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](image1.png)

- 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

![Figure 4 Starting the MO diagram](image)

• 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
Figure 5 Combining AOs to form MOs

- the px and py AOs "perpendicular to the bond" orbitals combine in a bonding and antibonding pairs (two px orbitals and then 2py orbitals),

Figure 6

- the px and py 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

\[
\begin{align*}
\text{in-phase} & \rightarrow \text{bonding} \\
\text{out-of-phase} & \rightarrow \text{antibonding}
\end{align*}
\]

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 2px AOs have combined, and have strong (end on) overlap so they have a large energy splitting, they form they σ MOs
- the 2px and 2py AOs have poor (side by side) overlap and so they have a significantly smaller energy splitting, they form the π 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?
  o orbitals symmetric around the C\(\infty\) axis are \(\sigma\)-orbitals, Figure 8
  o any rotation of a \(\sigma\)-orbital down the bond axis maps it onto itself
  o \(\pi\)-orbitals have a phase change on a 180º rotation around the bond axis

\[
\Delta E(\sigma) \gg \Delta E(\pi)
\]
the \(\sigma\) interaction is stronger than the \(\pi\) because the orbitals overlap better

\[
\begin{align*}
3\sigma_g & \quad \text{2p} \\
\text{fragment orbitals in grey (FOs)} & \quad \Delta E(\sigma) \\
\text{the } \sigma \text{ antibonding MO lies below the } & \quad \Delta E(\pi) \\
\text{bonding MO} & \quad \text{2p}
\end{align*}
\]

\[
\begin{align*}
\text{2s} & \quad \text{2s}
\end{align*}
\]

\[
\begin{align*}
\text{cylindrical axis} & \quad \text{cylindrical axis}
\end{align*}
\]

looking down the axis

point after rotation **
end of p-orbital

point at start

rotate

\[
\begin{align*}
\Delta E(\sigma) & \quad \Delta E(\pi)
\end{align*}
\]

Figure 7 Form the MO diagram

Figure 8 \(\sigma\) and \(\pi\) symmetry

• then the "u" and the "g" relate to the inversion symmetry of the orbitals, go back and have a look at, Figure 2
  o 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
  o 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.
  o 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 F₂ and O₂ but not for the other first row diatomics, such as C₂ or N₂, these molecules exhibit MO mixing, which we revise now.

- **MO mixing**
  - 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.
  - "mixing" in this sense applies ONLY to molecular orbitals
  - in the homonuclear diatomic there are two σₕ and two σₜ* MOs with the same symmetry, but not from the same bonding -antibonding pair and thus they could mix, these are the MO pairs 2σₕ & 3σₕ and 2σₜ* & 3σₜ*
  - the closer two orbitals are in energy the stronger they mix
  - these MO pairs are not particularly close in energy and so any mixing is expected to be rather weak.
  - 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 (i.e., $x+x=2x$), combining the negative parts makes the function more negative (i.e., $-x + (-x) = -2x$), 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 destabalisng 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

![Diagram of mixing $\sigma_g$ orbitals](image)

**Figure 11** Mixing the $\sigma_g$ orbitals

![Diagram of mixing $\sigma_u$ orbitals](image)

**Figure 12** Mixing the $\sigma_u$ orbitals

○ 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?
Answer!

Figure 13 Mixing the σ_u orbitals
tending to non-bonding as the internuclear out-of-phase component is reduced and electrons are polarised outside of the bond region

Figure 14 Mixing the σ_u orbitals
highly anti-bonding as the out-of-phase internuclear component has increased
the final MO diagram is shown in Figure 15,
- the pre-mixing orbital energy levels are shown in blue, the post mixing energy levels and MOs are shown in red
- note that the $\sigma_g$ MOs shift more because they were originally closer together in energy (and hence have a stronger interaction) than the $\sigma_u^*$.  

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.
- for example, the first row diatomics are all represented by the diagram you have just created.
- thus a single MO diagram can provide qualitative information about the stability of related compounds, without the necessity of complicated calculations.
- 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 O₂ ensure the spin state is a triplet
• additional information, energies of the MOs in au
  o notice the swap in energy for the 1π and 3σᵣ
  o note that the unoccupied 3σᵤ* LUMO for F₂ is still negative in energy!
  o the equivalent 3σᵤ* LUMO+3 for N₂ is very positive in energy

<table>
<thead>
<tr>
<th></th>
<th>C₂</th>
<th>N₂</th>
<th>O₂</th>
<th>F₂</th>
</tr>
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<tbody>
<tr>
<td>3σᵤ*</td>
<td>+0.26617</td>
<td>+0.39144</td>
<td>+0.31182</td>
<td>-0.15300</td>
</tr>
<tr>
<td>1πᵣ*</td>
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<td>-0.02410</td>
<td>-0.31182</td>
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<tr>
<td>2σᵤ*</td>
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<td>-0.79189</td>
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<td>-1.31486</td>
<td>-1.35305</td>
</tr>
</tbody>
</table>

Table 1 MO energies in au.

• comparing the 3σᵣ and 3σᵤ MOs of N₂ and F₂ (Figure 17)
  o the LCAO prediction is fairly accurate
  o however the 3σᵤ* of N₂ is not well-predicted

Figure 17 Real computed MOs
Molecular Orbitals and Energy Level Diagrams for Diatomic Molecules

Molecular Orbitals for Diatomic Molecules Formed from a Linear Combination of Atomic Orbitals
(the LCAO-MO Approximation)

\[
\begin{align*}
\text{Atomic Orbitals} & \quad \text{Molecular Orbitals} \\
\begin{array}{c}
+ \\
+ \\
- \\
-
\end{array}
& \quad \begin{array}{c}
+ \\
+ \\
- \\
-
\end{array}
& \quad \begin{array}{c}
\sigma_g \\
\sigma_g^* \\
\pi_u \\
\pi_u^*
\end{array}
\end{align*}
\]
Molecular Orbital Energy Diagram for Homonuclear Diatomic Molecules

For diatomic molecules, the atomic orbitals of each atom can be combined using the LCAO-MO method to form molecular orbitals. An approximate energy-ordering scheme is shown below for homonuclear diatomic molecules including N\(_2\) and those formed from atoms with lower atomic numbers, including Li\(_2\), Be\(_2\), B\(_2\), and C\(_2\). The molecular orbital energy diagram is not shown to scale (that is, the 1s orbitals are the corresponding MOs are much lower in energy than the 2s or 2p orbitals).

For homonuclear diatomic molecules formed from atoms with atomic numbers greater than that of nitrogen, including O\(_2\), F\(_2\), and Ne\(_2\), the energy ordering of the 1\(\pi\) and 3\(\sigma\) molecular orbitals is reversed.
Lecture 10: Molecular Orbital Theory for Homonuclear Diatomic molecules

The MO theory can be generalized to many electron atoms. Here the atomic orbitals will have the same quantum numbers as those of hydrogen but can be quite different. If we use the basic ideas of MO theory for $H_2^+$ and fill electrons, we can get a good picture about the bonding in diatomic molecules.

The set of molecular orbitals of diatomic molecules with atoms from the first two rows of the periodic table are usually represented in the form of a molecular orbital diagram. The Molecular orbital diagram gives the list of molecular orbitals which are filled with the required number of electrons starting from the lowest energy level onwards. Hund’s maximum multiplicity rule is followed when filling electrons in degenerate levels, so two electrons in two degenerate levels will be unpaired.

The relative energies of $3\sigma_g$ and $1\pi_u$ cannot be predicted. However, through calculations it is shown that for all atoms up to Nitrogen ($Z=7$), we have the energy of $1\pi_u$ to be less than $3\sigma_g$ but from Oxygen onwards this trend is reversed. On filling the electrons in the oxygen molecular orbitals, we see that the lowest energy state corresponds to 2 electrons in the $1\pi_u$ orbitals and thus Oxygen molecule is paramagnetic. The other quantity of interest is the bond order which is given by

$$\text{bondorder} = \frac{1}{2} (n_{\text{bonding}} - n_{\text{antibonding}})$$

where $n_{\text{bonding}}$ is the number of electrons in the bonding Molecular orbitals and similarly for $n_{\text{antibonding}}$. The bond order is a measure of the bond strength.

We will end this section with a two comments. The first is that only AOs of the same energy overlap in homonuclear diatomic molecules. This is a
general principle, that overlap is significant only for AOs with comparable energies, but the energies need not be exactly the same (e.g., heteronuclear diatomic molecules). The second statement about the nature of the nuclear motions in a diatomic molecule. From the energy curve, we can see that the equilibrium length of the bond $R_e$ and the nature of the energy curve near this minimum. Clearly, as the nuclei move near this distance, they feel a restoring force that brings them back to this separation. Thus, for small amplitude motions, the atoms move in a harmonic potential. The energy states for this motion are given by the Harmonic oscillator energy states. This will be the main idea behind analyzing the results of vibrational spectroscopy.
The MOs of a Homonuclear Diatomic Molecule

Calculations

Consider a homonuclear diatomic molecule A₂, whose two atoms A are identical. For the sake of simplicity, we will assume that each atom uses one (and only one) valence AO to form the bond. These interacting AOs, which we will call \( \phi_1 \) and \( \phi_2 \), are chosen so as to be mathematically real. The following procedure is used to calculate the resulting MOs:

1. The two nuclei are held at a certain fixed distance from each other (i.e. we apply the Born–Oppenheimer approximation).
2. The time-independent Schrödinger Equation (2.4) is written for the molecule, multiplied on the left-hand side by \( \Psi \), and integrated over all space [Equation (2.5)]:
   \[
   H\Psi = E\Psi \tag{2.4}
   \]
   \[
   \langle \Psi | H | \Psi \rangle = E \langle \Psi | \Psi \rangle \tag{2.5}
   \]
3. Each MO is expressed as a linear combination of atomic orbitals (LCAOs):
   \[
   \Psi = c_1 \phi_1 + c_2 \phi_2 \tag{2.6}
   \]
In Equation (2.6), we know \( \phi_1 \) and \( \phi_2 \). Calculating an MO \( \Psi \) therefore involves evaluating its associated energy \( E \), and the coefficients \( c_1 \) and \( c_2 \) of its LCAO expansion. Incorporating Equation (2.6) in Equation (2.5) gives
   \[
   \langle c_1 \phi_1 + c_2 \phi_2 | H | c_1 \phi_1 + c_2 \phi_2 \rangle = E \langle c_1 \phi_1 + c_2 \phi_2 | c_1 \phi_1 + c_2 \phi_2 \rangle \tag{2.7}
   \]
The linearity of integrals (p. 7), allows the left-hand side of Equation (2.7) to be expressed as
   \[
   \langle c_1 \phi_1 + c_2 \phi_2 | H | c_1 \phi_1 + c_2 \phi_2 \rangle = \langle c_1 \phi_1 | H | c_1 \phi_1 \rangle + \langle c_1 \phi_1 | H | c_2 \phi_2 \rangle + \cdots \\
   = c_1^2 \langle \phi_1 | H | \phi_1 \rangle + c_2^2 \langle \phi_2 | H | \phi_2 \rangle + \cdots 
   \]
To express this more simply, let us set
   \[
   \langle \phi_i | H | \phi_i \rangle = \alpha_i, \quad \langle \phi_i | H | \phi_j \rangle = \beta_{ij}, \quad \langle \phi_i | \phi_j \rangle = S_{ij}
   \]
where \( \alpha_i \) is termed the Coulomb integral, \( \beta_{ij} \) the resonance integral and \( S_{ij} \) the overlap integral. We are using normalized AOs, so \( S_{ii} = 1 \). Furthermore, the two atoms are identical,\(^3\) so
   \[
   \alpha_1 = \alpha_2 \quad \text{and} \quad \beta_{12} = \beta_{21}
   \]
\(^3\)In physical terms, \( \beta_{12} = \beta_{21} \) simply means that the force binding atom 1 to atom 2 is the same as the force binding 2 to 1.
Thus, Equation (2.7) can be written as
\[(c_1^2 + c_2^2)\alpha + 2c_1c_2\beta - E(c_1^2 + c_2^2) + 2c_1c_2S = 0\] (2.8)
where \(\alpha, \beta\) and \(S\) are parameters and \(c_1, c_2\) and \(E\) are unknowns.

4. Let us now choose \(c_1\) and \(c_2\) so as to minimize \(E\) (variational method). To do this, we differentiate Equation (2.8), and set the partial derivatives to zero:
\[\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0\]
thus obtaining the secular equations:
\[(\alpha - E)c_1 + (\beta - ES)c_2 = 0\]
\[(\beta - ES)c_1 + (\alpha - E)c_2 = 0\] (2.9)
These equations are homogeneous in \(c_i\). They have a nontrivial solution if the secular determinant (i.e. the determinant of the coefficients of the secular equations) can be set to zero:
\[
\begin{vmatrix}
\alpha - E & \beta - ES \\
\beta - ES & \alpha - E
\end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0
\] (2.10)
The solutions to Equation (2.10) are
\[E_1 = \frac{\alpha + \beta}{1 + S}\] and \[E_2 = \frac{\alpha - \beta}{1 - S}\] (2.11)
\(E_1\) and \(E_2\) are the only energies which an electron belonging to the diatomic molecule \(A_2\) can have. Each energy level \(E_i\) is associated with a molecular orbital \(\Psi_i\) whose coefficients may be obtained by setting \(E = E_i\) in Equation (2.9) and solving these equations, taking into account the normalization condition:
\[\langle \Psi_i | \Psi_i \rangle = c_{i1}^2 + c_{i2}^2 + 2c_{i1}c_{i2}S = 1\] (2.12)
The solutions are
\[\Psi_1 = \frac{1}{\sqrt{2(1 + S)}}(\varphi_1 + \varphi_2)\] and \[\Psi_2 = \frac{1}{\sqrt{2(1 + S)}}(\varphi_1 - \varphi_2)\] (2.13)
Figure 2.2 gives a pictorial representation of Equation (2.11) and (2.13).

\[\text{Figure 2.2} \quad \text{The MOs of the homonuclear diatomic } A_2. \varphi_1 \text{ and } \varphi_2 \text{ are arbitrarily drawn as s orbitals. Note that the destabilization of } \Psi_2 \text{ is greater than the stabilization of } \Psi_1.\]
The Parameters

The Coulomb Integral $\alpha$

To a first approximation, the Coulomb integral $\alpha_A$ gives the energy of an electron occupying the orbital $\phi_A$ in the isolated atom $A$. Therefore, its absolute value represents the energy required to remove an electron from $\phi_A$ and place it at an infinite distance from the nucleus where, by convention, its energy is zero. Consequently, $\alpha_A$ is always negative and its absolute value increases with the electronegativity of $A$.

The Resonance Integral $\beta$

The absolute value of the resonance integral gives a measure of the $A_1A_2$ bond strength. It increases with increasing overlap. We will see that $S_{12}$ measures the volume common to $\phi_1$ and $\phi_2$, which encloses the electrons shared by $A_1$ and $A_2$. Large values of $S_{12}$ thus imply strong bonding between $A_1$ and $A_2$. When $S_{12}$ is zero, $\beta_{12}$ is also zero. It follows that two orthogonal orbitals cannot interact with each other. Conversely, the more two orbitals overlap, the more they interact. Stereoelectronic control results from this principle of maximum overlap: the best trajectory is that corresponding to the best overlap between the reagent and the substrate. The principle of maximum overlap is often expressed in terms of the Mulliken approximation:

$$\beta_{12} = kS_{12}$$

(2.14)

where the proportionality constant $k$ is negative. Basis AOs are generally chosen with the same sign, so the overlap integrals are positive and the resonance integrals negative.

The Overlap Integral

Consider two overlapping orbitals $\phi_i$ and $\phi_j$. They define four regions in space:

- Region 1 lies outside $\phi_i$ and $\phi_j$, where both orbitals have small values. The product $\phi_i \phi_j$ is negligible.
- Region 2 (enclosed by $\phi_i$ but outside $\phi_j$) and region 3 (enclosed by $\phi_j$ but outside $\phi_i$) also have negligible values for $\phi_i \phi_j$: one component is appreciable, but the other is very small.
- Region 4, where both $\phi_i$ and $\phi_j$ are finite. The value of $S_{ij}$ comes almost exclusively from this region where the two orbitals overlap (hence the term "overlap integral").

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$^6$\(\beta_{12}\) is sometimes said to represent the coupling of $\phi_1$ with $\phi_2$. This originates in the mathematical analogy between the interaction of two AOs and the coupling of two pendulums. The term resonance integral has similar roots (Coulson C. A., Valence, Oxford University Press, Oxford, 2nd edn, p. 79).
Mulliken Analysis

The MOs in the diatomic molecules discussed above have only two coefficients, so their chemical interpretation poses few problems. The situation becomes slightly more complicated when the molecule is polyatomic or when each atom uses more than one AO. Overlap population and net atomic charges can then be used to give a rough idea of the electronic distribution in the molecule.

Overlap Population

Consider an electron occupying $\Psi_1$. Its probability density can best be visualized as a cloud carrying an overall charge of one electron. To obtain the shape of this cloud, we calculate the square of $\Psi_1$:

$$\langle \Psi_1 | \Psi_1 \rangle = c_{11}^2 \langle \varphi_1 | \varphi_1 \rangle + 2c_{11}c_{12}S_{12} + c_{12}^2 \langle \varphi_2 | \varphi_2 \rangle = 1$$  \hspace{2cm} (2.15)

Equation (2.15) may be interpreted in the following way. Two portions of the cloud having charges of $c_{11}^2$ and $c_{12}^2$ are essentially localized within the orbitals $\varphi_1$ and $\varphi_2$ and ‘belong’ to $A_1$ and $A_2$, respectively. The remainder has a charge of $2c_{11}c_{12}S$ and is concentrated within the zone where the two orbitals overlap. Hence this last portion is termed the overlap population of $A_1A_2$. It is positive when the AOs overlap in phase (as in $\Psi_1$) and negative when they are out of phase (as in $\Psi_2$). The overlap population gives the fraction of the electron cloud shared by $A_1$ and $A_2$. A positive overlap population strengthens a bond, whereas a negative one weakens it. We can therefore take $2c_{11}c_{12}S$ as a rough measure of the $A_1A_2$ bond strength.

Net Atomic Charges

It is often useful to assign a net charge to an atom. This allows the nuclei and electron cloud to be replaced by an ensemble of point charges, from which the dipole moment of the molecule can be easily calculated. It also allows the reactive sites to be identified: positively charged atoms will be preferentially attacked by nucleophiles, whereas negatively charged atoms will be favored sites for electrophiles.

The net charge on an atom is given by the algebraic sum of its nuclear charge $q_n$ and its electronic charge $q_e$. The latter is usually evaluated using the Mulliken partition scheme, which provides a simple way of dividing the electron cloud among the atoms of the molecule. Consider an electron occupying the molecular orbital $\Psi_i$ of the diatomic $A_1A_2$. The contribution of this electron to the electronic charge of $A_i$ is then $c_{ii}^2$ plus half of the overlap population. In the general case:

$$q_e(A) = \sum_{i,j} n_i c_{ix}c_{ij} S_{xj}$$  \hspace{2cm} (2.16)

---

1In a polyelectronic molecule, it is necessary to sum over all electrons and calculate the total overlap population to obtain a measure of the bond strength.

2This rule is not inviolate. See pp. 87, 96 and 175.
where $S_{ij}$ is the overlap integral of $\varphi_i$ and $\varphi_j$, $n_i$ is the number of electrons which occupy $\Psi_i$ and $c_{iA}$ and $c_{ij}$ are the coefficients of $\varphi_A$ and $\varphi_j$ in the same MO. The summation takes in all of the MOs $\Psi_i$ and all of the atoms $j$ in the molecule.

**MOs of a Heteronuclear Diatomic Molecule**

**Calculations**

A heteronuclear diatomic molecule is comprised of two different atoms A and B. For simplicity, we will again assume that only one AO on each atom is used to form the bond between A and B. The two relevant AOs are then $\varphi_A$, of energy $\alpha_A$, and $\varphi_B$ of energy $\alpha_B$. The calculation is completely analogous to the case of the homonuclear diatomic given above. For a heteronuclear diatomic molecule AB, Equation (2.10) – where the secular determinant is set to zero – becomes

$$(\alpha_A - E)(\alpha_B - E) - (\beta - ES)^2 = 0 \quad (2.17)$$

Equation (2.17) is a second-order equation in $E$ which can be solved exactly. However, the analogs of expressions Equation (2.11) and (2.13) are rather unwieldy. For qualitative applications, they can be approximated as follows:

$$E_1 \approx \alpha_A + \frac{(\beta - \alpha_A S)^2}{\alpha_A - \alpha_B} \quad E_2 \approx \alpha_B + \frac{(\beta - \alpha_B S)^2}{\alpha_B - \alpha_A} \quad (2.18)$$

$$\Psi_1 \approx N_1 \left( \varphi_A + \frac{\beta - \alpha_A S}{\alpha_A - \alpha_B} \varphi_B \right) \quad \Psi_2 \approx N_2 \left( \varphi_B + \frac{\beta - \alpha_B S}{\alpha_B - \alpha_A} \varphi_A \right) \quad (2.19)$$

where $N_1$ and $N_2$ are normalization coefficients. Equations (2.18) assume that $E_1$ and $E_2$ are not very different from $\alpha_A$ and $\alpha_B$, respectively. Using this approximation, it is possible to rewrite Equation (2.17) in the form

$$\alpha_A - E_1 = \frac{(\beta - E_1 S)^2}{\alpha_B - E_1} \approx \frac{(\beta - \alpha_A S)^2}{\alpha_B - \alpha_A} \quad (2.20)$$

which is equivalent to Equations (2.18). Equations (2.18) and (2.19) are shown pictorially in Figure 2.3.

![Figure 2.3](image-url) MOs of a heteronuclear diatomic molecule. $\varphi_A$ and $\varphi_B$ are arbitrarily shown as s orbitals.
Huckel Molecular Orbital theory (HMO theory).

An approximate theory that gives us a very quick picture of the MO energy diagram and MO’s of molecules without doing a lot of work.

Structure and bonding in highly conjugated systems nicely treated by HMO. Look at examples:

Ethene – look at the \( \pi \) bond in this simple molecule first.

Each carbon has a \( 2p_z \) orbital perpendicular to plane of molecule. Use LCAO-MO to get two MO’s, which gives rise to 2x2 secular determinant:

\[
\begin{vmatrix}
\alpha_A - E_{\text{trial}} & \beta - E_{\text{trial}} S \\
\beta - E_{\text{trial}} S & \alpha_B - E_{\text{trial}}
\end{vmatrix} = 0
\]

HMO approx:

Set all overlap integrals \( S = 0 \)

Recognize the \( \alpha \) integrals are equal

\[
\begin{vmatrix}
\alpha - E & \beta \\
\beta & \alpha - E
\end{vmatrix} = 0
\]

This gives quadratic \( (\alpha - E)^2 - \beta^2 = 0 \)

Roots \( E = \alpha + \beta, \alpha - \beta \)

Total \( \pi \) bond energy = \( 2(\alpha + \beta) \)

Stabilization due to bond formation = \( 2\beta \)

\( \beta \) is intrinsically negative and \( \sim -2.4 \text{ eV} \) for C-C bond (\( \sim -230 \text{ kJ/mol} \))
Butadiene.

Treat sigma bonding framework using VB theory as follows:

Still have an unused p orbital available on each C, perpendicular to plane of molecule.

Edge on view:

These extensively overlap to form a delocalized \( \pi \) system.

Treat \( \pi \) system by HMO as follow:

a. basis set is composed of four \( 2p_z \) orbitals (perpendicular to plane).

Therefore will get \( 4 \times 4 \) matrix or secular determinant

b. HMO approx:

1) Set all overlap integrals \( S = 0 \)
2) Set all resonance integrals between non-neighbors = 0
   $\beta_{13}, \beta_{14}, \beta_{24}$ etc. = 0

3) Set all other resonance integrals ($\beta$) equal to one another.

Resulting Sec detm

$$
\begin{vmatrix}
\alpha - E & \beta & 0 & 0 \\
\beta & \alpha - E & \beta & 0 \\
0 & \beta & \alpha - E & \beta \\
0 & 0 & \beta & \alpha - E \\
\end{vmatrix} = 0
$$

Generates a quartic polynomial in $E$ which has four roots.

Therefore 4 $\pi$-orbital MO
4 energies (roots of secular determinant)

They are: $E = \alpha \pm 1.62 \beta, \alpha \pm 0.62 \beta$

Energy diagram:
Spectroscopic transition HOMO $\rightarrow$ LUMO (called frontier orbitals)

HOMO = highest occupied molecular orbital (here MO $2\pi$)

LUMO = lowest unoccupied molecular orbital (here MO $3\pi$)

$\Delta E_{\text{trans}} = \text{LUMO} - \text{HOMO} = (\alpha - 0.62 \beta) - (\alpha + 0.62 \beta) = -1.24 \beta$

Compare wave functions with particle in box:

Delocalized system have extra stability (=deloc energy DE)

Calculate it:

$\text{DE} = \text{Energy of } c\equiv c\equiv c\equiv c - \text{Energy of } c=c\equiv c=c$

Allow electrons To delocalize

2 separate $\pi$ bonds like in ethene

$= [2(\alpha + 1.62 \beta) + 2(\alpha + 0.62 \beta)] - 2(2\alpha + 2\beta)$

$= 4\alpha + 4.48\beta - (4\alpha + 4\beta)$

$= 0.48\beta \sim -110 \text{ kJ/mol of stabilization}$
Benzene – cyclic delocalized system.

$6 \times 6$ secular determinant =

\[
\begin{vmatrix}
\alpha-E & \beta & 0 & 0 & 0 & \beta \\
\beta & \alpha-E & \beta & 0 & 0 & 0 \\
0 & \beta & \alpha-E & \beta & 0 & 0 \\
0 & 0 & \beta & \alpha-E & \beta & 0 \\
0 & 0 & 0 & \beta & \alpha-E & \beta \\
\beta & 0 & 0 & 0 & \beta & \alpha-E \\
\end{vmatrix} = 0
\]

due to cyclic connection

=Energy eigenvalues are $E = \alpha + 2\beta, \alpha + \beta, \alpha + \beta$

---

Calculate delocalization energy $DE$:

Total pi electron energy = $2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$

Energy of three C=C in ethane = $2\alpha + 2\beta$

$DE$ = difference = $2\beta = -460 \text{ kJ/mol}$
Introduction to Frontier Molecular Orbital Theory

- General Reviews
  Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*
  Kirby, A. J. *Stereoelectronic Effects*.

Universal Effects Governing all Chemical Reactions

- **Steric Effects**
  Nonbonding interactions (van der Waals repulsion) between substituents within a molecule or between reacting molecules.

- **Nondirectional Electronic Effects (Inductive Effects):**
  Rate decreases as R becomes more electronegative.

- **Stereoelectronic Effects**
  Geometrical constraints placed upon ground and transition states by orbital overlap considerations.

  **Fukui Postulate for reactions:**
  During the course of chemical reactions, the interaction of the highest filled (HOMO) and lowest unfilled (antibonding) molecular orbital (LUMO) in reacting species is very important to the stabilization of the transition structure.

- **General Reaction Types**
  **Radical Reactions (~10%):**
  \[ A^- + B^- \rightarrow A^+B^- \]
  **Polar Reactions (~90%):**
  \[ A(\cdot^-) + B(\cdot^+) \rightarrow A^-B^+ \]

FMO concepts extend the donor-acceptor paradigm to non-obvious families of reactions.

- **Consider** stabilization energy (\(\Delta E\)) when bringing atoms A & B together:
  \[
  \Delta E = -\frac{Q_A Q_B}{\varepsilon R} + \sum_{m\neq n} \frac{(c_{m\varepsilon c_{n\beta}})^2}{(E_m - E_n)}
  \]
  **Coulomb Term**  **Orbital Term**

Q: Charge density
\(\varepsilon\): Dielectric constant
R: distance of A to B
\(c\): coefficient of MO
m: species A, or MO n of species B
\(\beta\): Overlap Integral
E: Energy of MO
The H₂ Molecule (again!!)

Let's combine two hydrogen atoms to form the hydrogen molecule. Mathematically, linear combinations of the 2 atomic 1s states create two new orbitals, one is bonding, and one antibonding:

**Rule one**: A linear combination of n atomic states will create n MOs.

![Diagram of H₂ MOs](image)

Let's now add the two electrons to the new MO, one from each H atom:

![Diagram of H₂ with electrons](image)

Note that ΔE₁ is greater than ΔE₂. Why?

Linear Combination of Atomic Orbitals (LCAO): Orbital Coefficients

Each MO is constructed by taking a linear combination of the individual atomic orbitals (AO):

- **Bonding MO**: $\sigma = C_1\psi_1 + C_2\psi_2$
- **Antibonding MO**: $\sigma^* = C^*_1\psi_1 - C^*_2\psi_2$

The coefficients, $C_1$ and $C_2$, represent the contribution of each AO.

**Rule Two**: $(C_1)^2 + (C_2)^2 = 1$

The squares of the C-values are a measure of the electron population in the neighborhood of atoms in question.

**Rule Three**: bonding $(C_1)^2 +$ antibonding $(C^*_1)^2 = 1$

In LCAO method, both wave functions must each contribute one net orbital.

Consider the pi-bond of a C=O function: In the ground state pi-C–O is polarized toward oxygen. Note (Rule 2) that the antibonding MO is polarized in the opposite direction.
Bonding Generalizations

- Bond strengths (Bond dissociation energies) are composed of a covalent contribution ($\delta E_{\text{cov}}$) and an ionic contribution ($\delta E_{\text{ionic}}$).

  Bond Energy (BDE) = $\delta E_{\text{cov}} + \delta E_{\text{ionic}}$

When one compares bond strengths between C–C and C–X, where X is some other element such as O, N, F, Si, or S, keep in mind that covalent and ionic contributions vary independently. Hence, the mapping of trends is not a trivial exercise.

The following generalizations on covalent bonding are useful.

- Overlap between orbitals of comparable energy is more effective than overlap between orbitals of differing energy.

For example, consider elements in Group IV, Carbon and Silicon. We know that C–C bonds are considerably stronger by Ca. 20 kcal mol$^{-1}$ than C–Si bonds.

- Orbital orientation strongly affects the strength of the resulting bond.

  For $\sigma$ Bonds:

  ![Diagram of $\sigma$ Bond Orientation]

  This is a simple notion with very important consequences. It surfaces in the delocalized bonding which occurs in the competing anti (favored) syn (disfavored) E2 elimination reactions. Review this situation.

- An anti orientation of filled and unfilled orbitals leads to better overlap.

  This is a corollary to the preceding generalization. There are two common situations.

Case-1: Anti Nonbonding electron pair & C–X bond

- Weak bonds will have corresponding low-lying antibonds.

Formation of a weak bond will lead to a corresponding low-lying antibonding orbital. Such structures are reactive as both nucleophiles & electrophiles.

Case-2: Two anti sigma bonds
Donor-Acceptor Properties of Bonding and Antibonding States

Donor Acceptor Properties of C-C & C-O Bonds
Consider the energy level diagrams for both bonding & antibonding orbitals for C-C and C-O bonds.

- The greater electronegativity of oxygen lowers both the bonding & antibonding C-O states. Hence:
  - \(\sigma^*\) C-O is a better acceptor orbital than \(\sigma\) C-C
  - \(\sigma\) C-O is a better donor orbital than \(\sigma^*\) C-C

Donor Acceptor Properties of C\(_{\text{sp}^3}\)-C\(_{\text{sp}^3}\) & C\(_{\text{sp}^3}\)-C\(_{\text{sp}^2}\) Bonds

- The greater electronegativity of C\(_{\text{sp}^2}\) lowers both the bonding & antibonding C-C states. Hence:
  - \(\sigma\) C\(_{\text{sp}^3}\)-C\(_{\text{sp}^3}\) is a better donor orbital than \(\sigma\) C\(_{\text{sp}^3}\)-C\(_{\text{sp}^2}\)
  - \(\sigma^*\) C\(_{\text{sp}^3}\)-C\(_{\text{sp}^2}\) is a better acceptor orbital than \(\sigma^*\) C\(_{\text{sp}^3}\)-C\(_{\text{sp}^3}\)

Hierarchy of Donor & Acceptor States
Following trends are made on the basis of comparing the bonding and antibonding states for the molecule CH\(_3\)-X where X = C, N, O, F, & H.

- Decreasing \(\sigma\)-donor capacity
  - \(\sigma^*\)-acceptor capacity
  - \(\sigma\)-anti-bonding States: (C–X)
  - \(\sigma\)-bonding States: (C–X)

The following are trends for the energy levels of nonbonding states of several common molecules. Trend was established by photoelectron spectroscopy.

- Decreasing donor capacity
  - HCl:
  - H\(_2\)O:
  - H\(_3\)N:
  - H\(_2\)S:
  - H\(_3\)P:

Nonbonding States

- Decreasing donor capacity
- poorest donor
**Electrons in 2s states "see" a greater effective nuclear charge than electrons in 2p states.**

This becomes apparent when the radial probability functions for s and p-states are examined: The radial probability functions for the hydrogen atom s & p states are shown below.

Electrons in s-states "see" a higher nuclear charge. This is even more obvious in an electron density map (see http://www.shef.ac.uk/chemistry/orbitron/). The s-orbitals have maximal electron density at the nucleus, and the p-orbitals have none.

---

The above trend indicates that the greater the % of s-character at a given atom, the greater the electronegativity of that atom.

There is a linear relationship between %s character & Pauling electronegativity

There is a direct relationship between %s character & hydrocarbon acidity

---

This correctly implies that the stability of nonbonding electron pairs is directly proportional to the % of s-character in the doubly occupied orbital.

![Least stable](https://www.shef.ac.uk/chemistry/orbitron/)

Most stable

**Hybridization vs Electronegativity**
Hyperconjugation: Carbocation Stabilization

- The interaction of a vicinal bonding orbital with a p-orbital is referred to as hyperconjugation.

This is a traditional vehicle for using valence bond to denote charge delocalization.

The graphic illustrates the fact that the C-R bonding electrons can "delocalize" to stabilize the electron deficient carbocationic center.

Note that the general rules of drawing resonance structures still hold: the positions of all atoms must not be changed.

Stereoelectronic Requirement for Hyperconjugation: coplanar orientation between interacting orbitals

The Molecular Orbital Description

- Take a linear combination of σ C–R and Csp₂ p-orbital:
  
  The new occupied bonding orbital is lower in energy. When you stabilize the electrons in a system you stabilize the system itself.

Physical Evidence for Hyperconjugation

- Bonds participating in the hyperconjugative interaction, e.g. C–R, will be lengthened while the C(+)–C bond will be shortened.

First X-ray Structure of an Aliphatic Carbocation

The Adamantane Reference (MM2)


More substituted carbocations have more adjacent C-R bonds to act as donors to the empty p orbital

Hence, more substituted carbocations are more stable.
"Negative" Hyperconjugation/Anomeric Effect

Delocalization of nonbonding electron pairs into vicinal antibonding orbitals is also possible.

This delocalization is referred to as "negative" hyperconjugation.

Since nonbonding electrons prefer hybrid orbitals rather than p orbitals, this orbital can adopt either a syn or anti relationship to the vicinal C–R bond.

The Molecular Orbital Description

Overlap between two orbitals is better in the anti orientation as stated in "Bonding Generalizations" handout.

The Expected Structural Perturbations

<table>
<thead>
<tr>
<th>Change in Structure</th>
<th>Spectroscopic Probe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shorter C–X bond</td>
<td>X-ray crystallography</td>
</tr>
<tr>
<td>Longer C–R bond</td>
<td>X-ray crystallography</td>
</tr>
<tr>
<td>Stronger C–X bond</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>Weaker C–R bond</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>Greater e-density at R</td>
<td>NMR Spectroscopy</td>
</tr>
<tr>
<td>Less e-density at X</td>
<td>NMR Spectroscopy</td>
</tr>
</tbody>
</table>
The Anomeric Effect and Related Issues

Infrared evidence for lone pair delocalization into vicinal antibonding orbitals.

The N–H stretching frequency of cis-methyl diazene is 200 cm⁻¹ lower than the trans isomer.

\[ \nu \text{N–H} = 2188 \text{ cm}^{-1} \]

\[ \nu \text{N–H} = 2317 \text{ cm}^{-1} \]

The low-frequency shift of the cis isomer is a result of N–H bond weakening due to the anti lone pair on the adjacent (vicinal) nitrogen which is interacting with the N–H antibonding orbital. Note that the orbital overlap is not nearly as good from the trans isomer.

N. C. Craig & co-workers JACS 1979, 101, 2480.

Aldehyde C–H Infrared Stretching Frequencies

The IR C–H stretching frequency for aldehydes is lower than the closely related olefin C–H stretching frequency. For years this observation has gone unexplained.

\[ \nu \text{C–H} = 2730 \text{ cm}^{-1} \]

\[ \nu \text{C–H} = 3050 \text{ cm}^{-1} \]

We now conclude that this is another example of negative hyperconjugation.

The Anomeric Effect

It is not unexpected that the methoxyl substituent on a cyclohexane ring prefers to adopt the equatorial conformation.

\[ \Delta G^\circ = +0.8 \text{ kcal/mol} \]

What is unexpected is that the closely related 2-methoxytetrahydropyran prefers the axial conformation:

\[ \Delta G^\circ = -0.6 \text{ kcal/mol} \]

That effect which provides the stabilization of the axial OR conformer which overrides the inherent steric bias of the substituent is referred to as the anomeric effect.

Principal HOMO-LUMO interaction from each conformation is illustrated below:

Since the antibonding C–O orbital is a better acceptor orbital than the antibonding C–H bond, the axial OMe conformer is better stabilized by this interaction which is worth ca 1.2 kcal/mol.

Other electronegative substituents such as Cl, SR etc. also participate in anomeric stabilization.

This conformer preferred by 1.8 kcal/mol

Why is axial C–Cl bond longer?
HOMO and LUMO Energies and Orbital Coefficients of Common Alkenes

<table>
<thead>
<tr>
<th>Alkene</th>
<th>HOMO (eV)</th>
<th>c₁</th>
<th>c₂</th>
<th>LUMO (eV)</th>
<th>c₃</th>
<th>c₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CH₂</td>
<td>-10.52</td>
<td>0.71</td>
<td>0.71</td>
<td>+1.5</td>
<td>0.71</td>
<td>-0.71</td>
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<td>CH₂=CHCl</td>
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<td>-0.54</td>
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<td>CH₂=CHMe</td>
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<td>MeCH=CHMe</td>
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<td></td>
<td>+2.22</td>
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<td></td>
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<tr>
<td>CH₂=CH₂</td>
<td>-9.63</td>
<td></td>
<td></td>
<td>+2.01</td>
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<td></td>
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<tr>
<td>CH₂=CHMe</td>
<td>-8.94f,g</td>
<td></td>
<td></td>
<td>+2.18</td>
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<td></td>
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<tr>
<td>CH₂=CHOMe</td>
<td>-9.05;8.93</td>
<td>0.61</td>
<td>0.39</td>
<td>+2.0</td>
<td>0.66</td>
<td>-0.72</td>
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<td>CH₂=CHSMe</td>
<td>-8.45</td>
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<td>0.17</td>
<td>+1.0</td>
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<td>-0.48</td>
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<td>CH₂=CHNMMe₂</td>
<td>-9.0</td>
<td>0.50</td>
<td>0.20</td>
<td>+2.5</td>
<td>0.62</td>
<td>-0.69</td>
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<tr>
<td>CH₂=CHCO₂Me</td>
<td>-10.72</td>
<td>0.43</td>
<td>0.33</td>
<td>0</td>
<td>0.69</td>
<td>-0.47</td>
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<tr>
<td>CH₂=CHCN</td>
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<td>0.49</td>
<td>0</td>
<td>0.66</td>
<td>-0.54</td>
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<td>CH₂=CHNO₂</td>
<td>-11.4</td>
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<td>+0.7</td>
<td>0.54</td>
<td>-0.32</td>
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<td>CH₂=CHPh</td>
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<td>0.32</td>
<td>+0.8</td>
<td>0.48</td>
<td>-0.33</td>
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<td>CH₂=CHCHO</td>
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<td>CH₂=CHCHO/BF₃b</td>
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<td>+0.43</td>
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<td>CH₂=CHCO₂Hb</td>
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<td>-1.91</td>
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Influence of a conjugating substituent on alkene HOMO and LUMO energies.
Relative HOMO and LUMO energies of electron-rich and -poor dienes.
HOMO, LUMO Energies and Orbital Coefficients for Substituted Dienes

<table>
<thead>
<tr>
<th>Diene</th>
<th>HOMO $^a$</th>
<th>$\xi_1$</th>
<th>$\xi_2$</th>
<th>LUMO</th>
<th>$\xi_3$</th>
<th>$\xi_4$</th>
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<tr>
<td></td>
<td>$-9.07; -8.85^b$</td>
<td>0.57</td>
<td>-0.57</td>
<td>$+1.0; 3.38^b$</td>
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<td>0.56</td>
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<td>Me</td>
<td>$-9.78^a; -8.54$</td>
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<td>0.315</td>
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<td>0.617$^c$</td>
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<tr>
<td>Me$^b$</td>
<td>$-9.04^a; -8.72$</td>
<td>0.340</td>
<td>0.296</td>
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<td>Me</td>
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<td>Ph</td>
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<td>MeO$^b$</td>
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<td>0.103$^b$</td>
<td>$+3.60^b$</td>
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<td>SMe$^b$</td>
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<td>0.240</td>
<td>0.256</td>
<td>$+3.25$</td>
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<tr>
<td>SMe$^b$</td>
<td>$-8.37$</td>
<td>0.399</td>
<td>0.201</td>
<td>$+3.25$</td>
<td></td>
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HOMO_{butadiene}–LUMO_{ethene} interactions that control the Diels–Alder cyclization.
HOMO_{diene}–LUMO_{alkene} interactions of butadiene and representative alkenes
Regioselectivity of 1-Alkyl-1,3-butadienes with Electron Deficient Alkenes

\[
\begin{align*}
R & \quad Z & \quad \text{Ratio} \\
\text{Me} & \quad \text{CHO} & \quad 8:1 \\
\text{Me} & \quad \text{C}≡\text{N} & \quad 10:1 \\
\text{Me} & \quad \text{CO}_2\text{Me} & \quad 6.8:1 \\
i\text{-Pr} & \quad \text{CO}_2\text{Me} & \quad 5:1 \\
n\text{-Bu} & \quad \text{CO}_2\text{Me} & \quad 5.1:1 \\
t\text{-Bu} & \quad \text{CO}_2\text{Me} & \quad 4.1:1
\end{align*}
\]
In this lecture we will understand how the molecular orbitals are formed from the interaction of atomic orbitals.

We will see how the electrons occupy these molecular orbitals.

To start, we take up examples of simple diatomic homonuclear molecules and then we will discuss some heteronuclear molecules.

As the atomic orbitals are important in case of atoms, the molecular orbitals are needed to understand the structure of molecule.
Molecular orbitals are formed from the combinations of atomic orbitals. Since orbitals are wavefunctions, they can combine either constructively to form bonding molecular orbitals or destructively to form antibonding molecular orbitals.

Why do we need Molecular Orbital theory? Valence bond theory generally fails to explain the bonding in simple molecules. On the other hand, molecular orbital theory is better approach for the molecules those are having extended $\pi$ systems. With the help of molecular orbital one can understand the electronic transitions in molecules.
We have seen in the previous lecture that H$_2^+$-ion is stable because of the bonding between the two hydrogen atoms which form a bound state with one electron. Similar to this, if we consider two hydrogen atoms to form hydrogen molecule, we expect that the wavefunctions of two hydrogen atoms $\phi(a)$ and $\phi(b)$ will interact constructively or destructively.

If they interact constructively then the molecular wavefunction

$$\psi_+ = \frac{1}{\sqrt{2}} (\phi_s(a) + \phi_s(b))$$

This will form bonding orbital. And if they interact destructively, it will form antibonding orbital

$$\psi_- = \frac{1}{\sqrt{2}} (\phi_s(a) - \phi_s(b))$$

We have also realized that the degenerate levels of the two hydrogen atoms will be separated as the two nuclei come closer to each other.

As shown in figure 27.1, the ground state of two hydrogen atomic orbitals split into two energy levels – bonding $\psi_+$ and antibonding $\psi_-$. 

| Figure-27.1 |
Figure-27.2 explains the energies of bonding and anti-bonding molecular orbitals for first row diatomic molecules.

Two electrons in $H_2$ occupy bonding molecular orbital, with anti-parallel spins. If irradiated by UV light, molecule may absorb energy and promote one electron into its anti-bonding orbital.

The filling of lower molecular orbital indicates that the molecule is stable compared to two individual atoms.

“+” and “-“ sign indicates the sign of the wavefunction.

$\sigma_{1s}$ is symmetric with respect to the center of inversion (middle point of the bond), this sometimes called as symmetric or gerade and designate as $\sigma_{1s,g}$

$\sigma^*_{1s}$ is not symmetric with respect to the center of inversion (middle point of the bond), this sometimes called as asymmetric or ungerade and designate as $\sigma^*_{1s,u}$
Molecular orbital form when atomic orbitals with similar energies and proper symmetry spatially overlap each other.

For homonuclear molecule such as H₂, N₂, …etc.

s-orbitals combine with s-orbitals and p-orbitals combine with p-orbitals. In figure 27.2 we have seen the interaction of s orbital with another s orbital.

For p-orbitals:
There are three pₓ, pᵧ, and pₗ orbitals. If we consider X-axis coincides with internuclear axis then for pₓ orbitals, there will be end-on-end overlap along the bond axis as shown in figure 27.3. It forms σ bonding and nonbonding orbitals.

For σ bonding orbital, it is symmetric about the center of inversion and thus it is $\sigma_{2p,τ}$

For σ antibonding orbital, it is asymmetric about the center of inversion and thus it is $\sigma^*_{2p,τ}$
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The other \( p_x \) and \( p_y \) orbitals overlap side-by-side. This is known as \( \pi \)-bonding. This overlap is less than the overlap along the bond axis.

Note that, the overlap is more → it will be more stable and thus energy will be lower.

Thus, the \( \pi \)-bonding orbital will be higher in energy than that of the \( \sigma \)-orbital.

\( \pi \)-orbitals are asymmetric with respect to the bond axis as shown in figure-27.4. No electron density surrounding the bond axis. It has node along the internuclear axis.

\( \pi_{2p} \) is asymmetric about the center of inversion, and thus \( \pi_{2p,u} \)

\( \pi^*_{2p} \) is symmetric about the center of inversion, and thus \( \pi^*_{2p,g} \)
Figure-27.5 shows the total energy level diagram for p-orbitals interaction.

Note that $\sigma$-orbital is the lowest in energy due to maximum overlap.

Note:
Electron can occupy molecular orbital that are lower in energy.
Molecular orbitals may be empty or contain one or two electrons.
For two electrons occupied orbitals, electrons must be spin paired due to Pauli exclusion principle.
When occupying molecular orbitals, electrons occupy separate orbitals with parallel spin before pairing.
The highest occupied molecular orbital is known as HOMO.
The lowest unoccupied molecular orbital is known as LUMO.
Let us take an example of oxygen molecule.

Oxygen atom is having electron configuration \(1s^22s^22p^4\). So the oxygen molecule is having total of 16 electrons.

\[
\begin{align*}
1s^2,1s^2 & \Rightarrow \sigma_{1s} \rightarrow \sigma_g \\
& \Rightarrow \sigma_{1s}^* \rightarrow \sigma_g^*
\end{align*}
\]

\[
\begin{align*}
2s^2,2s^2 & \Rightarrow \sigma_{2s} \rightarrow \sigma_g \\
& \Rightarrow \sigma_{2s}^* \rightarrow \sigma_g^*
\end{align*}
\]

\[
\begin{align*}
2p^2,2p^2 & \Rightarrow \sigma_{2p} \rightarrow \sigma_g \\
& \Rightarrow \pi_{2p} \rightarrow \pi_g \\
& \Rightarrow \pi_{2p}^* \rightarrow \pi_g^* \\
& \Rightarrow \sigma_{2p}^* \rightarrow \sigma_g^*
\end{align*}
\]

The figure-27.6 shows that for oxygen molecule, there are two unpaired electrons.

Bond order indicates the strength of a bond and is defined as

\[
\text{Bond order} = \frac{\text{(no. of electrons in bonding orbitals)}}{2} - \frac{\text{(no. of electrons in the antibonding orbitals)}}{2}
\]

For oxygen, considering only the valence electrons (2p orbital)

Bond order \(= (8-4)/2 = 2\). So the result is a double bond.

Bond order \(=1\) (single bond); Bond order \(= 2\) (double bond) e.t.c
For heteronuclear atoms, due to the small energy gap between $s$ and $p$ orbitals, $s$ and $p$ orbitals overlap is possible. Figure-27.7 shows the overlap between $s$ and $p$ orbital. This interaction could be constructive or destructive.

Let us take an example of HF molecule. Figure 27.8 shows the energy level diagram of the HF molecule. Hydrogen 1$s$ orbital interact with 2$s$ and 2$p_x$ orbitals of fluorine. 2$p_y$ and 2$p_z$ orbitals do not have the proper symmetry to interact with 1$s$ orbital. So these are nonbonding orbital.
Let us take another example of CO as shown in figure 27.9.

Generally to simplify the things, interactions of the orbitals containing valence electrons are considered to form the molecular orbitals.

The molecular orbital $2\sigma$ is the highest filled orbital and is HOMO.

The molecular orbital $3\sigma$ is the lowest unfilled orbital and is LUMO.
In this lecture we learnt the formation of molecular orbital from the atomic orbitals. We also came to know about their symmetry such as gerade (g) and ungerade (u) depending on electronic distribution about the center of inversion. This arises only for the symmetric molecules that have inversion symmetry. We have also understood how to distribute electrons into the molecular orbitals. We have also learnt that the overlap is more, orbital will be more stable and thus energy will be lower. Thus, the $\pi$-bonding orbital will be higher in energy than that of the $\sigma$-orbital. We have also learnt that for heteronuclear molecule due to the small energy gap between $s$ and $p$ orbitals, $s$ and $p$ orbital overlap is possible.
Homonuclear Diatomic Molecules: Molecular Orbital Theory

Molecular orbital diagram: N₂

N₂ : \((1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4(2\sigma_g)^2\)

\[
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow \\
\downarrow & \downarrow & \downarrow & \downarrow \\
b & ab & b & b \\
\end{array}
\]

bond order = \(\frac{1}{2}(8 - 2) = 3\)

\(\text{:N≡N:}\)

Molecular orbital diagram: O₂ and F₂

O₂ : \((1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g)^2\)

\[
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\
b & ab & b & b & b & ab & ab \\
\end{array}
\]

bond order = \(\frac{1}{2}(8 - 4) = 2\)

\(\text{:O=O:}\)

F₂ : \((1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g)^4\)

\[
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\
b & ab & b & b & b & ab & ab & ab \\
\end{array}
\]

bond order = \(\frac{1}{2}(8 - 6) = 1\)

\(\text{:F−F:}\)

• MO bond orders agree with Lewis structures

• MO theory correctly predicts observed magnetic properties:
  N₂ and F₂ have 0 upe, O₂ has 2 upe