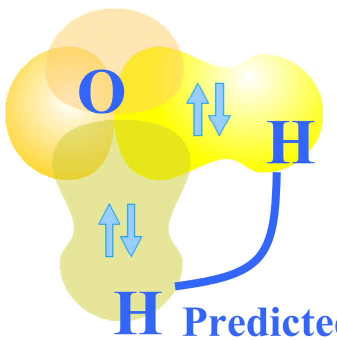
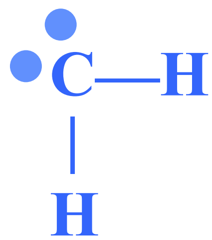
Relief for the VB Theory: Promotion and Hybridization



Prediction: CH_2



⇒ Trick 1: Promote a valence electron

C: $[He]2s^2 2p_x^1 2p_y^1 \rightarrow [He]2s^1 2p_x^1 2p_y^1 2p_z^1$

↓

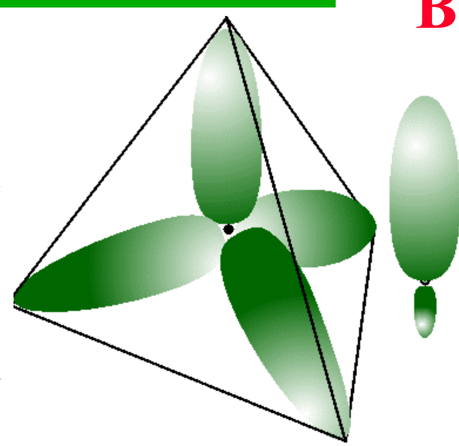
4 σ bonds can now form: CH_4

⇒ Overall huge gain in energy
⇒ Tetravalent carbon leads to organic chemistry

⇒ Trick 2: Describe the same electron distribution as composed of four singly occupied hybrid orbitals

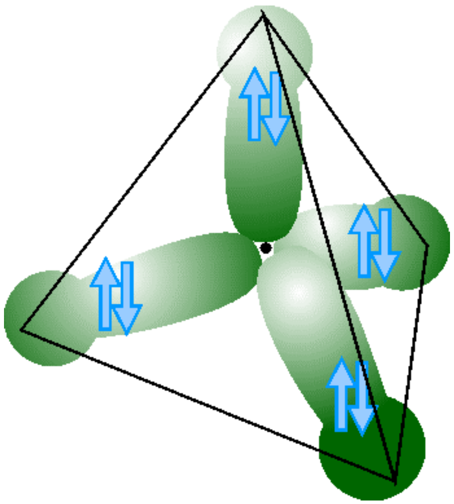
BUT: One bond is from a 2s orbital, the other three from 2p orbitals

$$h_1 = s + p_x + p_y + p_z$$
$$h_2 = s - p_x - p_y + p_z$$
$$h_3 = s - p_x + p_y - p_z$$
$$h_4 = s + p_x - p_y - p_z$$



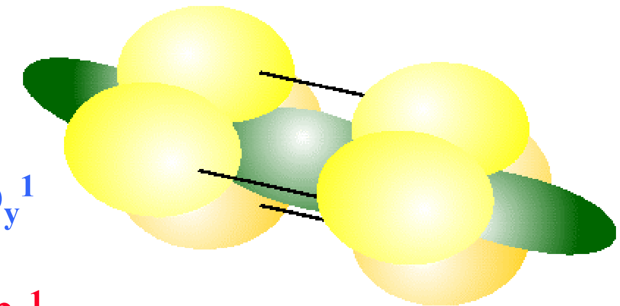
⇒ four sp^3 hybrid orbitals

Now VB Theory Gets the Molecular Geometries Right



Methane CH_4:
sp^3, tetrahedral, 109.5°
C: $[He]2s^22p_x^{\,1}2p_y^{\,1}$
→
$[He]2s^12p_x^{\,1}2p_y^{\,1}2p_z^{\,1}$

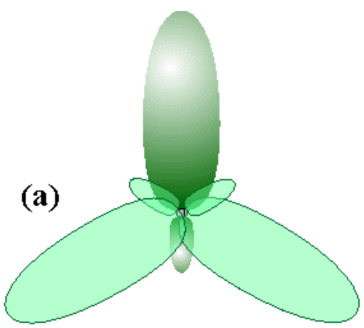
Ethyne C_2H_2:
sp, linear, 180°
C: $[He]2s^22p_x^{\,1}2p_y^{\,1}$
→
$[He]2s^12p_x^{\,1}2p_y^{\,1}2p_z^{\,1}$



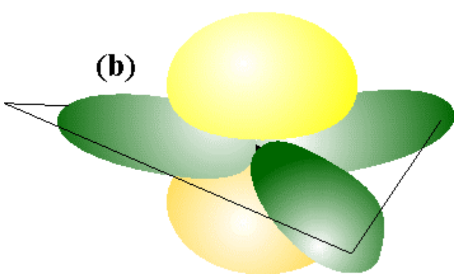
$$h_1 = s + p_z \qquad h_2 = s - p_z$$

⇒ hybridization of N atomic orbitals results in N hybrid orbitals

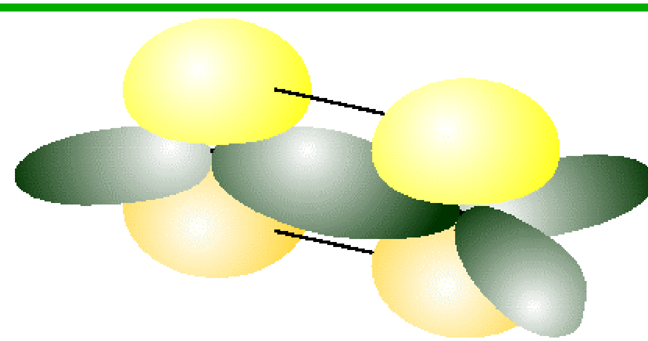
(a)



(b)



Ethene C_2H_4:
sp^2, trigonal pyramidal, 120°
C: $[He]2s^22p_x^{\,1}2p_y^{\,1}$
→
$[He]2s^12p_x^{\,1}2p_y^{\,1}2p_z^{\,1}$



$$h_1 = s + \sqrt{2}\,p_x$$

$$h_2 = s + \sqrt{\frac{3}{2}}\,p_x - \sqrt{\frac{1}{2}}\,p_y \qquad h_3 = s - \sqrt{\frac{3}{2}}\,p_x - \sqrt{\frac{1}{2}}\,p_y$$

But What About Polar Molecules? Resonance!

E.g., HCl: $\Psi_{\text{covalent}} = \Psi_H(1)\times\Psi_{Cl}(2) + \Psi_H(2)\times\Psi_{Cl}(1)$

for a purely covalent bond: electrons only can exchange

$\Rightarrow$ Allow for both electrons to be on Cl, i.e., H^+Cl^-:

$$\Psi_{\text{ion}} = \Psi_{Cl}(1)\times\Psi_{Cl}(2)$$

$\Rightarrow$ In reality: superposition $\boxed{\Psi = \Psi_{\text{covalent}} + \lambda\Psi_{\text{ion}}}$ Ionic-covalent resonance

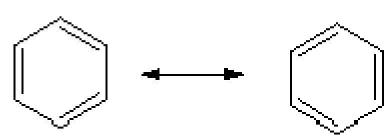
λ^2 = relative proportion (probability) of the ionic contribution

To find λ the Variation Theorem is used:

The energy of a trial wavefunction is never less than the true energy

Similar: benzene

$$\Psi = \Psi_{\text{Kek1}} + \Psi_{\text{Kek2}}$$



1 **2**

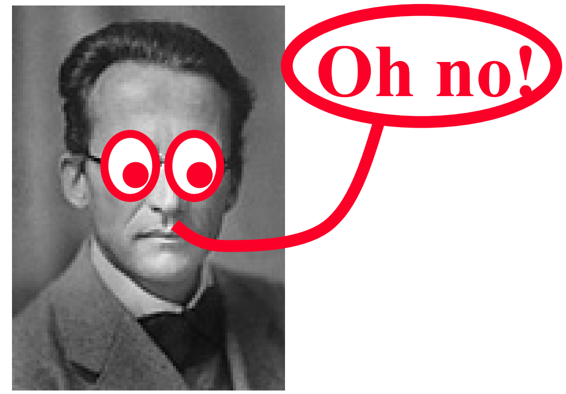
Resonance hybrid

$\Rightarrow$ Resonance stabilization

Even Better for Polar Molecules: Molecular Orbital Theory

Basic ideas:

- Every electron contributes to every bond
- Electrons spread through the entire molecule
- Each electron may be found in any of the atomic orbitals involved

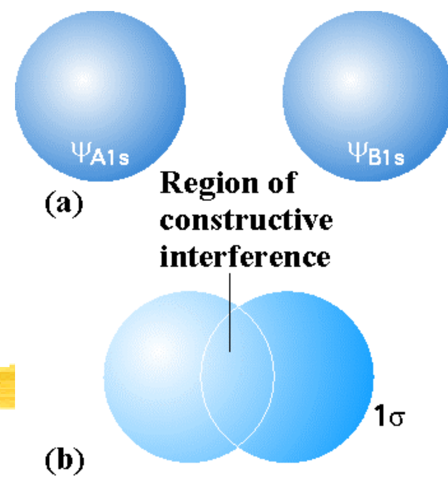


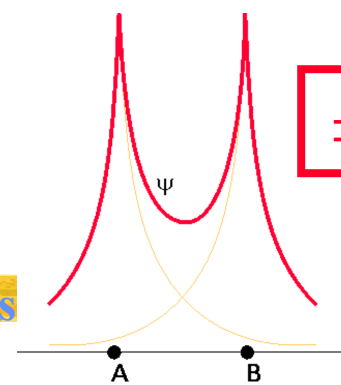
⇒ Approximation: Linear Combination of Atomic Orbitals (LCAO)

Example: H_2^+ $\quad \Psi(H_2^+) = c_A\Psi_A + c_B\Psi_B$ ⇒ c_A^2, c_B^2 = relative contributions of the atomic orbitals to the molecular orbital (MO)

$\boxed{\text{Homonuclear diatomic molecule} \Rightarrow c_A^2 = c_B^2}$

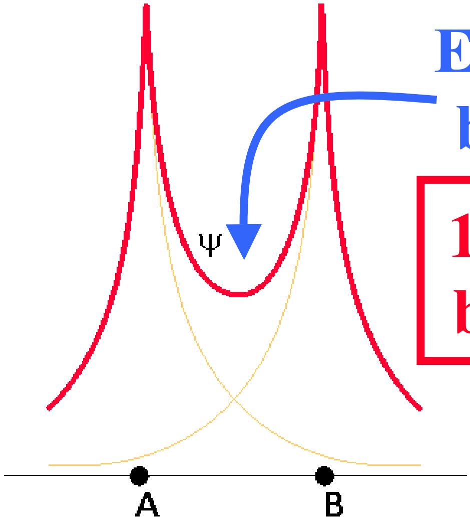
⇒ $\boxed{\Psi(H_2^+) = \Psi_A \pm \Psi_B}$





$\boxed{\Rightarrow 1\ \sigma\ \text{MO}}$

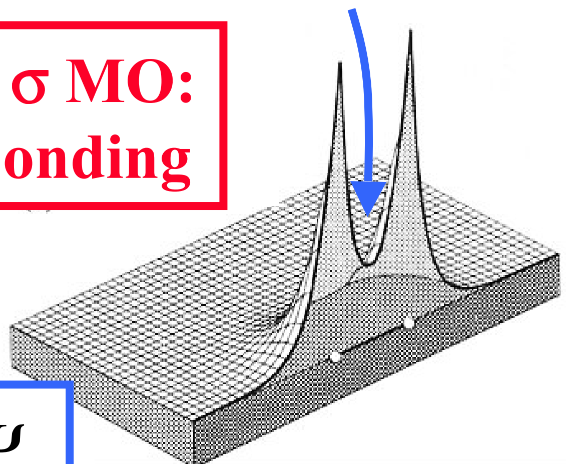
Bonding and Antibonding Orbitals

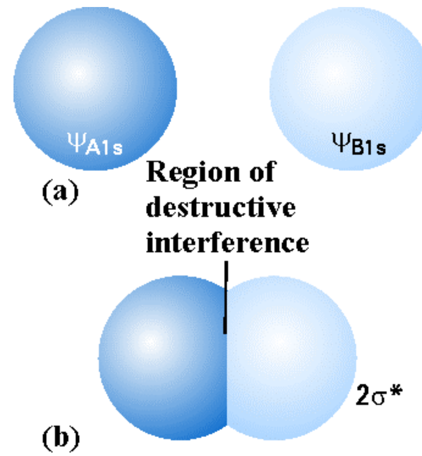


Electron density between nuclei

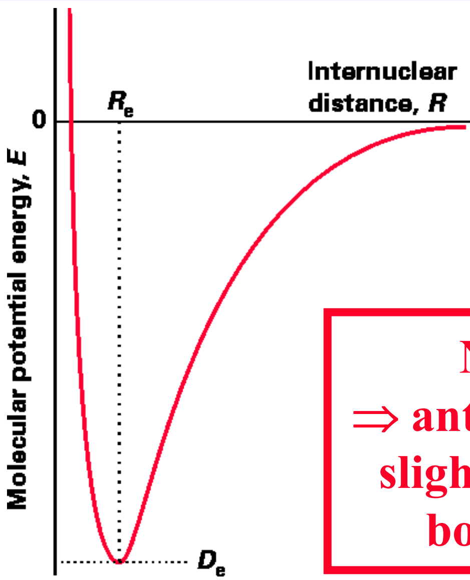
$$\Psi(H_2^{\ +}) = \Psi_A - \Psi_B$$

1 σ MO: bonding

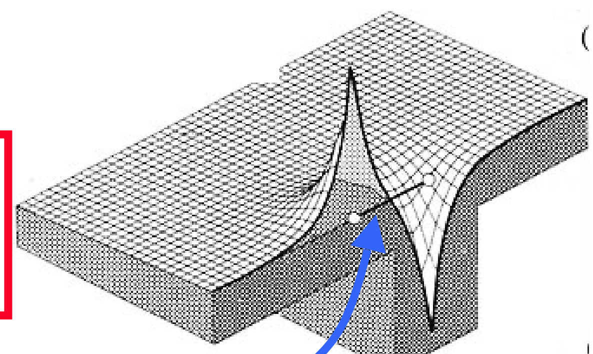




$$\Psi(H_2^{\ +}) = \Psi_A + \Psi_B$$



2 σ* MO: antibonding



Nuclei repel each other
⇒ antibonding MOs are typically slightly more antibonding than bonding MOs are bonding

No electron density between nuclei (nodal plane) ⇒ electrons pull nuclei apart