Boranes

- Boranes have structures and bonding that frequently cannot be adequately described by Lewis conventions.

- The simplest borane, BH$_3$, does not exist as a stable species, although it may be a transient species in the reactions producing higher boranes.

- The simplest stable borane is B$_2$H$_6$.

- Many higher boranes exist with complex cage-like structures.
Bonding Types in Boranes

- Bonds in boranes consist of types that can and cannot be described by conventional Lewis concepts.

- In the “semitopological” description of Lipscomb\(^1\) five distinct bonding types are identified, only two of which conform to Lewis concepts:

  - B—H: terminal 2-center-2-electron BH bond (2c-2e)
  - B—B: 2-center-2-electron BB bond (2c-2e)
  - open 3-center-2-electron B-bridge bond (3c-2e)
  - closed 3-center-2-electron B-bond (3c-2e)

- Diborane has four 2c-2e B–H bonds and two 3c-2e B–H–B bridge bonds, represented in semitopological notation as follows:

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H···H ligand distances are close to those calculated for BH$_4^-$ (202 pm) and BH$_3$ (203 pm).

Bridging H···H distance is short, suggesting that attraction between negatively charged bridging hydrogens and two positively charged borons causes the two hydrogens’ electron densities to be compressed.

Compression of bridging hydrogens allows terminal hydrogens to move apart, similar to C$_2$H$_4$, giving $\angle$H–B–H of 121.8°.
**Bonding Models of B$_2$H$_6$**

- With only 12 valence electrons, rather than 16 needed for complete 2c-2e bonding, diborane is an example of an electron deficient compound.

- Given the large atomic charges (B, +1.78; H, –0.60±0.01), B$_2$H$_6$ is approximately tetrahedrally arranged H$^-$ ions around two B$^{3+}$ cations.

- Using $sp^3$ hybridized B, the bridge bonds are represented as 3c-2e.

- From this, the two bridge bonds can be represented by the following MO scheme:
AIM Model of $\text{B}_2\text{H}_6$

Contour map in $\text{B}_2\text{H}_4$ plane

Contour map in H–B–H bridge plane

✔ Bond paths exist for terminal B–H 2c-2e bonds

✔ No bond path exists between boron atoms

✔ Bond paths exist between each boron and the two bridging hydrogen atoms, but they do not correspond to two 2c-2e bonds.

✔ Electron density across the B–H–B bridge corresponds to one electron pair, consistent with the 3c-2e model.

✔ AIM analysis of higher boranes similarly shows bond paths between all adjacent atoms, but all bonds cannot be considered conventional Lewis 2c-2e type.