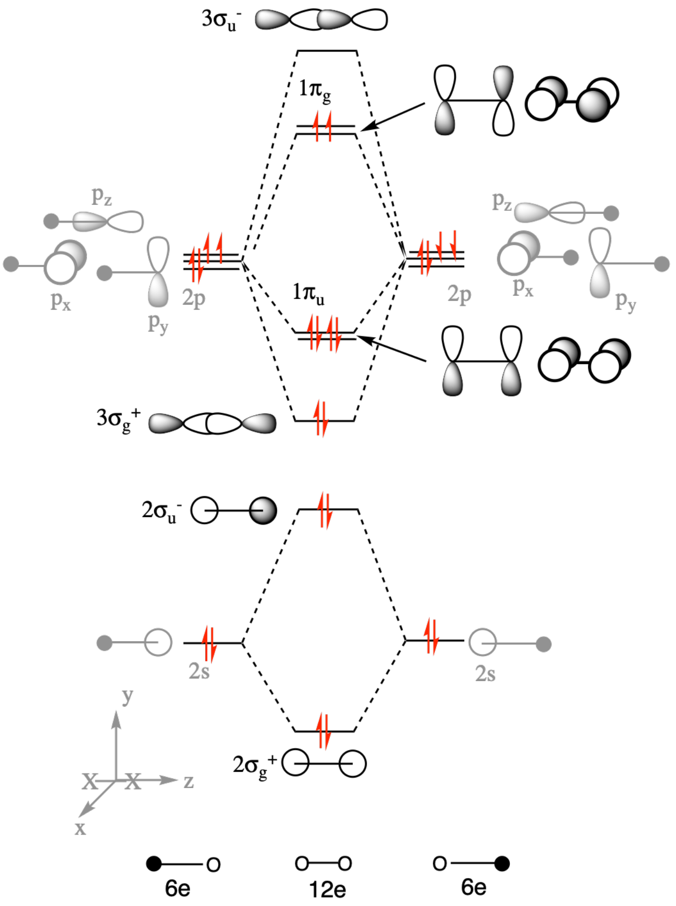
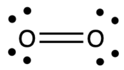


Figure 18 Filling in the electrons

Using the MO Diagram to Understand Bonding

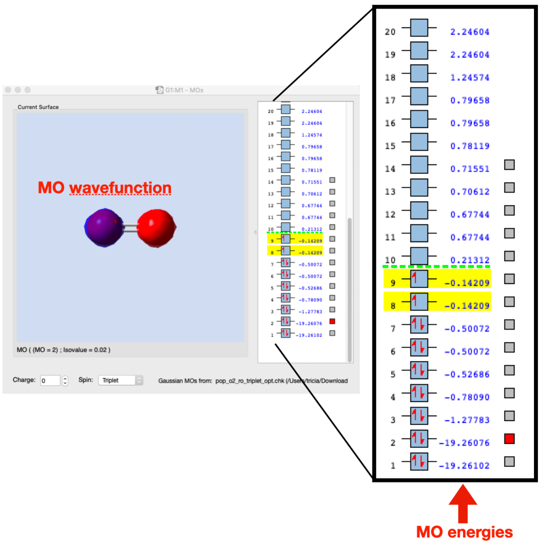


6 valence electrons each
2 into the double bond
2 lone pairs

- we are now at the key stage of MO theory, using the MO diagram to understand bonding
- at the beginning of the lecture we noted that the VSEPR theory of bonding predicted that O^2 should be diamagnetic with all electrons spin paired in bonds or as lone pairs
- however experimentally (liquid) O_2 is found to be paramagnetic, under the influence of a magnetic field the electrons align creating their own induced magnetic field, for this to occur the molecule must have *unpaired electrons*
- we can see easily from this MO diagram that O_2 does have unpaired electrons! The highest occupied MOs (HOMOs) are a degenerate set of π MOs, which are only partially occupied with a pair of electrons which by Hund's rules remain unpaired.
- VSEPR theory is an excellent method to make a *first guess* at molecular structure and bonding, however this should always be followed up with MO theory as the *more accurate* representation of bonding

How Realistic are the MOs?

- pen-and-paper MO diagrams are *qualitative*, they provide a good approximation for full MO theory
- to accurately establish the bonding we must carry out a *calculation* solving the **molecular Schrödinger equation**
- in forming the qualitative MO diagram we are "solving" the Schrödinger equation *without any maths*!!!
- I have run a calculation on O_2 (B3LYP/6-311G(d,p) level) and we can look at the results, **Figure 19** shows an output of the MO energies



MO ((MO = 2) ; Isovalue = 0.02)

Charge: 0 Spin: Triplet Gaussian MOs from: pop_o2_ro_triplet_opt.chk (/Users/tricia/Download

```
20  2.24604
19  2.24604
18  1.24574
17  0.79658
16  0.79658
15  0.78119
14  0.71551
13  0.70612
12  0.67744
11  0.67744
10  0.21312
 9 -0.14209
 8 -0.14209
 7 -0.50072
 6 -0.50072
 5 -0.52686
 4 -0.78090
 3 -1.27783
 2 -19.26076
 1 -19.26102
```

Figure 19 output of MO energies from a calculation

  - the energies are in atomic units or Hartree, a conversion is 1au=2625.5 kJ/mol or reversing this 1 kJ/mol=0.00038=$3.8*10^{-4}$ au
  - the energies at ≈-19au are very deep, you can see why we only form a valence MO diagram, most valence energies occur around ±1au

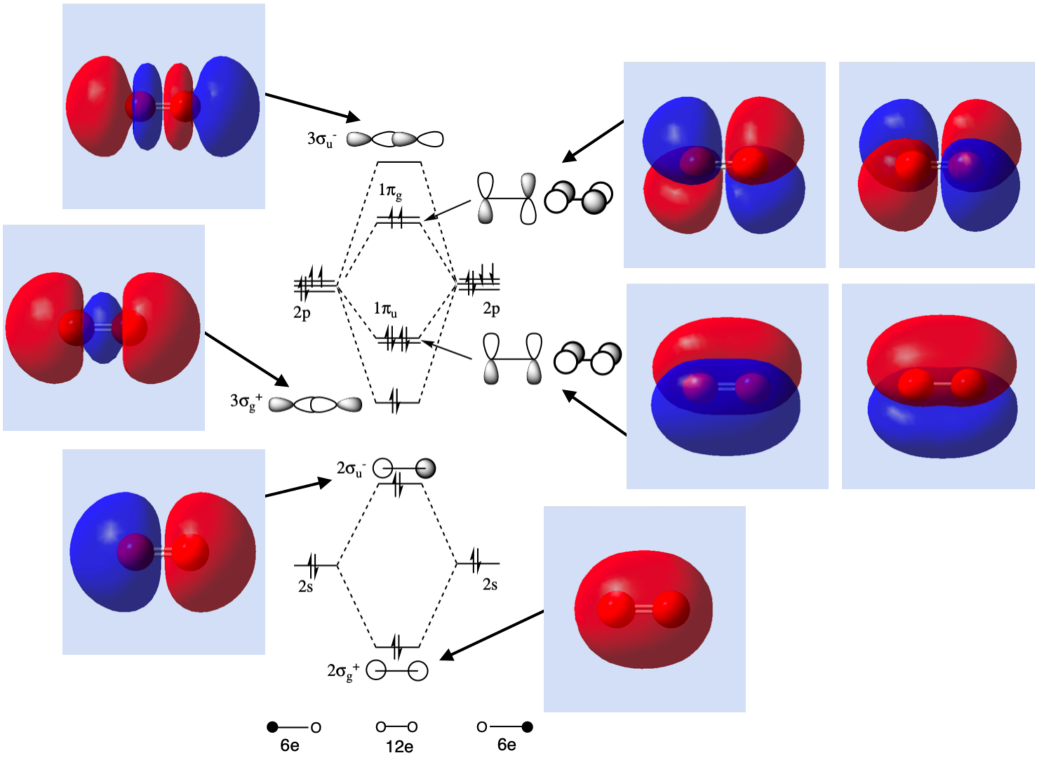


Figure 20 MO wavefunctions matched to those predicted using a qualitative MO diagram

- **Figure 20** shows the output MOs matched against the MO shapes we have predicted by forming a qualitative MO diagram, our predictions are very good!

Photoelectron Spectroscopy (PES)

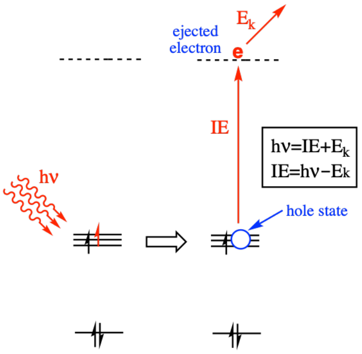


Figure 21 photo-electron process

- we can compare the qualitative (and computed) energy ordering of the MOs to experimental data
- photoelectron spectroscopy uses high energy light to eject an electron from a molecule or atom (M)
    - the process is $M + h\nu \rightarrow M^+ + e$ (h=planks constant, ν=frequency)
- photoelectron spectroscopy measures the distribution of kinetic energy of the ejected electrons, **Figure 21**
    - the energy required to eject the electron is the ionization energy (IE)
    - excess energy is in the kinetic energy (E_k) of the ejected electron
    - and from this we can determine the ionization energy $IE = h\nu - E_k$
- the IE gives us the "energy level" for each MO in a molecule
- the photoelectron spectrum (PES) of O_2 **Figure 22** shows 3 peaks in the positions we expect for the higher energy MOs, these peaks also show significant vibrational fine structure

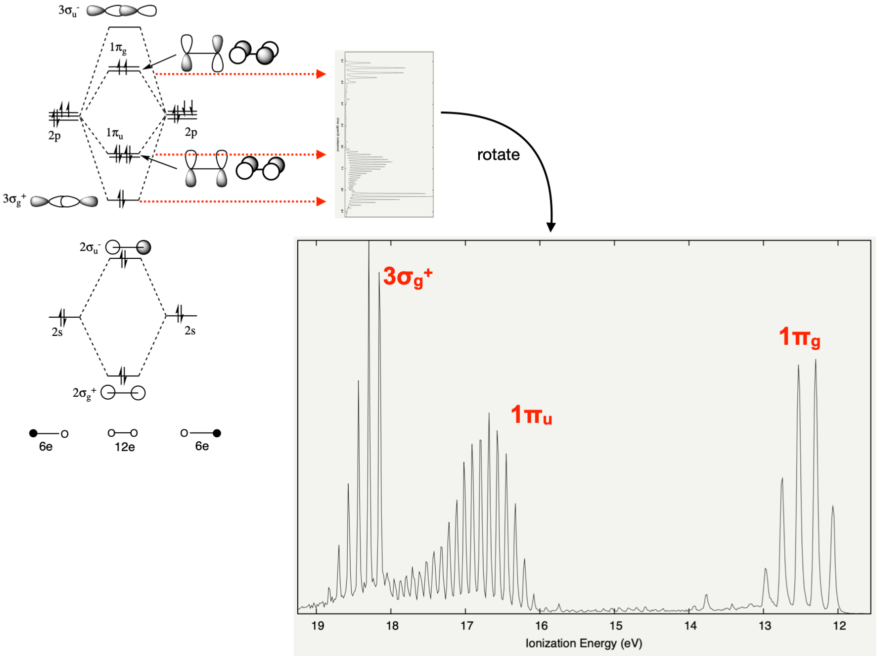


Figure 22 Relating MO diagram of O_2 to the PES

- vibrational fine structure often appears on IE peaks
    - this occurs when M^+ is formed in a vibrationally excited state
    - removal of an electron from a strongly bonding or antibonding MO can cause large changes in bond length
    - this shifts the excited state PES and consequently generates extensive vibrational fine structure, **Figure 23**

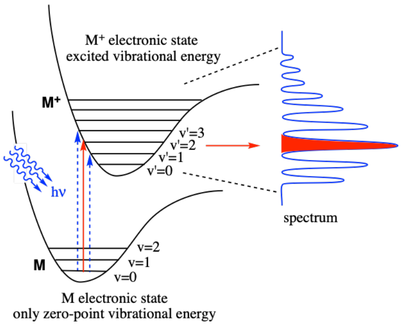


Figure 23 vibrational fine structure

Key Points

- be able to write down the MO checklist
- be able to draw a MO diagram for a homonuclear diatomic X_2
- be able to discuss how the 2s-2p energy gap changes across the first row and be able to use this knowledge in constructing MO diagrams
- be able to evaluate, discuss and illustrate bonding and antibonding MOs
- be able to evaluate, discuss and illustrate the splitting energy
- be able to determine and explain the symmetry of MOs
- be able to recognise the accuracy of qualitative MO diagrams relative to full MO theory
- be able to describe how a PES is generated and to discuss the origin of vibrational fine structure
- be able to interpret a PES in terms of a MO diagram, and alternatively be able to predict the PES of a molecule from knowledge of the MO diagram

Self-study Problems / Test Preparation

- **Q1** draw the MO diagram for F_2
- **Q2** draw the MO diagram for He_2, and use it as a basis to discuss the electronic structure of $[He_2]^+$ and $[He_2]^-$. Use your MO diagram to rationalize which of these diatomic molecules is stable. Identify if each molecule will be diamagnetic or paramagnetic.
- **Q3** using the MO diagram 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)