B_2H_6 MO Diagram

Complex MO diagrams: B_2H_6

- complex molecules are often built up by combining a series of simpler fragments. To illustrate this we are going to form the MO diagram for B_2H_6
- we will form an **intermediate MO diagram** from two BH_2 fragments and then add H_2 to form the final MO diagram for B_2H_6, **Figure 1**
- one could expect B_2H_6 to be similar to C_2H_6, however boron is formally electron deficient. Each B atom has only 3 electrons, and cannot form 4 separate bonds. The VSEPR counting for B_2H_6 is shown below in **Figure 2**

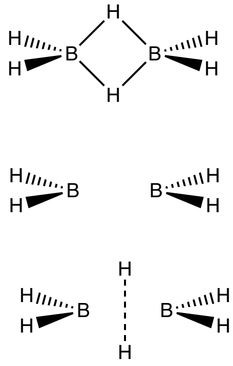
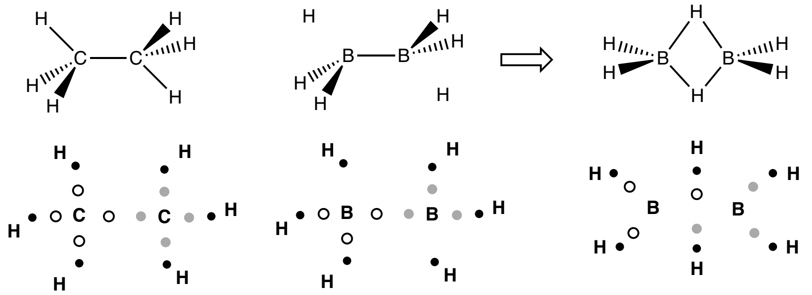


Figure 1 Fragments of B_2H_6



not enough electrons to form standard bonds

3 center B-H-B bonds with 2 electrons

Figure 2 VSEPR for C_2H_6 and B_2H_6

- to explain the deficiency of the VSEPR model with respect to B_2H_6 the idea of 3 centre–2 electron bonds was developed, with the B-H-B bridging bond (or "bent" bond) having 3 atomic centres but sharing only 2 electrons
- However MO theory can explain the bonding in B_2H_6 naturally and easily without making *ad-hoc* corrections.

Combining two BH_2 fragments

- the MOs for B_2H_6 are easily developed using the MO diagram checklist
- *determine the molecular shape and identify the point group of the molecule*: convince yourself (at home) that this molecule has D_{2h} symmetry, **Figure 3**
- *define the axial system and find all of the symmetry elements of the point group*: see **Figure 3**
- *identify the chemical fragments, and put them along the bottom of the diagram*: we will combine two BH_2 fragments to form B_2H_4 and then add an H_2 fragment across the centre.

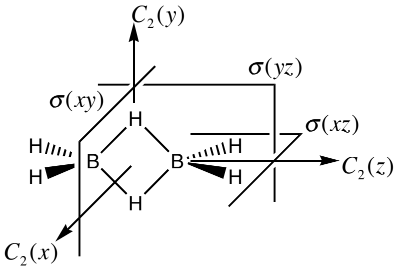


Figure 3 D_{2h} symmetry elements for B_2H_6

- *determine the energy levels and symmetry labels of the fragment orbitals assess interactions for the orbitals which overlap when the fragments are brought together*
- normally only fragment orbitals up to the LUMO+1 are included in the MO diagram, to work this out you need to know the configuration
  - the B atoms will contribute 6e and the 4H atoms 4e, so we fill the diagram with 10e.
- FIRST work out the MOs then analyse to work out the splitting energy

- there are two considerations when determining the splitting energy:
  - interactions between degenerate fragments are large.
  - but the BH_2 fragments are not directly bonded and are far apart in space, thus reducing interactions
  - note that σ_s interactions are stronger than σ_p interactions, which are stronger than π interactions
  - however the directed σ_p interactions will also be strong
  - the exact energy ordering is difficult to predict without explicit calculation
- next we need to determine the symmetry of the MOs in **Figure 4**, add the labels into the boxes provided
  - label symmetry of the totally symmetric MO
  - label the symmetry of any orbitals with the same phase pattern as the x, y and z axes.
  - label the symmetry of any orbitals with the same phase pattern as a dAO.
  - there remains a single orbital with an unknown symmetry, and this has to be worked out the long way, **Figure 5** what is the symmetry label of this MO?
  - for the model answers look at the end of the document!

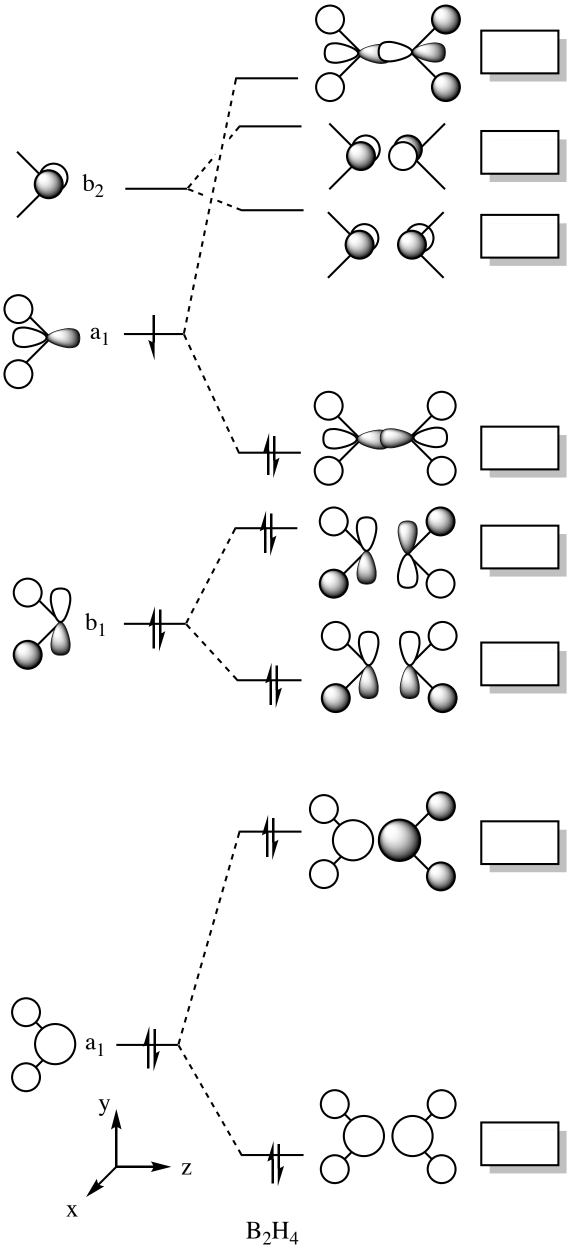


Figure 4 combining fragment orbitals for for B_2H_6

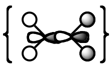
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ 	1	1	-1	-1	-1	-1	1	1

Figure 5 Character table for fragment orbital

Adding the H_2 fragments

- We now combine H_2 with B_2H_4. The MOs just derived now form the FOs for the new MO diagram.
  - the H_2 fragment (**Figure 6**) has a bonding component that is totally symmetric (a_g) and an antibonding component has the same symmetry as the x-axis (b_{3u})

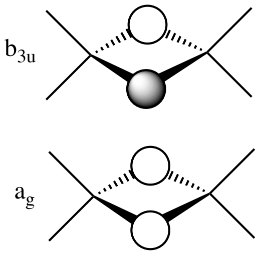


Figure 6 Fragment MOs for H_2

  - the H_2 fragment orbitals are not directly bonded, so will not exhibit a large splitting, they are sAOs but are neither strongly bonding or antibonding and so will lie near the non-bonding region of the B_2H_4 manifold of fragment orbitals, **Figure 7**
- *combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs*
  - the full MO diagram is shown in **Figure 7**
  - it will be sufficient for you to obtain the correct LCAO and a rough estimate of energy ordering based on the relative bonding antibonding character of the orbitals. Ordering that has been well explained with suitable arguments will be accepted in the test/assignment!
  - calculations are required to obtain accurate energy ordering of the MOs,

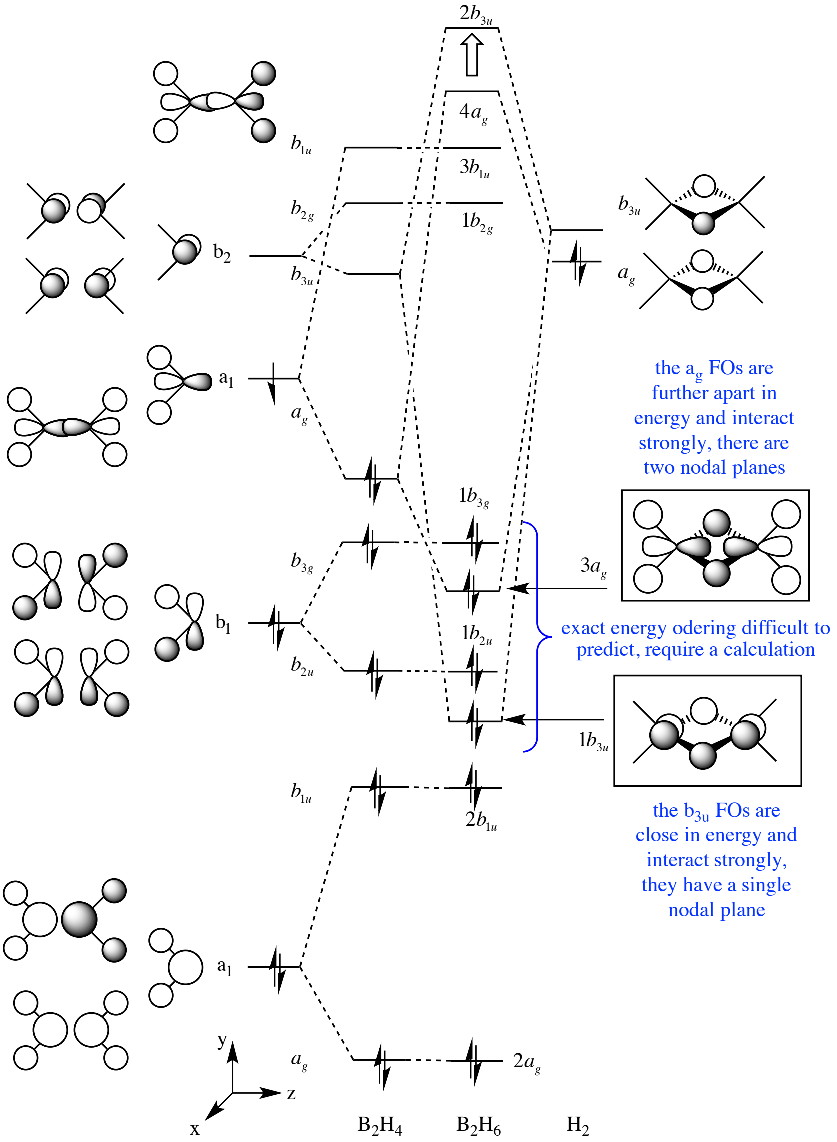


Figure 7 MO diagram for B_2H_6

- *determine the electronic configuration*
  - the two boron atoms each contribute 3 valence electrons ($2s^2 2p^1$) while the six hydrogen atoms contribute 1e each giving a total of 6+6=12e.
- *identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs*
  - no mixing is expected for this molecule
  - the $2a_g$ is a deep orbital and $3a_g$ MOs is too far apart in energy
  - the $2b_{1u}$ and $3b_{1u}$ are also too far apart in energy

- *use the MO diagram check-list*!
    - ie check the MO diagram, does it have all the required components?
- *analysis of the MO diagram*
    - this is an area where students have not performed well in the past, just drawing the MO diagram is not enough!
    - four of the MOs, $2a_g$, $2b_{1u}$, $1b_{2u}$ and $1b_{3g}$ are "non-bonding" with respect to the H_2 fragment. The $2a_g$ B_2H_4 fragment orbital lies too deep in energy to interact, and the $2b_{1u}$, $1b_{2u}$ and $1b_{3g}$ fragment orbitals are of the wrong symmetry to interact with the H_2 fragment orbitals. These MOs all describe bonding within each of the *terminal* BH_2 units.
    - two of the MOs, the $1b_{3u}$ and $3a_g$, primarily describe bonding in the *bridging* region and have strong interactions between the B atoms and the bridging H_2 fragment
    - the next $1b_{2g}$ MO is unoccupied and "non-bonding" with respect to the H_2 fragment. It is antibonding between the boron atoms, but these are not particularly close and the antibonding nature of this MO is small. Thus the LUMO is relatively low in energy and if two electrons were added because of its non-bonding character the molecule would not be strongly destabilised. Thus we expect that $B_2H_6^{2-}$ to be relatively easily formed, and once formed will be stable, which is the case.
    - in the MO picture of bonding in B_2H_6, there has been no need to treat B_2H_6 in any special way, no special bonding modes such as 3 center 2 electron bonds have need to be invoked.
- the computed orbitals for HOMO and three lower energy orbitals are shown in **Figure 8**

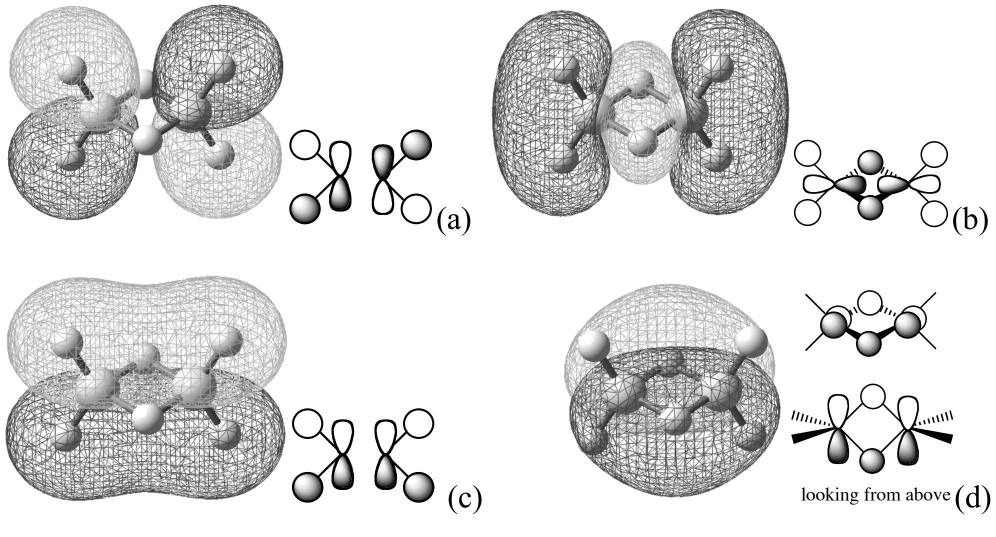


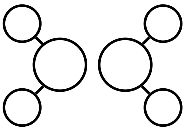
Figure 8 the (a) HOMO b_{3g}, (b)HOMO-1 $3a_g$ (c)HOMO-2 b_{2u} and (d)HOMO-3 b_{3u}

Special Comment

- text books can differ in the ordering of the energy levels for B_2H_6!
- some text books simplify the interactions for B_2H_6 by showing a modified orbital diagram, in which all the orbitals that don't interact with the H_2 fragment are grouped at lower energy
- other text books may also show a larger MO energy splitting for the $3a_g$ and $4a_g$ orbitals, thus putting the $3a_g$ MO below the $1b_{3u}$ MO.
- these are all equally valid approximations if starting from a qualitative MO approach.
- often for complex molecules we cannot tell the exact ordering of the MOs using qualitative MO theory alone. However, once we have carried out a calculation we have well defined energy ordering and we can understand how the bonding and antibonding interactions arise.

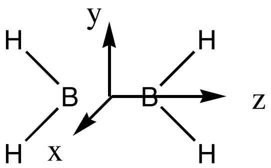
Determining the Symmetry of MOs

- label symmetry of the totally symmetric MO



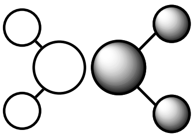
has a_g symmetry

- what symmetry label is associated with each of the x, y and z axes?

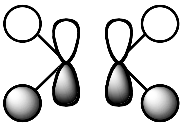


x-axis => b_{3u}
y-axis => b_{2u}
z-axis => b_{1u}

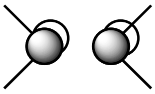
- label the symmetry of any orbitals with the same phase pattern as the x, y and z axes.



has phase distribution like the z-axis hence b_{1u}



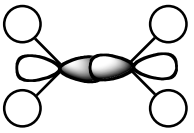
has phase distribution like the y-axis hence b_{2u}



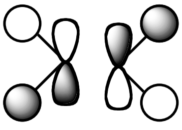
has phase distribution like the x-axis hence b_{3u}

Figure 9 Short cuts for determining the symmetry for complex MOs

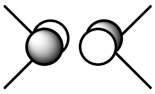
- What are the symmetry labels for the dAOs under D_{2h}?
  dz^2 has a_g symmetry
  dx^2-y^2 has a_g symmetry
  dxy has b_{1g} symmetry
  dzx has b_{2g} symmetry
  dyz has b_{3g} symmetry
- label the symmetry of any orbitals with the same phase pattern as a dAO.



has phase distribution like the dz^2 AO hence a_g



has phase distribution like the dyz AO hence b_{3g}



has phase distribution like the dxz AO hence b_{2g}