Molecular Orbital Diagram for a Homonuclear Diatomic

- The point group for the molecule
  - symmetric linear molecules have $D_{\infty h}$ symmetry
  - on the flow chart
    1. is the molecule linear? YES
    2. is there a center of inversion? YES
  - where does the "infinity" come from? The infinite number of possible rotation axes, Figure 1
  - where does the "h" come from? The mirror plane perpendicular to the highest axes of symmetry (the infinity axis)
  - $D_{\infty h}$ symmetry is special in that there is also an infinite number of $C_2$ axes perpendicular to the principle axis, and an infinite number of mirror planes aligned with the principle axis

![Figure 1](image)

- we also need to consider the centre of inversion in this molecule
- this is where g (gerade) and u (ungerade) labels come from, Figure 2
- the symmetry is gerade when there is no change in on moving from one side of the inversion point to the other ie from (+x, +y, +z) to (-x, -y, -z)
- the symmetry is ungerade when there is a change in phase on moving from one side of the inversion point to the other

- setting up the diagram
  - start by considering the axial definition
  - always put the z-axis along the bond in diatomics, Figure 3
  - always add a diagram clearly showing how the axial system related to your molecule on your MO diagram
  - then start the diagram itself, remember the vertical "axis" of the whole diagram is energy and the horizontal axis are the fragments, atoms in the case of a simple diatomic
  - add the molecule in the centre at the bottom, and the individual atomic fragments either side, don't forget to add placeholders so that you know where the orbitals should "sit", see Figure 4
• now you need the atomic orbitals, **Figure 4**
  o the 1s AOs are not shown, generally only the valence orbitals are shown in MO diagrams.
  o for C the gap between the 2s and 2p orbitals is small, this is why C forms sp hybrids
  o however for all the other elements to the right of C such as N, O, F the sp gap is larger and gets increases long the periodic table, thus for F the gap is very large
  o put the 2s and 2p AOs on the diagram taking note of the distance between the energy levels

![Diagram](image)

**Figure 4** Starting the MO diagram

• now form the molecular orbitals
  o when forming a bonding antibonding pair always combine the AOs once "as is" and once "out of phase" ie with one orbital "reversed", **Figure 6**
  o the $p_z$ AOs “along the bond” combine in a bonding and antibonding pair

![Diagram](image)
Figure 5 Combining AOs to form MOs

- the $p_x$ and $p_y$ AOs "perpendicular to the bond" orbitals combine in a bonding and antibonding pairs (two $p_x$ orbitals and then $2p_y$ orbitals), Figure 6

- the $p_x$ and $p_y$ based MOs remain degenerate, this means they have the same energy, I've only shown one of this set of the MOs in Figure 6

$$\begin{align*}
\begin{array}{c}
\text{in-phase $\rightarrow$ bonding} \\
\begin{array}{c}
\hspace{0.5cm}
\end{array}
\end{array}
\end{align*}$$

Figure 6 Combining AOs to form MOs

- **first** decide the relative energy splitting and **then** put the MOs on the diagram, Figure 7

- the 2s AOs combine in a bonding and antibonding pair, the 2s AOs are so deep in energy that the bonding and antibonding pair still lie below the p AOs orbitals. Nevertheless the splitting will be large because these are sAOs.

- the 2p_z AOs have combined, and have strong (end on) overlap so they have a large energy splitting, they form they $\sigma$ MOs

- the 2p_x and 2p_y AOs have poor (side by side) overlap and so they have a significantly smaller energy splitting, they form the $\pi$ MOs

- these two orbitals are also very similar, they have the same kind of symmetry and remain degenerate when they form a MO, we represent this as a double line as shown on Figure 7
how do I know what symmetry to label the orbitals?

- orbitals symmetric around the C\(_\infty\) axis are \(\sigma\)-orbitals, Figure 8
- any rotation of a \(\sigma\)-orbital down the bond axis maps it onto itself
- \(\pi\)-orbitals have a phase change on a 180º rotation around the bond axis

then the "u" and the "g" relate to the inversion symmetry of the orbitals, go back and have a look at, Figure 2
- each orbital is labelled according to its symmetry, and within each symmetry type each orbital is labelled incrementally eg 1, 2, 3 … as shown in Figure 9
- the first orbital is labelled 2\(\sigma_g\) because of the \(\sigma_g\) and \(\sigma_u^*\) MOs formed from the 1s AOs form 1\(\sigma_g\) and 1\(\sigma_u^*\) which are not shown on a valence MO diagram.
- sometimes orbitals have a "star" which indicates an antibonding orbital, this does not relate to the symmetry so does not initiate a new numbering sequence.
• Figure 9 is appropriate for $F_2$ and $O_2$ but not for the other first row diatomics, such as $C_2$ or $N_2$, these molecules exhibit MO mixing, which we revise now.

• MO mixing
  o MOs that have the same symmetry label (but are NOT from the same bonding-antibonding pair) can "mix" and form a new bonding and antibonding combination.
  o "mixing" in this sense applies ONLY to molecular orbitals
  o in the homonuclear diatomic there are two $\sigma_g$ and two $\sigma_u^*$ MOs with the same symmetry, but not from the same bonding-antibonding pair and thus they could mix, these are the MO pairs $2\sigma_g$ & $3\sigma_g$ and $2\sigma_u^*$ & $3\sigma_u^*$
  o the closer two orbitals are in energy the stronger they mix
  o these MO pairs are not particularly close in energy and so any mixing is expected to be rather weak.
  o to "mix" MOs take them once "as is" and once with one MO "phase inverted" to form two new mixed MOs
Figure 10 positive and negative combination of $\sigma_g$ MOs

- we will start by considering the two $\sigma_g$ orbitals as shown in Figure 10. Draw the orbitals one on top of the other, then "add" the orbitals on a single atomic centre
- 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 negative
- 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 ($-x + x =0$)
- the resultant orbitals look very much like hybrid orbitals because they are made from an s and p component
- in this example the positive combination has increased bonding character because there is more overlap of in-phase orbitals in the inter-nuclear or bond region
- next take the "negative" of one of the MOs, by taking the phase inverted MO and do the same again
- in this example 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 bond.
- however we don't have a strong antibonding overlap in the inter-nuclear region, so this is not a strongly antibonding orbital, so this orbital is more "non-bonding" than antibonding.
- the net effect of mixing has been to strongly stabilise one mixed-MO while destabilising the other mixed-MO
- in Figure 11 plots show how the "real" computed MOs look while the cartoons show LCAOs (linear combination of atomic orbitals)
• your turn you try mixing of the $\sigma_u$ MOs

- now draw the energy shift diagram analogous to that shown in Figure 11
  which orbital is the high energy one and which is the low energy one?
o Answer!

![diagram](image1.png)

**Figure 13** Mixing the $\sigma_u$ orbitals

tending to non-bonding as the internuclear out-of-phase component is reduced and electrons are polarised outside of the bond region

![diagram](image2.png)

**Figure 14** Mixing the $\sigma_u$ orbitals

highly anti-bonding as the out-of-phase internuclear component has increased
• the final MO diagram is shown in Figure 15,
  o the pre-mixing orbital energy levels are shown in blue, the post mixing energy levels and MOs are shown in red
  o note that the $\sigma_g$ MOs shift more because they were originally closer together in energy (and hence have a stronger interaction) than the $\sigma_u^*$. 

![MO Diagram](image)

Figure 15 Perturbed MO diagram for homonuclear diatomics

• it is important to realise that molecules with the same type of valence orbitals have similar MO diagrams.
  o for example, the first row diatomics are all represented by the diagram you have just created.
  o thus a single MO diagram can provide qualitative information about the stability of related compounds, without the necessity of complicated calculations.
  o whether or not significant mixing occurs for homonuclear diatomics of the first row depends on the 2s-2p energy gap, very electronegative elements O and F have a large gap, and so only a small amount of mixing, mixing then increases significantly from N -> C, Error! Reference source not found.

Figure 16
the "cross-over" of the $3\sigma_g$ and $1\pi_u$ occurs between O$_2$ and N$_2$, the valence electronic configurations of O$_2$ and N$_2$ are given below, notice how there is a switch in the orbital occupation, as the 2s-2p gap changes,

**Figure 16**

- 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) $(2\sigma_g)^2 (2\sigma_u^*)^2 (1\pi_u)^4 (3\sigma_g)^2$

- if two compounds have the same number of electrons then they are called **isoelectronic**. For example, C$_2$ and N$_2^{2+}$ are isoelectronic.

• this course also requires that you carry out calculations on the molecules we examine in class (**this is part of the course and is examinable**)

- revise the first year workshop found here: http://www.huntresearchgroup.org.uk/teaching/year1_lab_start.html

- **compute** the MOs for N$_2$ and confirm the position of the $3\sigma_g$ MO, and that mixing has occurred (by looking at the shape of the MO)

- **compute** the MOs for F$_2$ and confirm that the $1\pi_u$ lies above the $3\sigma_g$ MO, has there been any mixing in the $3\sigma_g$ MO?

- **ensure** you first optimise the geometry, then check you have found a minima by checking that you have all positive vibrational frequencies, finally carry out a MO (population) analysis. Step by step instructions can be found in the online material.
• calculations carried out at the B3LYP/6-311G(d,p) level
  o (for experts!) if you want to optimise $O_2$ ensure the spin state is a triplet
• additional information, energies of the MOs in au
  o notice the swap in energy for the $1\pi$ and $3\sigma_g$
  o note that the unoccupied $3\sigma_u^*$ LUMO for $F_2$ is still negative in energy!
  o the equivalent $3\sigma_u^*$ LUMO+3 for $N_2$ is very positive in energy

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<tr>
<th></th>
<th>$C_2$</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>$F_2$</th>
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<td>$3\sigma_u^*$</td>
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<td>+0.31182</td>
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Table 1 MO energies in au.

• comparing the $3\sigma_g$ and $3\sigma_u$ MOs of $N_2$ and $F_2$ (Figure 17)
  o the LCAO prediction is fairly accurate
  o however the $3\sigma_u^*$ of $N_2$ is not well-predicted

![Figure 17 Real computed MOs](image-url)