Classic VB Model of Water

- $sp^3$ hybridized oxygen contributes six electrons
- Two hydrogens contribute one electron each in $1s$ orbitals
- Two sigma bonds formed by $sp^3$-$s$ overlap
- Two "lone pairs" in $sp^3$ hybrid orbitals
Electron Density Maps of H₂O

The X-Y plane shows your location inside the molecular plane. The ρ axis shows how much electron density there is at this location.

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.

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

atorium Is all the electron density on the back side the result of two lone pairs?
MO Scheme of $\text{H}_2\text{O}$
Hydrogen SALCs

- Taking the two hydrogens as a basis for the SALCs

\[ \begin{array}{c}
\text{O} \\
\text{H}_a \\
\text{H}_b \\
\end{array} \]

we obtain the following reducible representation:

\[
\begin{array}{c|cccc}
C_{2v} & E & C_2 & \sigma_v & \sigma_v' \\
\hline
\Gamma_H & 2 & 0 & 0 & 2 \\
\end{array}
\]

for which $\Gamma_H = A_1 + B_2$.

- The equations for the SALCs are

\[
\Phi_{a_1} = \frac{1}{\sqrt{2}} (s_{\text{H}_a} + s_{\text{H}_b})
\]

\[
\Phi_{b_2} = \frac{1}{\sqrt{2}} (s_{\text{H}_a} - s_{\text{H}_b})
\]
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 $\text{H}_2\text{O}$

\[
\sigma (s) - a_1 \quad \sigma^* (s) - a_1
\]

\[
\sigma (z) - a_1 \quad \sigma^* (z) - a_1
\]

\[
\sigma (y) - b_2 \quad \sigma^* (y) - b_2
\]

\[
\pi (x) - b_1
\]

Mixed as one $\sigma^*$
Qualitative MO Scheme for H$_2$O

Hashed lines indicate lesser contributions arising from $s$-$p$ mixing.
PES of H$_2$O 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.