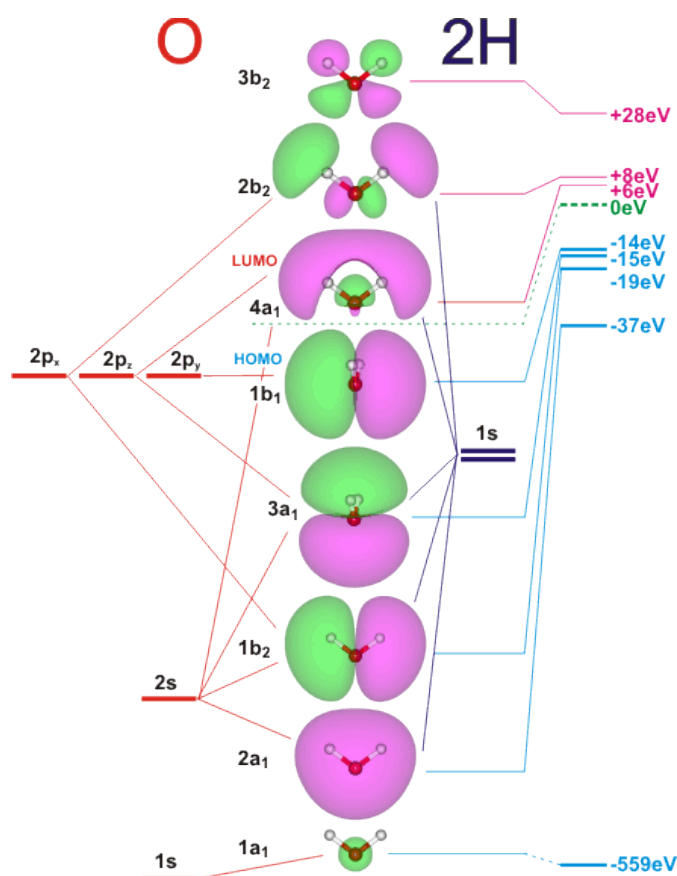


Molecular Orbitals for Water (H₂O)



The five occupied and the lowest three unoccupied molecular orbitals of the isolated molecule ($1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$) were calculated using the Restricted Hartree-Fock wave function (RHF) using the 6-31G** basis set (experimental data is given in [1289]). They are set out with the lowest energy (that is, most negative energy) molecular orbitals at the bottom. They are all given in the xz plane (z-axis upwards) except $1b_1$ and $3a_1$, which are in the yz plane (z-axis upwards).^a The two lowest energy orbitals $1a_1$ and $2a_1$ are contributed from the 1s and 2s (mostly) orbitals of the oxygen atom, respectively, and are consequentially approximately spherical. The three highest energy occupied orbitals ($1b_2$, $3a_1$, $1b_1$) are orthogonal around the oxygen atom and without obvious sp^3 hybridization characteristics.

The relative energies of these orbitals have been found to be somewhat different from these theoretical values. The lowest energy transitions are broad at 7.61 and 9.36 eV for the $3s/4a_1 \leftarrow 1b_1$ ($\tilde{A} 1^1B_1$) and $3s/4a_1 \leftarrow 3a_1$ ($\tilde{B} 2^1A_1$) transitions respectively [1561] for the gas phase and at 8.09 and 9.74 eV in the liquid [1561, 1562].

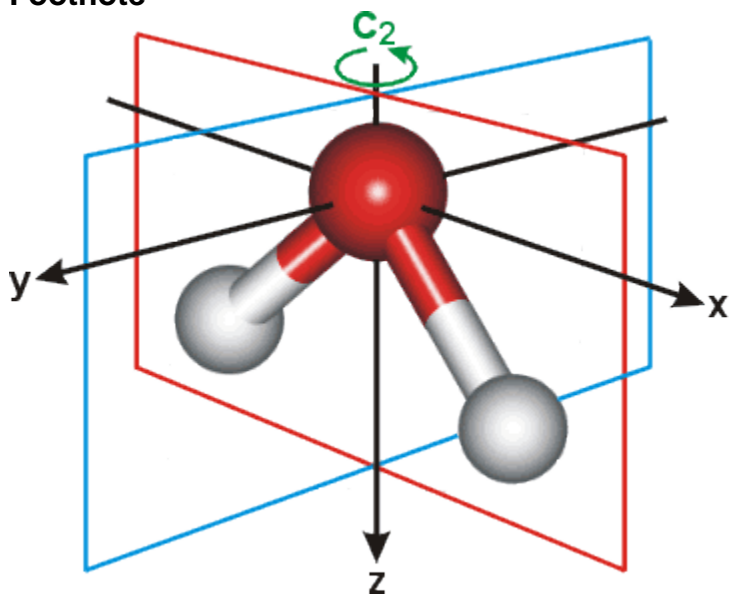
The highest occupied molecular orbital (HOMO), $1b_1$, is predominantly p_z^2 in character with no contribution from the hydrogen 1s orbital and mainly contributes to the "lone pair" effects. The $2a_1$, $1b_2$ and $3a_1$ all contribute to the O-H bonds. The two lowest unoccupied molecular orbitals $4a_1$ (LUMO) and $2b_2$ are O-H antibonding orbitals, seen in X-ray spectroscopy. They have greatest

electron densities around the O-atom whereas orbital $3b_2$ has greatest electron density around the H-atoms. The experimental binding energy of the $1a_1$ orbital in the gas phase is 539.9 eV [1227].

These orbitals are appreciably changed in ice and water; the experimental electron binding energies in liquid water being $2a_1$ 30.90 eV, $1b_2$ 17.34 eV, $3a_1$ 13.50 eV, $1b_1$ 11.16 eV [877]. The experimental binding energy of the $1a_1$ orbital in the liquid phase consists of a broad energy distribution centered about 538.1 eV plus a smaller contribution at 536.6 eV within the tetrahedrally hydrogen bonded bulk [1227]. The $1b_2$ and $3a_1$ orbitals are largely responsible for the donation of hydrogen bonding with the $3a_1$ orbital shown experimentally to contribute the most [411]. Also, the $4a_1$ and $2b_2$ antibonding orbitals are reported to be partially occupied in hydrogen bond formation, receiving electron density from donor $1b_1$ orbitals [814].

An interactive structure with orbitals is available (COW [Plug-in, ActiveX] only).

Footnote



^a The nomenclature is based upon the symmetry of the orbitals. The figure right shows the planes of symmetry (xz and yz) and the two-fold axis of rotation (C_2 , z-axis).

If the orbitals are unchanged (that is, symmetric) with respect to the planes of symmetry (xz and yz) and the two-fold axis of rotation (C_2) then they are denoted as ' a_1 ' orbitals and numbered from the lowest energy (*i.e.* $1a_1$ is the lowest energy a_1 orbital). If the sign of the orbital changes with respect to 180° rotation about C_2 and reflection through the xz plane it is b_1 , whereas if the sign of the orbital changes with respect to 180° rotation about C_2 and reflection through the yz plane it is b_2 . An a_2 orbital has no change in sign with respect to 180° rotation about C_2 but changes sign on reflection through both xz and yz planes (for example, the 9th lowest unoccupied molecular orbital for H_2O). [Back]

Source:<http://www1.lsbu.ac.uk/water/h2oorb.html>