Heteronuclear Diatomic Molecules

In a heteronuclear diatomic molecule, there is an electronegativity difference between the atoms, which leads to an asymmetric distribution of the electronic probability density, weighted more heavily toward the element with the greater electronegativity.

Consider constructing a MO from two \(\langle 2s\rangle\) orbitals for nuclei with different \(\langle Z\rangle\) values. Let atom A have an atomic number \(Z_A\) and atom B have an atomic number \(Z_B\). For a single electron interacting with the two nuclei, an LCAO guess wave function could be

\[
\psi_g (r) = C_A \psi_{2s(Z=Z_A)}^{A}(r) + C_B \psi_{2s(Z=Z_B)}^{B}(r)
\]

Recall the energies \(H_{AA}\) and \(H_{BB}\) that were defined for LCAO in the homonuclear case:

\[
\begin{align*}
H_{AA} &= \int \psi_{2s(Z=Z_A)}^{A}(r)\hat{H}_{elec}\psi_{2s(Z=Z_A)}^{A}(r)dV \\
H_{BB} &= \int \psi_{2s(Z=Z_B)}^{B}(r)\hat{H}_{elec}\psi_{2s(Z=Z_B)}^{B}(r)dV
\end{align*}
\]

For the heteronuclear case, \(H_{AA} \neq H_{BB}\). If atom B is the more electronegative, then its \(Z\) will be larger (in the second period), and the energy will be more negative due to the large Coulomb attraction between the electrons and the nuclei. Thus, in this case \(H_{BB} < H_{AA}\) (remember \(H_{AA}\) and \(H_{BB}\) are both negative). Now, if we calculate the guess of the ground-state energy

\[
E_g = \frac{\int \psi_g (r)\hat{H}_{elec}\psi_g (r)dV}{\int \psi_g^2 (r)dV}
\]

we find the more general result

\[
E_g = \frac{\int \psi_g (r)\hat{H}_{elec}\psi_g (r)dV}{\int \psi_g^2 (r)dV}
\]

and then perform the minimization of \(E_g\):

\[
\frac{dE_g}{dC_A} = 0; \frac{dE_g}{dC_B} = 0
\]

we obtain the conditions

\[
\begin{align*}
\frac{dE_g}{dC_A} &= \frac{2C_A H_{AA} + 2C_B H_{AB}}{D} - \frac{H_{AA} C_A^2 + H_{BB} C_B^2 + 2C_A C_B H_{AB}}{D^2}(2C_A + 2SC_B) = 0 \\
\frac{dE_g}{dC_B} &= \frac{2C_B H_{BB} + 2C_A H_{AB}}{D} - \frac{H_{AA} C_A^2 + H_{BB} C_B^2 + 2C_A C_B H_{AB}}{D^2}(2C_B + 2SC_A) = 0
\end{align*}
\]

If we make the simplifying approximation that the overlap \(S\approx 0\), then these conditions lead to the following relationship between \(C_A\) and \(C_B\):

\[
\frac{dC_A}{C_B} = \frac{H_{AA} - H_{BB}}{2H_{AB}} \pm \sqrt{\frac{(H_{AA} - H_{BB})^2}{4H_{AB}^2} + 1}
\]

In order to make the analysis a bit easier, let us expand the square root using the fact that

\[
\sqrt{1+x} \approx 1 + \frac{1}{2}x
\]
Then
\[\frac{C_A}{C_B}=\frac{H_{AA}-H_{BB}}{2H_{AB}}\pm\left[1+\frac{(H_{AA}-H_{BB})^2}{8H_{AB}^2}\right]\]

Now, we know that
\[\left[1+\frac{(H_{AA}-H_{BB})^2}{8H_{AB}^2}\right] > \\left|\frac{H_{AA}-H_{BB}}{2H_{AB}}\right|\]

First, look at the \(\psi_+ (r)\). If \(H_{AA}>H_{BB}\), \(B\) is more electronegative because its energy is lower (think of the Bohr formula \(E_n =-Z^2/n^2\)), which shows that as \(Z\) increases, the energy decreases. Generally, a not so easy calculation of \(H_{AB}\) shows that \(H_{AB}\) is not very different. Thus, if \(H_{AA}>H_{BB}\), then
\[\frac{H_{AA}-H_{BB}}{2H_{AB}}<0\]
and this means that \(C_A/C_B <1\) or \(C_A <C_B\), which is what we would expect if \(B\) is more electronegative.

Similarly, if \(H_{AA}<H_{BB}\), \(A\) is more electronegative. We would then find
\[\frac{H_{AA}-H_{BB}}{2H_{AB}}>0\]
and \(C_A /C_B >1\), and \(C_A >C_B\), which is what we would expect if \(A\) is more electronegative.

Another consequence we can derive from the above result is that if \(H_{AA}\ll H_{BB}\) or \(H_{AA}\gg H_{BB}\), then the coefficients will be very different, e.g. \(C_A \gg C_B\) or \(C_A \ll C_B\), in which case, the resulting MO is not really an MO at all, but rather more like the AO with the larger coefficient. Thus, it is clear that \(H_{AA}\) and \(H_{BB}\) cannot be very different if we are to have a reasonable amount of mixing of the two AOs. This supports the idea that only orbitals with similar energies can be combined in the LCAO scheme.

We can no longer use the "g" and "u" designators because the orbitals have no particular symmetry when \(r\rightarrow-r\). That is
\[\psi_+ (-r)\neq \psi_+ (r)\;\psi_- (-r)\neq -\psi_- (r)\]
Thus, we denote \(\psi_+ (r)\) simply as \(\sigma_{2s}\) and \(\psi_- (r)\) simply as \(\sigma_{2s}^*\).

Let us now construct a correlation diagram for the heteronuclear diatomic \(\text{BO})\). Boron has an electronic configuration
\[\text{[1s}^2 \text{2s}^2 \text{2p}_x\text{]}\]
while oxygen’s is
\[\text{[1s}^2 \text{2s}^2 \text{2p}_x\text{]}^2\text{2p}_y \text{2p}_z\text{]}
Since we are interested in the chemical bond that forms between them, we only consider the valence electrons explicitly, and these are the electrons in the \(\text{n=2}\) shell. In \(\text{BO})\), oxygen is the more electronegative, so its orbitals are lower in energy than those of boron. This must be indicated on the correlation diagram. Thus, the correlation diagram appears as in the figure below:
Note that the ordering of the MOs follows the pattern we would expect for boron rather than oxygen. Only high-level calculations can predict this, but physically, the simple explanation is that there is only one electron in the \(\sigma_{2p_z}\) orbital, and only one of the two atoms has a large nuclear charge (unlike in \(O_2\), where they both do). There is, therefore, insufficient Coulomb attraction for this one electron to pull the energy of the \(\sigma_{2p_z}\) orbital below the energy of the \(\pi\) bonding orbitals.

The electronic configuration of \(BO\) is, therefore

\[
\text{[(sigma}(2s)^2 (sigma}(2s)^*^2 (pi}(2p_x)^2 (pi}(2p_y)^2 (sigma}(2p_z)^1]
\]

and the bond order is \((1/2)(7-2)=5/2\). The fraction bond order indicates that the molecule is paramagnetic, as with \(O_2\).
As another example, consider the molecule \(\text{NO}\). \(\text{NO}\) has 11 valence electrons and has the electronic configuration:
\[
(\sigma_{2s})^2 (\sigma_{2s}^{*})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^2 (\pi_{2p_x}^{*})^1
\]
The bond order is also \(5/2\), and the molecule is paramagnetic as well.

What about the molecule \(\text{HF}\)? Here, the \(1s\) and \(2s\) orbitals of \(\text{F}\) are so low in energy compared to the \(1s\) orbital in \(\text{H}\) that they cannot be combined to form MOs. At the same time, the \(2p_x\) and \(2p_y\) orbitals of \(\text{F}\) have an insignificant spatial overlap with the \(1s\) orbital in \(\text{H}\) (assuming that the two nuclei lie along the z-axis) that they also do not form MOs. Only the \(2p_z\) orbital of \(\text{F}\) has significant overlap with the \(1s\) orbital in \(\text{H}\) and can mix with it energetically. Thus, the LCAO guess wave function takes the form
\[
\psi_+ (r)=C_A \psi_{1s}^{A}(r)+C_B \psi_{2p_z}^{B}(r)
\]
where atom A is \(\text{H}\) and atom B is \(\text{F}\). If \(\text{H}\) lies to the left of \(\text{F}\), then this orbital has antibonding character, while the orbital
\[
\psi_- (r)=C_A \psi_{1s}^{A}(r)-C_B \psi_{2p_z}^{B}(r)
\]
has bonding character because there is significant amplitude in the region between the nuclei. See the figure below:

**Figure:** Illustration of the overlap between the \(\langle 2s\rangle\) and \(\langle 2p\rangle\) orbitals of \(\text{F}\) with the \(\langle 1s\rangle\) of \(\text{H}\) in the molecule \(\text{HF}\).
The orbital \(\psi_-\) is denoted simply as \(\sigma\) while the orbital \(\psi_+\) is denoted \(\sigma^*\) for bonding and antibonding, respectively. The \(2s\), \(2p_x\) and \(2p_y\) orbitals of F do not mix with anything and are, therefore, called nonbonding orbitals. They are denoted \(\sigma^{nb}\) and \(\pi_{x}^{nb}\) and \(\pi_{y}^{nb}\), respectively. The orbital ordering is \(\sigma^{nb}\) (since it is a low-energy \(2s\) orbital), followed by \(\sigma\), then the two nonbonding \(\pi\) orbitals and finally \(\sigma^*\). Therefore, the correlation diagram for \(HF\) is as shown in the figure below:
Another look at the correlation diagram in HF.

The bond order of HF is easily seen to be 1.

**Frontier molecular orbitals**

While we are looking at HF, it is worth digressing to discuss (briefly) the concept of frontier molecular orbitals (to which you will be exposed more in organic chemistry). The term "frontier" refers to the orbitals that are at the outer edges of a molecule. These tend to be the orbitals that are the most spatially delocalized and hence, the orbitals with the highest energies (either occupied or unoccupied). In particular, two orbitals are of particular importance. These are the **highest occupied molecular orbital** (HOMO) and the **lowest unoccupied molecular orbital** (LUMO). "Highest" and "lowest" refer to the energies. In HF, the HOMO orbital(s) are the double degenerate \( |\pi_{2p_x}\rangle \) and \( |\pi_{2p_y}\rangle \) orbitals, while the LUMO is the \( |\sigma_{2p_z}^{\star}\rangle \) orbital.
The HOMO and LUMO can help us predict what will happen in a chemical reaction. Consider the reaction of \(\text{HF}\) with \(\text{H}_2\text{O}\):

\[
\text{HF} + \text{H}_2\text{O} \rightarrow \text{F}^- + \text{H}_3\text{O}^+
\]

In terms of Lewis structures, the reaction can be depicted as shown below:

**Figure:** Reaction of \(\text{HF}\) with \(\text{H}_2\text{O}\) in Lewis structures.

![Lewis structure of HF + H2O reaction](image)

Here we see the \(H\) of \(\text{HF}\) trading the shared pair in the \(\text{HF}\) bond for one in the \(\text{H}_3\text{O}^+\) (as depicted by the arrow in the diagram). The arrow attempts to convey that the water molecule donates one of its lone pairs to the \(\text{HF}\) molecule, causing the \(\text{HF}\) bond to rupture, thereby allowing liberated proton to attach to the water molecule.

In terms of frontier molecular orbitals, we can view the reaction as follows: The electron pair donated by the water molecule must go into the LUMO of \(\text{HF}\). Since the LUMO is a \(\sigma_{2p_z}^{*}\) orbital, the occupancy of this orbital by two electrons changes the bond order of \(\text{HF}\) from 1 to 0, and this causes the bond to be destabilized and rupture, thereby freeing up the proton \(\text{H}^+\) to react with the \(\text{H}_2\text{O}\).

**Constructing MOs for the water molecule**

In this section, we will construct approximate molecular orbitals for a water molecule by considering a simple linear triatomic of the general form \(\text{HXH}\), where \(\text{X}\) is a second row element. The linear form clearly does not apply to \(\text{H}_2\text{O}\), but we can still construct a reasonable argument for the energetic ordering and structure of the MOs. We first note that each \(\text{H}\) will donate a \(1s\) orbital in the LCAO scheme, and \(\text{X}\) will likely donate at least \(2s\) and possible \(2p\) orbitals, depending on its chemical identity. Let atom \(A\) be an \(\text{H}\), let atom \(B\) be \(\text{X}\) and let atom \(C\) be \(\text{H}\). What orbitals can we construct? Note that the molecule is symmetric about the center (the position of \(\text{X}\)), hence the orbitals have to have the same symmetry.

As with \(\text{HF}\), the only \(2p\) orbital of \(\text{X}\) that will overlap with \(1s\) of \(\text{H}\) is the \(2p_z\). Hence, consider the combination

\[
|\psi_{1}(r)=|C_A|\psi_{1s}^{A}(r)-|C_B|\psi_{2s}^{B}(r)+|C_A|\psi_{1s}^{C}(r)|
\]

Note that the two coefficients in front of the \(1s\) orbitals are the same by symmetry.

How big should the \(2s\) orbital of \(\text{X}\) be compared to the \(1s\) orbital of \(\text{H}\)? This depends on several things. First, is the nuclear charge on \(\text{X}\) and the second is the electronegativity difference between \(\text{H}\) and \(\text{X}\). The first determines how quickly the \(2s\) orbitals, remembering that the exponential part is \(\exp(-Zr/a_0)\), and the electronegativity difference determines the relative magnitude of \(|C_A|\) compared to \(|C_B|\). In the case of \(\text{BeH}_2\), the \(2s\) orbital on \(\text{Be}\) multiplied by the coefficient \(|C_B|\) (which is smaller than that of \(|C_A|\) due to \(\text{Be's}\) lower electronegativity) causes the \(2s\) orbital to be smaller than the \(1s\) on \(\text{H}\). For \(\text{H}_2\text{O}\), the \(2s\) orbital decays at about the same
rate in \(r\) as does the \(1s\) orbital of \(H\), however, the coefficient \(|C_B|\) will be larger than \(|C_A|\) because \(O\) is more electronegative. Hence, for \(O\), the \(2s\) orbital should be larger than that of the \(1s\) on \(H\).

However, this is a technical issue that is less important than the qualitative features of the MOs that we now seek. The orbital \(\psi_1 (r)\) constructed above is purely bonding because the \(2s\) orbital is positive near the oxygen nucleus but becomes negative as we go away from the nucleus. Note that the book gets this wrong throughout Chapter 7. This orbital is also even, so we can denote it as a \(\sigma_{g2s}\) orbital signifying that it is constructed from a \(2s\) orbital of \(O\) combined with the \(1s\) orbital of \(H\) (no designator is needed for this \(1s\) orbital since this is the only orbital \(H\) can donate and hence, is obvious). The only other MO that can be constructed that has the right symmetry is

\[
\psi_2 (r) = |C_A|\psi_{1s}^{A}(r)+|C_B|\psi_{2s}^{B}(r)+|C_A|\psi_{1s}^{C}(r)
\]

which will be antibonding, as shown in the figure above. The orbital is even, so we can denote it as \(\sigma_{g2s}^{*}\). Next, if we combine a \(2p_z\) orbital of \(O\) with the \(1s\) of \(H\), there are two possibilities that have the right symmetry. The first is

\[
\psi_3 (r) = |C_A|\psi_{1s}^{A}(r)-|C_B|\psi_{2p_z}^{B}(r)-|C_A|\psi_{1s}^{C}(r)
\]

which is a bonding orbital as shown in the figure above. Since it is odd, we can denote it as \(\sigma_{u2p_z}\). Finally, there is

\[
\psi_4 (r) = |C_A|\psi_{1s}^{A}(r)+|C_B|\psi_{2p_z}^{B}(r)-|C_A|\psi_{1s}^{C}(r)
\]

which is purely antibonding (see figure above) and odd. Hence, we denote this as \(\sigma_{u2p_z}^{*}\). The orbitals \(2p_x\) and \(2p_y\) from \(O\) are nonbonding and become \(\pi_{2p_x}\) and \(\pi_{2p_y}\) nonbonding orbitals.

The figure below illustrates the difference between the actual linear case we just analyzed and the truly bent molecule, e.g. \(H_2O\). The geometry changes the ordering somewhat, but the qualitative picture we obtain from the linear case makes it a useful construction.

**Figure:** MOs of linear vs. bent triatomics.
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