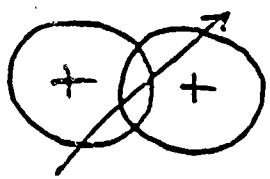
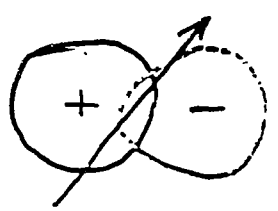


Parity : behavior of an orbital under inversion through the center of the molecule



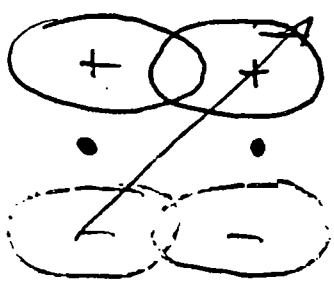
σ_g

$g \equiv$ gerade



σ_u^*

$u \equiv$ ungerade

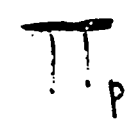


π_g

Term Symbols

Consider the orbital angular momentum about the internuclear axis

Σ analogous to S

$2S+1$ 

\uparrow multiplicity \nwarrow parity u, g

analogous to P

--- work out for all electrons

$g \times g = g$
 $u \times u = g$
 $u \times g = u$

Consider 2 electrons with orbital angular momenta = 1 --- π electrons

both in opposite directions $\equiv \Sigma$
 both in same direction $\equiv \Delta$

Homonuclear Diatomics

non-polar
bond

Heteronuclear Diatomics

- charge "drifts"

toward one of the atoms -
the non-polar bond goes in
the direction of becoming a polar
one.

Covalent bonds - both atoms share,
at least to some degree, the electrons.

Ionic bonds - (some) electrons
nearly completely transferred

LCAO

$$\Psi = C_A \Psi_A + C_B \Psi_B$$

proportion of Ψ_A in the
bond depends on C_A^2

For non-polar $C_A^2 = C_B^2$

For totally ionic $C_A^2 = 0$

Determining Energies & C's

Variation Principle: If arbitrary wave function is used to calculate the energy, the value is never less than the true energy.

The true energy is the energy minimum

Procedure

- guess a wave function (trial ψ)
- calc. energy of electron
- repeat with better guess

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$$

Choose a basis set

ψ - - - -

minimize E wrt C_A, C_B

To determine which orbitals overlap in a molecule, and hence participate in bonding, Calc. S
the overlap integral

(Continued)

$$\alpha_A = \int \psi_A H \psi_A d\tau$$
$$\alpha_B = \int \psi_B H \psi_B d\tau$$

} energy of electron in orbital on A
Coulomb Integral

Homonuclear diatomic $\alpha_A = \alpha_B$

$$\beta = \int \psi_A H \psi_B d\tau$$

— resonance integral
vanishes when orbitals don't overlap



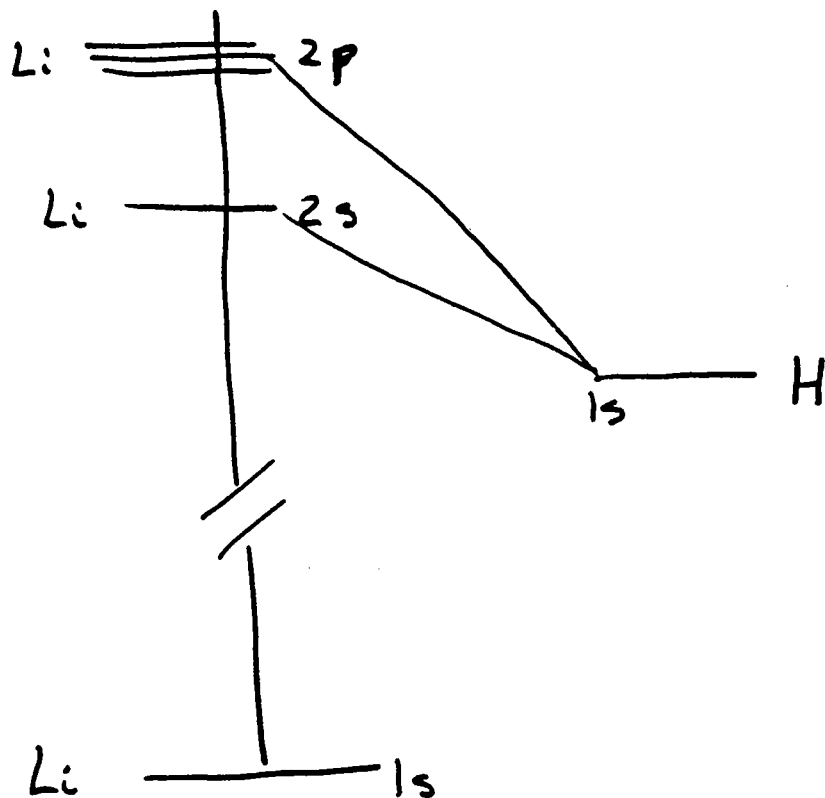
Strength of bond depends on this.

$$E = \frac{\alpha_A c_A^2 + \alpha_B c_B^2 + 2\beta c_A c_B}{c_A^2 + c_B^2 + 2c_A c_B S}$$

Take derivatives & minimize

Heteronuclear Diatomic

Hybridization : LiH



minimal basis set : $(H(1s), Li(2s))$

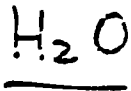
better basis set : $(H(1s), Li(2s), Li(2p))$

Linear combination of all three

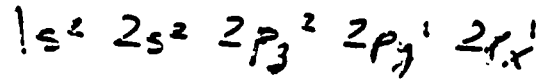
Variational Calc.
$$\psi = 0.323(Li(2s)) + 0.231(Li(2p)) + 0.685(H(1s))$$

Best considered as $H(1s) +$ hybridized orbital from Li

Hybridization



○ ≡ 2 electrons

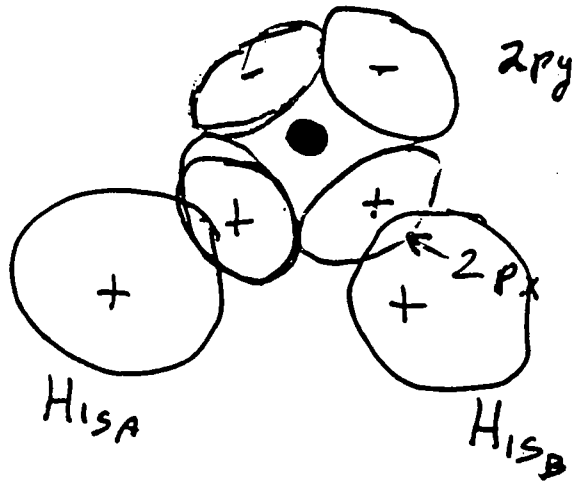
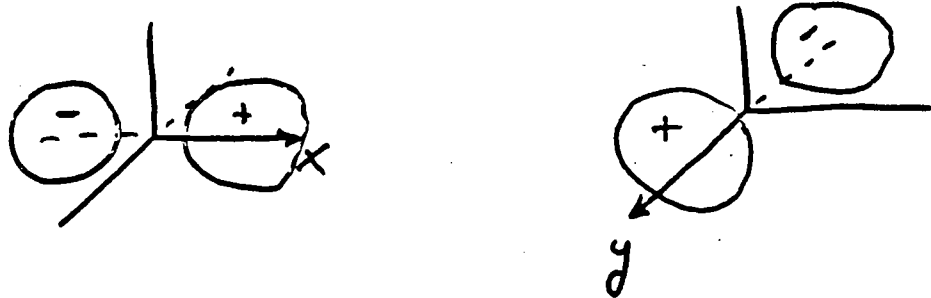


minimal basis set

○ : $2p_y 2p_x$

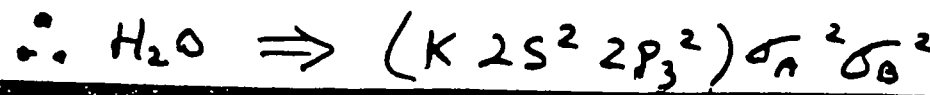
H : $1s_A 1s_B$

∴ 4 electrons to accommodate



predicts 90°
get 2
σ bonds

H_{1s} + O_{2p}
bonding : each MO gets 2 electrons.



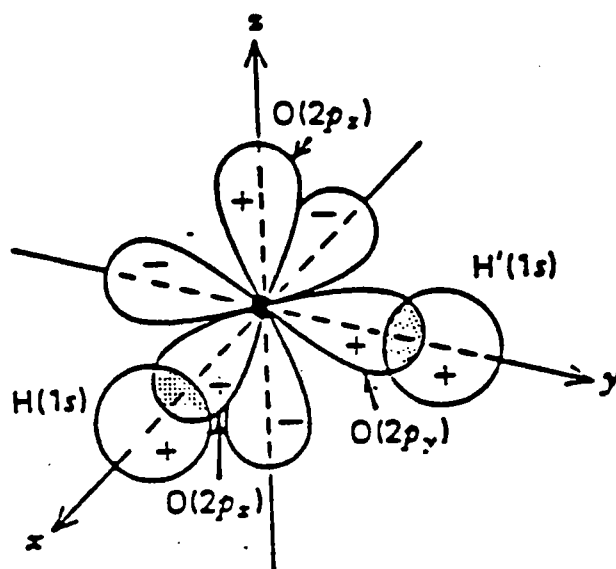


FIGURE 8.5

Localized-bond picture of H₂O. The two bonds are formed by overlap (indicated by shading) of the oxygen 2p_x and 2p_y orbitals with one hydrogen 1s orbital each. The oxygen 2p_z orbital is non-bonding, as are the oxygen 1s and 2s orbitals (not shown).

H₂O (continued)

9

But

O :

2s orbital is
close in energy - can
include via
hybridization

With Hybridization :

H-O-H angle = 104.45°

Orbitals are no longer orthogonal

to include 2s - requires some
promotion energy -

but bonding improves to
compensate

SP³ hybrid orbitals

∴ 8 electrons

Figure 9-26. The tetrahedral sp^3 hybrid orbitals also can be used as a model for H_2O .

