Nixing the 3-Center Orbital Bond Concept of Diborane

By Joel M Williams (text and images ©2014)

Abstract

The bonding of the hydrogen atom in the B—H—B sequence of diborane is just a standard overlapping of atomic orbitals. With the MCAS model, hydrogen naturally has the capacity to form linear and non-linear bonds between two atoms when necessary. There is no need for the nebulous 3-center, two-electron, bond that has been used to honor the unassailable s-orbital of the spdf-QM model.

INTRODUCTION

A century or so ago, the electronic structure of atoms began to take shape. Spectral physics and mathematics led the charge. Making some assumptions, like electrons not behaving near the nucleus like they do between anodes and cathodes of a battery, but instead "buddy up", the spdf-quantum mechanical (spdf-QM) model arose. The physicists were satisfied, got lots of Nobel prizes, and ventured off to dig into the nucleus and its particles.

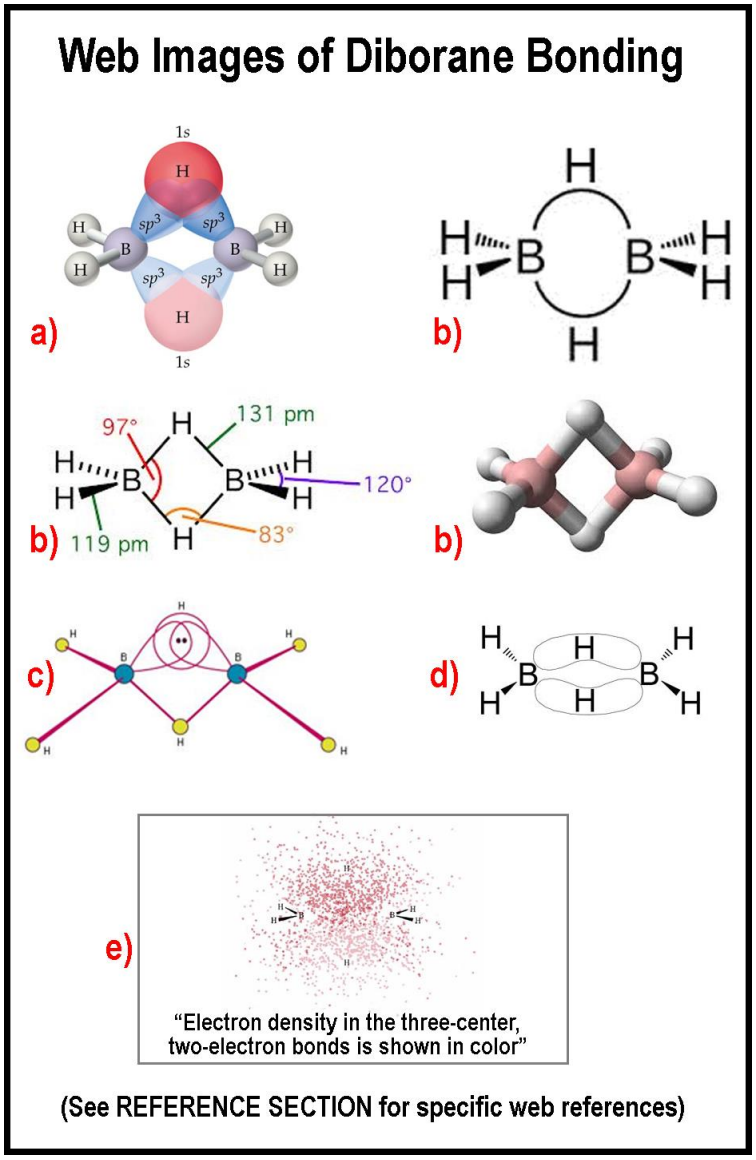
Chemists were left with an "unassailable" model of how electrons could be arranged around various atoms and thus be connected to one another to form the polyatomic matter of the world. That the spdf-QM model could not even model a simple molecule, like methane, was the chemists' problem. Brew up some "hybrids" of the orbitals, if you need to, but do not mess with the hydrogen s-orbital. The spdf-QM model is based on the "holiest of holies" – the electron spin-paired sphere. The hydrogen orbital can be nothing else.

While organic chemists generated polymers, dyes, metal complexes, assorted drugs, etc., physical chemists and chemical physicists brewed in their caldrons complex hybrid orbitals that sometimes looked like misty particle clouds. Treatises were received and published as long as the "holiest-of-holies" was treated with respect.

Hydrogen atoms bonded to something singularly glided along smoothly. Hydrogen bonding in things like water was glossed over as not a real molecular bond, but an electrostatic addition to its real covalent bond. That a proton might have two "real" molecular bonds when placed between some oxygen atoms hardly caused a ripple, although it should have.

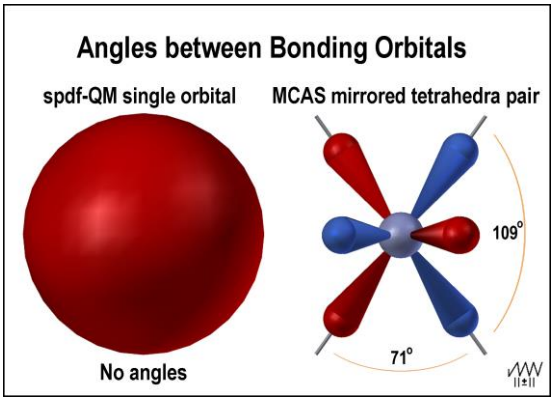
When chemists began studying boron chemistry, multiple molecular bonding of hydrogen to boron atoms became a more onerous problem. Did the scientific world "hybridize" hydrogen as it had carbon to convert s+3p's to $4sp^3$'s? Nope. The "holiest-of-holies" was unassailable. Thus was born the 3-center, two-electron, bond.

1 The figure at the right contains a sampling of some of the images that appear on the web to portray the B—H—B, 3-center, two-electron, bond. The red letters correspond to those in the reference at the end of this paper.[1] The upper left image[1a] indicates that a spherical hydrogen bonds with two sp^3 hybrid orbitals. Just how is unclear; it just does. The upper right image[1b] indicates that there are B-to-B bonds, just what those bonds are is not clear, and that somehow hydrogen gets involved. The left middle image[1b] gives physical data and indicates two bonds for the middle hydrogen atoms, but orbital types are indicated; a 122-degree bond angle instead of the 120-degree angle is listed elsewhere.[2] The middle right image[1b] makes the hydrogen atoms appear a bit like an oxygen atom of a water molecule with the electrons omitted. The next lower left image[1c] presumably indicated what a 3-center, two-electron, bond is; well, it shows 3 orbitals at a juncture. How those orbitals interact is not clear. This is especially problematic now that electrons are being detected as particles flowing in orbits.[3] The next lower right image[1d] looks like there is a pi-cloud between the boron atoms and somehow the hydrogen atoms are afloat in it. Experimental evidence shows that electrons really are particulate at the nuclear level, however.[3] The very bottom image[1e] takes the cake in my estimation and shows what happens when folks get carried away with those dot matrix representations of orbitals![3] The website[1e] claims that this is "the current picture of bonding in diborane". You have to wonder what students are learning from this sort of imagery. Little information about the bonding mechanics of the hydrogen atoms is forthcoming from these images, except for the physical location of the hydrogen atoms and that two of the hydrogen atoms ARE each attached to two boron atoms, contrary to the spdf-QM precept that hydrogen forms single, 2-electron, bonds!



While I was studying supercritical fluids,[4] it became clear to me that hydrogen atoms should not have orbitals that differed from those of other atoms and certainly not spherical ones. Indeed, WHY should those of hydrogen be different? So, I sent a submission to the academic press in 1993 indicating that hydrogen should have a tetrahedral orbital rather than a spherical one.[5] This was the birth of the MCAS atomic orbital model.

The figure at the right contrasts the spherical orbital of the spdf-QM model with the mirrored tetrahedral pair of the MCAS model. What differentiates hydrogen and helium from other elements is the tightness (extent) of the first energy level. At the first energy level, each tetrahedral unit (red or blue here) is dimensionally too small to handle more than a single electron. Thus, hydrogen and helium are the only elements of the first period of the periodic table. As orbital extents increase with higher energy levels, the orbitals contain one electron each at first (pairing) and then three more each until there are eight. Thus, a periodicity of eight occurs in the outer energy level as it does in the periodic table. Creating the periodic table via the MCAS model is presented elsewhere.[6] The first level orbitals of hydrogen (and helium) need to be no different than those of any other element![7]

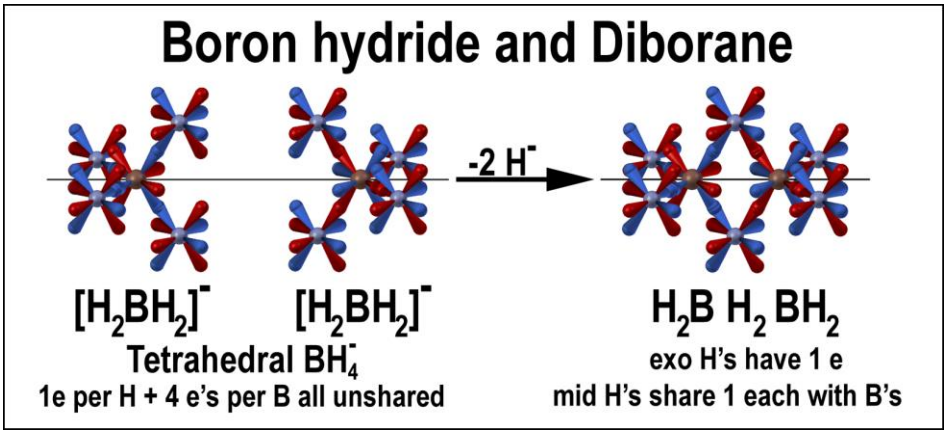


MULTIPLE BONDING OF HYDROGEN ATOMS

Having pointed out that the MCAS atomic orbitals are the same for all atoms, multiple bonds for hydrogen atoms should not be strange at all. The main reason that they are not common results from the fact that a single electron in the non-bonding tetrahedral set is electrostatically sufficient for the singly positive proton. The diametrically opposed tetrahedral sets of the MCAS model signal the logic of linear X—H—X bonds, however. Such linear arrangements are found for protons between two oxygen atoms (O—H—O).[8]

Diborane presents a different problem as the B—H—B bonds are NOT linear!

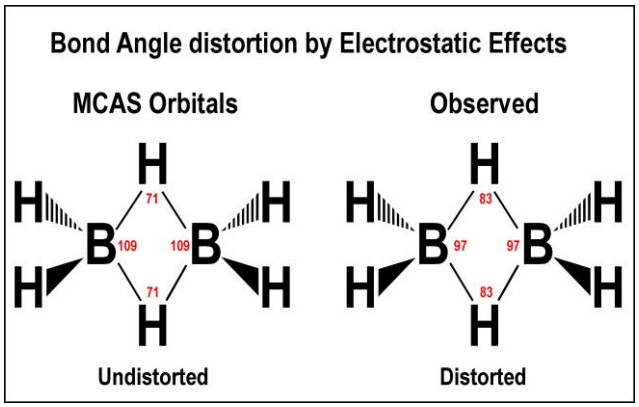
Boron hydride is a "methane analog". Each of the four hydrogen atom is identical and surrounds the boron atom tetrahedrally. A single electron moves around each hydrogen atom in the non-overlapped (bond) orbital set. Since 4 electrons move around the boron atom in its non-bonding set, the negative charge of the boron hydride unit is centered. The images in the left of the figure below show the orbital alignments. The two boron hydride images are reverse color-coded for the purpose of demonstrating their combination to diborane.



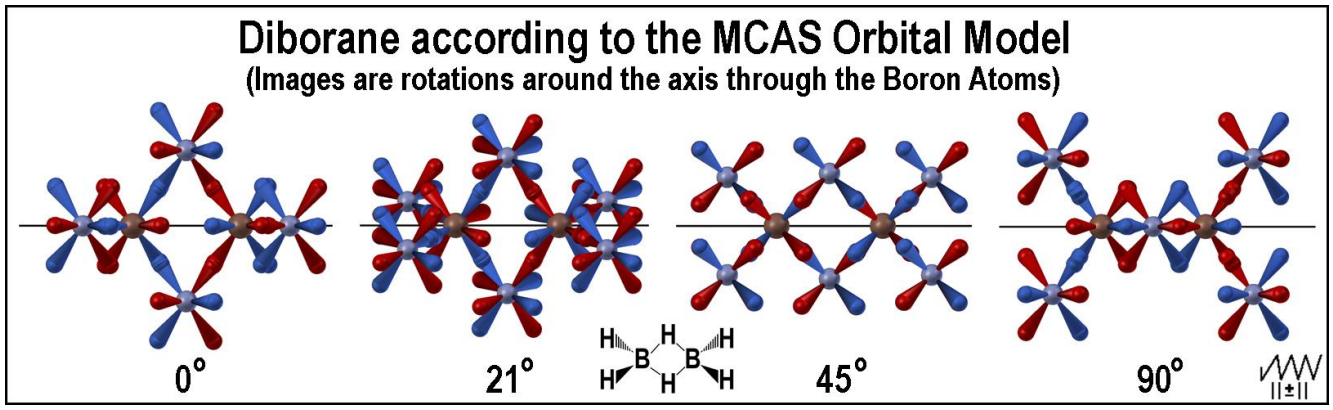
Diborane is a molecule wherein two boron hydride anions are merged with the removal of 2 protons and 4 electrons. The figure at the right illustrates this process. The two types of hydrogen atoms differ in their connectivity. Four (4) hydrogen atoms have a normal, single orbital overlapped bond with their electron in the non-overlapped tetrahedral set and thus not shared. Two (2) hydrogen atoms have two bonds formed

by the overlap of an orbital of each its tetrahedral sets with that of two different boron atoms. These atoms share electrons with each other and the boron atoms through the bond linkages. There are two different paths: one is indicated “blue” and the other “red”.

The undistorted bond angles of the center bridge are 109º for the H—B—H connections and 71º for the B—H—B connections. Repulsion between the boron nuclei forces them apart and narrows the H—B—H angles while lengthen the B—H bonds and widening the B—H—B angle. This is illustrated in the figure at the right.



The following figure shows the undistorted orbitals of diborane as the molecule is rotated around the boron-boron nuclear axis.



One wonders, as a reader has pointed out, why linear $(H_2B)_nH_2$ molecules would not occur. The main reason is that boron can form B—B bonds, too. These will promote electron flow through 3D with occasional double-bonded hydrogen atoms.

CONCLUSIONS

The bonding of the hydrogen atom in the B—H—B sequence of diborane is just a standard overlapping of atomic orbitals. With the MCAS model, hydrogen naturally has the capacity to form linear and non-linear bonds between two atoms when necessary. There is no need for the nebulous 3-center, two-electron, bond that has been used to honor the unassailable s-orbital of the spdf-QM model.

REFERENCES

[1] Web reference for the images of diborane in the text:
a) http://wps.prenhall.com/wps/media/objects/948/971150/ch19_04.htm
b) http://en.wikipedia.org/wiki/Diborane
c) http://www.britannica.com/EBchecked/media/956/The-structure-of-the-three-centre-two-electron-bond-in
d) http://de.wikipedia.org/wiki/Diboran
e) http://chempaths.chemeddl.org/services/chempaths/?q=book/General Chemistry Textbook/2568/chemistry-representative-elements&title=CoreChem:Group_IIIA

[2] http://www.chemteam.info/VSEPR/diborane.html

[3] Joel M Williams, *Nixing the 'Balloons-of-Electron-Dots' Atomic Orbital Models, http://pages.swcp.com/~jmw-mcw/Nixing the 'Balloons-of-Electron-Dots Atomic Orbital Models.htm*

[4] Joel M Williams and George H. Sprenger, *THE 4TH STATE OF MATTER: THE DELTA STATE, http://arxiv.org/html/physics/9904001*

[5] The submission was neither accepted nor peer-reviewed.

[6] Joel M Williams, *Creating the Familiar Periodic Table via MCAS Electron Orbital Filling, http://pages.swcp.com/~jmw-mcw/The Familiar Periodic Table of Elements and Electron Orbital Filling.htm*

[7] Joel M Williams, *Comparing Several Orbital Approaches to the Hydrogen Molecule*, http://pages.swcp.com/~jmw-mcw/Orbital Models and the Hydrogen%20Molecule; and *Electron Orbitals for Ortho and Para Helium*, http://pages.swcp.com/~jmw-mcw/electron orbitals for ortho and para helium.htm

[8] Joel M Williams, *Hydrogen Bonding and Orbital Models*, http://pages.swcp.com/~jmw-mcw/Hydrogen Bonding and Orbital Models.htm