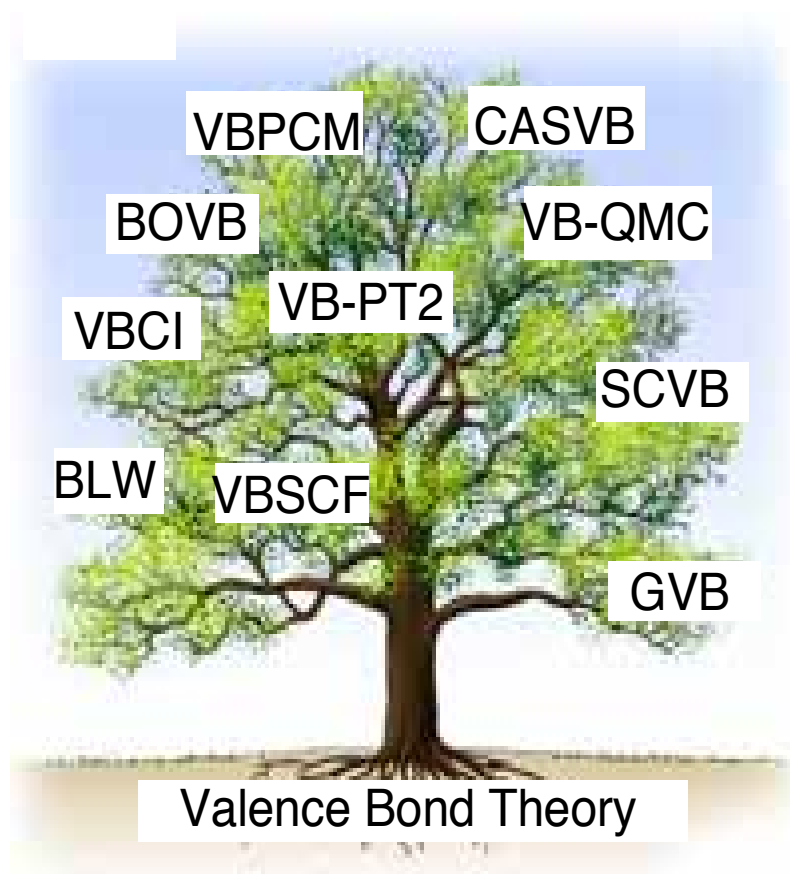
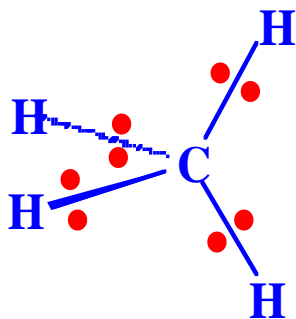


Valence bond, a class of modern ab initio methods

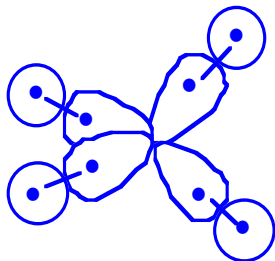


First, some basic principles...

The Valence Bond model



electron pairs are in *local* bonds



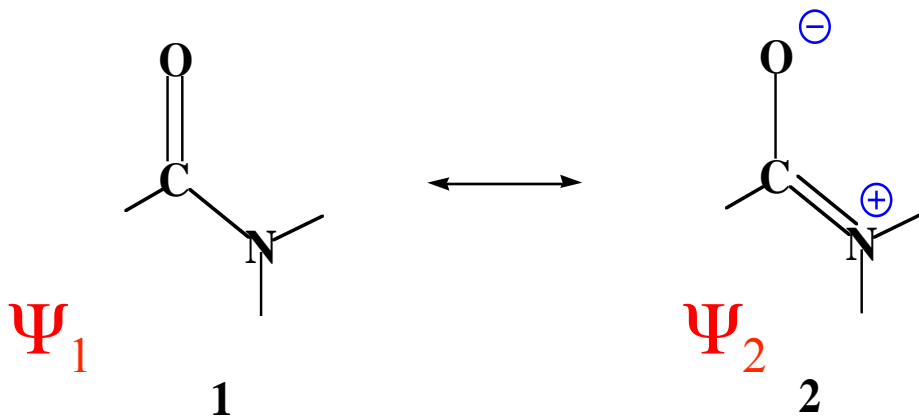
one bond = an interaction between two singly occupied atomic orbitals

Each bond is **mainly covalent**, but has some **minor ionic** character

The Valence bond wave function is the Quantum Mechanical translation of the Lewis structure

Systems that cannot be described by a single Lewis structure:

- Molecules displaying electron conjugation



The VB wave function $\Psi(1 \leftrightarrow 2)$ for the ground state is a combination of two VB structures Ψ_1 and Ψ_2 :

$$\Psi(1 \leftrightarrow 2) = C_1(\Psi_1) + C_2(\Psi_2)$$

Estimation of C_1 , C_2 , resonance energy = $E(\Psi_1) - E(\Psi(1 \leftrightarrow 2))$

Why Doing Valence Bond and not only MO?

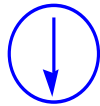
- Some vital concepts
 - hybridization
 - IR frequencies of C-H bonds:
 sp^3 -H, sp^2 -H, sp -H
 - resonance
 - VSEPR (based on local electron pairs)
 - Lewis structures
 - Arrow-pushing language
 - Application to reactivity (the VBSCD model)
- Standard teaching:
 - VB has failed
 - The only correct theory is MO

Writing VB functions Example: the covalent H₂ bond

H H



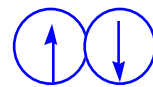
φ_a



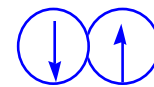
φ_b

Working hypothesis:
the electrons remain in atomic orbitals

At equilibrium distance,
2 possible determinants :



$$\left| \varphi_a \bar{\varphi}_b \right|$$

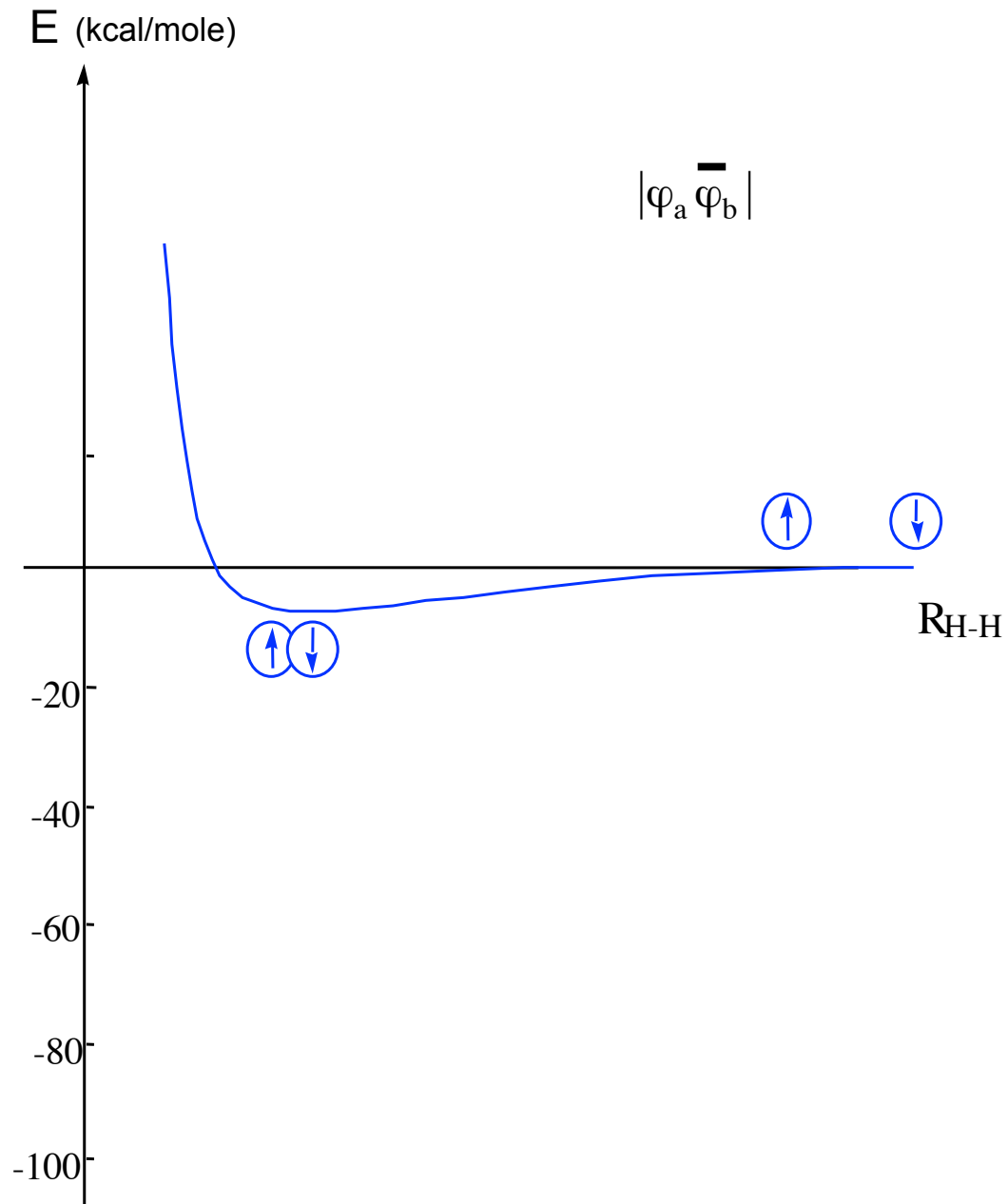


$$\left| \varphi_b \bar{\varphi}_a \right|$$

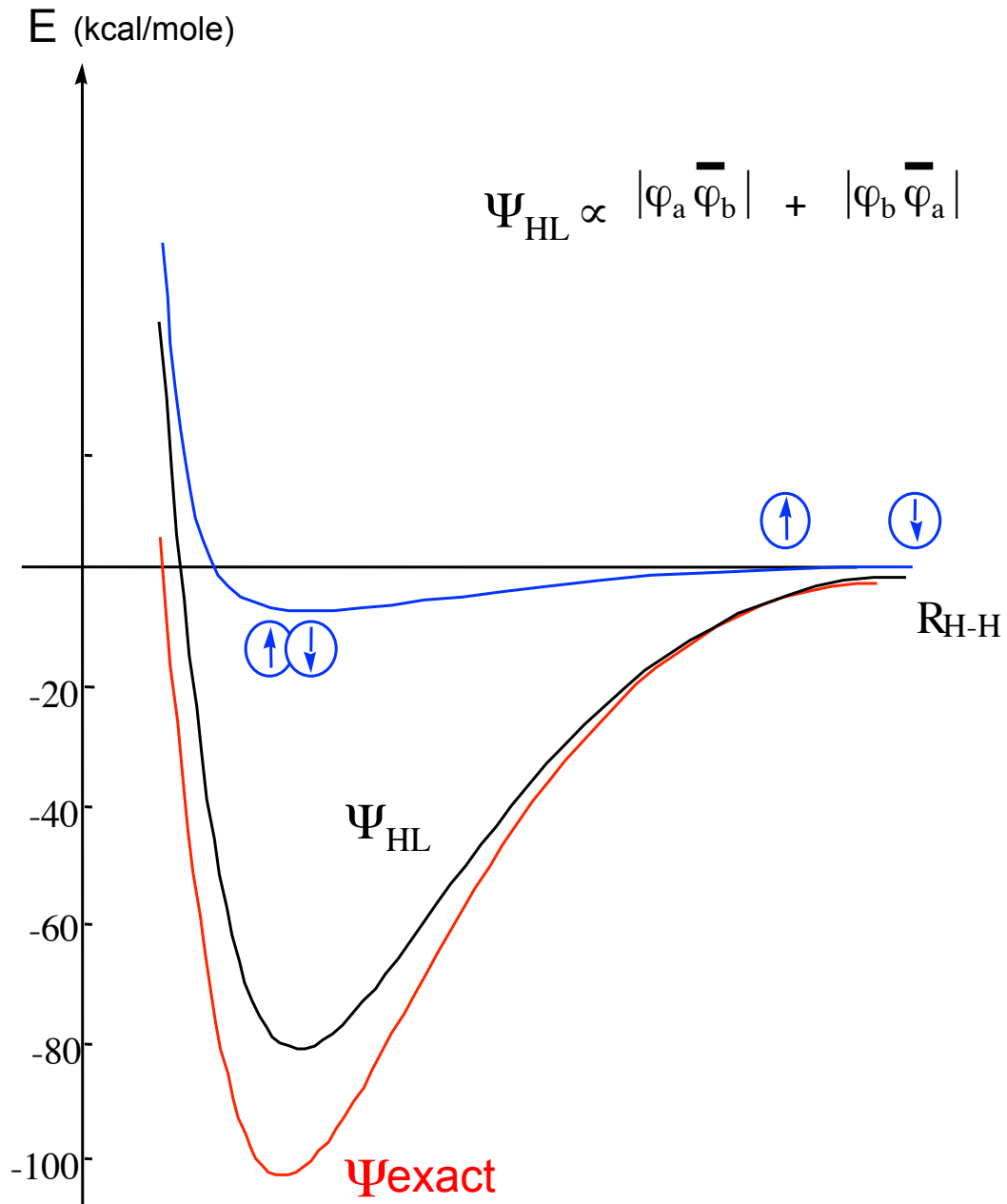
Correct wave function
(for the covalent bond) :

$$\Psi_{\text{HL}} = \frac{\left| \varphi_a \bar{\varphi}_b \right| + \left| \varphi_b \bar{\varphi}_a \right|}{\sqrt{2+2S^2}}$$

Dissociation curve of H₂



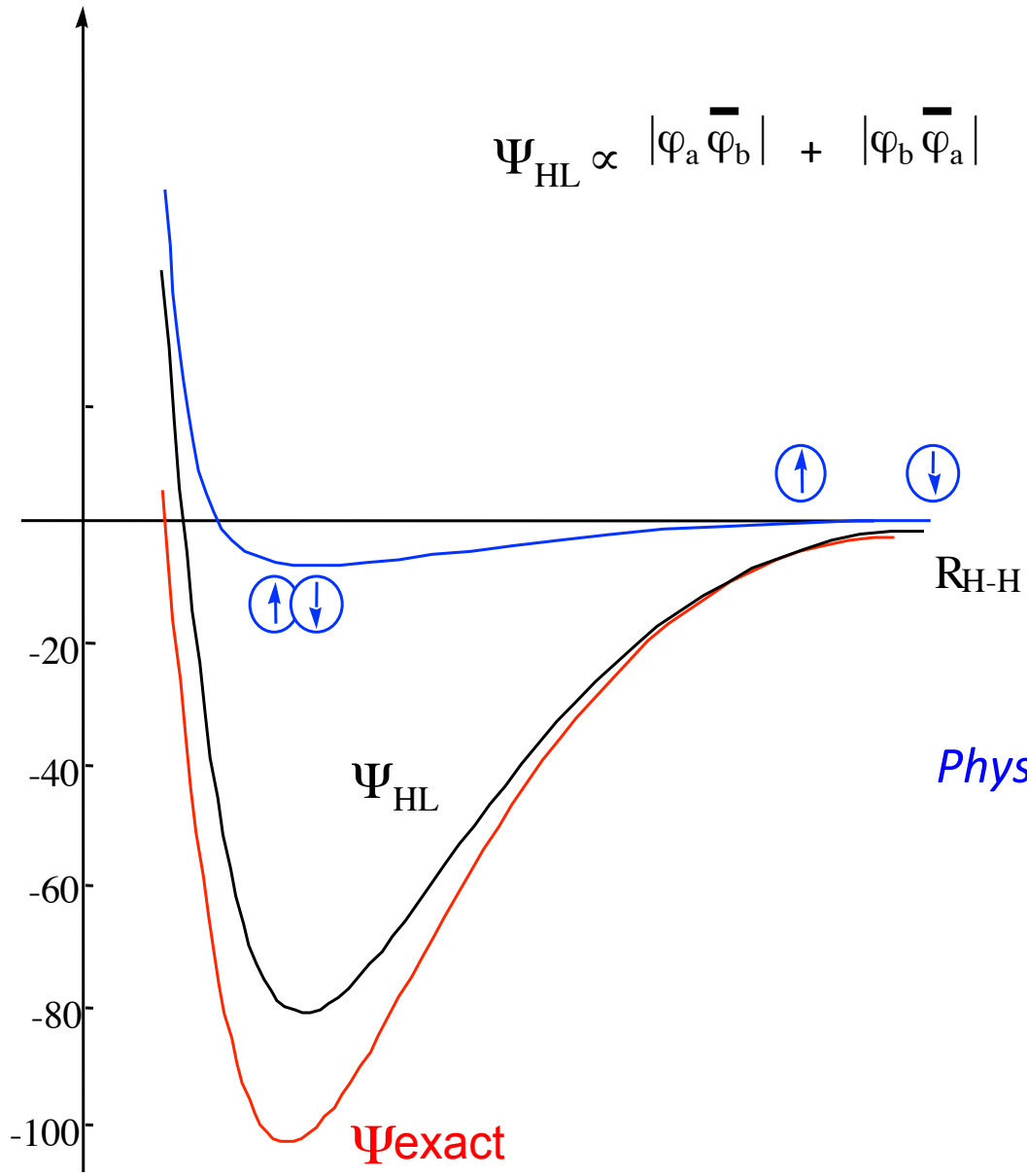
Dissociation curve of H₂



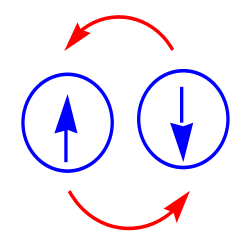
Dissociation curve of H₂

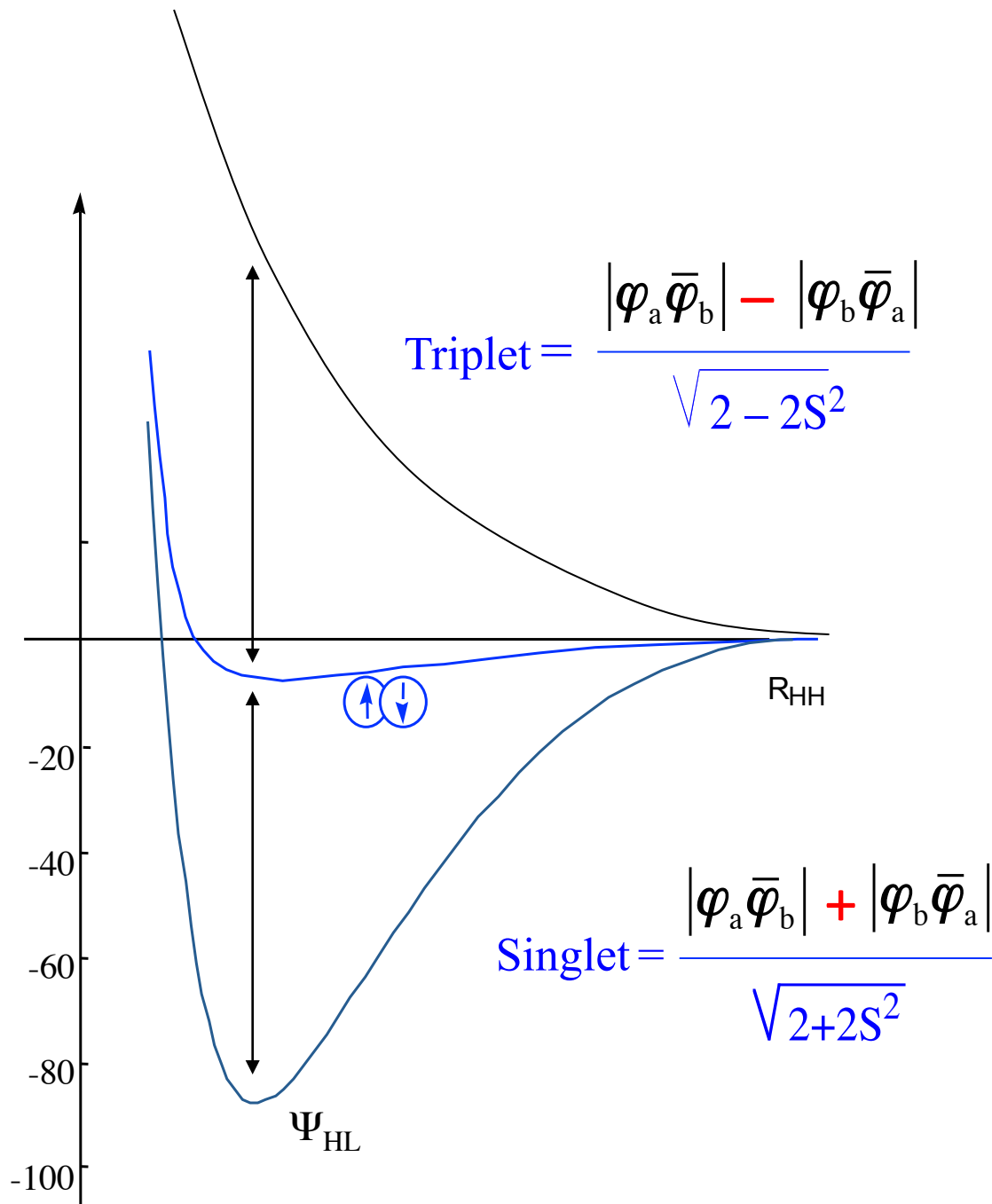
E (kcal/mole)

$$\Psi_{\text{HL}} \propto |\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|$$

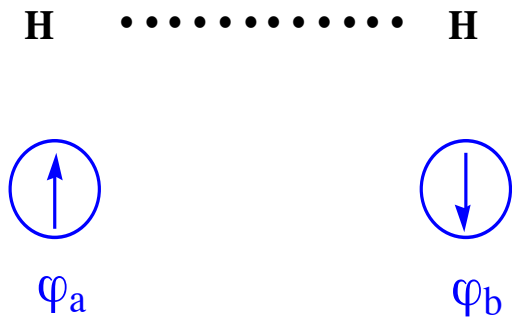


*Physical origin of the covalent bond:
spin exchange between AOs*






Bonding energy of the covalent H₂ bond (qualitative expression)



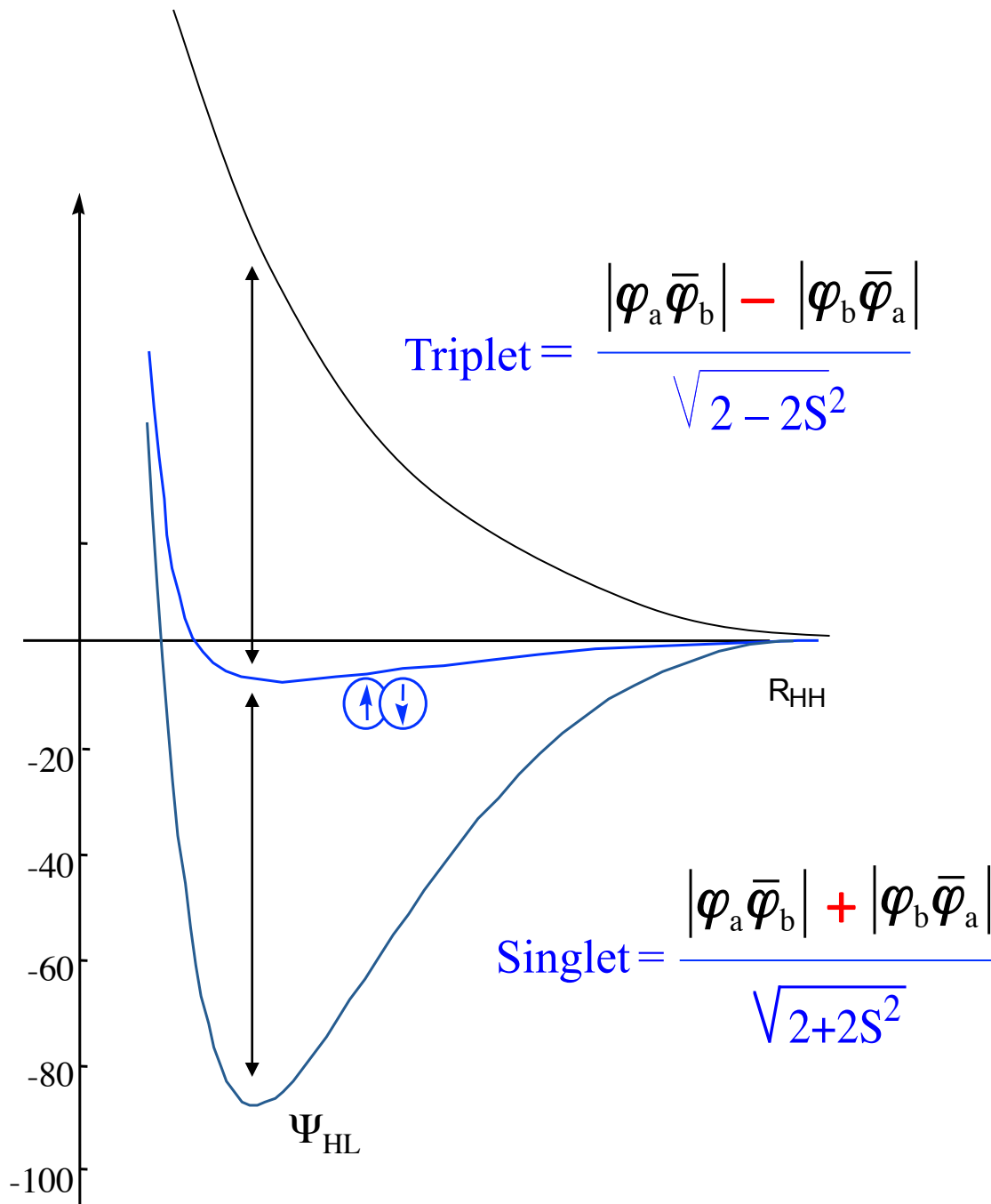
$$\Psi_{\text{HL}} = \frac{|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|}{\sqrt{2+2S^2}}$$

Since $|\varphi_a \bar{\varphi}_b|$ is non-bonding, its energy is ~ 0

 $D_e(\text{H}_2) = \langle \Psi_{\text{HL}} | \hat{H} | \Psi_{\text{HL}} \rangle = \frac{2 \langle \varphi_a \bar{\varphi}_b | \hat{H} | \varphi_b \bar{\varphi}_a \rangle}{1+S^2}$

Notation in qualitative VB theory:

$$D_e(\text{H}_2) = \frac{2\beta S}{1+S^2}$$



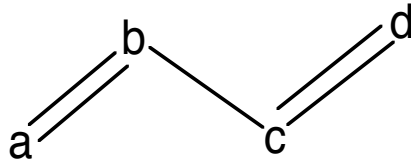
$$E(\text{triplet}) = \frac{-2\beta S}{1 - S^2}$$

$S \rightarrow T$ gap $\approx 2D_e$

$$E(\text{singlet}) = \frac{2\beta S}{1 + S^2}$$

Writing VB functions beyond the two-electron/two center case

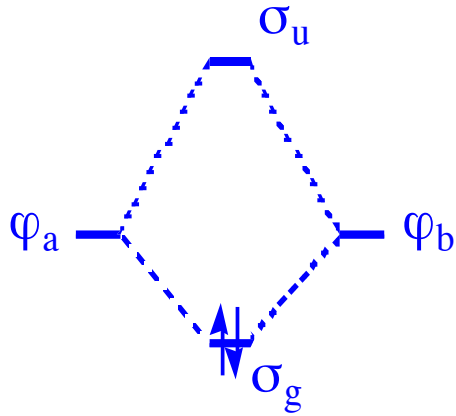
Exemple: the π -system of butadiene



$$\Psi_{\text{cov}} = |(\bar{a}\bar{b} + \bar{b}\bar{a})(\bar{c}\bar{d} + \bar{d}\bar{c})|$$

$$\Psi_{\text{cov}} = |\bar{a}\bar{b}\bar{c}\bar{d}| + |\bar{a}\bar{b}\bar{d}\bar{c}| + |\bar{b}\bar{a}\bar{c}\bar{d}| + |\bar{b}\bar{a}\bar{d}\bar{c}|$$

Comparison with MO description (Hartree-Fock)



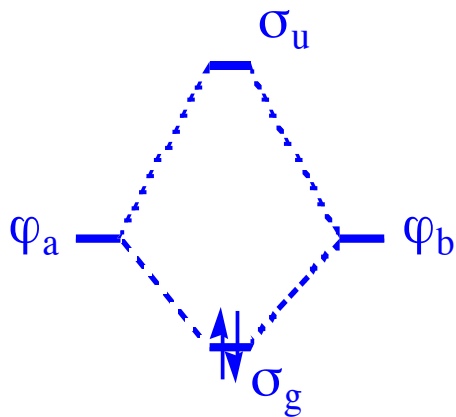
$$\sigma_u = \varphi_a - \varphi_b = \text{[Diagram: two circles, one white, one shaded blue]}$$

$$\sigma_g = \varphi_a + \varphi_b = \text{[Diagram: two overlapping white circles]}$$

$$\Psi_{\text{HF}} = \left| \sigma_g \bar{\sigma}_g \right| \propto \underbrace{\left| \varphi_a \bar{\varphi}_b \right| + \left| \varphi_b \bar{\varphi}_a \right|}_{\text{H}\cdot\text{---}\cdot\text{H}} + \underbrace{\left| \varphi_a \bar{\varphi}_a \right| + \left| \varphi_b \bar{\varphi}_b \right|}_{\text{H}^-\text{H}^+ + \text{H}^+\text{H}^-}$$

- Simple MO description $\left| \sigma_g \bar{\sigma}_g \right| = 50\% \text{ covalent } 50\% \text{ ionic}$
- Simple VB description $\Psi_{\text{HL}} = 100\% \text{ covalent}$

Comparison with MO description (Hartree-Fock)



$$\sigma_u = \varphi_a - \varphi_b = \text{[Diagram: two circles, one white, one shaded blue]}$$

$$\sigma_g = \varphi_a + \varphi_b = \text{[Diagram: two overlapping white circles]}$$

$$\Psi_{\text{HF}} = \left| \sigma_g \bar{\sigma}_g \right| \propto \underbrace{\left| \varphi_a \bar{\varphi}_b \right| + \left| \varphi_b \bar{\varphi}_a \right|}_{\text{H}\cdot\text{---}\cdot\text{H}} + \underbrace{\left| \varphi_a \bar{\varphi}_a \right| + \left| \varphi_b \bar{\varphi}_b \right|}_{\text{H}^-\text{H}^+ + \text{H}^+\text{H}^-}$$

• Simple MO description $\left| \sigma_g \bar{\sigma}_g \right| = 50\% \text{ covalent } 50\% \text{ ionic}$

• Simple VB description $\Psi_{\text{HL}} = 100\% \text{ covalent}$

• Exact description **72-79% covalent 21-28% ionic**

Exact description

• In the VB framework $\Psi_{\text{exact}} = \lambda(|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|) + \mu(|\varphi_a \bar{\varphi}_a| + |\varphi_b \bar{\varphi}_b|)$

$\text{H}\cdot\text{---}\cdot\text{H} \qquad \text{H}^-\text{H}^+ + \text{H}^+\text{H}^-$

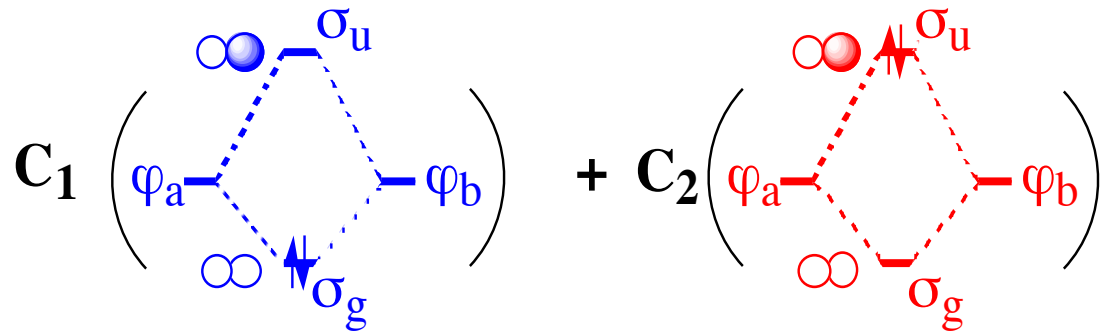
λ , μ and the orbitals are optimized simultaneously:
VBSCF method (Balint-Kurti, van Lenthe)

Exact description

• In the VB framework $\Psi_{\text{exact}} = \lambda(|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|) + \mu(|\varphi_a \bar{\varphi}_a| + |\varphi_b \bar{\varphi}_b|)$

$\text{H}\cdot\text{---}\cdot\text{H}$
 $\text{H}^-\text{H}^+ + \text{H}^+\text{H}^-$

• In the MO framework



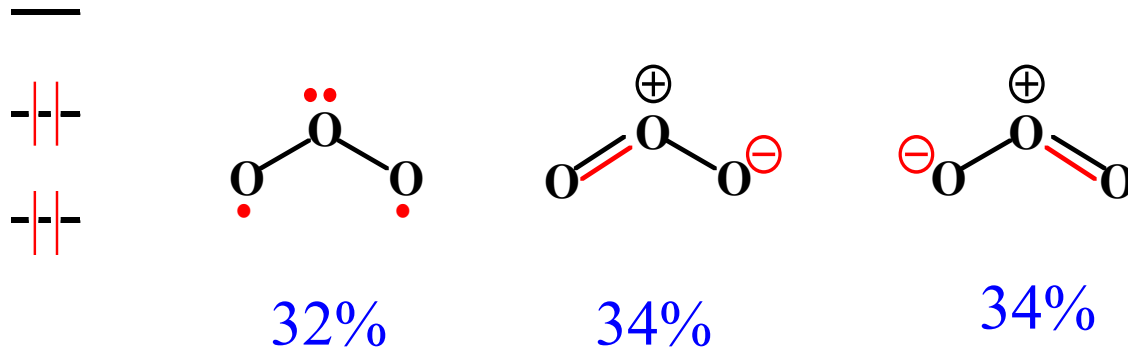
$$|\sigma_g \bar{\sigma}_g| = |\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a| + (|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|)$$

$$|\sigma_u \bar{\sigma}_u| = |\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a| - (|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|)$$

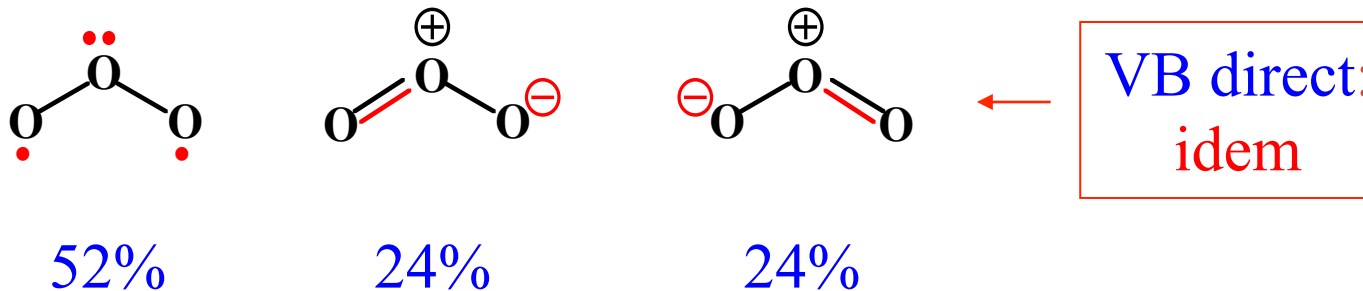
$$C_1 |\sigma_g \bar{\sigma}_g| + C_2 |\sigma_u \bar{\sigma}_u| = \Psi_{\text{exact}}$$

Transformation MO \rightarrow VB (Example: ozone)

- Fonction Hartree-Fock (expanded in VB structures)

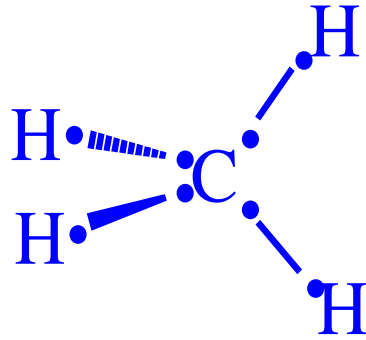


- Configuration Interaction



- Any MO wave function can be converted to VB, and vice versa
- If Complete CI, VB and MO-CI become equivalent !

Generalisation to polyatomic molecules



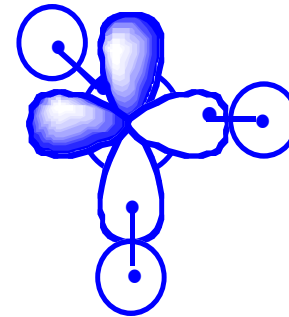
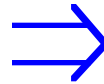
= four equivalent local $\text{C}\cdot\text{---}\cdot\text{H}$ bonds

Which atomic orbitals?

First try: « pure » AOs

H : 1s

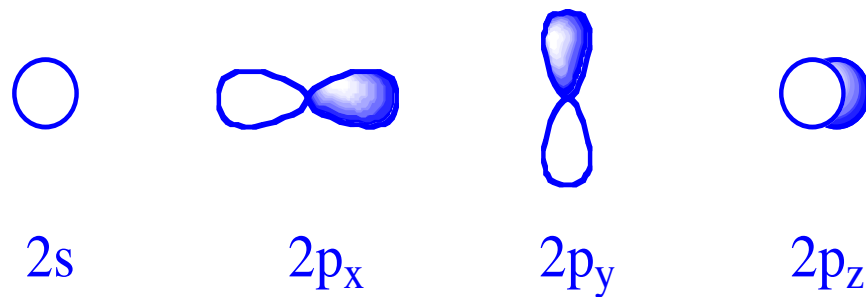
C : 2s, 2p_x, 2p_y, 2p_z



- 90° angles

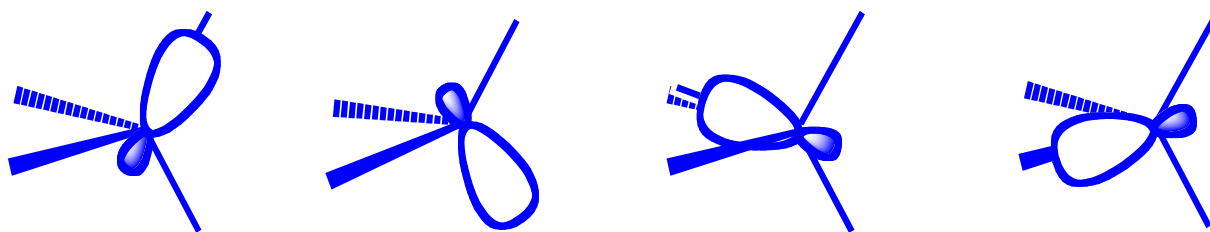
- non-equivalent bonds

The answer: hybridization of the atomic orbitals



... rotation ... \Rightarrow

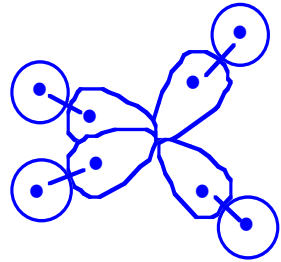
4 equivalent « hybrid » atomic orbitals (HAOs)



Orthogonal, pointing in tetrahedral directions

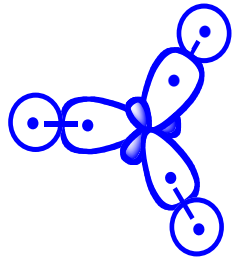
Hybrid atomic orbitals

CH₄



sp³ hybrids
(all alkanes...)

BH₃



sp² hybrids
(ethylene, all alkenes...)

BeH₂



sp hybrids
(acetylene, all alkynes...)

Local bonds \Leftrightarrow Hybrid atomic orbitals

Conclusions

- VB and MO: two complementary theories.
 - lower level: MO too much ionic, VB not enough
 - elaborate level: MO \equiv VB
 - *There is nothing such as VB failures*
- VB specific concepts:
 - Lewis structures, arrow pushing language,
 - transferable local bonds, hybridization, resonance energy
- Applications to chemical reactivity
 - Valence bond state crossing diagrams (next lecture, S. Shaik))