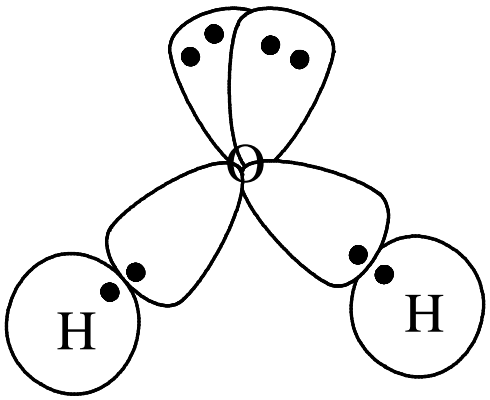
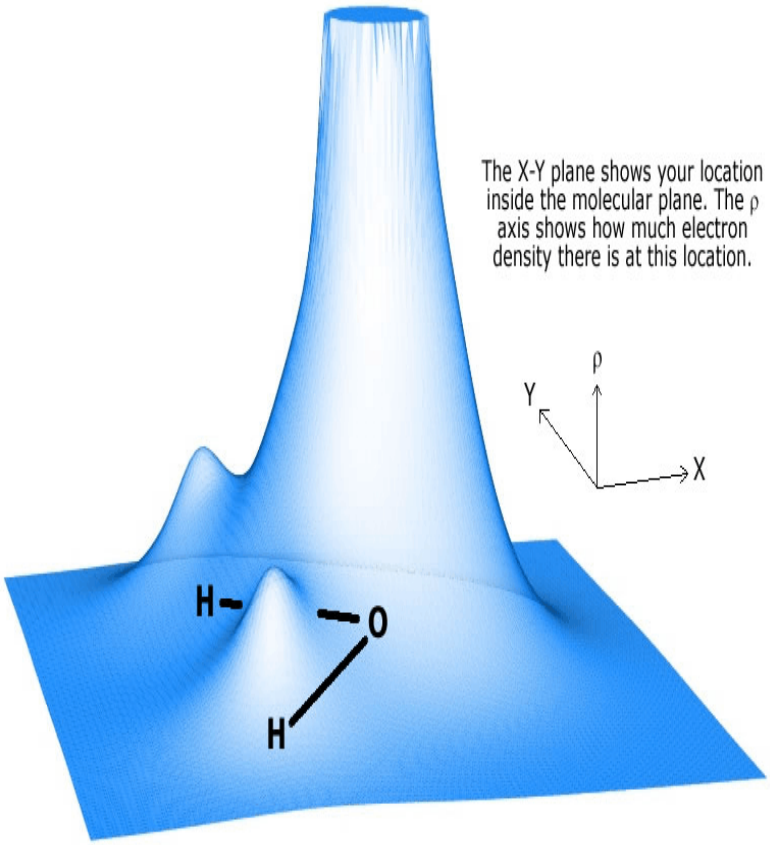
Classic VB Model of Water



- ✔ sp^3 hybridized oxygen contributes six electrons
- ✔ Two hydrogens contribute one electron each in 1*s* orbitals
- ✔ Two sigma bonds formed by sp^3-*s* overlap
- ✔ Two "lone pairs" in sp^3 hybrid orbitals

Electron Density Maps of H_2O



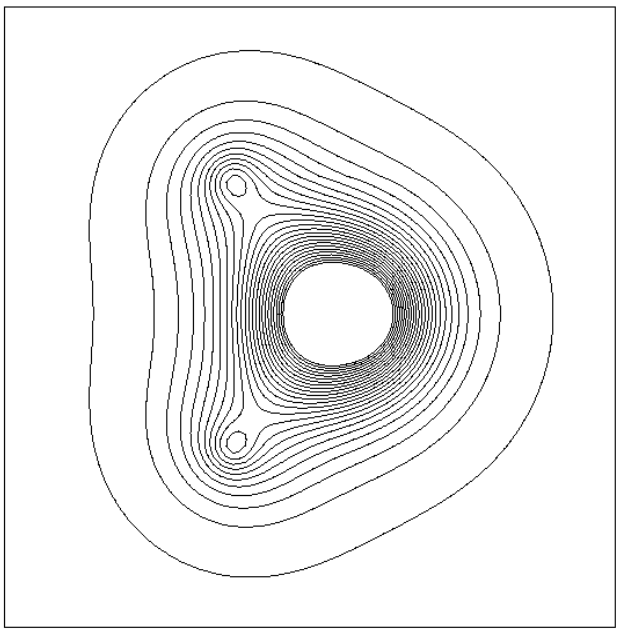


Image sources: (top) www.reed.edu/chemistry/roco/Density/graphs.html; (bottom) www.ccl.net/cca/documents/dyoung/water/lp3.html

Conclusions and Questions

✔ The electron density maps show significant electron density on the back side of water, but there is no indication of separate regions.

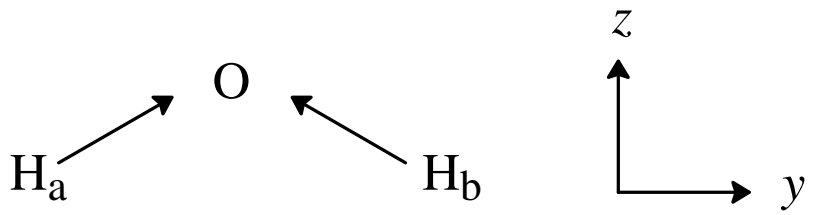
✔ The electron density maps do not indicate the bonding or non-bonding nature of the electron density on the back side.

☹ Is the electron density on the back side strictly non-bonding?

☹ Is all the electron density on the back side the result of two lone pairs?

MO Scheme of H_2O
Hydrogen SALCs

- Taking the two hydrogens as a basis for the SALCs



we obtain the following reducible representation:

C_{2v}	E	C_2	σ_v	σ_v'
Γ_H	2	0	0	2

for which $\Gamma_H = A_1 + B_2$.

- The equations for the SALCs are

$$\Phi_{a_1} = \frac{1}{\sqrt{2}}(1s_{H_a} + 1s_{H_b})$$

$$\Phi_{b_2} = \frac{1}{\sqrt{2}}(1s_{H_a} - 1s_{H_b})$$

Symmetries of Oxygen AOs

- From the C_{2v} character table, oxygen AO symmetries are

$$s = A_1 \quad p_x = B_1 \quad p_y = B_2 \quad p_z = A_1$$

- The p_x AO (B_1) has no matching SALC and must be nonbonding.

- The p_y orbital can form bonding and antibonding combinations with the B_2 SALC.

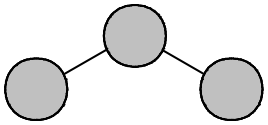
- Both *s* and p_z orbitals on oxygen match with the A_1 SALC, so *s*-*p* mixing can be expected.

☹ If we formed bonding and antibonding combinations for both of these, we would end up with more MOs in the final scheme (seven) than there are available AOs on the component atoms (six).

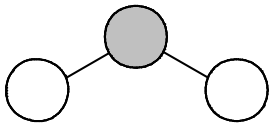
  ☛ To avoid this, we must make only three MOs from the A_1 AOs and SALC.

☺ For simplicity, we will assume that the *s* and p_z orbitals on oxygen both form bonding MOs, and together they form one *s*-*p* mixed antibonding orbital.

LCAOs for H_2O

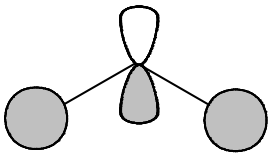


σ (s) - a_1

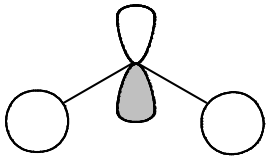


σ^* (s) - a_1

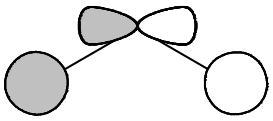
Mixed as one σ^*



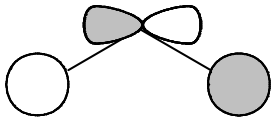
σ (z) - a_1



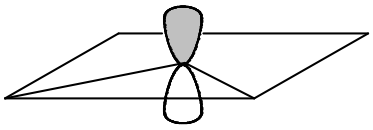
σ^* (z) - a_1



σ (y) - b_2

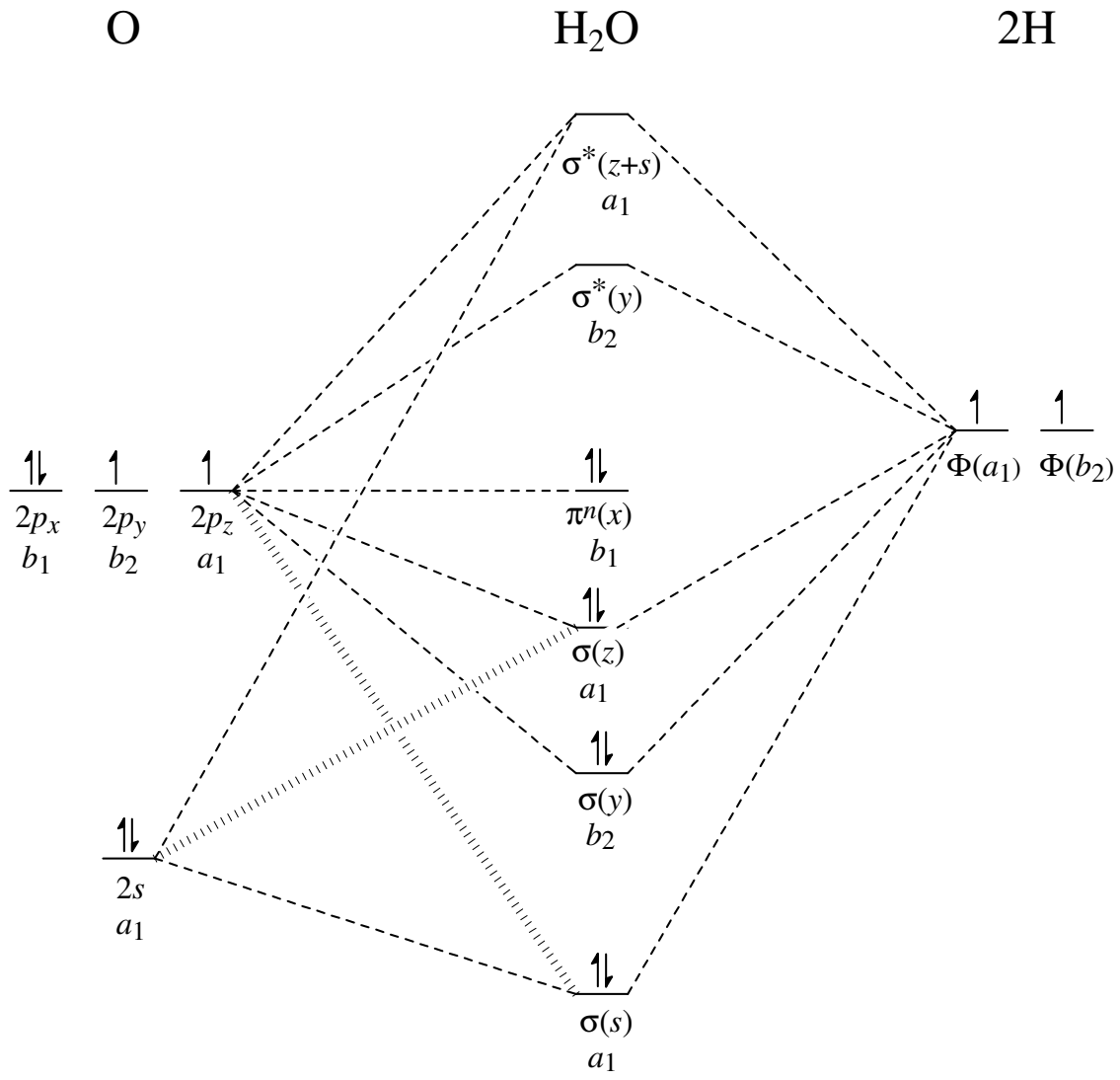


σ^* (y) - b_2



π (x) - b_1

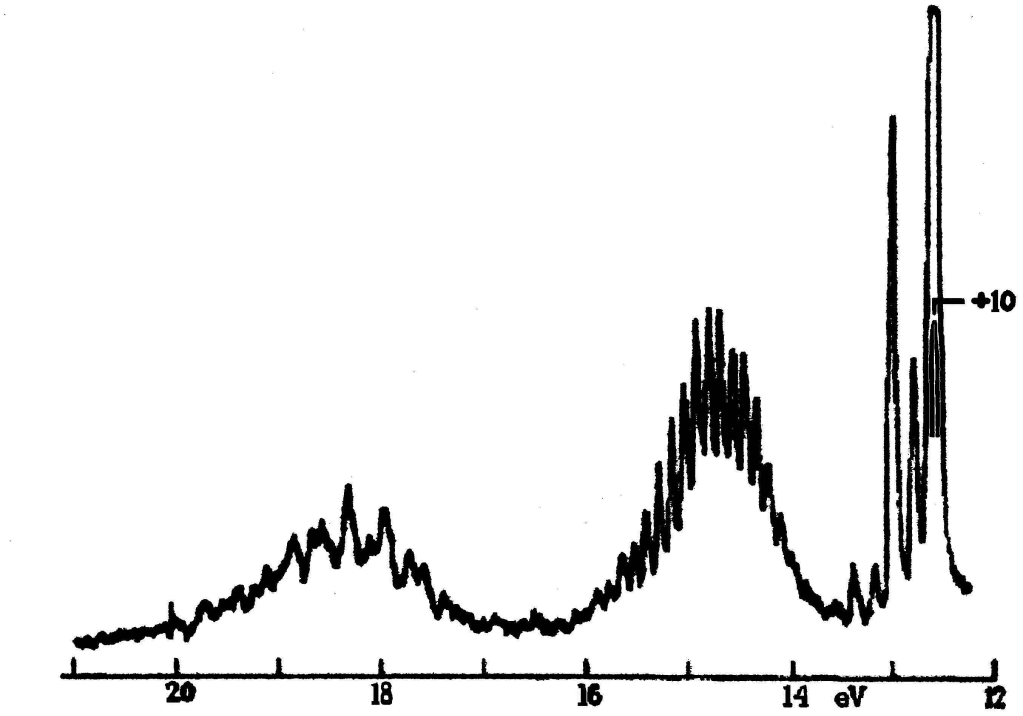
Qualitative MO Scheme for H_2O



☞ Hashed lines indicate lesser contributions arising from *s*-*p* mixing.

PES of H_2O and MO Model[1]

- Four bands:
  - Three with highest energy have fine structure.
  - Least energetic band has no fine structure, consistent with ionization from nonbonding $\pi^n(x)$.



☞ The P.E.S. results are consistent with the MO scheme.

- Rather than two lone pairs in approximately sp^3 hybrids, the MO scheme suggests a single region of electron density protruding from the back side of the molecule, created by the combination of the nonbonding $\pi^n(x)$ MO and the weakly bonding $\sigma(z)$ MO.

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[1]C. R. Brundle and D. W. Turner, *Proc. Roy. Soc., A*, **1968**, *307*, 27-36.