

Structure and Bonding of Second-row Hydrides

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Abstract The structure and bonding of the hydrides of boron, carbon, nitrogen and oxygen are described using the concepts of the valence state and hybrid atomic orbitals. The tetrahedral arrangement of orbitals in CH₄, NH₃ and H₂O is explained. A rationalization is proposed for the unique bridged structure of diborane B₂H₆.

Keywords: hydrides, valence state, hybrid atomic orbitals, methane, ammonia, water molecule, boron hydrides

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1. Introduction

The simplest hydrides of boron, carbon, nitrogen and oxygen provide an elementary picture of atomic orbitals, hybridization and chemical bonding, which can be very instructive for beginning chemistry students [1]. The valence shells of the free atoms of B, C, N and O in their ground states have the electron configurations $2s^2 2p^1$, $2s^2 2p^2$, $2s^2 2p^3$, $2s^2 2p^4$, respectively, (apart from their $1s^2$ inner shells). The three degenerate $2p$ orbitals are singly occupied, except for O, in which one of the $2p$ orbitals must double up. These configurations are represented graphically in Figure 1, with the electrons, shown as white dots, occupying the orbitals, whose geometrical forms are drawn schematically.

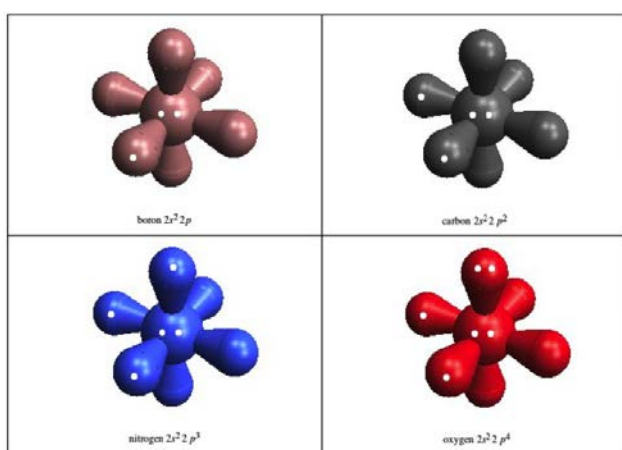


Figure 1. Ground state electron configurations of boron, carbon, nitrogen and oxygen atoms

2. Carbon

Carbon, with its two unpaired electrons, appears to be a naturally divalent atom, and indeed the compound CH₂ can exist in the gas phase. But much more stable

compounds can be formed if carbon invests a relatively small amount of energy to excite one of its $2s$ -electrons to the remaining unoccupied $2p$ orbital, and thereby becomes quadrivalent, thus recouping the $2s$ - $2p$ excitation energy in the formation of two additional chemical bonds. A further transformation, first suggested by Linus Pauling[2] is the linear combination of the nearly degenerate $2s$ and three $2p$ orbitals into four identically-shaped hybrid orbitals, directed toward the corners of a tetrahedron. These are called sp^3 -hybrid orbitals, which can be designated t_1 , t_2 , t_3 , and t_4 . The carbon atom with the four singly-occupied tetrahedral hybrids is now in what can be designated as its "valence state," a construct introduced independently by J. H. Van Vleck[3] and W. E. Moffitt[4], as the conceptual precursor of bond formation to hydrogen atoms (or other elements). The quadrivalent valence state of carbon atom, along with the four hydrogen atoms ready to form bonds, is represented in Figure 2.

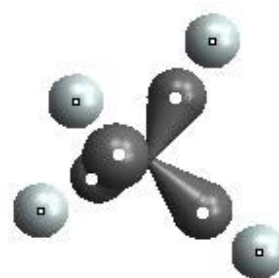


Figure 2. Valence state of carbon atom in methane



Figure 3. Molecular plot of methane, CH₄

Indeed, the methane molecule CH_4 , formed by covalent bonding with four hydrogen atoms has a tetrahedral shape with identical angles of 109.5° between each pair of C-H bonds, as shown in the familiar ball and stick model of methane in Figure 3.

3. Nitrogen and Oxygen

Nitrogen and oxygen atoms also tend to produce tetrahedral hybrids. Except when four identical atoms bond to the central atom, the hybrids are slightly distorted from a perfect tetrahedral shape. This picture can be subsumed by the VSEPR model of chemical bonding, in which bonds and lone pairs of electrons adopt a configuration determined by their maximized repulsions. Nitrogen expresses its natural trivalence to form the ammonia molecule NH_3 . It still has an approximately tetrahedral structure with a lone pair of electrons occupying one of the vertices, The N-H bond angles are reduced to 107.8° because the lone pair repels the N-H bonds. Adding an additional proton produces the ammonium ion NH_4^+ , which is again a regular tetrahedron. Figure 4 shows the valence states which are precursors to NH_3 and NH_4^+ , resulting in the ammonia molecule and the ammonium ion, Figure 5.

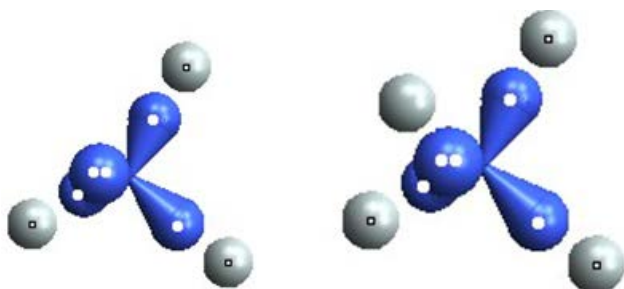


Figure 4. Valence states of nitrogen atom in NH_3 and NH_4^+ .

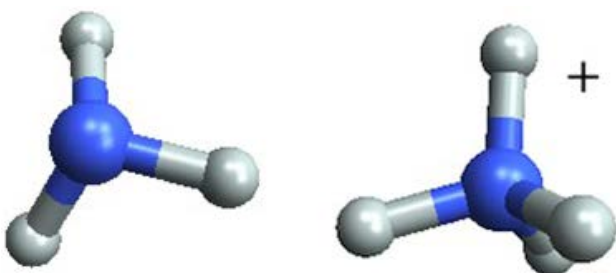


Figure 5. Ammonia molecule NH_3 and ammonium ion NH_4^+

The best-known compound of oxygen, and an essential for life, is, of course, water H_2O , which forms two bonds to hydrogen atoms in addition to two lone pairs. The H-O-H angle is reduced to 104.5° by repulsion of the lone pairs. A principal component of acids is the hydronium ion H_3O^+ , with a structure analogous to ammonia. Figure 6 and Figure 7 show the relevant valence states and molecular structures.

When water is involved in hydrogen bonding, the oxygen can momentarily be surrounded by four hydrogen atoms or ions in a tetrahedral configuration. This arrangement can occur in the crystal structure of ice.

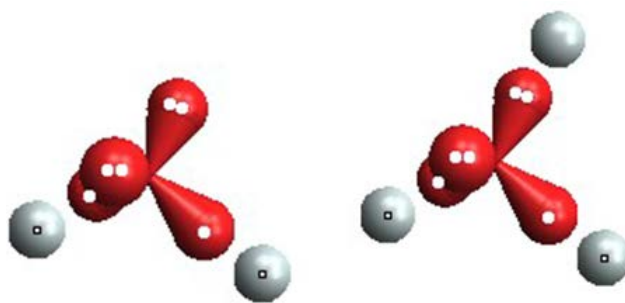


Figure 6. Valence states of oxygen in water and hydronium ion

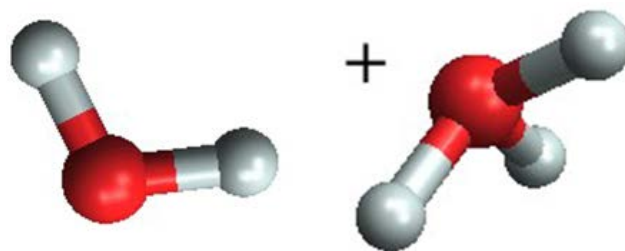


Figure 7. Molecular structures of water molecule H_2O and hydronium ion H_3O^+

4. Boron

We have saved for last, the hydrides of boron. Compounds of boron exhibit the behavior of "electron deficient" species. This means that there are not enough electrons to permit the formation of conventional 2-electron bonds. The simplest hydride, borane BH_3 , which can be expected to have a planar triangular structure, utilizes trigonal sp^2 -hybrid atomic orbitals (which can be designated tr_1 , tr_2 , tr_3). It is an extremely unstable compound, however, and spontaneously dimerizes to form diborane, B_2H_6 . (The fluorine analog BF_3 is a stable molecule, secured by the larger electronegativity of fluorine.) Figure 8 shows the valence state and molecular structure of BH_3

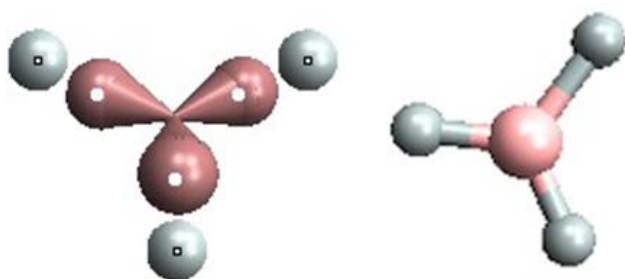


Figure 8. Trigonal valence state of boron and molecular structure of BH_3

For the more common valence state of boron, one can imagine a tetrahedron with one empty orbital. This can also be pictured as a resonance hybrid in which the 3 electrons are distributed among the 4 tetrahedral lobes (with an average of $3/4$ of an electron per orbital). This works to account for the tetrahedral structure of the borohydride ion BH_4^- , which requires combination with three hydrogen atoms, plus a hydride ion H^- . The valence state and the structure of the borohydride are shown in Figure 9.

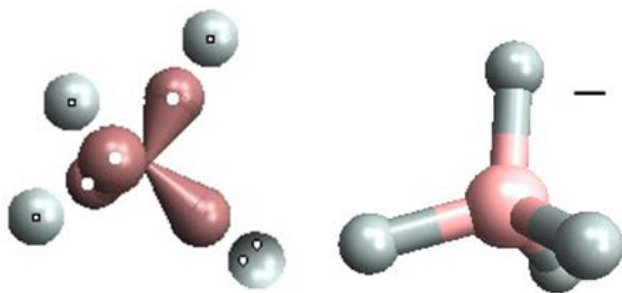


Figure 9. Tetrahedral valence state of boron and structure of BH₄⁻

A long controversial problem in chemistry has been the structure of diborane B₂H₆. We propose the following picture, beginning with two boron atoms in juxtaposition occupying their hypothetical tetrahedral valence states, as shown in the above graphic. Four hydrogen atoms can be added "normally" to the ends of the molecule. The four remaining valence orbitals on the two boron atoms, having only two electrons between them can then be imagined to form four one-electron bonds with two hydrogen atoms, as shown in Figure 10.

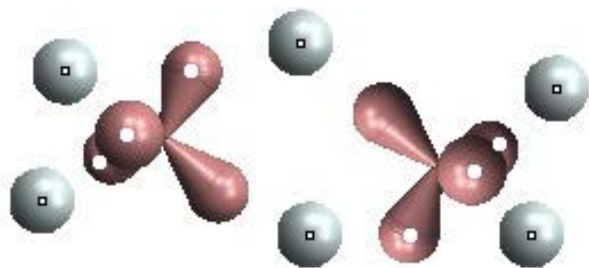


Figure 10. Proposed valence state for diborane formation

This produces the unique bridged structure of diborane, shown in Figure 11.

One of the first to propose such a bridged structure was H. C. Longuet-Higgins [5]. The structure has since been amply verified experimentally [6]. One-electron bonds are known to exist, for example in the H₂⁺ molecule-ion. Alternatively, the two B-H-B bridges can be

classified as 3-center, 2-electron bonds. Heavier boranes (hydrides of boron), such as B₄H₁₀, B₅H₉, etc., make extensive use of the theme of B-H-B and B-B-B bridge bonds [7].

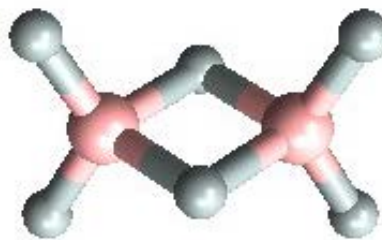


Figure 11. Structure of diborane B₂H₆

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