A homonuclear diatomic molecule is one in which the molecule is formed from two atoms of the same element.

The neutral hydrogen molecule $H_2$ is the simplest diatomic molecule.

$H_2$ is a two electron problem where we have to include the repulsion between the two electrons in the electron potential. This is a difficult problem and we try to avoid that.

Instead we will ignore electron-electron interaction and use the molecular hydrogen ion to describe at least some of the diatomic molecules.

We know that these few diatomic molecules are going to be satisfactorily by this approximation. However, as the number of valence electrons increases in the molecule using the molecular hydrogen ion approximation produces serious errors.
• In the $H_2$ molecule the two electrons will occupy the two spin (±1/2) states in $1\sigma$.

• We observe that the internuclear distance in the neutral molecule is smaller with a larger binding energy $E_b \sim 5 \text{ eV}$ as compared to $E_b \sim 3 \text{ eV}$ for the ion.

• One deduces that in $H_2$ the two electrons form a strong bond since the bond is relatively short with a somewhat large binding energy.

• The next molecule is $He_2$. In the $He$ atom the two electrons occupy the two spin states in the $1s$ AO.

• As we figured earlier the LCAO of the $1s$ AOs yields the $1\sigma$ and $1\sigma^*$ MOs. These are the MOs that would accommodate the four electrons in $He_2$. Therefore the electronic configuration in $He$ is $1\sigma^2$ and $1\sigma^*^2$.

• In the $Li_2$ molecule, however, the LCAOs involving the $2s$ AOs in the isolated Li atom ($Z = 3 ; 1s^22s^1$) produces the MOs $2\sigma$ and $2\sigma^*$. The $Li_2$ electron configuration becomes $1\sigma^21\sigma^*^22\sigma^2$.

• For beryllium ($Z = 4 ; 1s^22s^2$) the diatomic molecule $Be_2$ has the electron configuration $1\sigma^21\sigma^*^22\sigma^22\sigma^*^2$. 
• At this point we notice that there is some kind of pattern developing on the number of AOs involved in the LCAO and the number of MOs generated.

• We find that the number of AOs from the two atoms contributing in the LCAO is equal to the number of MOs produced in the molecule. This is the law of “conservation of states”.

• For boron \((Z = 5; 1s^22s^22p^1)\) we immediately see that the 2p AOs come to bear in the \(B_2\) molecule. We have shown that the 2p AOs comprise the 2p\(_x\), 2p\(_y\), and 2p\(_z\) orbitals.
• If we take the z-axis as the molecular axis of symmetry, then the overlap of the $2p_z$ AOs has the same cylindrical symmetry that distinguishes the $\sigma$ MOs.

• Therefore the LCAO involving the two $2p_z$ AOs produces the 3$\sigma$ and 3$\sigma^*$ bonding and antibonding MOs, respectively.

• Here we note the departure from the shell number $n$ in the individual atoms when it comes labeling the MO: e.g., for $n = 1$ the two 1s AOs give the 1$\sigma$ and 1$\sigma^*$ MOs and the $n = 2$ two 2s AOs give the two 2$\sigma$ and 2$\sigma^*$ MOs, but the $n = 2$ two $2p_z$ AOs result in 3$\sigma$ and 3$\sigma^*$.

• We immediately realize that the Greek letter designation of the MO is based on the symmetry and the number designation is based on the energy and not on the atomic shell in the isolated atoms making up the molecule.
• The overlap of the two 2p_x AOs results in two bonding and antibonding MOs designated, respectively, as 1\pi_x and 1\pi_x^*.
• Similarly the two 2\pi_y AOs result in the 1\pi_y and the 1\pi_y^* bonding and antibonding MOs, respectively.
• Since the 2\pi_x and 2\pi_y have the same symmetry the resulting bonding MOs 1\pi_x and 1\pi_y have the same energy, i.e., they are degenerate.
• So are the antibonding MOs and .
• The atomic configuration in B_2 is

\begin{array}{cccccccc}
1 & 2 & 1 & 2 & 2 & 1 & 1 & 1 \\
\end{array}

• We have pointed out that 1\pi_x and 1\pi_y are degenerate, but then the electrons in B_2 populate these levels in such a way that their spins are parallel.
• This is one of the rules that must be obeyed in filling the MOs with electrons: it is called Hund’s rule.
• In spite of the fact that B_2 has an even number of electrons, it still has a net non-zero spin, i.e., B_2 is paramagnetic.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electron Configuration</th>
<th>Bond Strength (eV)</th>
<th>Bond Length (nm)</th>
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<tbody>
<tr>
<td>$B_2$</td>
<td>$1\pi_x^1\pi_y^1$</td>
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<td>0.112</td>
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<tr>
<td>$N_2$</td>
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<td>6.7</td>
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<tr>
<td>$O_2$</td>
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<td>0.121</td>
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<tr>
<td>$F_2$</td>
<td>$1\pi_x^2\pi_y^2 3\sigma^2 1\pi_x^{*2} \pi_y^{*2}$</td>
<td>1.6</td>
<td>0.144</td>
</tr>
</tbody>
</table>
HETERONUCLEAR DIATOMIC MOLECULES

• In the homonuclear molecules discussed above the MOs are made from AOs, which have the same symmetries.
• These MOs are either symmetrical or unsymmetrical about the plane orthogonal to and midway in the axis of the molecule.
• At any given time, the electron in the bonding MO could be near one proton or near the other.
• Since the wavefunction is symmetrical about the orthogonal midway plane averaged over time the electron is shared equally by the two protons.
• This type of molecular bonding is referred to as purely covalent. In this case the LCAOs method is very straightforward and calculations are very much simplified by the symmetry.
• However in a heteronuclear diatomic molecule – a molecule made of two different atoms - the story is very different: the math becomes difficult and tedious in this case.
• Consider a heteronuclear diatomic molecule such as HF and let us treat it the same way we treated the molecular hydrogen ion.
• The electron in the ground state of hydrogen resides in the 1s AO and is bound to the nucleus at an energy of -13.6 eV.
• In F (Z = 9; 1s²2s²2p⁵) the weakest bound electron resides in 2p at an energy of -18.6 eV.
• The loosely bound electrons are the ones that bond to form the molecule. So we now have to form our MOs from the 1s in H and the 2p in F.
• We now need to specify one of the AOs at \( \phi_1 \) and the other as \( \phi_2 \) but before that we have to determine which one of the 2p AOs are we going to use.
• The answer to this lies in the definition of the bonding integral which is non-zero only for \( \phi_1 \) and \( \phi_2 \) that have the same symmetry.
• MOs are formed from AOs with the same symmetry: hence the choice for the AO from the F atom to be used in the LCAO is the 2p\(_z\).
• With this choice we may set \( \phi_1 \) as the 1s in H and set \( \phi_2 \) as the 2p\(_z\) in F and we may write the MO \( \psi \)

\[
\psi = a_1 \phi_1 + a_2 \phi_2
\]
• Using the above assignments for the AOs and

\[ E_e^+ = E_C + E_B \quad \text{and} \quad E_e = E_C - E_B \]
where

\[ E_C = 1 \quad 1 = 2 \quad 2 \quad \text{and} \quad E_B = 1 \quad 2 = 2 \quad 1 \]

• We now have no longer one value for the Coulombic integral. Instead we have two different Coulombic integrals \( E_C^H \) and \( E_C^F \).

\[ E_C^H = 1 \quad 1 \quad 13.6 \quad eV \]
and

\[ E_C^F = 2 \quad 2 \quad 18.6 \quad eV \]

• We then continue with evaluation of the expectation value for the energy and then minimize this value with respect to \( a_1 \) and \( a_2 \), and since \( \phi_1 \) and \( \phi_2 \) have different functional forms the minimization problem is not going to be mathematically as easy as that for the molecular hydrogen.
• One gets $\alpha_1 < \alpha_2$ for the bonding $\sigma$ MOs and $\alpha_1 > \alpha_2$ for antibonding $\sigma^*$ MOs.

• If we realize that $\alpha_1$ and $\alpha_2$ are weighing factors for the contributions of $\phi_1$ and $\phi_2$ in $\psi$ we immediately acknowledge that the electron is more affected by F and hence it spends more time residing closer to the F nucleus.

• Therefore the bond will be polar or ionic, i.e., there is a shift of negative charge from H to F.

• F is said to be more electronegative than H and the bond in HF is not purely covalent, instead it is a polar bond.
In polyatomic molecules using only the highest energy occupied AOs from each of the atoms in the molecule yields results that do not agree with experiments. Therefore more AOs will have to be used in explaining electronic structures in polyatomic molecules.

To illustrate the use of several AOs we take the example of the BeCl$_2$. 
In this molecule if we were to proceed as before we will be selecting the 2s orbital from the Be atom (Z = 4 : 1s\(^2\)2s\(^2\)) and the 2\(p_z\) AO from the Cl atom (Z=17 : 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^5\)).

But this selection is not able to explain experimental observations made on this molecule.

One here would have to take into account the angle between the bonds and come up with an alternative logical set of AOs. Instead of taking only the 2s AO from Be, we build up linear combinations of AOs made from the 2s and 2\(p_z\) AOs to represent Be in the MO.

The choice of 2\(p_z\) assumes that the z-axis is the molecular axis. If the 2s and 2\(p_z\) are equally mixed then the resulting orbitals will extend outward from Be along the z-axis in the directions of the bonds in BeCl\(_2\).

The orbitals made up of 2s and 2\(p_z\) are, hence,

\[
\begin{align*}
sp^+ &= \frac{1}{\sqrt{2}} \left( 2s + 2p_z \right) \\
and
sp^- &= \frac{1}{\sqrt{2}} \left( 2s - 2p_z \right)
\end{align*}
\]

where the factor \(1/\sqrt{2}\) takes care of the normalization.
The two orbitals, constructed from the AOs in Be, are called the sp hybrid AOs and they are the ones that are to be combined with the contribution from the other atom, Cl, to form the MOs for BeCl₂.

In spite of the 2pₓ being at a higher energy than the 2s its inclusion tends to lower the overall energy of the molecule, since the 2pₓ AO extends away from the Be atom much more than the 2s AO thereby resulting in more overlap with AOs from the Cl atom.

This larger overlap results in larger magnitude for the bond integral Eₜ (which is negative) and, hence, stronger bonds.

We also note that the 2s and the 2pₓ contribute equally to the sp hybrid, which is referred to as the diagonal hybrid.

These two sp hybrids from the Be AOs are to be used in the LCAO with the 3pₓ AO from Cl, i.e., one AO from the Cl atom, to form the MOs for BeCl₂.
As can be seen from the figure the bond is very highly polar where the two $2s$ electrons in the isolated Be atom spend most of their times near the Cl atoms. Chemists describe this type of bonding as ionic.
• An interesting molecule to consider at this stage is that of methane or CH₄.
• It is interesting because it is one of the simplest molecules that contain the carbon atom.
• The CH₄ molecule and bonding orientations are as shown
• The four C-H bonds are tetrahedrally arranged with an angle of 109.5° between bonds.

• These bonds correspond to MOs made of LCAO of the 1s AO in H (Z = 1 : 1s\(^1\)) and four sp\(^3\) hybrids involving the 2s and the three 2p AOs of the C atom (Z = 6 : 1s\(^2\)2s\(^2\)2p\(^2\)).

• The four normalized sp\(^3\) hybrids are given by

\[
\begin{align*}
\text{++++ } sp^3 &= \frac{1}{2} \left( 2s + 2p_x + 2p_y + 2p_z \right) \\
\text{++ ++ } sp^3 &= \frac{1}{2} \left( 2s + 2p_x + 2p_y + 2p_z \right) \\
\text{++ + } sp^3 &= \frac{1}{2} \left( 2s + 2p_x + 2p_y + 2p_z \right) \\
\text{++++ } sp^3 &= \frac{1}{2} \left( 2s + 2p_x + 2p_y + 2p_z \right)
\end{align*}
\]

• The sp\(^3\) hybrids in C are referred to as the tetrahedral hybrids.