Hydrogen Bonding and Orbital Models

By Joel M Williams (text and images ©2014)

Abstract

There is increasing evidence that the hydrogen atom in X—H—X connections is covalently bound to both X atoms in equal to varying degrees. A spherical s-orbital for hydrogen attached to two 2-electron covalent bonds clearly violates the spdf-QM concept of shared electron bonding. A short discussion of the situation is presented along with a simple alternative orbital model for hydrogen that allows hydrogen to have two, diametrically opposite, covalent bonds.

INTRODUCTION

Molecule interactions form our physical world. While solids indicate strong interactions between atoms and within molecules, e.g. crystals and polymers, water is the epitome of "loose" interactions. As such, water has been one of the most studied substances, both as object and solvent. Martin Chaplin has assembled a website with 2065 references entitled "*Water Structure and Science*"[1].

Since this paper will be about hydrogen bonding in O—H—O systems, the following figure is presented to give the reader a feel for the atomic distances. The figure is adapted from Chaplin[1]. Information presented in the **Data Appendix** at the end of this paper has been added to provide perspective.
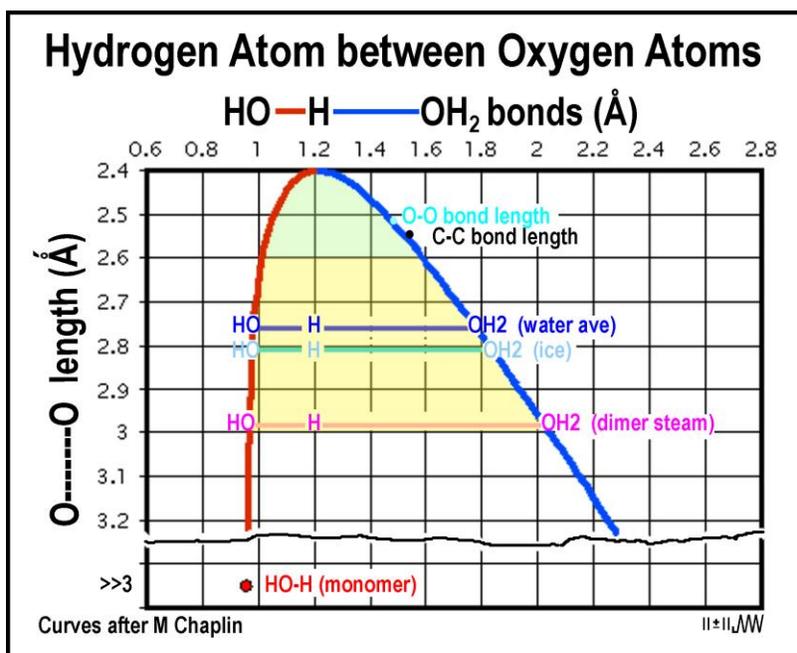
The figure clearly indicates the long bond that is associated with the term "hydrogen bonding" that allows H_2O to exist as water. The same bond in ice is just a bit longer. Surprisingly, the bond is much longer in the H_2O dimer that occurs about 1 in 1000 water molecules and about 1 in 20 steam molecules[1]. Chaplin indicates that the hydrogen bonding strength is 15kJ/mole at a length of 2.99Å. The light yellow zone reflects that an extended covalent bond is well within this distance.

Chaplin covers a number of articles dealing with the covalence of hydrogen bonds. A few of his comments (mainly from footnote 'd'[1]) are presented below to give the reader a feel for the situation. The reader should refer to Chaplin's website for references to each of these comments.

- *The (water)$_{JMW}$ network is essentially complete at ambient temperatures; that is, (almost) all molecules are linked by at least one unbroken hydrogen bonded pathway.*

- *If the water hydrogen bond (the long one)$_{JMW}$ is considered within the context of the complete range of molecular hydrogen bonding then it appears most probable that it is not solely electrostatic.*

- *If the hydrogen bond is substantially bent, it follows that the bond strength is weaker.*

- *The ionization of water, the continuous transformation of ice VII to ice X and the lower ionization potential for liquid water relative to water vapor would all seem to indicate a continuity of electron sharing between water molecules.*

- *In nucleic acids, inter-nucleotide N-H····N coupling (2JNN, using 15N nuclei) confirms some covalent nature in the N-H····N hydrogen bond.*

- *3-bond NMR (3JNC) splitting has been found through peptide N-H····O=C hydrogen bonds in proteins, confirming some covalent nature in the N-H····O hydrogen bonds.*

- *Hydrogen bonds in other molecules, such as DNA, also possess considerable covalent character.*

"Hydrogen bonding" is commonly associated with long, weak, O-----H interactions. When the oxygen atoms are closer, the hydrogen nucleus is more equally distant from each oxygen nucleus (the light green area in the figure above). Such short distances would be expected for proton-transfers from one oxygen atom to another. Proton-transfer might be a fleeting event, but the interaction of the oxygen orbitals with the hydrogen would be instantaneous with the hydrogen atom having two short covalent bonds. How can this occur when, in the current spdf-QM model, hydrogen has only a spherical s-orbital and by definition can only form a single covalent bond having 2 electrons?

A stable molecular arrangement with two oxygen atoms sharing a hydrogen atom equally at short range would definitely require the hydrogen to have two covalent bonds. Do such molecular arrangements exist? The answer is "Yes".

DISCUSSION

Dimethysulfoxide solvated proton (DMSO—H—OSDM)$^+$ is a stable molecular arrangement with a symmetrically placed proton between the two oxygen atoms (O—H—O). This molecular species was first reported by Williams and Kreevoy in 1967 when we studied methanesulfonic acid in DMSO.[2] A similar conclusion was drawn by Kirilova, etal.[3] in their 1986 study with ATR. No bands belonging to (DMSO—H—OSDM)$^+$ other than v(O—H—O) were found. X-ray studies have shown the occurrence of (DMSO—H—OSDM)$^+$ in crystalline salts.[4] In 2002, Denisov, etal.[5], determined the cation to be practically linear with a O—O distance of 2.403Å with the bridging proton located exactly in the center between the two oxygen atoms.

In their 2005 study of crystalline $H_5O_2^+ClO_4^-$, Vener and Sauer[6] found the equilibrium O—O distances to be 2.431Å in the isolated cation and 2.426Å in the crystal.

The covalent orbital reach of an oxygen atom is greater than 0.74Å (½ of O—O) and that of a hydrogen atom is greater than 0.37Å (½ of H—H). The full reach of each atom to the other will be

greater than this 1.11Å sum. It is reasonable to expect them to span the 1.2Å distance of O—H bonds easily. In each of the molecular arrangements above, the hydrogen atom is thus clearly involved with two covalent bonds which, in the current spdf-QM bonding model, require it to be coordinated with 4 electrons.

The current spdf-QM electron orbital model is a forced one based on the precept of a sphere as the starting point. The spdf-QM model not only requires that macro-physical laws, such as e-e repulsion, cease in the near-nucleus area, but has a basic set of orbitals with little resemblance to those needed to model the materials of our substantive world. To address how atoms actually bond to one another, the orbitals of spdf-QM model had to be "hybridized". For the simplest orbital connections, sp^3, sp^2 and sp^1 orbital sets were created. Eventually, when inorganic complexes were modeled more "hybridizing" was needed with d-orbitals becoming involved. Interestingly, with all of this "hybridizing" of orbitals, the spherical s-orbital of hydrogen was consciously excluded (avoided?). In the bond formation part of the currently accepted spdf-QM hybridized model, bonds contain 2 paired electrons. Consequently, hydrogen is able to form only 1 covalent bond as its unhybridized orbital can only handle 2 electrons. From the real-world cases above, a hydrogen atom does form more than one covalent bond is necessary. Clearly, the spherical s-orbital for hydrogen is incorrect for such bonding. It is even incorrect for a solo hydrogen atom and a helium atom[7].

The upper image in the figure at the right indicates the problem with the current spdf-QM spherical hydrogen orbital. Two identical covalent bonds are needed for the O—H—O connection. Each oxygen atom (only one of their orbital protuberances is shown) supplies 2 electrons, but the hydrogen atom is able to form only one 2-electron bond. Thus, two covalent bonds being attached to the hydrogen atom violates a prime tenet of the spdf-QM orbital approach to molecular bonding.

Atomic Orbital Model Approaches to Hydrogen Bonding and Transfer

Hybridized spdf-QM approach

$(CH_3)_2S$-O-$\overset{+}{H}$-O-$S(CH_3)_2$
Williams and Kreevoy, JACS (1967)

MCAS model approach
(Only H is MCAS modeled)

The MCAS model[8] was created as the result of the need for hydrogen atoms to have two covalent bonds as well as to eliminate the need for spin-reversed electron pairing. "Mirrored tetrahedral orbital twins" (center of the bottom image in the figure at the right) provide precisely the needed orbital configuration for hydrogen. The oxygen atoms are not MCAS-modeled here (shown as spheres with an orbital protuberance), so that the focus is on the MCAS character of the hydrogen orbitals; their orbitals, too, are "mirrored orbital twins". Electrons are not corralled in the covalent bond, but flow through the orbital sets. The mirrored hydrogen orbital pair establishes an opposing linear orientation of the covalent bonds from the hydrogen atom.

The MCAS model negates the need to "hybridize" an atom's orbitals for the simplest bonding between atoms! Dogged adherence of the scientific community to Bohr's orb-turned-sphere for the hydrogen atom has stifled the search for physical model alternatives to the spdf-QM atomic model. Strong pi-bonds from parallel p-orbitals that can hardly touch, and do so at an acute angle, counter experimental evidence that bonds become progressive weaker as they deviate from linearity. Molecular orbital diagrams remove the physical aspects of the orbitals. In essence, MOs simply indicate that bonds are formed without worrying about how electrons in them actually move or reside. How and where electrons move in the atomic and molecular systems is the aim of the MCAS model. A spherical orbital with spin-reversed paired electron twins in highly localized, interatomic, bond space is not part of this model.
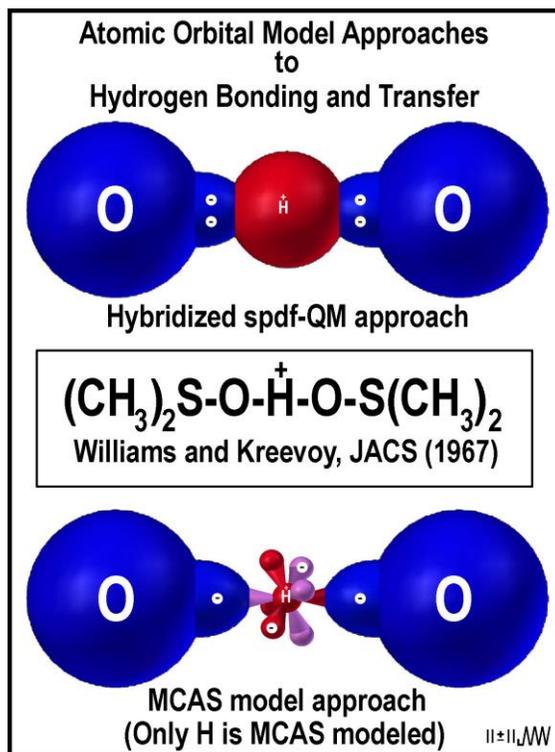
Data Appendix

From Martin Chaplin, *Water Structure and Science*, http://www1.lsbu.ac.uk/water/hbond.html and http://www1.lsbu.ac.uk/water/molecule.html
- o The experimental values for gaseous water molecule O—H length is 0.95718 Å
- o The O—O distance in ice Ih varies between 2.75 Å (0 K) and 2.764 Å (253 K).
- o In ambient atmosphere the O—O in the water dimer is 2.985 Å (calculated by JMW); the short O—H bond is 0.948Å and the long bond is 2.037Å

From U. Bergmann, A.Di Cicco, P. Wernet, E. Principi, P. Glatzel, and A. Nilsson, *Nearest-neighbor oxygen distances in liquid water and ice observed by x-ray Raman based extended x-ray absorption fine structure*, J Chem Phys. 2007 Nov 7;127(17):174504, http://www.ncbi.nlm.nih.gov/pubmed/17994824
- o O—O of water average distance (2.81 Å for water and 2.76 Å for ice)
- o And a slightly shorter peak position (2.70 Å for water and 2.71 Å for ice)

From C Chieh, http://www.science.uwaterloo.ca/~cchieh/cact/c120/bondel.html
- o C—C 1.54 Å
- o O—O 1.48 Å
- o H—H 0.74 Å

REFERENCES

[1] Martin Chaplin, *Water Structure and Science*, http://www1.lsbu.ac.uk/water/hbond.html

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[5] G.S. Denisov, A. Koll, V.I. Lobadyuk, V.M. Schreiber, A.V. Shurukhina, V.N. Spevak, *Hydrogen bonding in coordination compounds containing homoconjugated bis-dimethylsulfoxide cation*, J Molecular Structure **605** (2002) 221-226; http://www.chemie.fu-berlin.de/~limbach/denisov/184.pdf

[6] V. Vener and J Sauer, *Environmental effects on vibrational proton dynamics in $H5O2^{+}$: DFT study on crystalline $H5O2^{+}ClO4^{-}$*, Phys . Chem. Chem. Phys . , 2005, **7** , 258-263; http://edoc.hu-berlin.de/oa/articles/recUjCiEZgtpY/PDF/247whSivydg.pdf

[7] Joel M Williams, *Electron orbitals for ortho and para Helium*, http://pages.swcp.com/~jmw-mcw/electron orbitals for ortho and para helium.htm; a pdf version is available at http://gsjournal.net/Science-Journals/Essays/View/4980; He (11±11) is a gas.

[8] A description of the MCAS atomic model is presented along with the spdf-QM atomic model in this reference: Joel M Williams, *Parsing the spdf electron orbital model*, http://pages.swcp.com/~jmw-mcw/Parsing the spdf electron orbital model.htm; a pdf version is available at http://gsjournal.net/Science-Journals/Essays/View/5032