

Tutorial Problem

- Draw the correlation diagram for the distortion of AH_3 from D_{3h} to C_{3v}
- Assume that BH_3 has been distorted to become trigonal pyramidal, will MO mixing occur? If BH_3 has accepted electrons from a base into the LUMO will MO mixing occur?

AH_3 Correlation Diagram (Model Answers)

- Draw the correlation diagram for the distortion of AH_3 from D_{3h} to C_{3v}
 - The tutorial for L3 involved the first step in this process, drawing the high symmetry MO diagram
 - Then we have two options:
 1. determine the MO diagram for trigonal pyramidal AH_3 from scratch
 2. use the MO diagram we have constructed and evaluate changes to MOs
- Option 2 is often more useful when forming a correlation diagram, **Figure 1**
- the far right column of **Figure 1** shows the center of the MO diagram for trigonal planar AH_3 , A less electronegative than H (you may want to think about what happens when A is more electronegative than H)
- when the shape of a molecule is distorted the AO components move with their atoms, they do not change direction or orientation. For example look at the pAOs of the central atom A in the $1e$ MO, the atom has not moved, so the AO does not move.

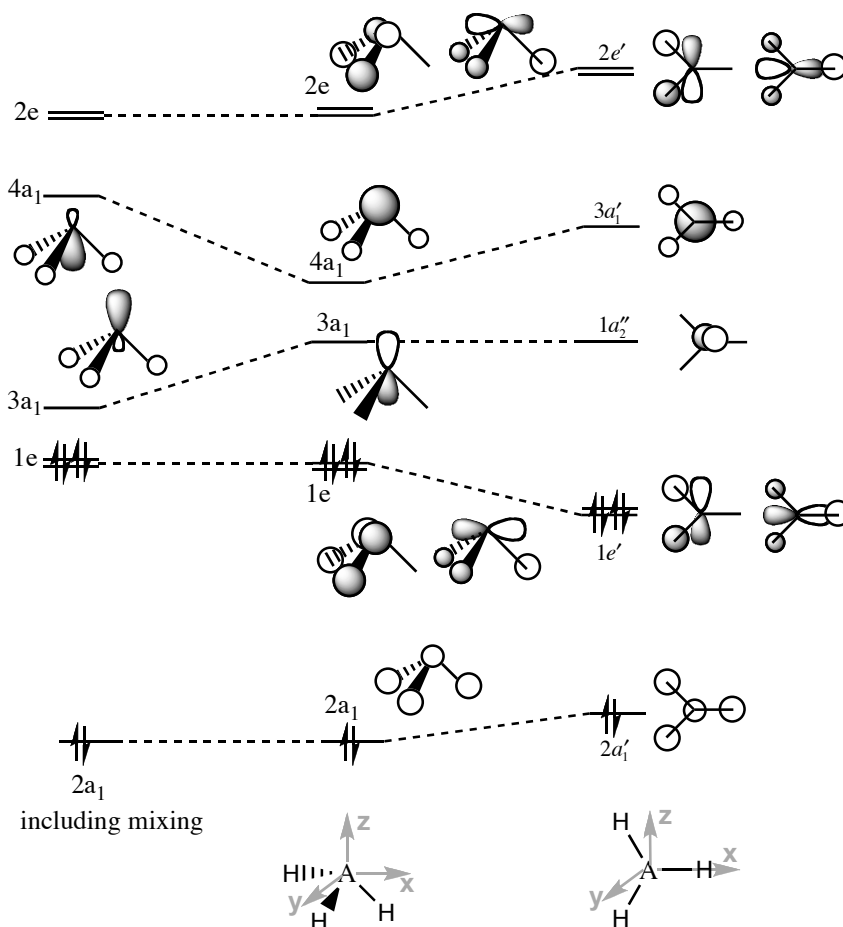


Figure 1 Setting up for a correlation diagram

- the shift in the energy levels has been determined solely by evaluating changes that occur in overlap and overall bonding character on distortion.
 - the $2a_1'$ MO is slightly stabilised due to an increase in the (through space) H sAO bonding overlap, this is a result of the H atoms getting slightly closer together as the molecule distorts. There is also a slight decrease in the bonding overlap of the central element sAO with the H sAOs and so overall the stabilisation is not large.
 - the $1e'$ MOs are destabilised due to a reduction in the bonding overlap of the central element pAO with the H sAOs, and an increase in the through space H sAO antibonding interaction, Both interactions contribute to destabilisation and hence the shift in energy is larger than for the $2a_1'$ MO. The converse is true for the $2e'$ MOs.
 - the $1a_2''$ MO is non-bonding and so the energy of this MO does not change
 - the $3a_1'$ MO is slightly stabilised due to an increase in the (through space) H sAO bonding overlap, there is also a slight decrease in the anti bonding overlap of the central element sAO with the H sAOs and so overall there is significant stabilisation (larger than that observed for the $2a_1'$ MO).
- there is also a change in point group on distortion from D_{3h} to C_{3v} , and the symmetry labels of the orbitals change
 - there is no significant effect on the $e' \rightarrow e$ MOs, or in the deep lying $2a_1' \rightarrow 2a_1$ MO
 - however the $1a_2''$ MO becomes the $3a_1$ (D_{3h}), and the $3a_1'$ MO becomes the $4a_1$ (D_{3h}).
 - these orbitals now have the same symmetry and can potentially mix, the extent of mixing is determined by the rules outlined in Lecture 3:
- Rules for MO mixing:
 - only MOs of the same symmetry can mix
 - mixing must stabilise the total energy of the molecule
 - mixing tends to be large when at least one of the following criteria are met:
 - MOs are close in energy
 - one of the MOs is non-bonding or unoccupied
 - MOs are in the HOMO-LUMO region
- we evaluate the effects of mixing between the $3a_1$ and $4a_1$ MOs (**Figure 2**) and include them on our diagram (**Figure 1**).

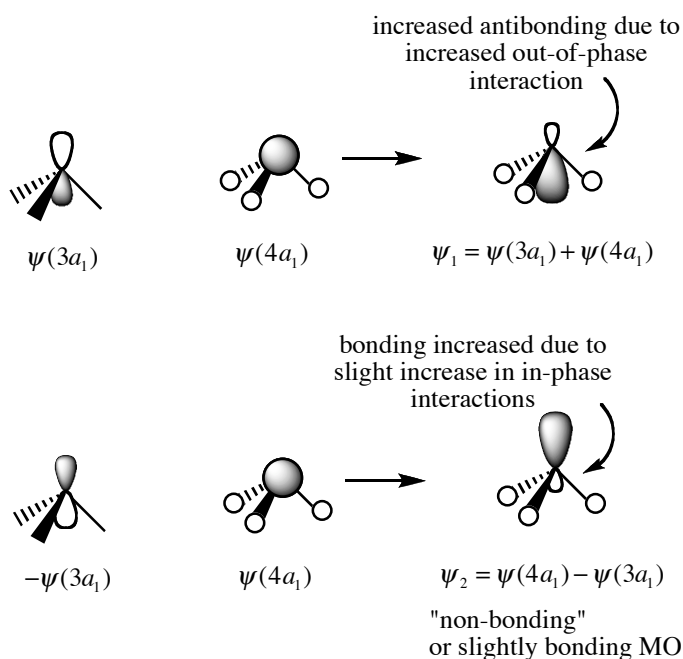


Figure 2 Mixing of the $3a_1$ and $4a_1$ MOs

- It is important to realise that mixing will be small unless there are electrons in the $4a_1$ LUMO, this is why NH_3 is pyramidal while BH_3 is planar! I'll discuss this a little more after the correlation diagram below, **Figure 3**

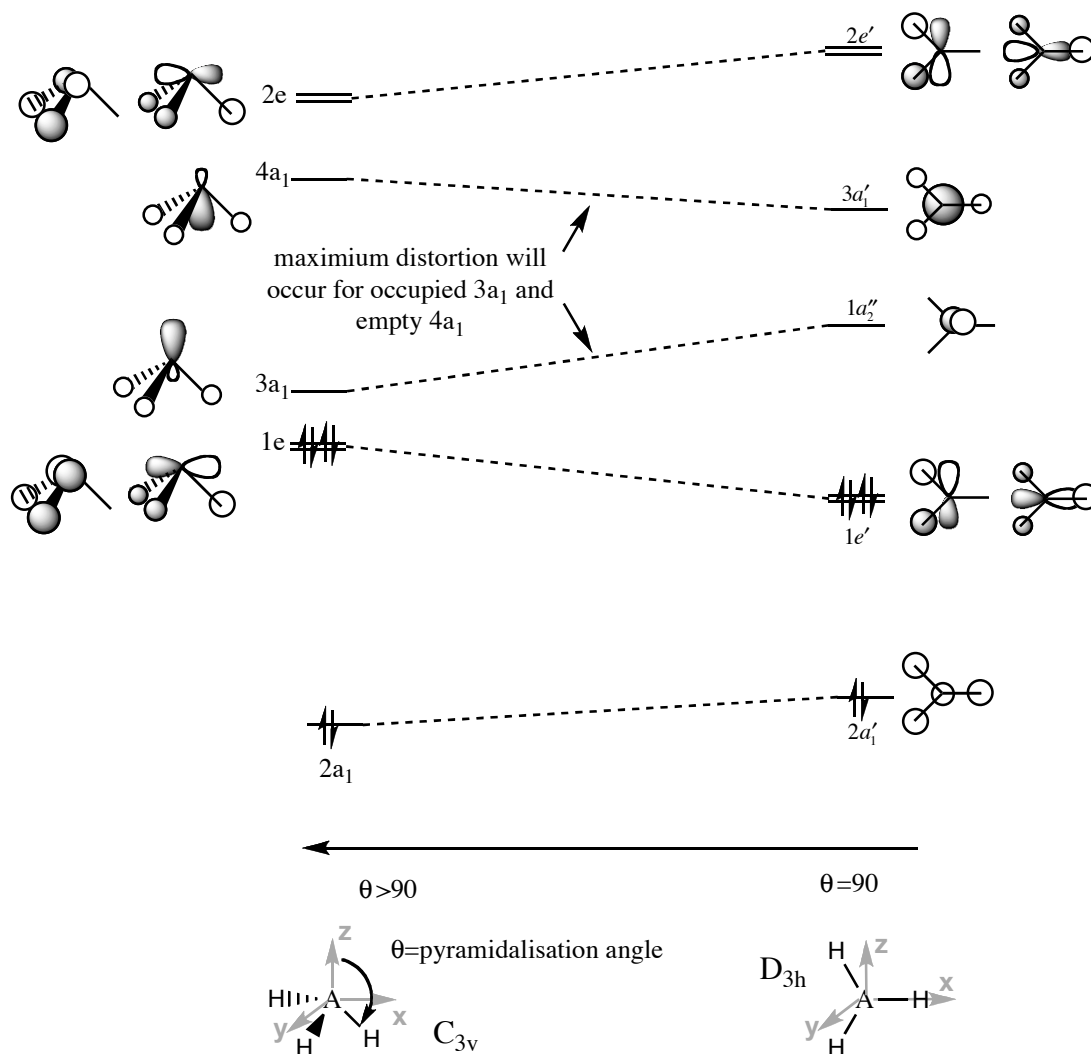
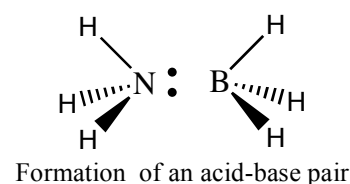


Figure 3 Correlation diagram for pyramidalisation

- BH_3 has 6e (3 from B and 3 from H_3) which fill this diagram to the $1e'$ (or $1e$) level. On distortion the $1e'$ level is destabilised, more than the $2a_1'$ is stabilised and hence BH_3 prefers to remain planar.
- NH_3 has 8e (5 from B and 3 from H_3) which fill this diagram to the $3a_1$ level. While the $3a_1$ MO is not stabilised by the geometry change, the loss of symmetry means that mixing can now occur between the occupied $3a_1$ and unoccupied $4a_1$ MO. This mixing is very strong and stabilises the $3a_1$ MO substantially and hence NH_3 is trigonal pyramidal and not planar.
- Assume that BH_3 has been distorted to become trigonal pyramidal, will MO mixing occur? If BH_3 is distorted (by some external influence) MO mixing will not occur because the $3a_1$ MO is not occupied.
- However the situation is more complex than you might think, for example when forming an acid-base adduct BH_3 distorts from a planar into a local pyramidal geometry. Two key things are happening
 - On forming an acid-base complex the symmetry of the whole adduct is reduced (due to the presence of the adduct) thus



- leading to reduction in (local) symmetry
- In the presence of the base electrons are being donated from the base into the $1a_2''$ (D_{3h}) or $3a_1'$ (C_{3v}) LUMO of BH_3
 - The reduced local symmetry of the BH_3 fragment changes the symmetry labels for the MOs allowing the HOMO and LUMO to mix, these orbitals only mix if there is some electron density in the $1a_2''$ (D_{3h}) or $3a_1'$ (C_{3v}) LUMO. The more electron density transferred into the $1a_2''$ LUMO by the base the greater the mixing that can occur and the larger the stabilisation and the greater the structural distortion.
 - Thus the extent of distortion of the BH_3 molecule in an acid-base adduct can be roughly correlated with the basicity of the base! ie the amount of electron density donated from the base into the LUMO of BH_3
 - *If BH_3 has accepted electrons from a base into the LUMO will MO mixing occur?* The answer therefore is yes.
 - More importantly the electronic structure (ie presence of electrons in the (D_{3h}) or $3a_1'$ (C_{3v}) LUMO) is affecting the nuclear structure. Thus this is a clear example of a **breakdown in the Born-Oppenheimer approximation!!** The electronic structure is influencing the nuclear geometry.