

Problem Class

- Form the MO diagram for BH_3 using as fragments H_3 and B. The fragment orbitals for H_3 are given in **Figure 1**

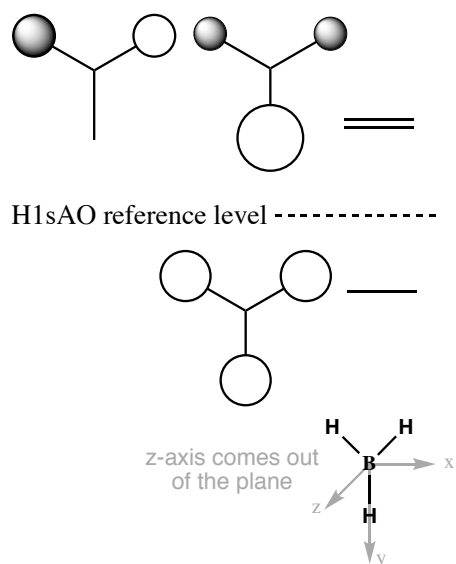


Figure 1 Fragment orbitals for H_3

Problem Class

- Form the MO diagram for BH_3 using as fragments H_3 and B. The fragment orbitals for H_3 are given in **Figure 2**
 - where do these FOs come from? These are called **symmetry adapted fragment orbitals** and they are the solution to the Schrödinger equation
 - is it correct that one orbital has no AO contribution? Yes! Not all atoms have to contribute to a MO, this is perfectly normal.
 - actually we don't need to solve the Schrödinger equation directly because the Hamiltonian and Symmetry operators commute, we can use symmetry to "find" the solutions without using a computer
 - how to do find the symmetry adapted orbitals used to be part of this course, but it has now been removed to make room for more transition metal orbital chemistry. If you want to know more, the old notes (from 2013) are available on my web-site.
 - another way to think about this orbital is to consider its symmetry, there is a mirror plane and if the missing orbital were present it would need to have one half dark and one half light to be of the correct symmetry. sAOs are all one phase, so the sAO does not have the right symmetry to contribute to the FO.
- First, use the MO checklist

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 $\text{H}1s$ as a reference)
 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
- *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.

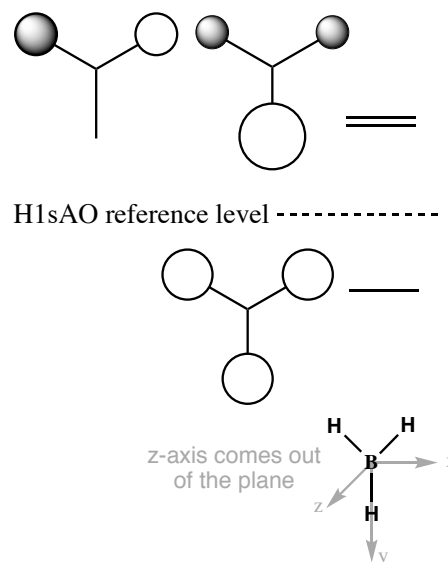


Figure 2 Fragment orbitals for H_3

- find all of the symmetry elements of the point group on the molecule: (homework problem from Lecture 1), **Figure 3**

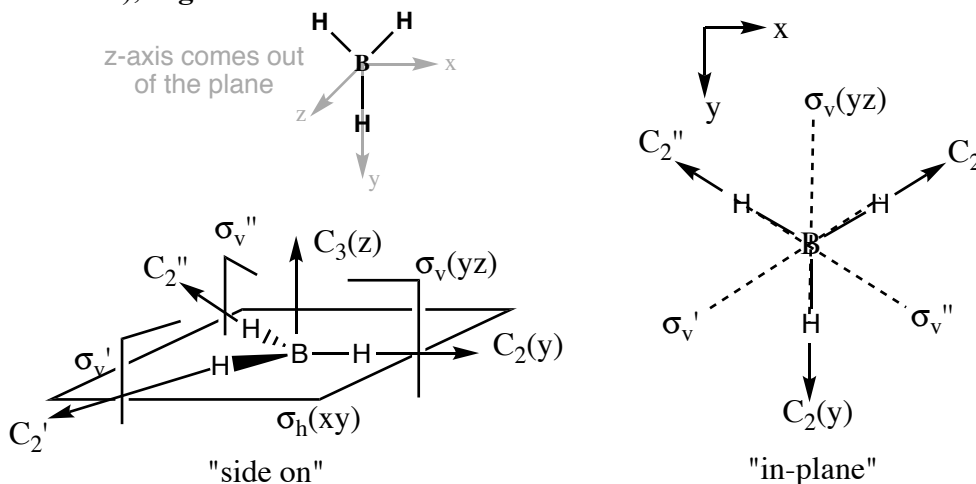


Figure 3 Axial system and symmetry elements for BH_3

- 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 4**)

- determine the energy levels and symmetry labels of the fragment orbitals: **Figure 4**

- 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 $\Rightarrow a_1'$

- 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 (p_x, p_y) are a degenerate e' pair and the p_z AO is a_2'' . The sAO is always totally symmetric and thus has a_1' symmetry.

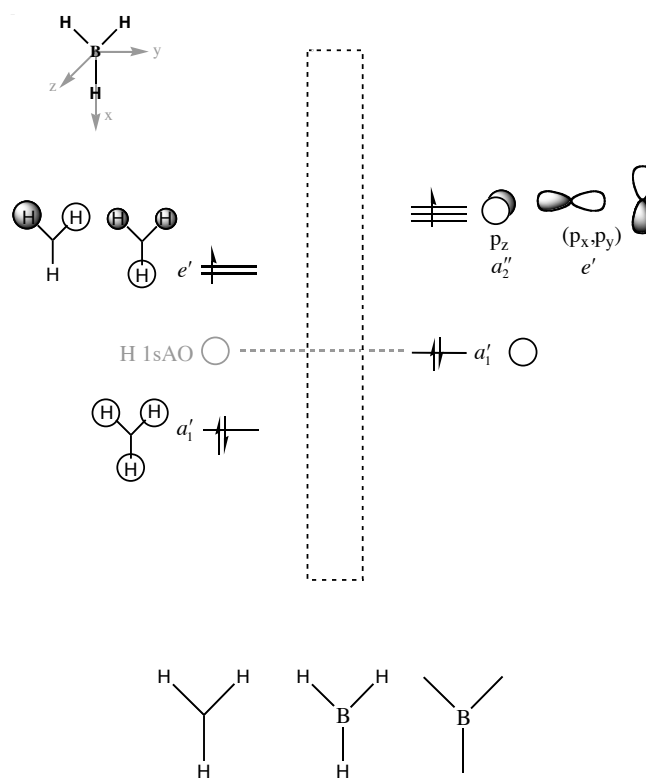


Figure 4 Fragment MO diagram BH_3

- 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 4**

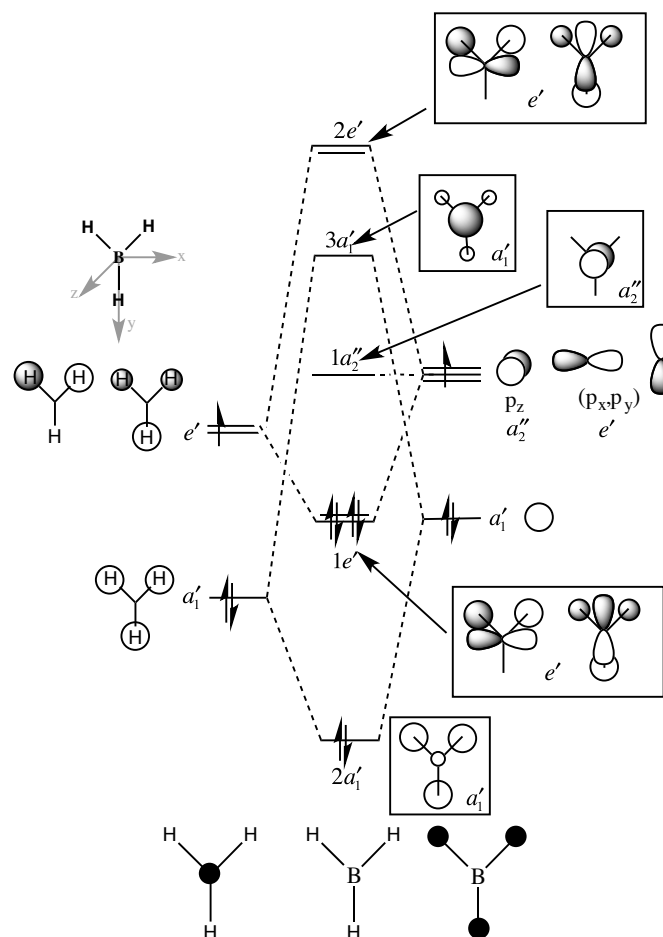


Figure 5 MO diagram for BH₃

- 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 5**
 - 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 H₃ orbitals of this symmetry.
- determine the number of electrons in each fragment and hence the central MO region, add them to the diagram: H₃ 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
- Annotate your diagram, **Figure 5** (next page)

