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Now let's put in the electrons –

six if we are talking about \( \text{BH}_3 \), or eight, if we are talking about \( \text{NH}_3 \).

(The carbon reactive intermediates \( \text{CH}_3^+ \) and \( \text{CH}_3^- \) will be treated later in the section on reactive intermediates.)

With 6 electrons, MO’s A-C only are occupied, and the planar form is clearly preferred, since both orbitals B and C are destabilized upon pyramidalization.

In contrast, with 8 valence electrons, \( \text{NH}_3 \) is clearly predicted to be pyramidal, since orbital \( \text{D}' \) is now occupied and it is highly stabilized by pyramidalization.
Walsh Diagram for Pyramidal $\text{AH}_3$
Walsh diagram for the AH₃ systems (A is a 1ˢᵗ or 2ⁿᵈ row element): the D₃ₕ to C₃ᵥ distortion

planar CH₃, D₃ₙ

pyramidal CH₃, C₃ᵥ
1.2.4 The CH$_2$ Group in Detail

If one does the same thing for the CH$_2$ group, the Walsh diagram with group orbitals can be described as

**Start with the linear structure:**

1. There is a low-lying, C-H bonding orbital A derived from the carbon 2s orbital.

2. Only one p orbital can bond to the H’s in the linear form – giving MO B, plus a degenerate pair of non-bonding p-orbitals.
Going from linear to bent:

1. Orbital A is slightly stabilized forming $\sigma(\text{CH}_3)$.
2. B is destabilized more, since C-H overlap decreases upon bending - $\pi(\text{CH}_3)$
3. Biggest change is the drop in energy of C, as it goes from non-bonding to bonding.
4. Orbital D remains an isolated, non-bonding p-orbital.
5. Secondary mixing between C and E results in an important hybrid orbital C' ($\sigma$-out).
Walsh Diagram for AH2
Qualitative Molecular Orbital Theory (QMOT)

Walsh diagram for the AH₂ systems (A is a 1ˢᵗ or 2ⁿᵈ row element): the D₅ᵥ to Cᵥ distortion

- 2pₓ, 2pᵧ, 2p₂ of carbon atom
- 2s AO of carbon
- 1s AO's of hydrogen atoms

linear CH₂ (D₅ᵥ)  bent CH₂ (Cᵥ)
Where are the H₂O Lone Pairs?

Putting in electrons:

For H₂O –

eight valence electrons, including two lone pairs

Where are the lone pairs?

In this bonding scheme, the lone pairs are considered to be in MO’s C’ and D, not in equivalent orbitals.
There is experimental evidence for this:

In the gas phase, the photoelectron spectrum of H$_2$O exhibits two ionizations corresponding to the two different lone pairs, separated by 2.2 eV. This observation certainly points out a limitation of the VB theory. Two equivalent lone pairs can be obtained for H$_2$O by taking in-phase and out of phase combinations of C' and D orbitals, and upon perturbation by an interacting species (such as a proton), this probably happens.

In practice, the two bonding models are generally indistinguishable.
Similarly, the photoelectron spectrum of \textit{methane}, which is represented in VB theory as having four equivalent C-H $\sigma$-bonds, consists of two bands, at about 23 and 12.7 eV, and not the single band that one would expect from four identical C-H bonds. (Of course a third band, corresponding to ionization of the 1s electrons can also be observed at much higher energy (290 eV).) \textit{See Carey and Sundberg for a relevant discussion of the bonding in methane.}

\textbf{Methane}

\begin{verbatim}
http://courses.chem.psu.edu/chem210/mol-gallery/methane-MO/methane-MO.html
\end{verbatim}
Fig. 1.14. Combinations of atomic orbitals leading to the methane molecular orbitals.
Mixing two orbitals produces an in-phase, bonding combination and an out-of-phase, antibonding combination. The former is stabilized and the latter is destabilized. It is important that the antibonding combination is raised in energy more than the bonding combination is lowered in energy.

The mixing of filled orbitals on two separate molecules is always destabilizing. This four-electron interaction is referred to as “closed shell repulsion.”

Figure 6. Orbital mixing. Simple spherical orbitals are used to illustrate the concept (A=first order, degenerate mixing, B= second order mixing)
Obviously, a different outcome arises when one only has two electrons in the system – then the two electrons end up in the lower orbital and the mixing is always stabilizing.

*It is favorable to mix a filled orbital with an empty one, or to mix two singly-occupied orbitals.*

The lower example in Figure 6 illustrates another important feature of non-degenerate orbital mixing.

In this situation, the lower energy, bonding orbital will have a larger contribution from the original orbital that was lower in energy. Conversely, the high energy, antibonding orbital will have a larger contribution from the originally higher energy orbital. Such mixing produces a polarization of the resulting orbitals.

First order, degenerate mixing is stronger than second order mixing

The larger the energy gap between the initial pair of orbitals, the smaller the interaction (*energy gap law*).
1.3.1 Using Group Orbitals to Make Ethane

Use the MO’s of pyramidal methyl as shown in Figure 7.

**Figure 7.** The orbital mixing diagram for formation of ethane from two pyramidal CH₃ groups.
1. Only consider the degenerate, 1\textsuperscript{st} order mixings – they will be strongest.

2. $\sigma(\text{CH}_3)$ and $\pi(\text{CH}_3)$ orbitals are primarily C-H bonding – they don’t point out into the C-C bonding region. Thus, overlap is small for them and the mixing interaction is small.
3. The most important mixing is that of the pair of $\sigma$(out) orbitals – they point out into the C-C bonding region and therefore they overlap very well and the mixing is strong.

Adding electrons: 14 valence electrons

It can be seen that the HOMO is a degenerate pair of orbitals that are best described as C-H bonding, but also slightly C-C antibonding.

Generalizing, whenever one sees a C-C single bond in a molecule, one can consider that the respective C-C bonding orbital derives from such a $\sigma$(out) + $\sigma$(out) interaction.

Likewise, once can also anticipate orbitals of $\pi$-like character for the C-H interactions.
Group Orbitals to Make Ethane

\[
\begin{align*}
\text{σ(out)} & \quad \text{π(CH}_3\text{)} & \quad \text{σ(out) + σ(out)} & \quad \π(CH}_3\text{)} \\
\text{π(CH}_3\text{)} & \quad \text{σ(out)} & \quad \text{π(CH}_3\text{)} & \quad \text{σ(CH}_3\text{) - σ(CH}_3\text{)} \\
\text{σ(CH}_3\text{)} & \quad \text{σ(CH}_3\text{)} & \quad \text{σ(CH}_3\text{) + σ(CH}_3\text{)} & \quad \text{σ(CH}_3\text{)} \\
\end{align*}
\]
Group Orbitals to Make Ethane

Figure 1.13
The computed MOs of ethane.
1.3.2 Using Group Orbitals to Make Ethylene

Using MO theory, we build ethylene by combining two \( \text{CH}_2 \) groups (six electrons each) as shown in Figure 8.

As was the case for ethane, the MO’s derived from \( \sigma(\text{CH}_2) \) and \( \pi(\text{CH}_2) \) make four MO’s that are primarily C-H bonding.

The interesting interactions involve the \( \sigma(\text{out}) \) orbital and the \( p \) atomic orbital.

The hybrid \( \sigma(\text{out}) \) orbital is strongly directional and strongly overlapping, and it produces the C-C \( \sigma \) bond.

The \( p + p \) interaction is weaker overlapping and produces the \( \pi \)-bond of ethylene.

Inserting the twelve electrons, one sees that the LUMO is the out-of-phase combination of \( p \) orbitals or the \( \pi^* \) orbital.
Group Orbital Picture of Ethylene
Figure 1.15
The computed MOs of ethylene. Note the molecule is shown in different orientations for different MOs.