Tutorial Problem

- Form the MO diagram for BH_3 using as fragments H_3 and B
  - the fragment orbitals for H_3 are given in **Error! Reference source not found.**
  - for the moment just use these MOs, you will be deriving these in a later lecture and will then understand where they come from
- What can the highest occupied MO and the lowest unoccupied MO tell us about the chemical nature of BH_3?

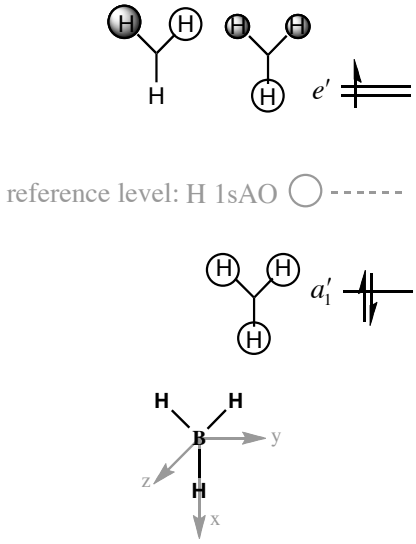

Figure 1 Fragment orbitals for H_3

The molecular orbital diagram for trigonal planar BH_3 **(Model Answers)**

- *determine the molecular shape*: BH_3 is trigonal planar
- *identify the point group of the molecule*: D_{3h}
- *define the axial system*: the z-axis is coincident with the highest rotation axis, which means the BH_3 molecule lies in the (x,y) plane with the z-axis pointing out-of-plane.
- *find all of the symmetry elements of the point group on the molecule*: (homework problem from Lecture 1), **Figure 2**

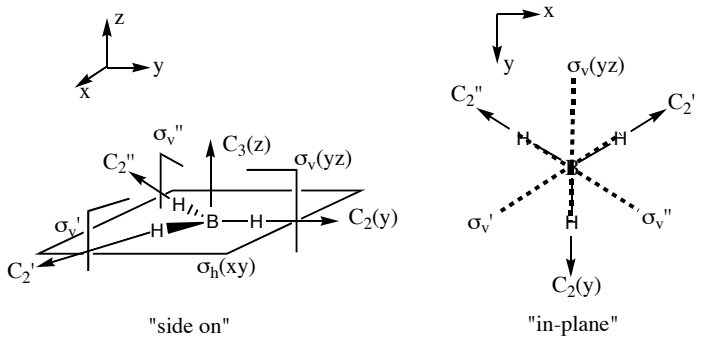

Figure 2 Axial system and symmetry elements for BH_3

- *identify the chemical fragments, and put them along the bottom of the diagram:* fragments are a central element B and an H_3 fragment. (**Figure 2** on next page)
- *determine the energy levels and symmetry labels of the fragment orbitals*: **Figure 2**
  - fragment orbitals for H_3 have been given to you, **Figure 1**
  - of the H_3 fragment the totally bonding fragment orbital must be totally symmetric => a_1'
  - of the H_3 fragment the degenerate fragment orbitals must have either e' or e" symmetry labels. The first of these orbitals has a phase distribution analogous to the x axis. Looking at the character table the x-axis has e' symmetry, therefore these orbitals have e' symmetry.
  - for the central boron atom, the fragment the orbital symmetries are determined by noting the symmetry labels of the x, y and z axes. Thus (px,py) are a degenerate e' pair and the pz AO is a_2''. The sAO is always totally symmetric and thus has a1' symmetry.

- the relative energy of the two fragments must be estimated. Boron and hydrogen are both electropositive elements and hence their s atomic orbitals will start at approximately the same level. However, the all in-phase bonding fragment orbital of the H_3 unit will be slightly stabilised. The stabilisation is only small because the H atoms are far apart (much further than a normal bond distance) and interactions between the orbitals are not large. The out-of-phase interactions will be slightly higher in energy than the lone sAO because of the antibonding component to the fragment orbitals, but not too high as these orbitals are not close enough to interact strongly, **Figure 2**

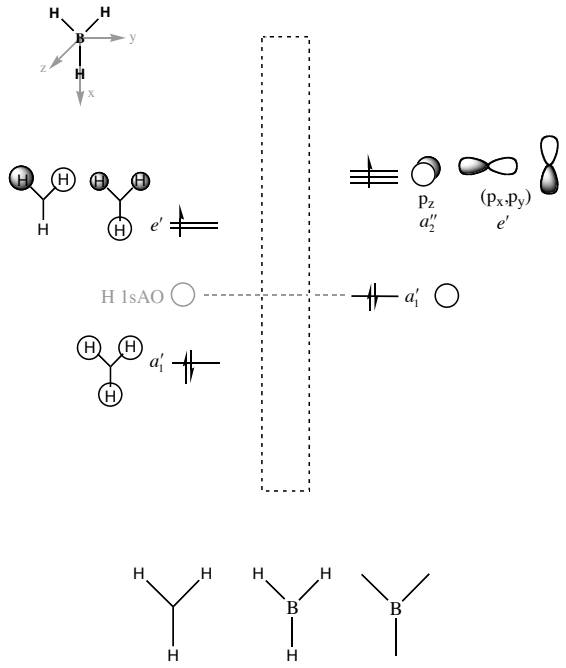

Figure 2 Fragment MO diagram BH_3

- *combine fragment orbitals of the same symmetry, estimate their bonding/antibonding character and the extent of energy splitting, then draw the MOs into your MO diagram,* **Figure 3**
  - the low energy a_1' fragment orbitals will combine, these orbitals are on atoms that are directly bonded, and they involve sAOs so the interactions will be very large.
  - the higher energy e' fragment orbitals will combine, the splitting will also be reasonably large as these interactions lie directly between bonded atoms
  - the a_2'' (p_z AO) on boron will remain non-bonding as there are no H_3 orbitals of this symmetry.

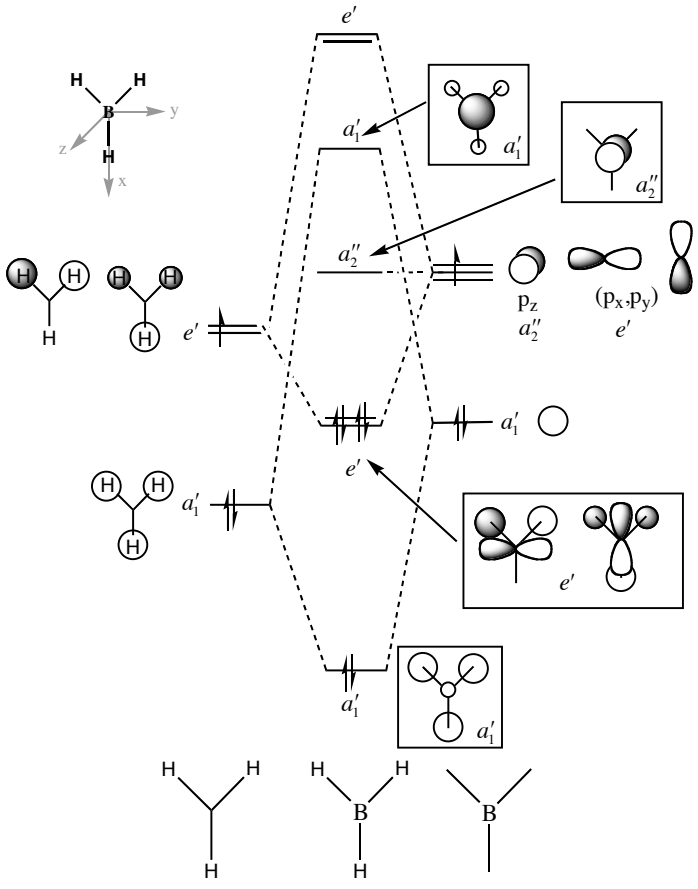

Figure 3 MO diagram for BH_3

- *determine the number of electrons in each fragment and hence the central MO region, add them to the diagram*: H_3 contributes 3 electrons while B contributes 3 valence electrons, thus 3 pairs of electrons are placed in the diagram, filling from the lowest energy MOs and moving up.
- *identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs*: Only MO of the same symmetry can mix, and they must not belong to the same bonding/antibonding pair! In this case there is no MO mixing.
- use the MO diagram check-list to make sure you have done everything

MO diagram check-list

1. determine the molecular shape and identify the point group of the molecule
2. define the axial system find all of the symmetry operations on the molecule
3. identify the chemical fragments, and put them along the bottom of the diagram
4. determine the energy levels and symmetry labels of the fragment orbitals (use H1s as a referece)
5. combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs (in pencil!)
6. determine the number of electrons in each fragment and hence the central MO region, add them to the diagram
7. identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
8. Annotate your diagram
9. Analyse the MO diagram

- *Annotate your diagram,* **Figure 5**

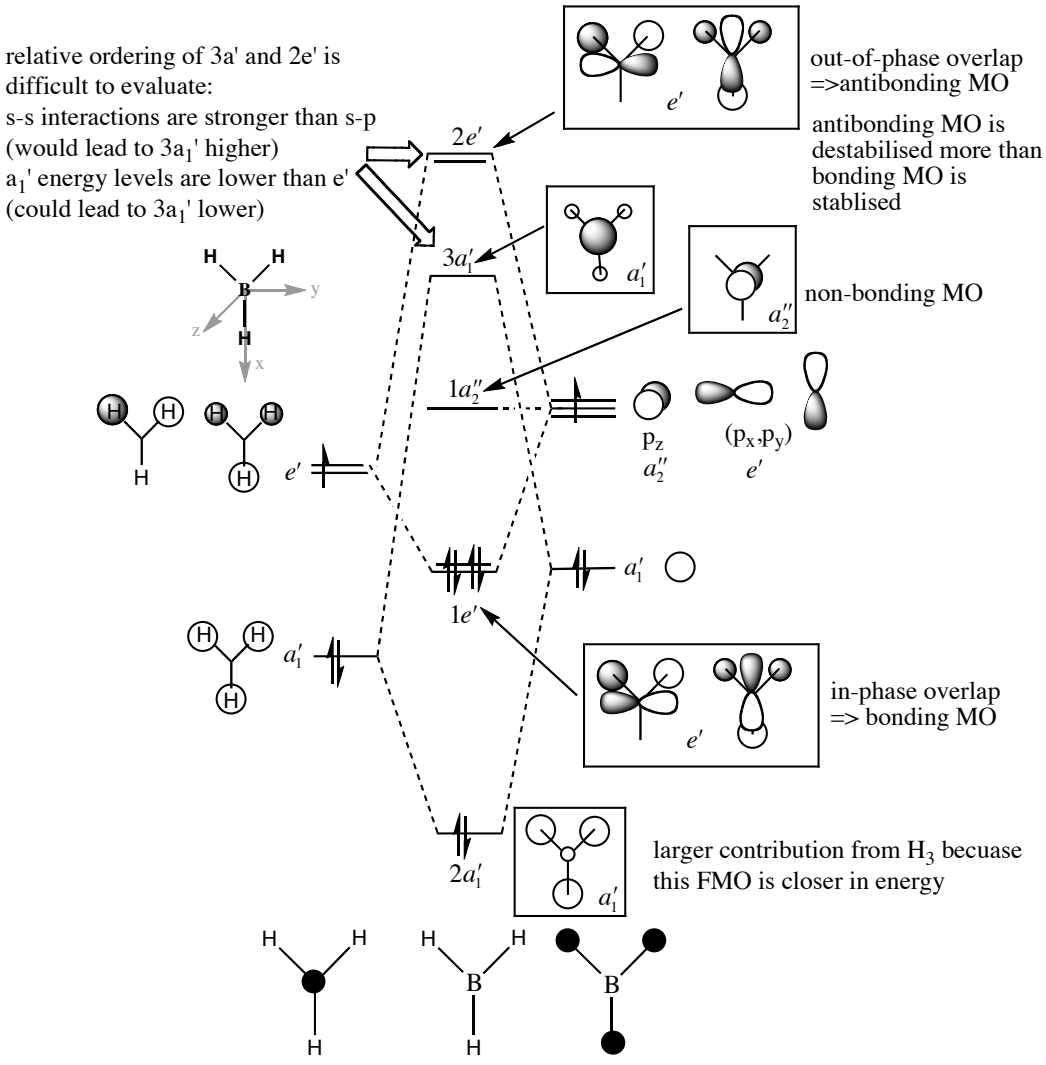

Figure 5 Annotated MO diagram for BH_3

- What can the HOMO and LUMO tell us about the chemical nature of BH_3?
  - the highest occupied molecular orbital or HOMO of BH_3 is a degenerate e' MO while the lowest unoccupied molecular orbital or LUMO is a non-bonding p_z orbital (a_2" symmetry) on the B atom. The a_2" orbital is low in energy because boron is an electropositive element and this is a non-bonding orbital (rather than a high energy antibonding orbital)
  - The low energy of the LUMO is a **key point,** this means that BH_3 will be susceptible to accepting electrons from species with higher energy HOMOs. Moreover donation of electrons from another molecule into the LUMO will not effect the overall bonding in the molecule, as the LUMO is non-bonding with respect to the H_3 fragment orbitals. Thus BH_3 is a Lewis acid an will accept electrons from a base.