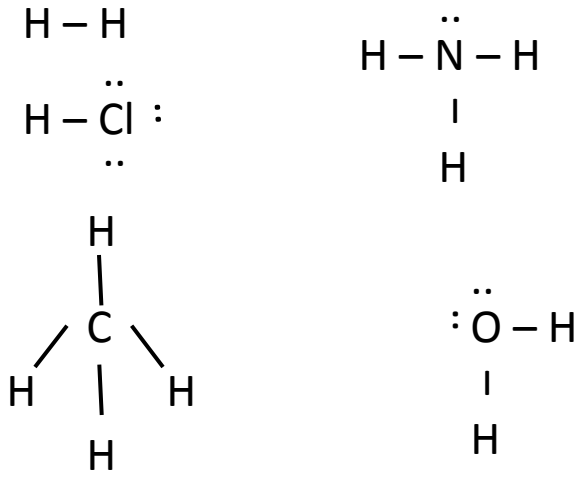
Valence bond *vs.* MO approaches

Valence-bond

localized orbitals

e.g. Lewis structures



Valence shell electron pair repulsion (VSEPR) model

- ligands and lone pairs around a central atom repel one another
- lone pair occupies more ∢ space than ligand
- amount of ∢ space occupied by ligand < as its electronegativity > as an EN of central atom >
- a multiply bonded ligand occupies more space than a singly bonded ligand

Failures

CH_3 planar

CaF_2, $SrCl_2$ bent rather than linear

SeF_6^{-2} octahedral even though has extra lone pair

Hybridization

$$sp^2: \quad 1s^2\left(2p_y\right)^1\left(\psi_a\right)^1\left(\psi_b\right)^1\left(\psi_c\right)^1$$

$$\psi_a = c_1\phi_{2p_z} - \frac{1}{\sqrt{3}}\phi_{2s} \qquad \rightarrow -\frac{1}{\sqrt{3}}\phi_{2s} + \sqrt{\frac{2}{3}}\phi_{2p_z}$$

$$\psi_b = c_4\phi_{2p_z} - \frac{1}{\sqrt{3}}\phi_{2s} - c_6\phi_{2p_x} \rightarrow -\frac{1}{\sqrt{3}}\phi_{2s} - \frac{1}{\sqrt{2}}\phi_{2p_z} - \frac{1}{\sqrt{2}}\phi_{2p_x}$$

$$\psi_c = c_4\phi_{2p_z} - \frac{1}{\sqrt{3}}\phi_{2s} + c_6\phi_{2p_x} \rightarrow -\frac{1}{\sqrt{3}}\phi_{2s} - \frac{1}{\sqrt{6}}\phi_{2p_z} + \frac{1}{\sqrt{2}}\phi_{2p_x}$$

Each orbital has one-third 2s and two-thirds 2p character

sp:

$$\begin{cases} \psi_a = \frac{1}{\sqrt{2}}\left(-\phi_{2s} + \phi_{2p_z}\right) \\ \psi_b = \frac{1}{\sqrt{2}}\left(-\phi_{2s} - \phi_{2p_z}\right) \end{cases}$$

sp^3

$$\begin{cases} \psi_a = \frac{1}{2}\left(-\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z}\right) \\ \psi_b = \frac{1}{2}\left(-\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z}\right) \\ \psi_c = \frac{1}{2}\left(-\phi_{2s} + \phi_{2p_x} - \phi_{2p_y} - \phi_{2p_z}\right) \\ \psi_d = \frac{1}{2}\left(-\phi_{2s} - \phi_{2p_x} + \phi_{2p_y} - \phi_{2p_z}\right) \end{cases}$$

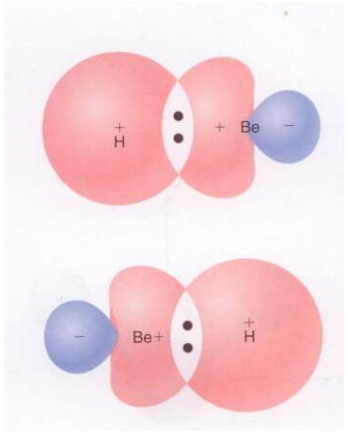
Need to modify mixing if ligands non equivalent

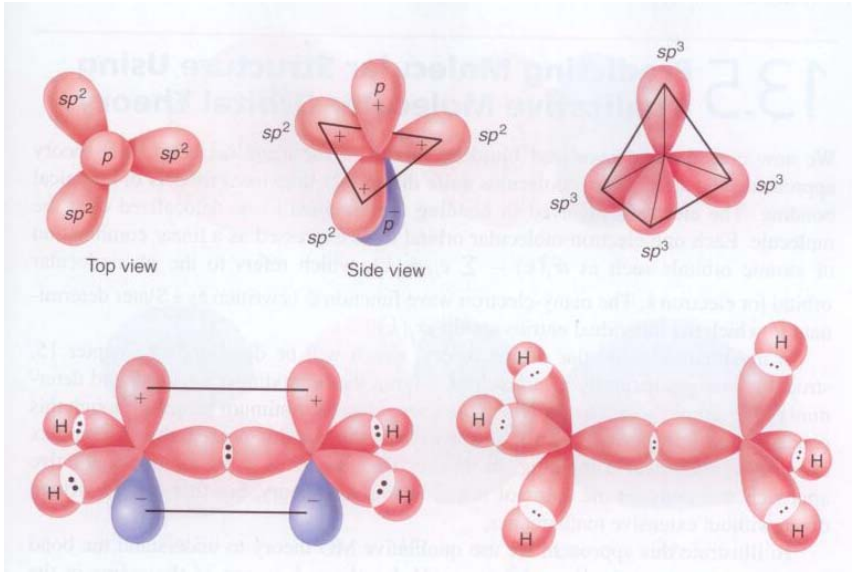
We are not going to worry about this

Chemical bonding

H Be H but if Be is $1s^2 2s^2$ – how does this bond?

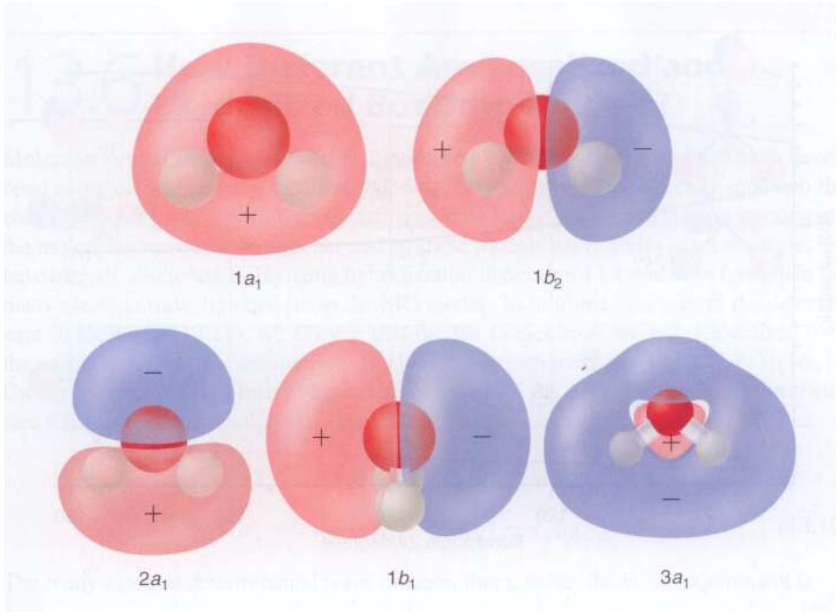
H Be H is linear so make sp hybrids

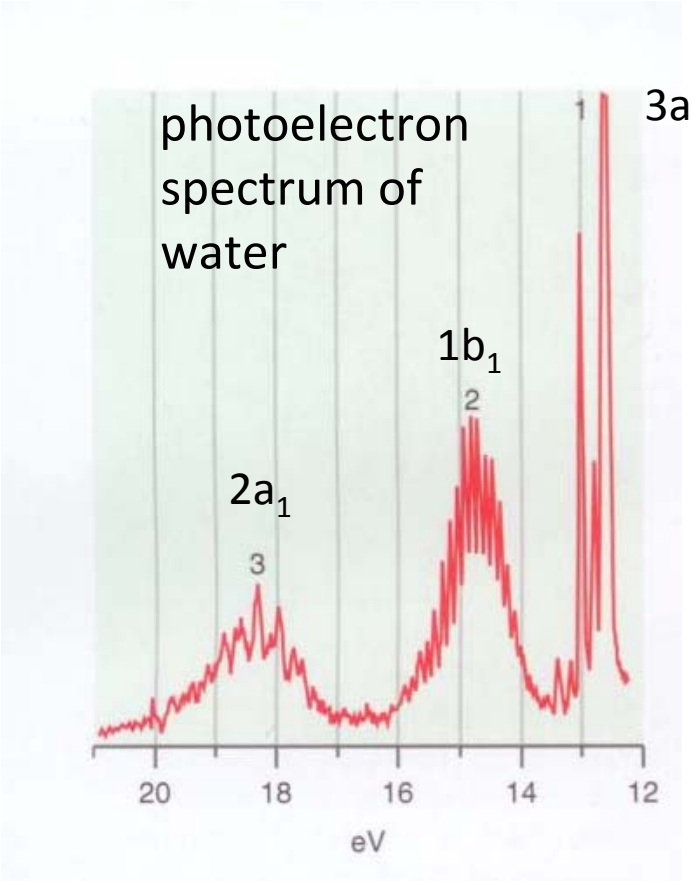


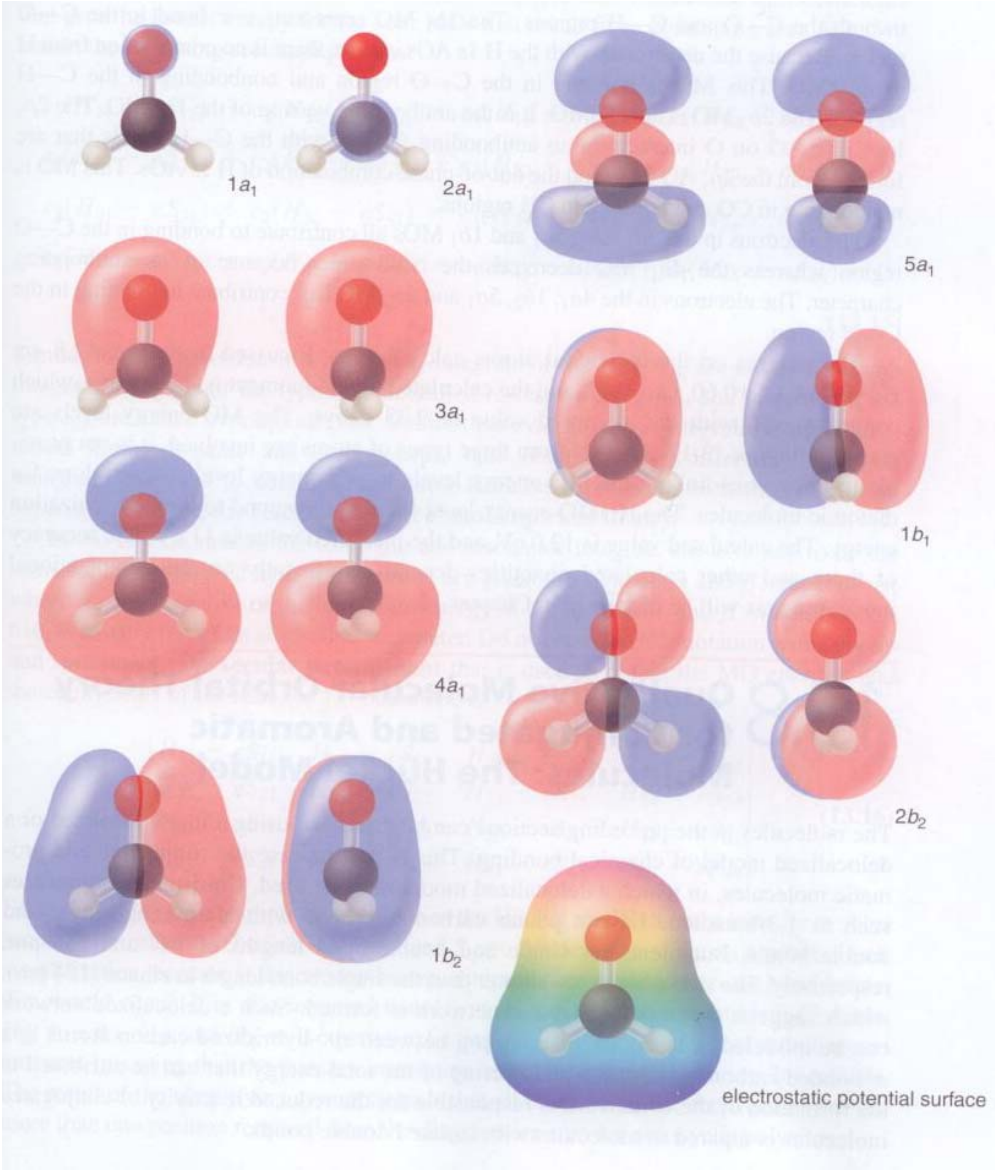


ethylene ethane

MO Theory
orbitals of
water







MOs of formaldehyde