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WATER STRUCTURE AND BEHAVIOR

Text

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The Water Molecule

Water is a tiny V-shaped molecule with the molecular formula H_2O ^a. In the liquid state, in spite of 80% of the electrons being concerned with bonding, the three atoms do not stay together as the hydrogen atoms are constantly exchanging between water molecules due to [protonation/deprotonation processes](#). Both acids and bases catalyze this exchange and even when at its slowest (at pH 7), the average residence time is only about a millisecond. As this brief period is, however, much longer than the timescales encountered during investigations into water's [hydrogen bonding](#) or [hydration properties](#), water is usually treated as a permanent structure.

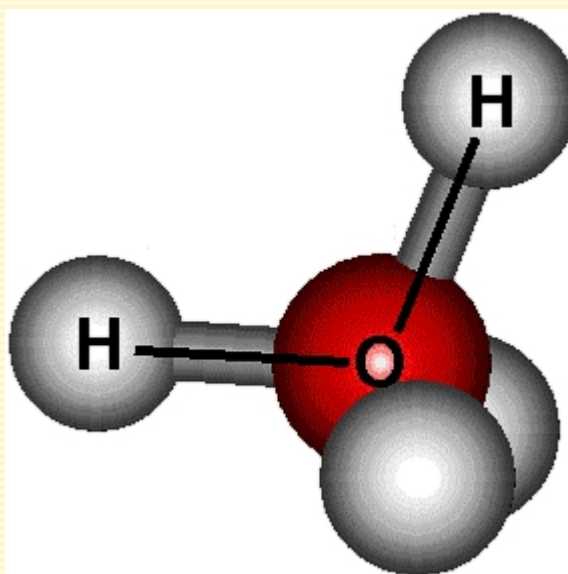
Water molecules (H_2O) are symmetric (point group C_{2v}) with two mirror planes of symmetry and a 2-fold rotation axis. The hydrogen atoms may possess parallel (paramagnetic ortho- H_2O) or antiparallel (nonmagnetic para- H_2O) [nuclear spin](#). The equilibrium ratio is all para at zero Kelvin shifting to 3:1 ortho:para at less cold temperatures ($> 50\text{ K}$);^c the equilibrium taking months to establish itself in ice and nearly an hour in ambient water [410]. This means that liquid H_2O effectively consists of a mixture of non-identical molecules and the properties of pur liquid ortho- H_2O or para- H_2O are unknown. Many materials preferentially adsorb para- H_2O due to its non-rotation ground state [410, 835]. The apparent difference in energy between the two states is a significant $1\text{--}2\text{ kJ mol}^{-1}$, far greater than expected from spin-spin interactions ($< \text{J mol}^{-1}$) [835].

The water molecule consists of two light atoms (H) and a relatively heavy atom (O). The approximately 16-fold difference in mass gives rise to its ease of rotation and the significant relative movements of the hydrogen nuclei, which are in constant and significant relative movement.

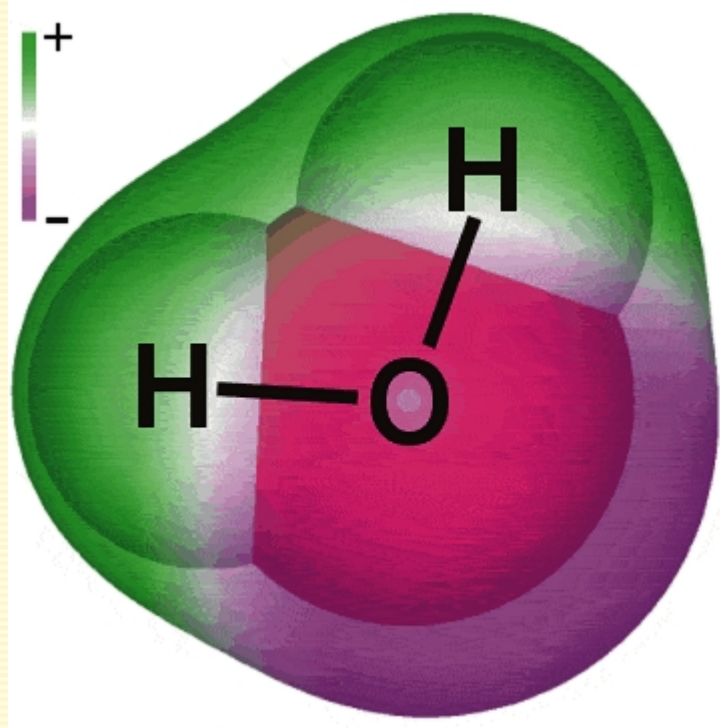
The water molecule is often described in school and undergraduate textbooks of as having four, approximately tetrahedrally arranged, sp^3 -hybridized electron pairs, two of which are associated with hydrogen atoms leaving the two remaining lone pairs. In a perfect tetrahedral arrangement the bond-bond, bond-lone pair and lone pair-lone pair angles would all be 109.47° and such tetrahedral bonding patterns are found in condensed phases such as [hexagonal ice](#).

[Ab initio calculations](#) on isolated molecules, however, do not confirm the presence of significant directed electron density where lone pairs are expected.

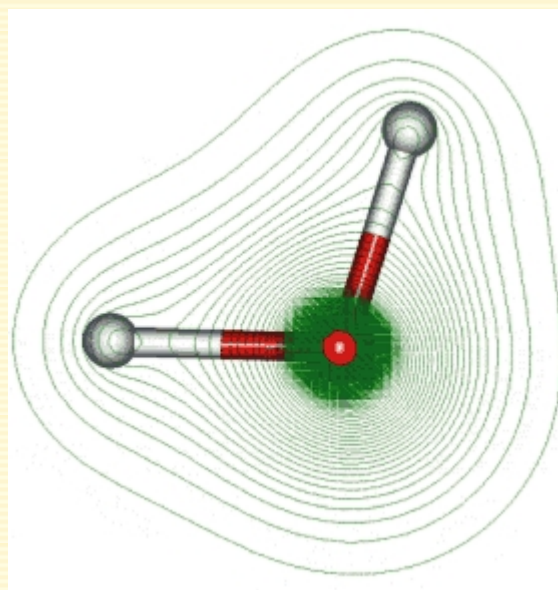
Early 5-point [molecular models](#), with explicit negative charge where the lone pairs are purported to be, fared poorly in describing hydrogen bonding, but a recent [TIP5P](#) model shows some promise. Although there is no apparent consensus of opinion [116], such descriptions of substantial sp^3 -hybridized lone pairs in the isolated water molecule should perhaps be avoided [117], as an sp^2 -hybridized structure (plus a p_z orbital) [is indicated](#). This rationalizes the formation of (almost planar) trigonal hydrogen bonding that can be found around some [restricted sites in the hydration of proteins](#) and where the numbers of hydrogen bond donors and acceptors are unequal.



Note. This cartoon of water does not represent its actual outline, which is more rotund ([see below](#))



The approximate shape and charge distribution of water.



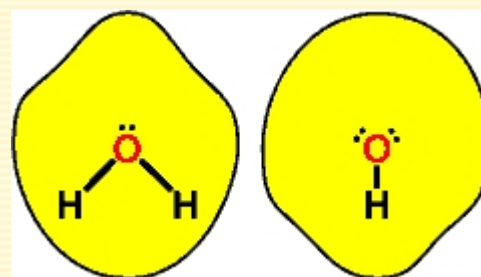
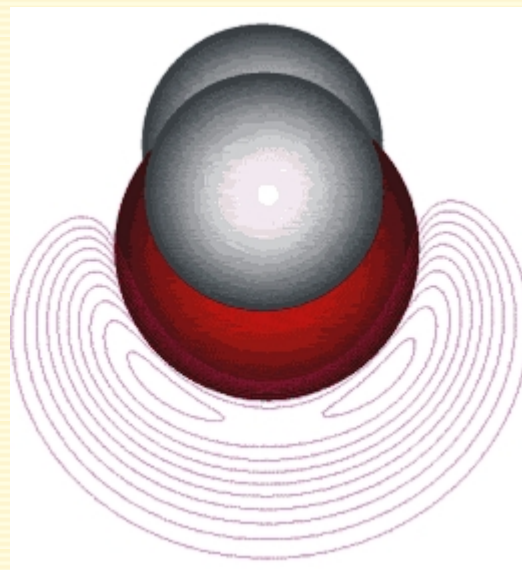
Note that the average electron density around the oxygen atom is about 10x that around the hydrogen atoms.

The electron density distribution for water is shown above right with some higher density contours around the oxygen atom omitted for clarity. The polarizability of the molecule is centered around the O-atom (1.4146 \AA^3) with only small polarizabilities centered on the H-atoms (0.0836 \AA^3) [736]. For an isolated H_2^{16}O , H_2^{17}O or H_2^{18}O molecule, the calculated O-H length is 0.957854 \AA and the H-O-H angle is 104.500° (D_2^{16}O , 0.957835 \AA , 104.490°) [836]. The charge distribution depends significantly on the atomic geometry and the method for its calculation but is likely to be about $-0.7e$ on the O-atom (with the equal but opposite positive charge equally divided between the H-atoms) for the isolated molecule [778].^d The experimental values for gaseous water molecule are O-H length 0.95718 \AA , H-O-H angle 104.474° [64].^e These values are not maintained in liquid water, where ab initio (O-H length 0.991 \AA , H-O-H angle 105.5° [90]) and neutron diffraction studies (O-H length 0.970 \AA , H-O-H angle 106° [91])^f suggest slightly greater values, which are caused by the hydrogen bonding weakening the covalent bonding. These bond lengths and angles are likely to change, due to polarization shifts, in different hydrogen-bonded environments and when the water molecules are bound to solutes and ions. Commonly used [molecular models](#) utilize O-H lengths of between 0.957 \AA and 1.00 \AA and H-O-H angles of 104.52° to 109.5° . ▲

The electronic structure has been proposed as $1s_{\text{O}}^{2.00} 2s_{\text{O}}^{1.82} 2p_{x_{\text{O}}}^{1.50} 2p_{z_{\text{O}}}^{1.12} 2p_{y_{\text{O}}}^{2.00} 1s_{\text{H1}}^{0.78} 1s_{\text{H2}}^{0.78}$ [71], however it now appears that the 2s orbital may be effectively unhybridized with the bond angle expanded from the (then) expected angle of 90° due to the steric and ionic repulsion between the partially-positively charged hydrogen atoms (as proposed by Pauling over 50 years ago [99]). The **molecular orbitals** of water, $(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2$, are shown on another page (24 KB).

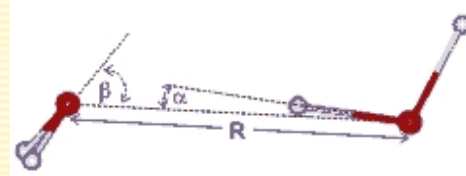
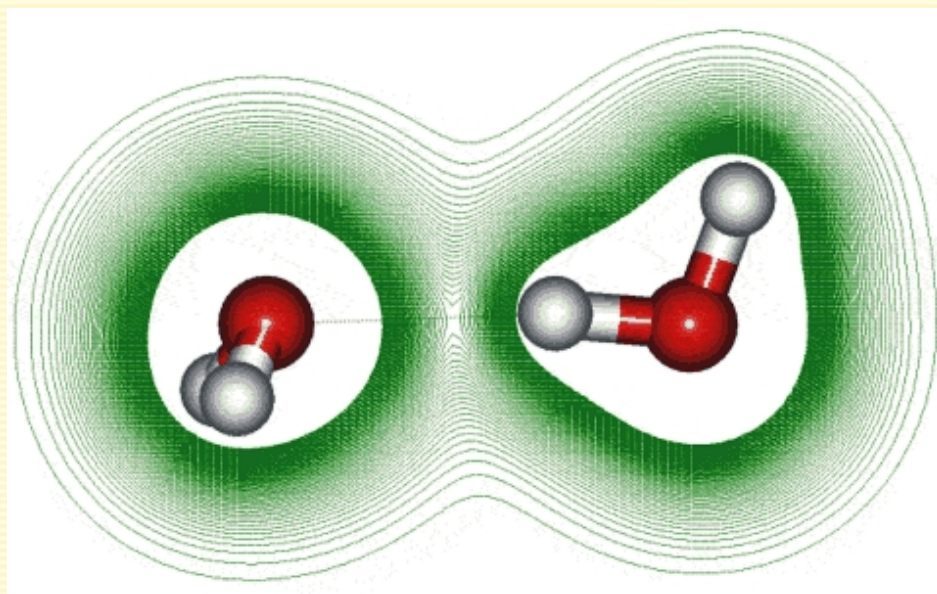
Shown opposite is the electrostatic potential associated with the water structure. Although the lone pairs of electrons do not appear to give distinct directed electron density in isolated molecules, there are minima in the electrostatic potential in approximately the expected positions.

The mean van der Waals diameter of water has been reported as identical with that of isoelectronic neon (2.82 Å) [112]. **Molecular model** values and intermediate peak **radial distribution data** indicates however that it is somewhat greater ($\sim 3.2\text{\AA}$). The molecule is clearly not spherical, however, with about a $\pm 5\%$ variation in van der Waals diameter dependent on the axis chosen; approximately tetrahedrally placed slight indentations being apparent opposite the (putative) electron pairs.



Van der Waals radii [206]

Much effort has been expended on the structure of small isolated water clusters. The most energetically favorable water dimer is shown below with a section through the electron density distribution (high densities around the oxygen atoms have been omitted for clarity). This shows the tetrahedrality^b of the bonding in spite of the lack of clearly seen lone pair electrons; although a small amount of distortion along the **hydrogen bond** can be seen. This tetrahedrality is primarily caused by electrostatic effects (i.e. repulsion between the positively charged non-bonded hydrogen atoms) rather than the presence of tetrahedrally placed lone pair electrons. The hydrogen-bonded proton has reduced electron density relative to the other protons [222]. Note that, even at temperatures as low as a few kelvin, there are considerable oscillations ($< \text{ps}$) in the hydrogen bond length and angles [591]. The **molecular orbitals** of the water dimer are shown on another page (50 KB)



$R = 2.976 (+0.000, -0.030) \text{ \AA}$, $\alpha = 6 \pm 20^\circ$, $\beta = 57 \pm 10^\circ$ [648]; α is the donor angle and β is the acceptor angle. The dimer (with slightly different geometry) dipole moment is 2.6 D [704]. Although β is close to as expected if the lone pair electrons were tetrahedrally placed ($= 109.47^\circ/2$), the energy minimum ($\sim 21 \text{ kJ mol}^{-1}$) is broad and extends towards $\beta = 0^\circ$.

Simplified models for the water molecule have been developed to agree with particular physical properties (e.g. agreement with the **critical parameters**) but they are not robust and resultant data are often very sensitive to the precise model parameters [206]. Models are still being developed and are generally more complex than earlier but they still generally have poor predictive value outside the conditions and physical parameters for which they were developed.

Although not often perceived as such, water is a very reactive molecule available at a high concentration. This reactivity, however, is greatly moderated at ambient temperatures due to the extensive **hydrogen bonding**. Water molecules each possess a strongly nucleophilic oxygen atom that enables many of life's reactions, as well as **ionizing** to produce reactive hydrogen and hydroxide ions. Reduction of the hydrogen bonding at high temperatures, or due to **electromagnetic fields**, results in greater reactivity of the water molecules. ▲

^a Water's composition (two parts hydrogen to one part oxygen) was discovered by the London scientist Henry Cavendish (1731-1810) in about 1781. He reported his findings in terms of phlogiston (later the gas he made was proven to be hydrogen) and dephlogisticated air (later this was proven to be oxygen). Cavendish died (1810) in his Laboratory just 30 minutes walk from the present site of [London South Bank University](#).

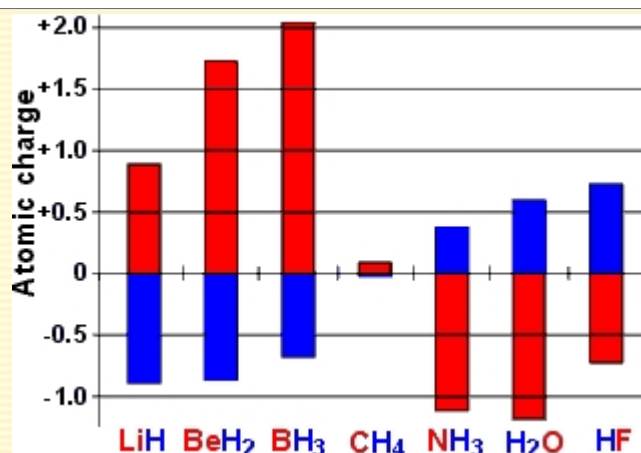


It has recently been suggested that $H_{1.5}O$ may better reflect the formula at very small (attosecond) timescales when some of the H-atoms appear invisible to neutron and electron interaction [515]. These results have been questioned [630] and are now thought erroneous [796], but such suggestions do add support to the view that observations concerning the structure of water should be tempered by the timescale used. [Back]

^b The tetrahedral angle is $180 - \cos^{-1}(1/3)^\circ$; $109.47122^\circ = 109^\circ 28' 16.39''$. Tetrahedrality (q , the orientational order parameter) may be defined as $q = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \psi_{jk} + \frac{1}{3} \right)^2$, where ψ_{jk} is the angle formed by lines drawn between the oxygen atoms of the four nearest and hydrogen-bonded water molecules [169]. It equals unity for perfectly tetrahedral bonding (where $\cos(\psi_{jk}) = -1/3$) and averages zero (± 0.5 SD) for random arrangements, with a minimum value of -3. The density order parameter is [described elsewhere](#). [Back]

^c Due to deuterium's nuclear spin of 1 (cf 1/2 for H's spin), the lowest energy form of D_2O is ortho. D_2O converts to a 2:1 ortho:para ratio at higher temperatures. HDO, having non-equivalent hydrogen atoms, does not possess an ortho/para distinction. T_2O behaves similarly to H_2O as tritium also possesses a nuclear spin of 1/2. [Back]

^d The charge on the hydrogen atoms across the periodic table are shown opposite [820]. The hydrogen atom charges are [blue](#) and the charges on the other atoms are indicated [red](#). [\[Back\]](#)



^e The actual values depend on the vibrational state of the molecule with even values of 180° being attainable during high order bend vibrations ($\nu_2 \geq 7$, $\lambda < 900$ nm) for the H-O-H angle [860].

Vibrations are asymmetric around the mean positions. In the ground state, the bond angle (104.5°) is much closer to the [tetrahedral angle](#) than that of the other Group VI hydrides, H₂S (92.1°), H₂Se (91°) or H₂Te (89°). [\[Back\]](#)

^f The H-O-H angle in ice Ih is reported as $106.6^\circ \pm 1.5^\circ$ [717], whereas recent modeling gives values of $108.4^\circ \pm 0.2^\circ$ for ice Ih and $106.3^\circ \pm 4.9^\circ$ for water [1028]. [\[Back\]](#)

Details of water's [molecular vibrations and absorptions](#) are given on another page.

Please submit any [comments and suggestions](#) you may have.

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This page was last updated by [Martin Chaplin](#)
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