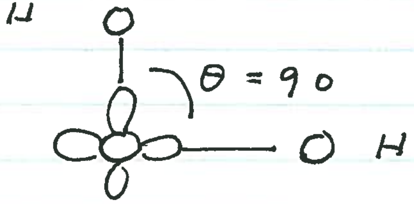
Chapter 10

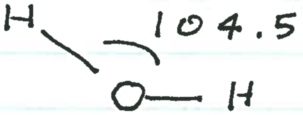
Bonding in Polyatomic Molecules

"Of two orbitals in an atom, the one that can overlap more with the orbital of another atom will form the strongest bond with that atom. Moreover the bond formed by a given orbital will tend to lie in that direction in which the orbital is concentrated"

Consider H_2O



O atom



experiment

Need to construct atomic orbitals that are "concentrated" in the direction of the two H atoms.

This is done by mixing or hybridizing atomic orbitals of similar energy.

Procedure

1. "point" p orbitals toward the H atoms

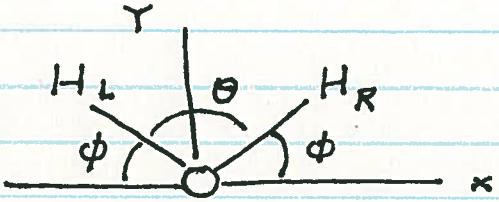
Consider the p orbitals as vectors of unit length

We can combine a p_x & p_Y orbital so that the resulting p is oriented at an angle ϕ relative to the x axis

$$p(\phi) = p_x \cos\phi + p_Y \sin\phi$$

note $p(\phi)$ or p_ϕ is normalized

$$\langle p_\phi | p_\phi \rangle = \cos^2\phi + \sin^2\phi = 1$$



$$\theta + 2\phi = 180$$

A p orbital pointing toward the right H is

$$p_R = p_x \cos\phi + p_Y \sin\phi$$

& one pointing towards the left H is

$$p_L = - p_x \cos\phi + p_Y \sin\phi$$

Note however these two oriented p orbitals are not (necessarily) orthogonal

$$\langle p_L | p_R \rangle = -\cos^2\phi + \sin^2\phi = \cos\theta$$

which is zero only when $\phi = 45$ & $\therefore$ $\theta = 90$.

We want to keep these new atomic orbitals orthogonal & to do so we add in some 2s or s character 2. Make orthogonal

$$\psi_L = (p_L + \lambda s)/\sqrt{1+\lambda^2}$$

$$\& \quad \psi_R = (p_R + \lambda s)/\sqrt{1+\lambda^2}$$

$$\langle \psi_L | \psi_R \rangle = \langle p_L + \lambda s | p_R + \lambda s \rangle / (1+\lambda^2)$$

$$= \left(\langle p_L | p_R \rangle + \lambda^2 \langle s | s \rangle \right) / (1+\lambda^2)$$

so if $\langle \psi_L | \psi_R \rangle = 0$

$$\cos\theta + \lambda^2 = 0$$

$$\& \quad \lambda = +\sqrt{-\cos\theta} \quad ; \quad \text{clearly } \theta > 90$$

3. Mix with ligands, in this case H atoms

We then form the bonding orbitals

$$b_L = (\psi_L + \mu s)/\sqrt{1+\mu 2\langle s|\psi_L\rangle + \mu^2}$$

$$b_R = (\psi_R + \mu s)\sqrt{1+2\mu\langle s|\psi_L\rangle + \mu^2}$$

where the amount of mixing is to be determined by the variation principle.

Note that we started with 3 oxygen atomic orbitals $2s$, $2p_x$ & $2p_y$ & constructed two hybrid orbitals ψ_L & ψ_R. We can form one more hybrid, orthogonal to the first two.

$$\psi_{lp} = (p_y + \gamma' s)/\sqrt{1+\gamma'^2}$$

ψ_{lp} is called a lone pair orbital. To make it ⊥ to ψ_L & ψ_R we require

$$\langle \psi_L|\psi_{lp}\rangle = 0 = \langle p_L + \lambda s|p_y + \gamma' s\rangle = 0$$

$$0 = \sin\phi + \lambda\gamma' \qquad \text{so } \gamma' = \frac{-\sin\phi}{\lambda}$$

Note $\langle \psi_R | \psi_{lp} \rangle = \langle p_R + \lambda s | p_\gamma + \gamma' s \rangle$.

$= \sin\phi + \lambda s = 0$ as with $\langle \psi_L | \psi_{lp} \rangle$

The remaining p orbital is p_z & is ⊥ to the molecular plane. The electronic configuration for H_2O is then

$$1s^2 \, b_L^2 \, b_R^2 \, \psi_{lp}^2 \, 2p_z^2 .$$

Energy of H_2O.

We can write down the Born Oppenheimer Hamiltonian for H_2O & compute the energy as

$\langle \psi | \hat{\mathcal{H}} | \psi \rangle = E$ where

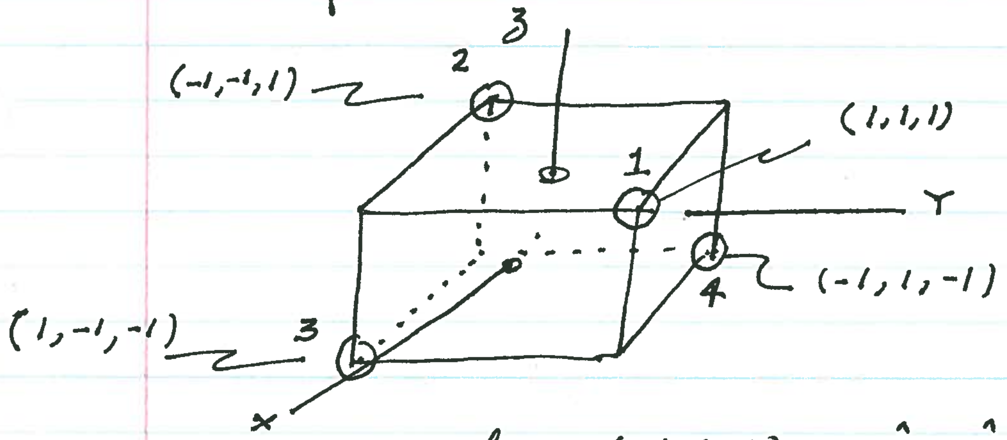
$$\psi = \mathcal{A} \, 1s\alpha \, 1s\beta \, b_L\alpha \, b_L\beta \, b_R\alpha \, b_R\beta \, \psi_{lp}\alpha \, \psi_{lp}\beta \, p_z\alpha \, p_z\beta$$

Note that the energy depends on θ, μ and the O-H bond lengths. We can determine these using the variation principle

$$\frac{\partial E}{\partial R} = 0 \; ; \; \frac{\partial E}{\partial \theta} = 0 \; \& \; \frac{\partial E}{\partial \mu} = 0$$

The same procedure can be used to describe CH_4, for example.

We will form hybrid orbitals using the carbon 2s & 2p orbitals. There are 4 ligands so we need 4 hybrid orbitals. Orient CH_4 so C is at the center of a cube with the H atoms at the corners.



where $(-1,1,-1) = -\hat{x} + \hat{y} - \hat{z}$ etc

1. first point the p orbitals towards the H atoms

$$p_1 = (p_x + p_y + p_z)/\sqrt{3}$$

$$p_2 = (-p_x - p_y + p_z)/\sqrt{3}$$

$$p_3 = (p_x - p_y - p_z)/\sqrt{3}$$

$$p_4 = (-p_x - p_y - p_z)/\sqrt{3}$$

2. mix in s so that ψ_i are orthogonal

$$\psi_i = (p_i + \lambda s)/\sqrt{1+\lambda^2}$$

$$\langle \psi_i | \psi_j \rangle = \langle p_i + \lambda s | p_j + \lambda s \rangle / (1+\lambda^2)$$

now $\langle p_i | p_j \rangle = -\frac{1}{3}$ if $i \neq j$

so if $\langle \psi_i | \psi_j \rangle = \delta_{ij} = -\frac{1}{3} + \lambda^2$

$$\lambda = \sqrt{\frac{1}{3}}$$

so $p_1 = (p_x + p_y + p_z + s)/\sqrt{3}$

etc.

These orbitals are called sp^3 (3 p's, 1 s)

As another example consider BeH_2, a linear molecule. The electron configuration of Be is $1s^2 2s^2$ so why is the molecule linear? Be forms hybrids as follows:

1. point the p orbitals.

This is trivial because there is only one p orbital pointing toward the H atoms. If we call the H-Be-H — line the z axis, then it's the $2p_z$ orbital

If we want it to point toward the ligands we write

$$p_R = p_z \qquad (R = \text{right};\ L = \text{left})$$

$$p_L = p_z$$

note $\langle p_R | p_L \rangle = 1$; not ⊥

2. mix in 2s to make an orthogonal pair

$$\varphi_R = (p_R + \lambda s)/\sqrt{1+\lambda^2}$$

$$\varphi_L = (p_L + \lambda s)/\sqrt{1+\lambda^2}$$

choose λ so that

$$\langle \varphi_R | \varphi_L \rangle = 0 = \langle p_R + \lambda s | p_L + \lambda s \rangle$$

$$0 = 1 + \lambda^2 \quad \text{so } \lambda = \pm 1$$

so $\varphi_R = (p_R + s)/\sqrt{1+\lambda^2}$

$\varphi_L = (p_L - s)/\sqrt{1+\lambda^2}$

φ_R & φ_L are called sp hybrids

The bonds would be $\quad (S = \langle \varphi_R | h \rangle = \langle \varphi_L | h \rangle)$

$$b_R = (\varphi_R + \mu h)/\sqrt{1 + 2S\mu + \mu^2}$$

$$b_L = (\varphi_L + \mu h)/\sqrt{1 + 2S\mu + \mu^2}$$