The Electron Deficient Borane Molecule

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Outline

Borane Dimerizes
What is the energy of the dimerization reaction?

- ΔH_f°(gas) for BH_3 = 25.5 kcal/mol
- ΔH_f°(gas) for B_2H_6 = 9.799 kcal/mol
- ΔH_{rxn}°(gas) for 2 BH_3 → B_2H_6 = 9.799 − 2(25.5) = −41 kcal/mol
- The C_2H_4 molecule is isoelectronic, how does its central bond energy compare?
- Look up the requisite ΔH_f° values in the NIST database
- We look to interpret the bonding in B_2H_6 using symmetry and MO theory

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Do we Expect to Find B-B Bonding in Diborane?
Examine the structure and check the B-B distance

- The covalent radius r_{cov} for boron is 0.81 Å

- Therefore, a B-B single bond is expected to be $2(r_{cov}) = 1.62$ Å

- Right-click in the diborane applet to get access to the interatomic distances

- We find the B-B distance to be 1.76 Å

- This is longer by 0.14 Å than a B-B single bond

- We might expect some partial B-B bonding

- Let's investigate the bonding with MO theory!

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Begin by Choosing our Coordinate System
This is not a planar molecule

- Take the B-B axis to define the z direction

- Take the pair of bridging H atoms H_b to define the y direction

- Then the four terminal atoms H_t lie in the xz plane but not on any of the Cartesian axes

- Note that there is no central atom in this problem!

- This carries the implication that none of the MOs can be as simple as one of the atomic orbitals on a central atom as was the case for the HOMO of the water molecule

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More Restrictions on the MOs
This is not a planar molecule

- Boron has four valence atomic orbitals: $2s, 2p_x, 2p_y, 2p_z$

- There are six H atoms each with a single 1s valence orbital

- All of the MOs will be combinations of the $4 + 4 + 6 = 14$ valence atomic orbitals; each combination must belong to one of the irreducible representations of the D_{2h} point group

- Will all 14 of the MOs be occupied?

- The number of valence electron pairs is six

- We expect the lowest-energy six MOs to be occupied, and the higher-energy MOs to be vacant

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The D_{2h} Character Table

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Finding the Symmetry Species of the MOs
Start by looking for sets of symmetry-related atoms/orbitals

- Atoms or atomic orbitals are "symmetry-related" if they are interchanged upon carrying out the operations of the group
  - The four terminal hydrogens H_t (each has a 1s atomic orbital) are symmetry related
  - The two bridging hydrogens H_b are symmetry related
  - None of the group operations interchanges any of the H_t with any of the H_b atoms/orbitals
  - We can use the H_t set to generate the reducible representation $\Gamma_{red} = 4\ 0\ 0\ 0\ 0\ 0\ 4\ 0$
  - The characters of $\Gamma_{red}(H_t)$ are obtained by noting how many atoms in the H_t set are unshifted upon carrying out the group operations
  - The characters of $\Gamma_{red}(H_t) = A_g + B_{2g} + B_{1u} + B_{3u}$

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- What about the pair of H_b atoms?

- We can use the H_b set to generate the reducible representation $\Gamma_{red} = 2\ 0\ 2\ 0\ 0\ 2\ 0\ 2$

- $\Gamma_{red}(H_b)$ can be reduced to $A_g + B_{2u}$

- Therefore, we expect the H_b 1s atomic orbitals to contribute to a pair of bonding MOs having A_g and B_{2u} symmetry

- Note, from the Lewis picture of B_2H_6, we can expect that all six valence electron pairs reside in MOs that have bonding character involving the hydrogen atoms

- Now, we expect the six occupied MOs to transform as $2A_g + B_{2g} + B_{1u} + B_{2u} + B_{3u}$

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How to Interpret the MO energies
Remember what you know about AO energies

- the Valence Orbital Ionization Energy (VOIE) for a hydrogen $1s$ orbital is 13.6 eV

- the Valence Orbital Ionization Energy (VOIE) for a boron $2s$ orbital is 14.0 eV

- the Valence Orbital Ionization Energy (VOIE) for a boron $2p$ orbital is 8.3 eV

- MOs constructed from low-energy (electronegative) AOs will tend to be low energy

- AO's of similar energy tend to mix strongly

- Good overlap leads to strong mixing

- The presence of antibonding nodes makes for a high-energy MO

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Inspect the Occupied MOs for Diborane
What would corresponding antibonding MOs look like?

- Use the drop-down menu in the diborane applet to get access to the MO isosurfaces

- How would you determine the symmetry species of the other 8 valence MOs?

- Use symmetry-related pairs of boron atom AOs as bases for reducible representations

- For example, the pair of boron $2p_z$ orbitals give $\Gamma_{red} = 2\ 2\ 0\ 0\ 0\ 0\ 2\ 2$

- $\Gamma_{red}(\text{boron } 2p_z) = A_g + B_{1u}$

- And so on!

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