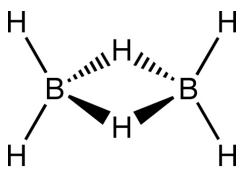
Diborane – B_2H_6

If we consider the molecule B_2H_6 (diborane ***Figure 1***), there are 12 valence electrons at our disposal for chemical bonding (B has 3, and H has 1, so 2xB + 6xH =12). Each terminal B–H bond is a standard vanilla two electron bond, and there are four of these, thus accounting for a total of eight electrons. This leaves a total of four electrons to share between the two bridging H atoms and the two B atoms. Consequently, two B–H–B bridging bonds are formed, each of which consists of two electrons (***Figure 2***), forming what are called three-center-two-electron bonds (i.e., 3 atoms share 2 electrons) – sometimes called 'banana' bonds, as they are not linear but curved. Each B atom is, approximately, sp^3 hybridized (hybridization is just a mathematical tool, so you can just as easily have $s^{1.05}p^{2.95}$ hybridized orbitals!), and if we consider just one of the B atoms, two of the four sp^3 hybrid orbitals form σ bonds to the terminal H atoms (1s orbitals). That leaves two B sp^3 hybrid orbitals, one of which contains an electron, one of which is empty. For each bridge therefore, one sp^3 orbital from each of the B atoms combines (***Figure 3***) with the 1s orbital of the bridging H atom to form three new molecular orbitals (MOs) – as always, *n* atomic orbitals (AO) form *n* MOs. One B atom gives its remaining valence electron to one bridge, and the other B atom gives to the other. Each bridge, therefore, has two electrons, which fill our new MO scheme starting with the lowest energy bonding MO.



Diborane

Figure 1. The structure of diborane

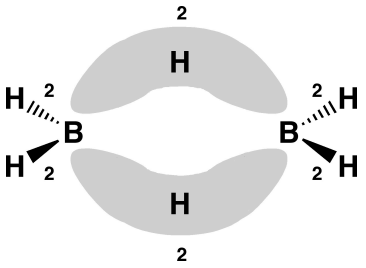


Figure 2. The terminal B–H bonds and the bridging B–H–B bonds each contain two electrons

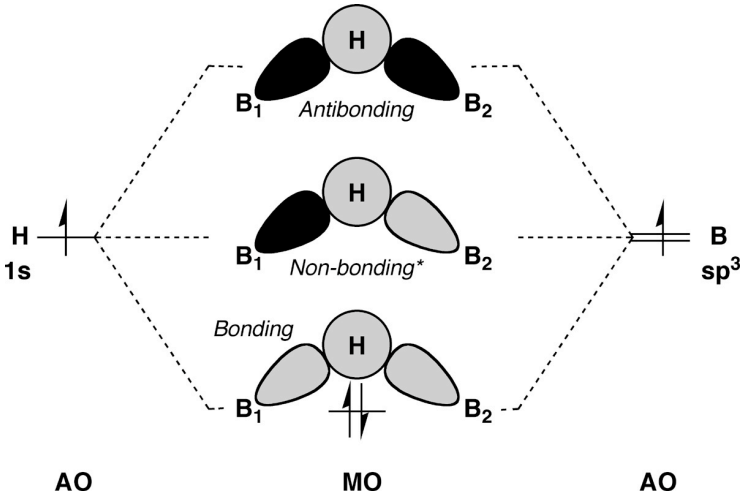


Figure 3. The MO scheme for one of the B–H–B bridging three center two electron bonds. *This picture is still a simplification of the actual MO scheme. The non-bonding orbital is actually of slightly lower energy than shown and so has slight bonding character. This arises from the fact that the orbitals involved in the terminal B–H bonding have the correct symmetry to overlap with the bridging bond orbitals, resulting in a stabilization of the 'non-bonding' orbital.

Figure 4. One final way of visualizing the bonding in diborane can be done by considering a dianion such as $B_2H_4^{2-}$, which has the same three-dimensional structure as ethene. There is π-electron density above and below the plane in which all six atoms lie (just like ethene) and so if we imagine embedding a proton in each face of this flat molecule, we balance the charge and arrive at the correct geometric structure.