The Electron Deficient Borane Molecule

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1 Why is Borane Electron-Deficient?
Borane Dimerizes
What is the energy of the dimerization reaction?

- \( \Delta H^\circ_f \) (gas) for BH\(_3\) = 25.5 kcal/mol
- \( \Delta H^\circ_f \) (gas) for B\(_2\)H\(_6\) = 9.799 kcal/mol
- \( \Delta H^\circ_{rxn} \) (gas) for 2 BH\(_3\) \(\rightarrow\) B\(_2\)H\(_6\) = 9.799 – 2(25.5) = \(-41\) kcal/mol
- The C\(_2\)H\(_4\) molecule is isoelectronic, how does its central bond energy compare?
- Look up the requisite \( \Delta H^\circ_f \) values in the NIST database
- We look to interpret the bonding in B\(_2\)H\(_6\) using symmetry and MO theory
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The covalent radius \( r_{\text{cov}} \) for boron is 0.81 Å.

- Therefore, a B-B single bond is expected to be \( 2(r_{\text{cov}}) = 1.62 \) 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!
Do we Expect to Find B-B Bonding in Diborane?
Examine the structure and check the B-B distance

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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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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

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<th>$D_{2h}$</th>
<th>$E$</th>
<th>$C_2(z)$</th>
<th>$C_2(y)$</th>
<th>$C_2(x)$</th>
<th>$i$</th>
<th>$\sigma(xy)$</th>
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</tr>
</tbody>
</table>

$R_z$, $xy$, $xz$, $yz$

$x^2$, $y^2$, $z^2$
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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 $\Gamma_{\text{red}} = 4 \ 0 \ 0 \ 0 \ 0 \ 0 \ 4 \ 0$.
- The characters of $\Gamma_{\text{red}}(H_t)$ are obtained by noting how many atoms in the $H_t$ set are unshifted upon carrying out the group operations.
- The characters of $\Gamma_{\text{red}}(H_t) = A_g + B_{2g} + B_{1u} + B_{3u}$. 

5.03 Lecture 4  Electron Deficient Molecules
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- What about the pair of $H_b$ atoms?
- We can use the $H_b$ set to generate the reducible representation $\Gamma_{\text{red}} = 2 \ 0 \ 2 \ 0 \ 0 \ 2 \ 0 \ 2$.
- $\Gamma_{\text{red}}(H_b)$ 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.

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- Since the characters of $\Gamma_{\text{red}}(H_t) = A_g + B_{2g} + B_{1u} + B_{3u}$, we expect the four 1s orbitals of the $H_t$ set to appear in MOs having these four symmetry species.
- What about the pair of $H_b$ atoms?
- We can use the $H_b$ set to generate the reducible representation $\Gamma_{\text{red}} = \begin{pmatrix} 2 & 0 & 2 & 0 & 0 & 2 & 0 & 2 \end{pmatrix}$
- $\Gamma_{\text{red}}(H_b)$ 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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Why is Borane Electron-Deficient?

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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5.03 Lecture 4 Electron Deficient Molecules
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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 $\Gamma_{red} = 2 \ 2 \ 0 \ 0 \ 0 \ 2 \ 2$
- $\Gamma_{red}(\text{boron } 2p_z) = A_g + B_{1u}$
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