

No Rabbit Ears on Water

The Structure of the Water Molecule: What Should We Tell the Students?

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In the vast majority of high school (1) and freshman university (2) chemistry textbooks, water is presented as a bent molecule whose bonding can be described by the Gillespie-Nyholm approach with the oxygen atom sp^3 hybridized. The lone pairs are said to be dominant causing the H-O-H angle to be reduced from the ideal $109\frac{1}{2}^\circ$ to 104° and are regularly shown as equivalent in shape and size even being described as "rabbit ears" (3). Chemists have even been advised to wear Mickey Mouse ears when teaching the structure and bonding of the H_2O molecule, presumably to emphasize the shape of the molecule (and possibly the two equivalent lone pairs) (4).

The question to ask is: are there good reasons for doing this, or are there sufficient grounds for handling the description of the bonding in a different way?

The best place to start is in the classic text "The Nature of the Chemical Bond" by Linus Pauling (5). In Chapter 4, he describes the concept of hybridization of $2s$ and $2p$ atomic orbitals to yield the set of tetrahedral sp^3 orbitals. He describes the difference in energy between the ground state s^2p^2 configuration of the C atom and the $2s2p^3$ configuration and introduces the term "promotion energy" (p 121). In the same chapter he describes the bonding in the H_2O molecule as being between the $2p$ orbitals on the O atom and the $1s$ orbitals of the H atom (p 111). He then explains that the $2s$ orbitals on oxygen are not involved because

A $2s$ electron of oxygen is more stable than a $2p$ electron by about 200 kcal/mole; and if the s orbital were used in bond formation ... rather than for an unshared pair the molecule would be made unstable to this extent.

He then ascribes the opening of the H-O-H angle from the ideal value of 90° to 104.5° to electrostatic repulsions between the two H atoms. It is

attributed in the main to the partial ionic character of the O-H bonds This would give a resultant positive charge to the hydrogen atoms, which would repel one another and thus cause an increase in the bond angle.

He also considers the possibility of s character in the bonding orbitals of OF_2 and OH_2 to improve the "strength" of the orbital (p 111) from 1.732 for pure p to 2.00 for the ideal sp^3 . Inclusion of s character in the hybrid will be "resisted in the case of atoms with an unshared pair ... in the s orbital, which is more stable than the p orbitals" (p 120). Estimates of the H-E-H angle range from 91.2° for AsH_3 to 93.5° for H_2O . He once again ascribes the anomalies for H_2O to "repulsion of the charges of the hydrogen atoms" (p 122).

In his famous book (6) Kitaigorodskii describes the bonding in water and H_2S (p 10). In both cases, he also begins with the simple model of the p orbitals of the central atom forming covalent bonds to the H atoms, with the two pairs remaining on the O atom occupying atomic $2s$ and $2p$ orbitals. He then confronts the problem of the H-O-H angle being 105° . His explanation is simple. The hydrogen atom has a van der Waals (contact) radius of 1.1 \AA . If the H-O-H angle were 90° then the two H atoms would interpenetrate (their van der Waals radii overlap—see Fig. 1). This physically cannot happen (this is equivalent to the Pauli exclusion principle) and therefore the angle must open until the two surfaces are in contact (see Fig. 2). The resulting H-O-H angle of 104.5° is thus a compromise between the van der Waals forces resisting compression of the two H atoms and the wave mechanical forces, which in the unstrained case would yield an angle of 90° . In H_2S , an angle close to 90° does not result in large van der Waals repulsions because the H-S bonds are so much longer (see Fig. 3).

These two descriptions represent the simple valence bond overlap-of-atomic-orbitals approximation but modified to account for the observed H-O-H bond angle. Notice that the two sigma bonding orbitals that form the OH bonds are identical in all aspects of shape and energy.

A totally different approach was described by Walsh in 1953 (7). He considered the building up of molecular orbitals for AH_2 molecules from atomic s and p orbitals of atom A

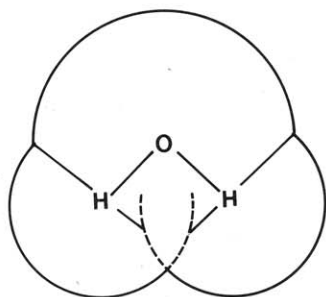


Figure 1. (left) Hypothetical water molecule with the H-O-H angle constrained to 90° . The van der Waals radii of the H atoms clearly overlap (as shown by the dotted lines); the two H atoms would penetrate each other.

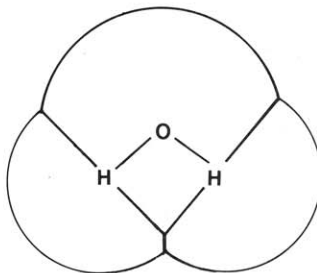


Figure 2. (center) The water molecule with the H-O-H angle set at 104.5° . The two H atoms are now in contact with slight compression.

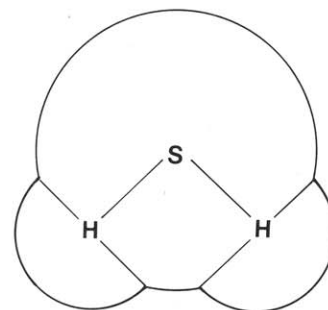


Figure 3. (right) The H_2S molecule, with the H-S-H angle of 90° . The longer S-H bond moves the H atoms apart thus eliminating the H · · · H interference which occurs in the H_2O molecule. Bond lengths are O-H, 1.0 \AA , S-H, 1.35 \AA ; van der Waals radii are O, 1.4 \AA , H, 1.1 \AA , S, 2.1 \AA .

under constraints of the symmetry properties of the combination of the contributing atomic orbitals and the molecular orbital that is formed. He begins with the assumption that the H-A-H angle is 90° , and that the two OH bonding orbitals are localized, and "formed by the overlap of a pure p atomic orbital of A with the $1s$ orbital of H". He then considers the in-phase and out-of-phase combination of these localized orbitals to give two nonlocalized orbitals labelled a_1 and b_2 . There remains a p orbital on A, perpendicular to the plane of H-A-H, and a nonbonding s orbital on A.

The combination of atomic orbitals to form these molecular orbitals are shown schematically in Figure 4 (8).

These pictorial representations should apply equally well to H_2S and H_2O . He then considers how the binding energy of each orbital should change with change in H-A-H angle, with the values for a_1 and b_2 being significantly affected as H-A-H opens from 90° to 180° . "At 90° the non-bonding a_{1s} orbital must be much more tightly bound than the non-bonding b_{1p} orbital."

In 1957, three pertinent papers were published in *Quarterly Reviews*. One discussed the concept of electron correlation (9), and one of the authors, Linnett, subsequently published an expanded and simplified version of his ideas as the "double quartet" approach (10).

The O^{2-} ion is expected to have the same electron configuration as the Ne atom, and therefore the H-O-H angle in the isoelectronic water molecule is predicted to be $109\frac{1}{2}^\circ$. The reduction in the angle is ascribed to the pairs of electrons in the OH bonds being "centered" further from the nucleus than the lone pairs. Because S^{2-} is larger than O^{2-} and S is less electronegative than oxygen, the regular tetrahedron of pairs of electrons about the S atom can be distorted more and hence the H-S-H angle will deviate more from the regu-

lar tetrahedral angle. He makes an important statement about methane:

The electron distribution will be most conveniently described in terms of tetrahedral, sp^3 , hybrid orbitals... but the means of description (hybrid orbitals) should not be regarded as the cause of the molecule being tetrahedral.

The second paper (11) is the most important, because it presented a very simple model based on electron-pair repulsions that accounted nicely for the shapes of a large number of simple inorganic compounds. This approach was subsequently expanded and published as the VSEPR theory (12) and had a marked influence on the treatment of bonding in textbooks. The O atom of the H_2O molecule is surrounded by four pairs of electrons in the valence shell, hence should be tetrahedral in shape. However, the H-O-H angle closes because the bonding pairs are drawn away from the nucleus of the O atom thus decreasing the repulsion between them. The much smaller H-S-H angle is attributed to the same effect, but enhanced by the decreased electronegativity of the S atom. What is important, is that this predominantly electrostatic model is then directly linked to the "corresponding hybrid orbitals" (in Table 1, p 344 of ref 11) where H_2O is described as V-shaped, tetrahedral sp^3 .

The third paper in that important year, by Pople, considered the molecular orbital and equivalent orbital approaches (13). He presents a set of molecular orbitals for the H_2O molecule that are similar to, but not identical with, those of Walsh (7); two bonding molecular orbitals and two nonbonding molecular orbitals. The nonbonding orbitals (lone pairs) are: a $2p$ orbital on oxygen perpendicular to the OH_2 plane, which "corresponds to the lone pair electron removed in the first ionization process", and a hybrid of the O $2s$ and O $2p$ in the plane of the OH_2 molecule, protruding on the side remote from the two H atoms and along the line bisecting the H-O-H angle. The combinations of atomic orbitals are shown schematically below (Fig. 5).

The question now is: are there any experimental data that can confirm or refute the bonding pictures put forward? The answer is unequivocally: yes.

Photoelectron spectroscopy has allowed the energies of the orbitals within atoms and molecules to be determined accurately. The technique has been fully described (14) and, in particular, the spectra of both water and H_2S have been determined and fully interpreted (15). The ground state configuration and orbital energies of the H_2O molecule were calculated by Ellison and Shull (16) to be approximately

| Orbital: | $(1s_0)^2$ | $(2s_0)^2$ | $(1b_2)^2$ | $(3a_1)^2$ | $(2px_0)^2$ |
|----------|------------|------------|------------|------------|-------------|
| Energy: | -577 | -36 | -18.5 | -13.2 | -11.8 eV |

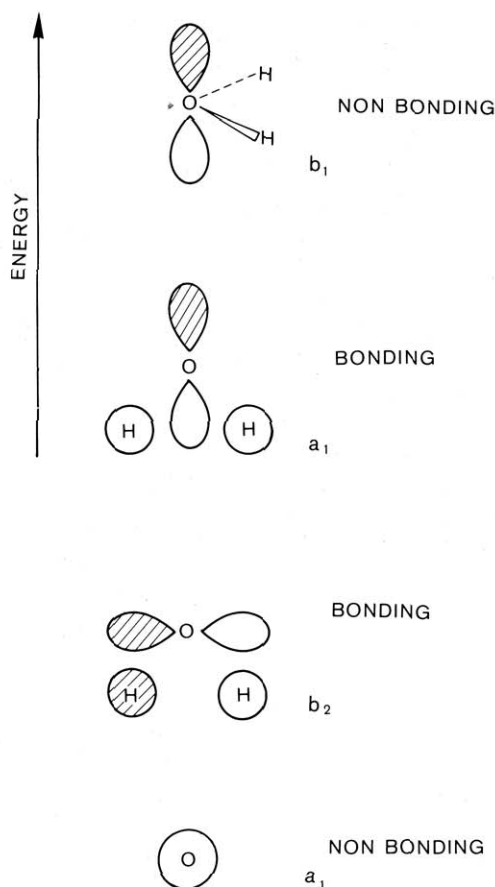


Figure 4. Combinations of atomic orbitals on O and H atoms to form the bonding and nonbonding orbitals in H_2O , as described by Walsh (7).

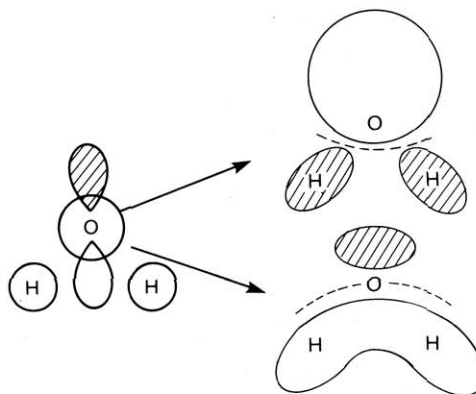


Figure 5. Combination of O $2s$, O $2p$, and H $1s$ orbitals giving a bonding orbital (below) and the nonbonding orbital (above). A simplified diagram showing the two nonbonding orbitals (lone pairs), the $2p$ orbital perpendicular to the OH_2 plane, and the hybrid molecular orbital is given in Figure 8.

and the three bands measured yielded ionization energies of 12.6, 13.7, and 17.2 eV, a pleasing correspondence. Turner states (15)

the highest electron-energy band relates to the removal of an oxygen 2p "lone-pair" electron. Since the oxygen 2s electrons are almost certainly at a much lower energy than 21.21 eV, the remaining two bands ... can be attributed to the O-H bonding molecular orbitals.

He also states—about the first I.P.—“we are concerned here with the removal of an essentially nonbonding electron (oxygen lone pair)”, and later says of H₂S, “the 1b₁ electron removed is even less bonding than is H₂O, and the orbital may be regarded as completely (3p)², a sulphur ‘lone-pair’”.

The photoelectron spectrum of H₂O is shown in Figure 6 together with the combination of atomic orbitals used to construct the molecular orbitals (15). The approach of teaching molecular orbital models by the interpretation of photoelectron spectroscopy was described in 1974 (17), and in particular, the spectra of H₂O and H₂S were interpreted with the aid of a correlation diagram in which the molecular orbitals are essentially the same as those described by Walsh in 1953. The detailed analysis of the lowest energy peak at 10.47 eV for H₂S “... verifies that here a nonbonding electron was removed ... a nonbonding ‘lone’ or ‘free’ electron pair ...” which was previously described as the 3p orbital. There is a discussion of how the difference in H-A-H bond angle affects the relative energies of the two bonding orbitals but *not* what is the cause of the H-S-H angle being 92° while the H-O-H angle is 105°.

More recently there have been published three excellent texts describing the qualitative molecular orbital approach to molecular bonding and shapes (18–20). Each treats the case of H₂O. The molecular orbitals for a bent AH₂ molecule are shown diagrammatically on p 34 of ref 18, p 52 of ref 19, and pp 55 and 88 of ref 20, and are essentially identical. Gimarc states that the lowest energy “1σg-1a₁ MO is mainly the oxygen 2s AO ... because the oxygen 2s is deep in energy

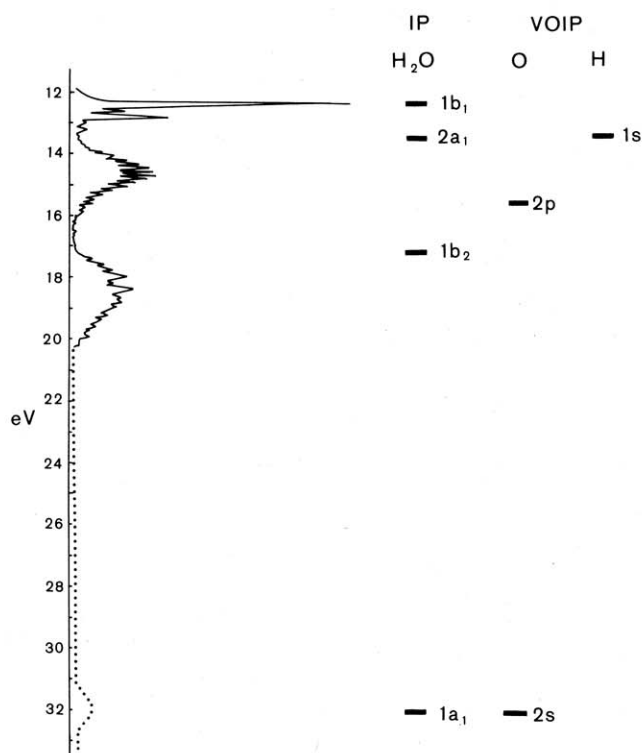


Figure 6. Photoelectron spectrum of the H₂O molecule with the ionization energies of the various molecular orbitals and atomic orbitals of the H and O atoms on the same energy scale.

(−36 eV) compared to the hydrogen 1s AOs (−13.6 eV)”. This concept of difference in energy of orbitals determining the degree of hybridization or mixing is stated clearly by these authors: “... atomic orbitals will only mix together strongly if their energy separation is small” (19, p 14); “... the magnitude of the interaction energy is inversely proportional to the energy difference between the interacting orbitals” (20, pp 17–18). The problem of the relatively large H-O-H angle of 104½° is considered (18, pp 40–41), and it is the small length of the O-H bond (0.958 Å) relative to the greater length of the S-H bond (1.336 Å) together with the difference in electronegativity that is said to account for the angle. More interestingly, Burdett (19, p 114) compares H...H separations in H₂S and H₂O in the observed geometry and for the hypothetical H-A-H angle of 90°. He concludes (a la Kitaigorodskii) that “the heavier hydrides [H₂S] because of their longer AH bonds, experience no strain at the 90° geometry ... but the lighter hydrides [NH₃, H₂O] are sterically strained at this structure and the ... larger HAH angles may be a direct result of this”. (The H...H contact distance in water is 1.519 Å and in NH₃ is 1.644 Å while in H₂S it is 1.914 Å and in PH₃ it is 2.068 Å. Assuming a contact radius of 1.1 Å, it is clear that in H₂S and PH₃ nonbonded repulsions due to van der Waals forces are negligibly small.)

It is important to recognize that the sp³ hybrid model of water (with the two equivalent “rabbit ear” lone pairs) indicates only *two* types of electrons, the bond pairs and the lone pairs (see Fig. 7). This implies that two bands should be observed in the photoelectron spectrum. This is clearly wrong because four well-defined bands are observed.

Finally, Hall in two papers published in 1978 considered the viability of Gillespie’s VSEPR approach and the stereo-

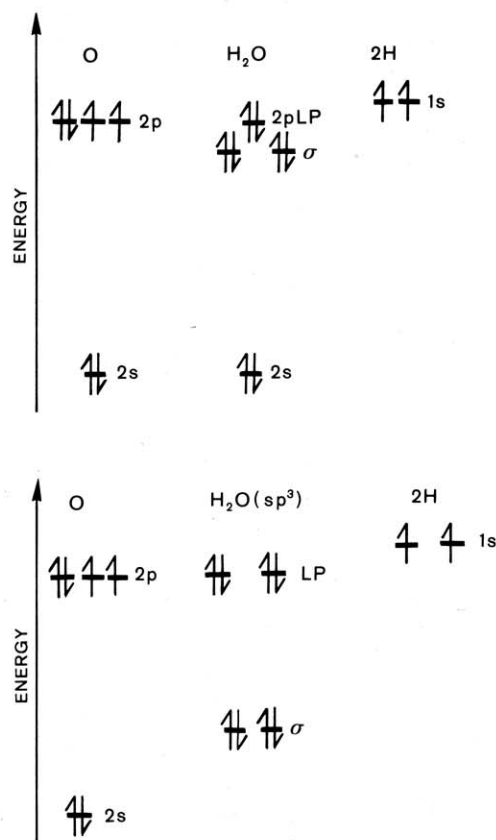


Figure 7. (above) The combination of the atomic orbitals of O and the H atoms *without* sp³ hybridization, resulting in an O 2s nonbonding orbital, two identical O 2p-H 1s sigma bonds, and a O 2p lone pair. This would yield a photoelectron spectrum of three peaks. (below) The sp³ model of the H₂O molecule, with two identical lone pairs and two sigma bonds. This would yield a photoelectron spectrum of only two peaks.

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