Valence bond, a class of modern ab initio methods
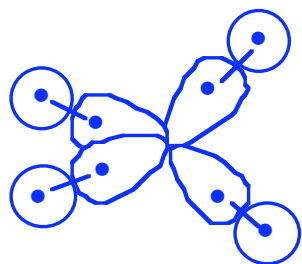

VBPCM
CASVB
BOVB
VB-QMC
VB-PT2
VBCI
SCVB
BLW
VBSCF
GVB
Valence Bond Theory
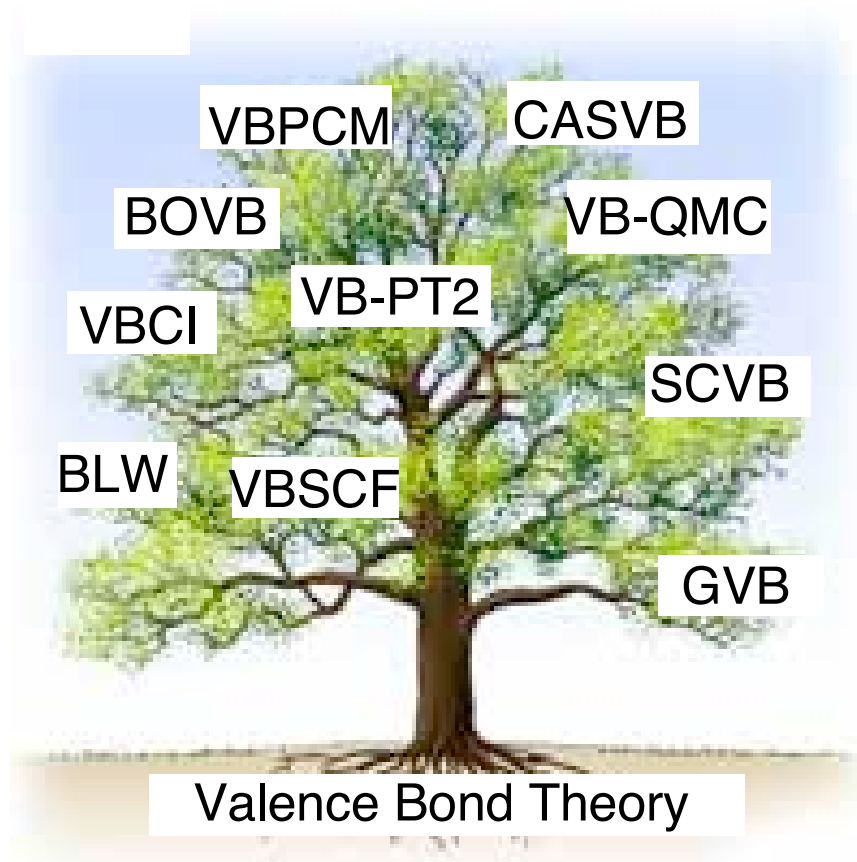
First, some basic principles…

# The Valence Bond model
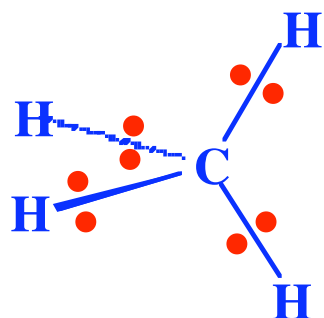
electron pairs are in *local* bonds

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**

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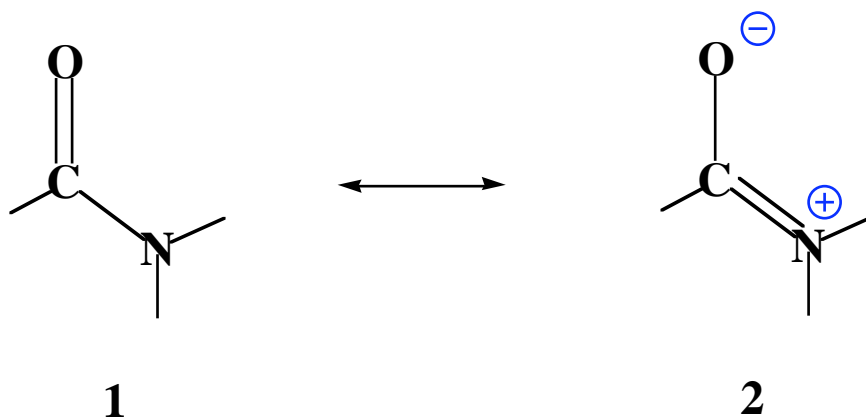
The VB wave function $\Psi(\mathbf{1}\leftrightarrow\mathbf{2})$ for the ground state
is a combination of two VB structures Ψ_1 and Ψ_2 :

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

Estimation of C_1, C_2, resonance energy…

Why Doing Valence Bond and not only MO?

- Some vital concepts
    - hybridization
    - resonance
    - VSEPR
    - Lewis structures
    - Arrow-pushing language
    - IR frequencies of C-H bonds:
        sp^3-H, sp^2-H, sp-H
- Application to reactivity (the VBSCD model)

- Standard teaching:

    VB has failed

    The only correct theory is MO

Writing VB functions   Exemple: the covalent H_2 bond

H • • • • • • • • • • • • • H

$\uparrow$ $\downarrow$
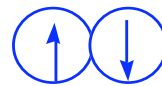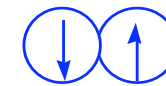
φ_a φ_b

Working hypothesis:

the electrons remain in atomic orbitals

At equilibrium distance,
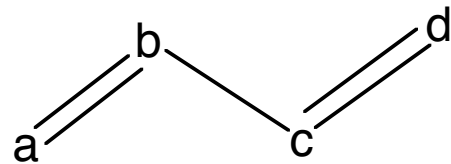2 possible déterminants :

$$\left| \varphi_a \, \bar{\varphi}_b \right| \qquad \left| \varphi_b \, \bar{\varphi}_a \right|$$

**Correct wave function
(for the covalent bond) :**

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

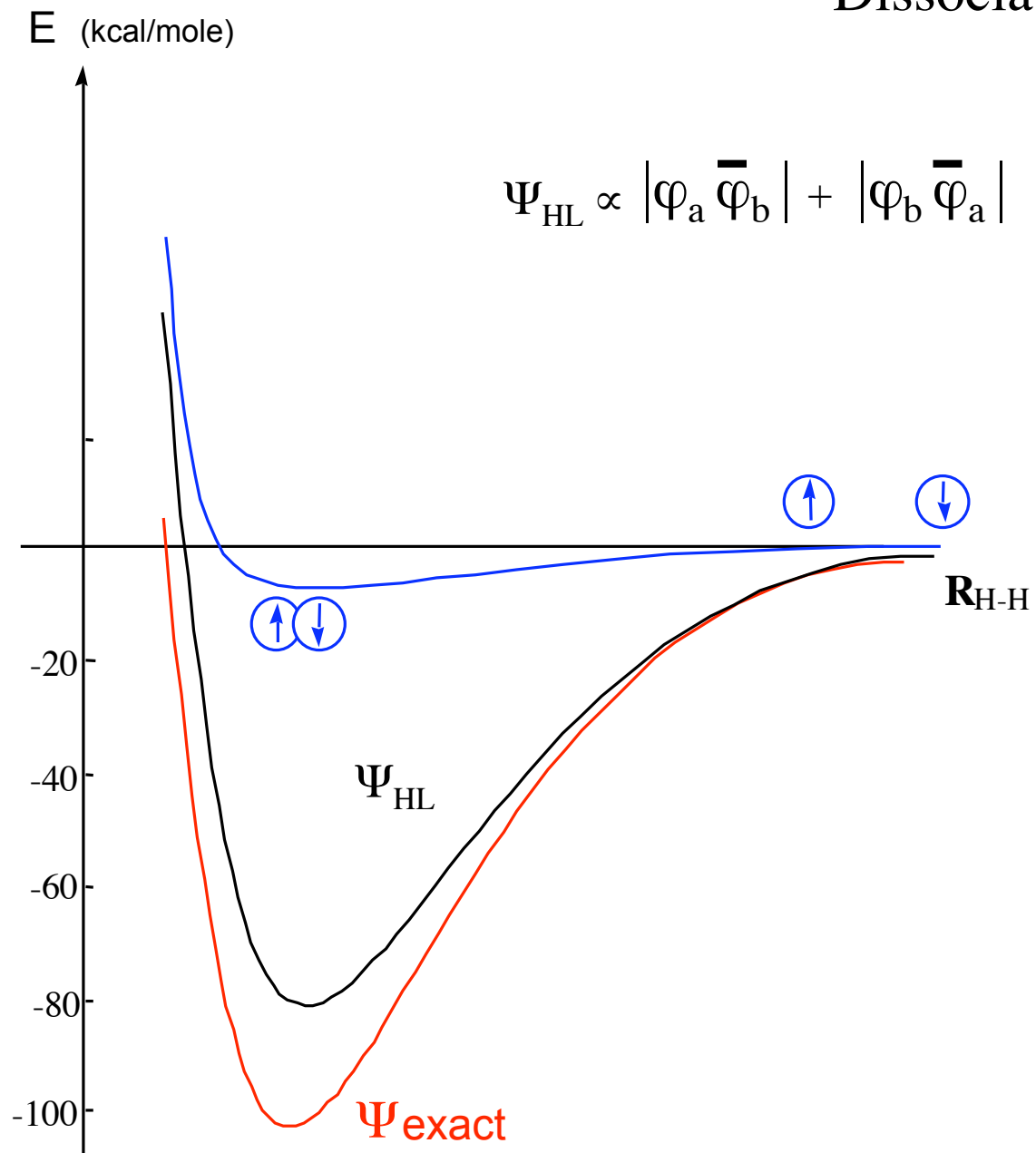# Writing VB functions beyond the two-electron/two center case

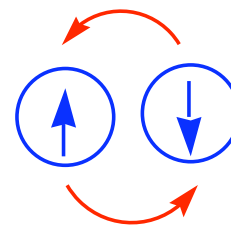**Exemple: the π-system of butadiene**

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

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

Dissociation curve of H_2

$$\Psi_{HL} \propto \left| \varphi_a \overline{\varphi}_b \right| + \left| \varphi_b \overline{\varphi}_a \right|$$

E (kcal/mole)

$R_{H\text{-}H}$

Ψ_{HL}

Ψ_{exact}

Physical origin of the bond:
spin exchange between AOs

$$\text{Triplet} = \frac{|\varphi_a \overline{\varphi_b}| - |\varphi_b \overline{\varphi_a}|}{\sqrt{2 - 2S^2}}$$

$$\text{S} \rightarrow \text{T gap} \approx 2D_e$$

R_{HH}

$$\text{Singlet} = \frac{|\varphi_a \overline{\varphi_b}| + |\varphi_b \overline{\varphi_a}|}{\sqrt{2 + 2S^2}}$$

Ψ_{HL}

-20

-40

-60

-80

-100
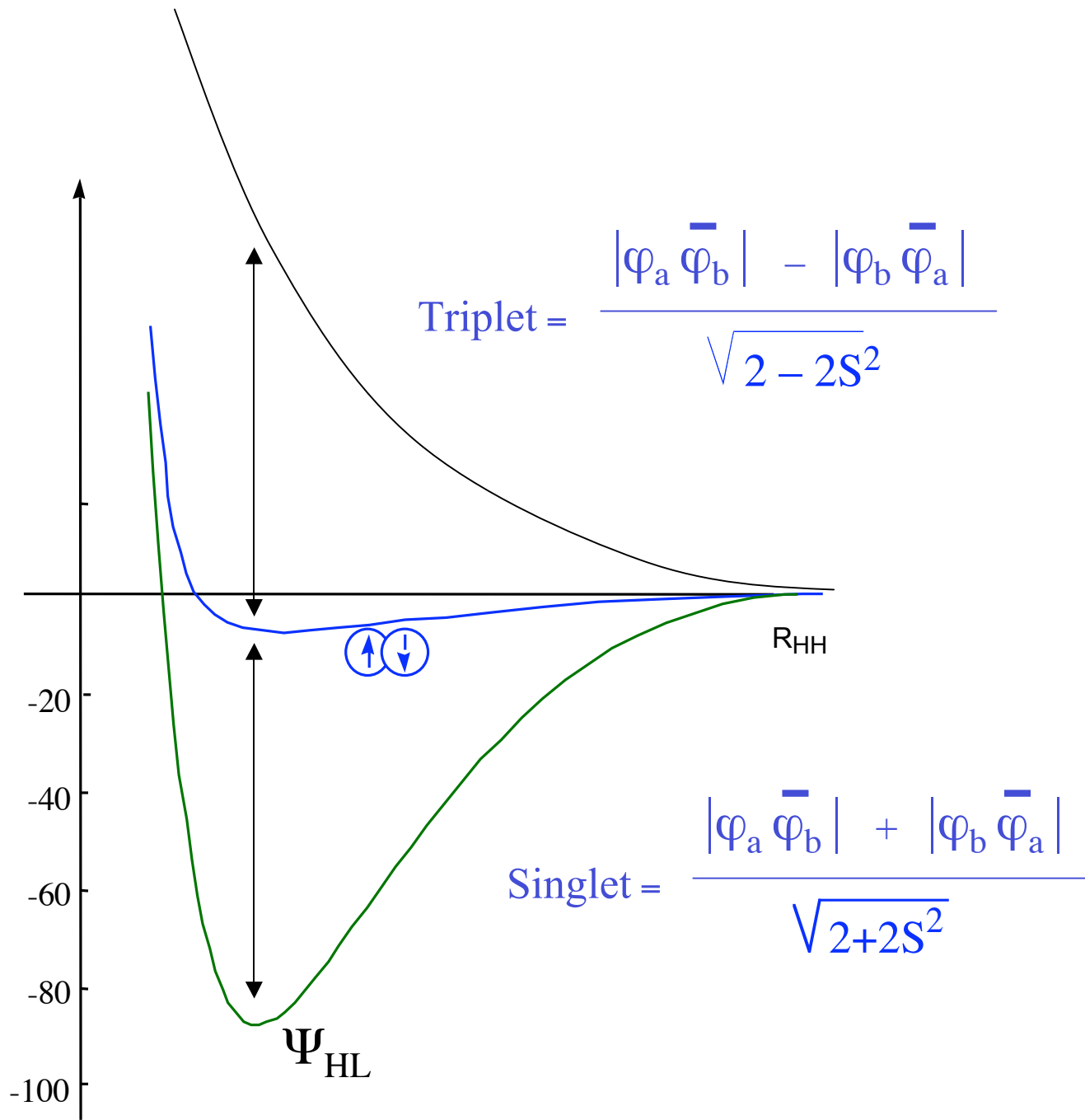
Comparison with MO description (Hartree-Fock)
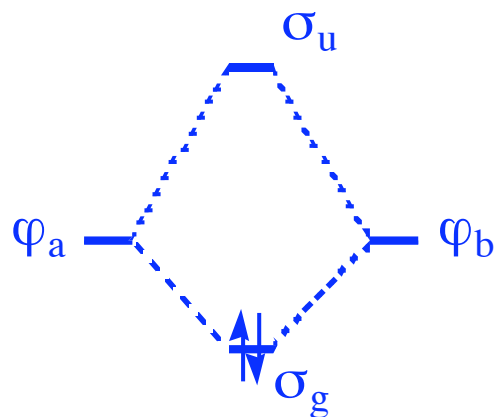
$$\sigma_u = \varphi_a - \varphi_b \quad =$$

$$\sigma_g = \varphi_a + \varphi_b \quad =$$

$$\Psi_{HF} = \left| \sigma_g \bar{\sigma}_g \right| \; = \left| \varphi_a \bar{\varphi}_b \right| + \left| \varphi_b \bar{\varphi}_a \right| \quad + \quad \left| \varphi_a \bar{\varphi}_a \right| + \left| \varphi_b \bar{\varphi}_b \right|$$

$$\underbrace{\qquad\qquad\qquad}_{\text{H•——•H}} \qquad\qquad \underbrace{\qquad\qquad\qquad}_{\text{H}^-\text{H}^+ \; + \; \text{H}^+\text{H}^-}$$

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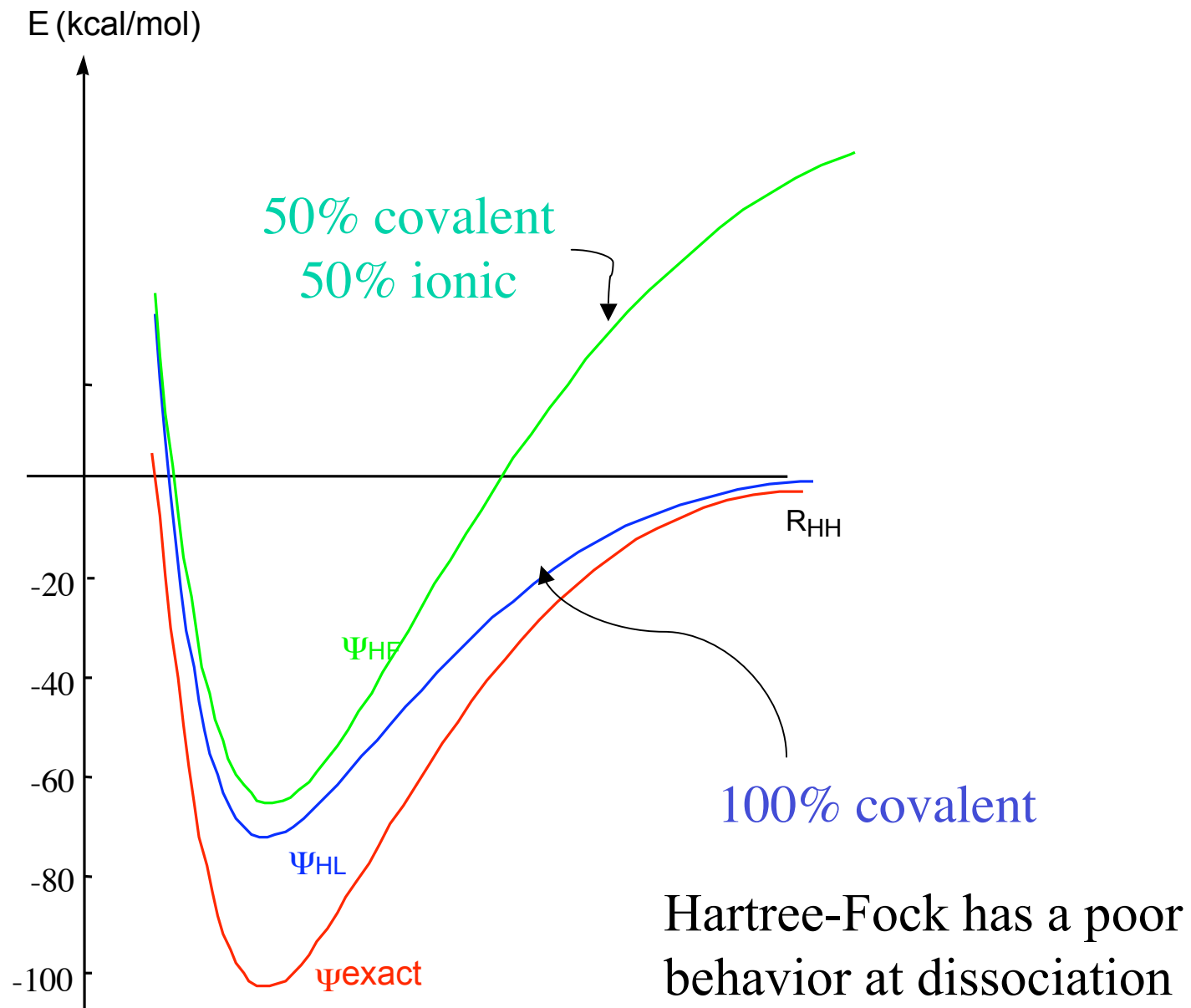
- **Simple VB description** $\Psi_{HL} = 100\%$ covalent

- **Exact description**   **72-79% covalent**   **21-28% ionic**
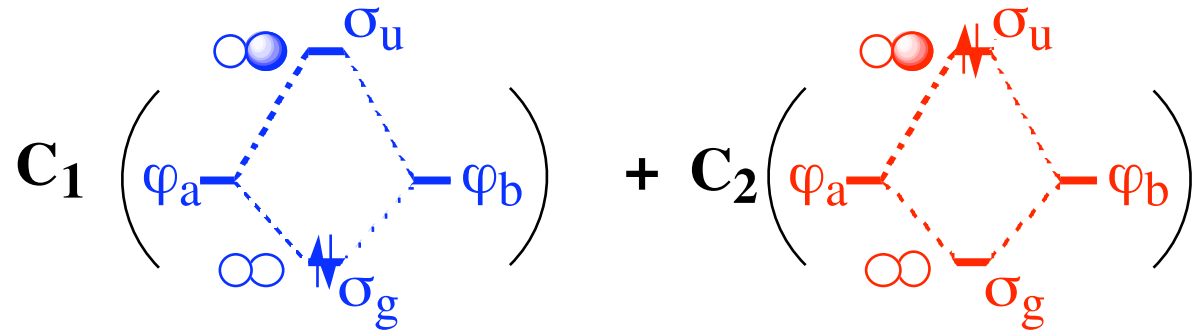
Dissociation curve MO vs VB

Exact description

- **In the VB framework**

$$\Psi_{exact} = \lambda(|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|) + \mu(|\varphi_a \bar{\varphi}_a| + |\varphi_b \bar{\varphi}_b|)$$

$$\text{H•——•H} \qquad\qquad \text{H}^-\text{H}^+ + \text{H}^+\text{H}^-$$

- **In the MO framework**
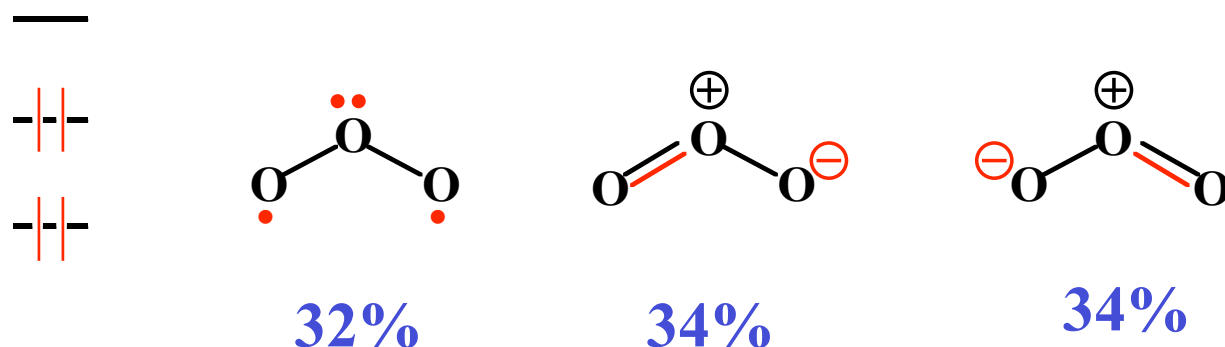

$$C_1 \qquad\qquad + \qquad C_2$$

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

$$|\sigma_u \bar{\sigma}_u| = |\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a| \quad - \quad |\varphi_a \bar{\varphi}_a| + |\varphi_b \bar{\varphi}_b|$$
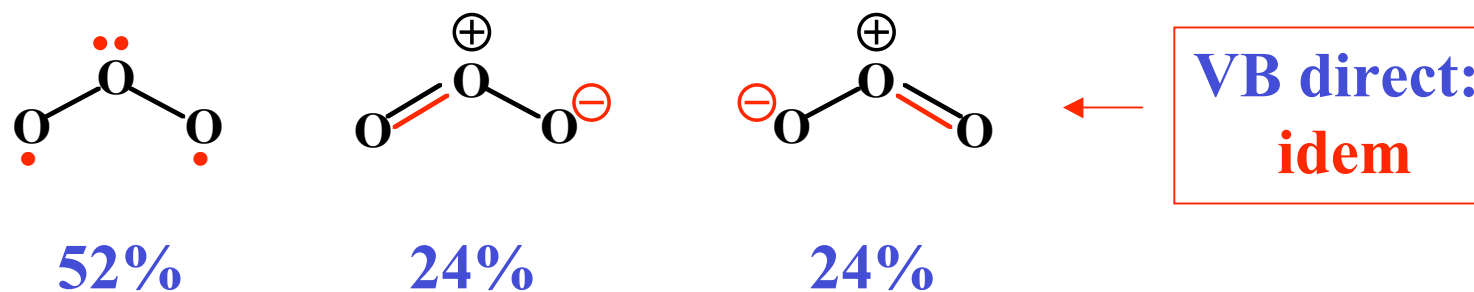
$$C_1 |\sigma_g \bar{\sigma}_g| + C_2 |\sigma_u \bar{\sigma}_u| = \Psi_{exact}$$

Transformation MO → VB   (Exemple: ozone)

- **Fonction Hartree-Fock** (expanded in VB structures)

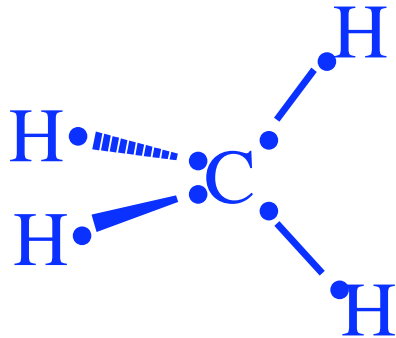**32%**   **34%**   **34%**

- **Configuration Interaction**

VB direct:
idem

52%   **24%**   **24%**

- *Any MO wave function can be converted to VB, and vice versa*
- *If Complete CI, VB and MO-CI become equivalent*
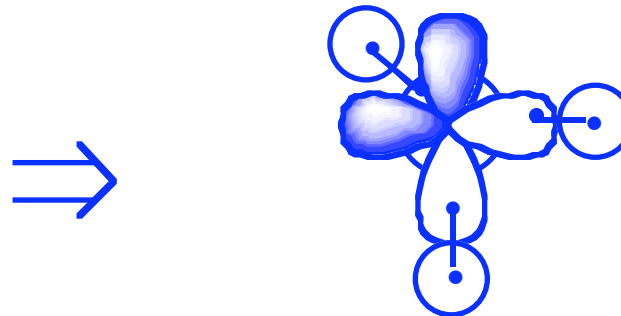
Generalisation to polyatomic molecules

= four equivalent local c•–•H bonds

Which atomic orbitals?

First try: « pure » AOs
H : 1s
C : 2s, 2px, 2py, 2pz
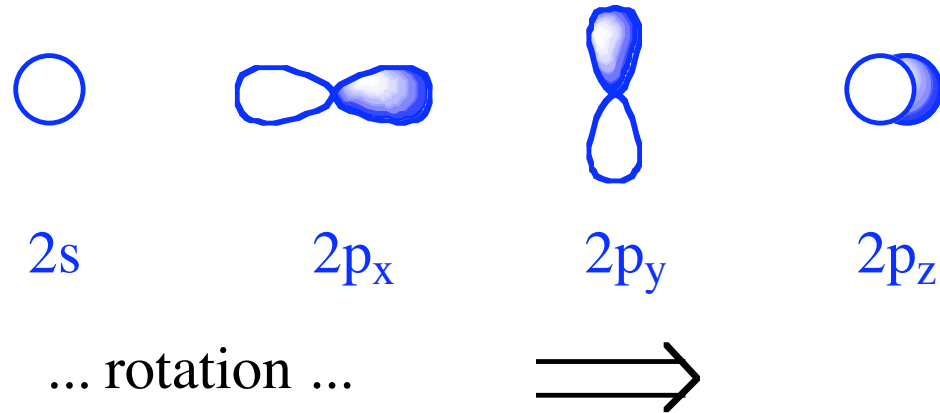
$\Rightarrow$

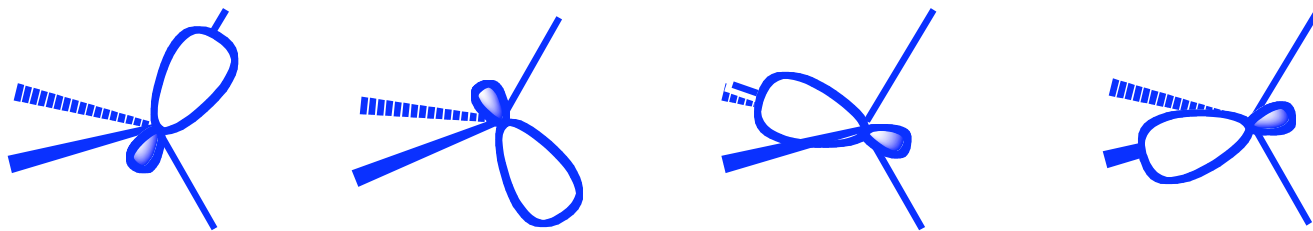
- 90° angles
- non-equivalent bonds

The answer: hybridization of the atomic orbitals

2s $2p_x$ $2p_y$ $2p_z$
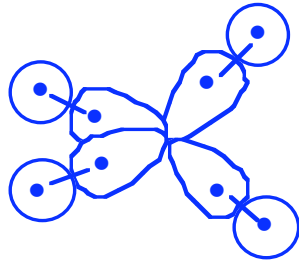
... rotation ... $\Longrightarrow$

4 equivalent « hybrid » atomic orbitals (HAOs)

Orthogonal, pointing in tetraedral directions
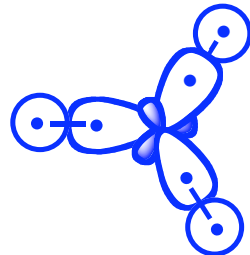
Hybrid atomic orbitals

CH$_4$

sp^3 hybrids
(all alkanes...)

BH$_3$

sp^2 hybrids
(ethylene, all alkenes...)

BeH$_2$

sp hybrids
(acetylene, all alkynes...)

A Qualitative valence bond theory[1]

Effective hamiltonian: $H^{eff} = (h(1) + h(2) + h(3) + ...)$

Parameters: β, S, ε

Similar model in the MO framework:

$$\frac{\varepsilon - \beta}{1 - S}$$

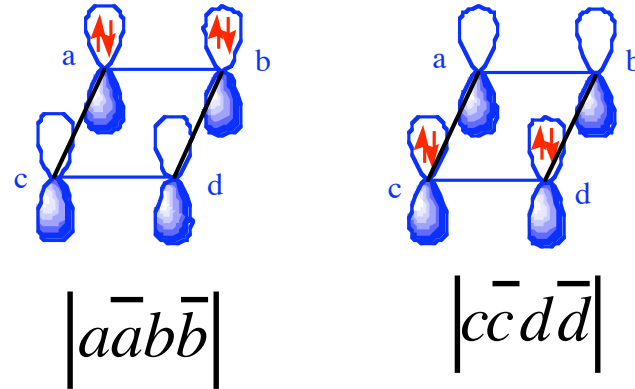$$\frac{\varepsilon + \beta}{1 + S}$$
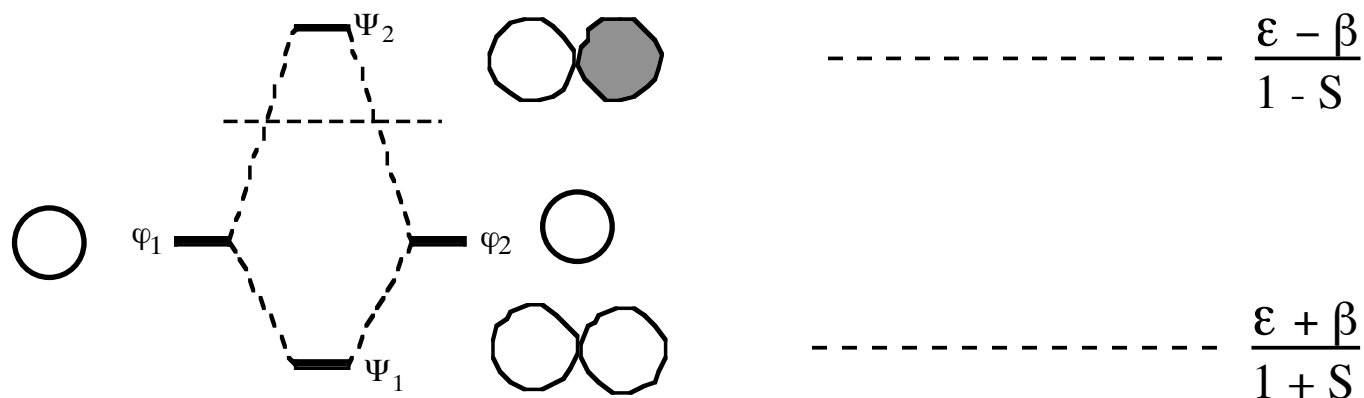
[1] "A Chemist's Guide to Valence Bond Theory", by Sason Shaik and P.C. Hiberty, Wiley, Interscience, 2008, **Chapter 3**

A Qualitative valence bond theory

Overlap between determinants:

Generate permutations…
- between identical spins
- only one side

$$\left|a\bar{a}b\bar{b}\right|$$

$$\left|c\bar{c}d\bar{d}\right|$$

$$\left\langle\left(\left|a\bar{a}b\bar{b}\right|\right)\middle|\left(\left|c\bar{c}d\bar{d}\right|\right)\right\rangle=\left\langle a\bar{a}b\bar{b}\middle|c\bar{c}d\bar{d}\right\rangle-\left\langle a\bar{a}b\bar{b}\middle|d\bar{c}c\bar{d}\right\rangle+....$$

$$= S_{ac}^2 S_{bd}^2 - S_{ad}S_{ac}S_{bc}S_{bd} - S_{ac}S_{ad}S_{bd}S_{bc} + S_{ad}^2 S_{bc}^2$$

$$\left\langle\left(\left|a\bar{a}b\bar{b}\right|\right)\middle|\left(\left|a\bar{a}b\bar{b}\right|\right)\right\rangle = 1 - 2S_{ab}^2 + 4S_{ab}^4$$

A Qualitative valence bond theory

Hamiltonian matrix elements:

$$\langle \Omega | H^{eff} | \Omega' \rangle = \langle \Omega | h(1) + h(2) + h(3) + h(4) | \Omega' \rangle$$

$$\langle (|a\,\bar{a}\,b\,\bar{b}|)|h(1)|(|c\,\bar{c}\,d\,\bar{d}|) \rangle = h_{ac}S_{ac}S_{bd}^2 - h_{ad}S_{ac}S_{bc}S_{bd} - h_{ac}S_{ad}S_{bd}S_{bc} + h_{ac}S_{ad}S_{bc}^2$$

$$h_{ac} = \langle a | h | c \rangle = \beta_{ac}$$

$$h_{aa} = \langle a | h | a \rangle = \varepsilon_a$$

Choice of an origin of energies: $\qquad \sum_i \varepsilon_i = 0$
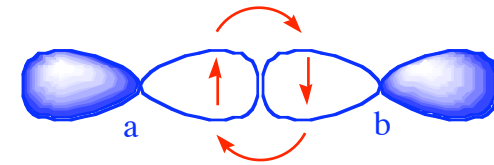
A Qualitative valence bond theory

The two-electron bond:

$$\Psi_{VB} = \frac{\left|a\,\overline{b}\right| + \left|b\,\overline{a}\right|}{\sqrt{2+2S^2}}$$

$$\left\langle \left(\left|a\overline{b}\right|\right)\left|h(1)+h(2)\right|\left(\left|a\overline{b}\right|\right)\right\rangle = \varepsilon_a + \varepsilon_b = 0$$

$$\left\langle \left(\left|a\,\overline{b}\right|\right)\left|h(1)+h(2)\right|\left(\left|b\,\overline{a}\right|\right)\right\rangle = 2\beta_{ab}S_{ab}$$

$$E(\Psi_{VB}) = \frac{2\beta S}{1+S^2} = D_e(2\text{-e})$$

Reminder, MO Theory:

$$\frac{-\beta}{1-S}$$

$$\frac{\beta}{1+S}$$

$$D_e = 2\beta/(1+S)$$
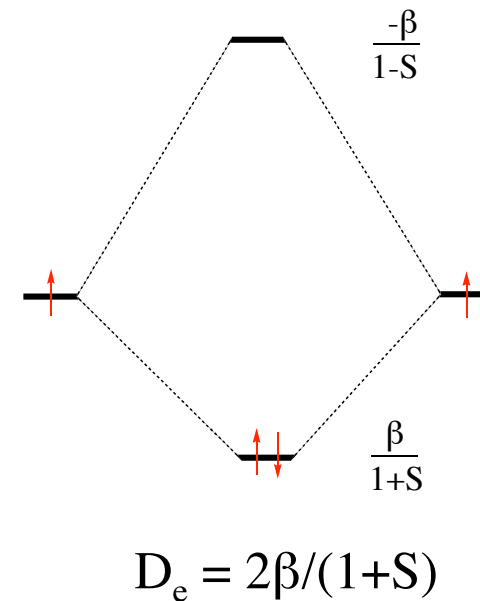
A Qualitative valence bond theory

The triplet Pauli repulsion:

$$\Psi_T = \frac{\left|a\,\bar{b}\right| - \left|b\,\bar{a}\right|}{\sqrt{2-2S^2}}$$

$$\left\langle \left(\left|a\bar{b}\right|\right)\left|H\right|\left(\left|a\bar{b}\right|\right)\right\rangle = \varepsilon_a + \varepsilon_b = 0$$

$$\left\langle \left(\left|a\bar{b}\right|\right)\left|H\right|\left(\left|b\bar{a}\right|\right)\right\rangle = 2\beta_{ab}S_{ab}$$

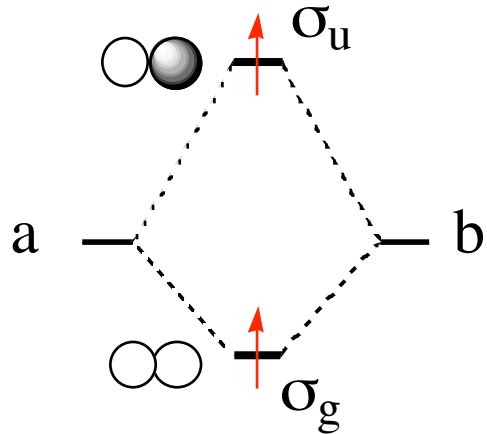$$E(\Psi_T) = \frac{-2\beta S}{1-S^2}$$
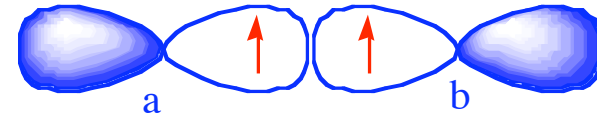
Reminder: MO theory:
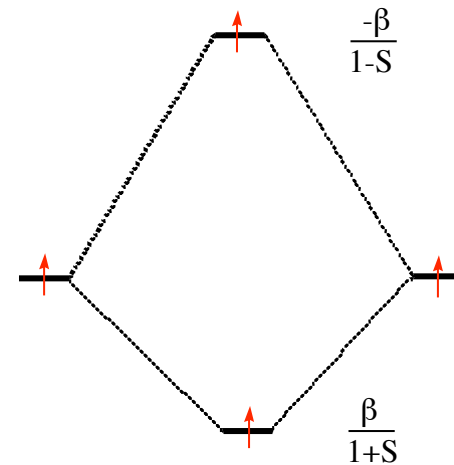
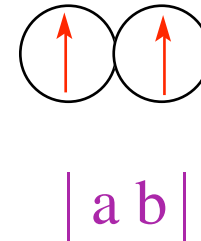$$E = \frac{\beta}{1+S} + \frac{-\beta}{1-S} = \frac{-2\beta S}{1-S^2}$$

The same!

Triplet Pauli repulsion:why $\Psi_{MO} = \Psi_{VB}$ **?**

• The MO picture:

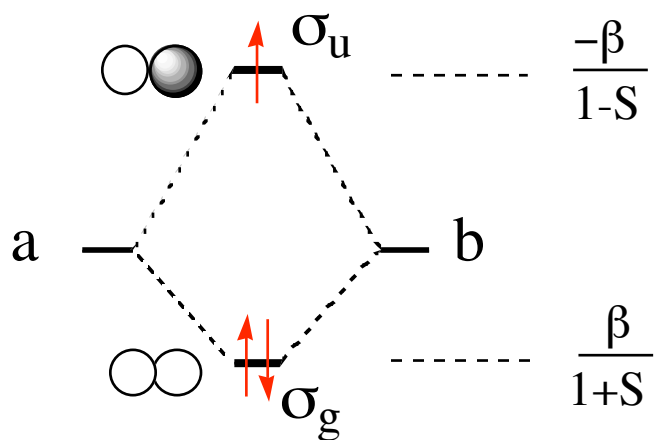**• The VB picture:**

σ_u

a

b

σ_g

$|\, a\ b\,|$

$$\Psi_{MO} = |\sigma_g\ \sigma_u| = |(a+b)(a-b)| = |\cancel{aa}| - |ab| + |ba| - |\cancel{bb}| = \Psi_{VB}$$

Whenever the MO and VB wave functions of an electronic state are equivalent, the VB energy can be estimated using qualitative MO theory
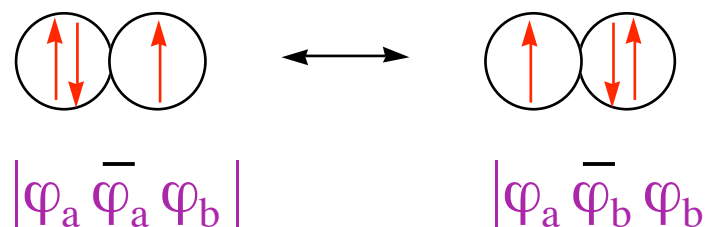
Other cases where $\Psi_{MO} = \Psi_{VB}$?

The three-electron bond   Example: the helium cation dimer He_2^+

• **The MO picture:**

$$\sigma_u \qquad \frac{-\beta}{1-S}$$

$$a \qquad\qquad b$$

$$\frac{\beta}{1+S}$$

$$\sigma_g$$

• **The VB picture:**

$$\left| \varphi_a \overline{\varphi}_a \varphi_b \right| \qquad\qquad \left| \varphi_a \overline{\varphi}_b \varphi_b \right|$$

$$\Psi_{MO} = \left| \sigma_g \overline{\sigma}_g \sigma_u \right| = \left| \varphi_a \overline{\varphi}_a \varphi_b \right| + \left| \varphi_a \overline{\varphi}_b \varphi_b \right| = \Psi_{VB}$$

Interaction energy: $D_e = E(He \therefore He)^+ - E(He) - E(He^+) = \dfrac{\beta(1-3S)}{1-S^2}$

Elementary interaction energies in qualitative VB *vs* MO theories

	VB	MO
One-electron bond (A↑ B) =	$\dfrac{ß}{1+S}$	$\dfrac{ß}{1+S}$
Two-electron bond (A–B) =	$\dfrac{2ßS}{1+S^2}$	$\dfrac{2ß}{1+S}$
Three-electron bond (A∴B) =	$\dfrac{ß(1-3S)}{1-S^2}$	$\dfrac{ß(1-3S)}{1-S^2}$
4-e repulsion (A↑↓ ↓↑B) =	$\dfrac{-4ßS}{1-S^2}$	$\dfrac{-4ßS}{1-S^2}$
Triplet repulsion (A↑ ↑B) =	$\dfrac{-2ßS}{1-S^2}$	$\dfrac{-2ßS}{1-S^2}$

Thumb rule: VB energies for typical interactions

Energy of a determinant with n (neighboring ↑ ↑) : $\dfrac{-2n\beta S}{1-S^2}$
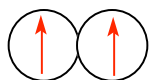
triplet repulsion	↑ ↑	$-2\beta S/(1-S^2)$	(VB and MO)
4-e repulsion	↑↓ ↑↓	$-4\beta S/(1-S^2)$	(VB and MO)
spin-alternated determinant		0	(VB only)
3-e repulsion	↑ ↑↓	$-2\beta S/(1-S^2)$	(VB only)
repulsion bond… single electron	↑ ↓ ↑	$-\beta S/(1-S^2)$	(VB only)
repulsion bond… bond	↑ ↓ ↑ ↓	$-\beta S/(1-S^2)$	(VB only)
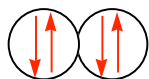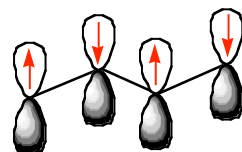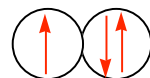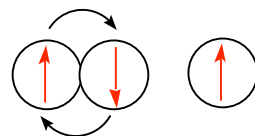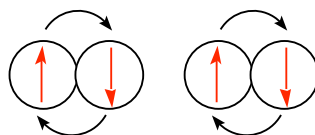
Thumb rule: off-diagonal Hamiltonian matrix elements

Determinants differing by one spin-orbital :

$$\left\langle \left(\left| a\,\bar{a}\,b \right|\right) \middle| H \middle| \left(\left| a\,\bar{b}\,b \right|\right) \right\rangle = \beta_{ab}$$

Determinants differing by spin inversion of two spin-orbitals :

$$\left\langle \left(\left| a\,\bar{b} \right|\right) \middle| H \middle| \left(\left| \bar{a}\,b \right|\right) \right\rangle = -2\beta_{ab} S_{ab}$$

Determinants differing by more than two spin-orbitals :

$$\left\langle D_i \middle| H \middle| D_j \right\rangle = 0$$

Application: ground state and 1^{rst} excited state of butadiene

Two covalent structures, R_1 and R_2:

$$R_1 = 0.5\left(\left|a\bar{b}c\,\bar{d}\right| + \left|\bar{a}bc\,d\right| - \left|\bar{a}bc\,\bar{d}\right| - \left|a\bar{b}c\,d\right|\right) \quad = $$

$$R_2 = 0.5\left(\left|ab\bar{c}\,\bar{d}\right| + \left|\bar{a}\bar{b}c\,d\right| - \left|a\bar{b}c\,\bar{d}\right| - \left|\bar{a}bc\,d\right|\right) \quad = $$
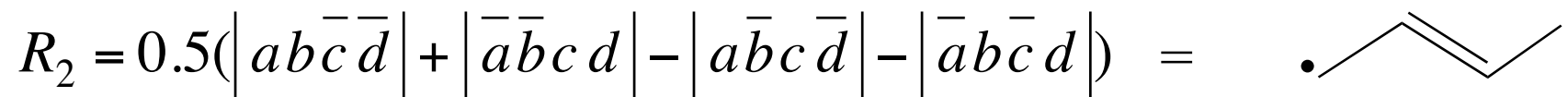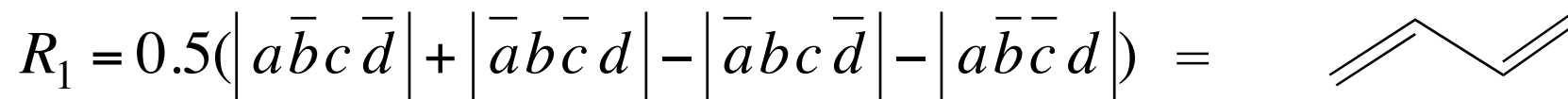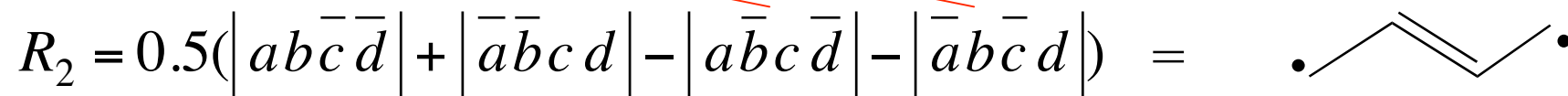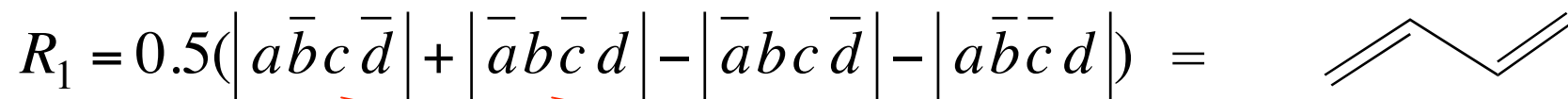

Energies:

$$E(R_1) = 2\beta S \times 2 - \beta S = 3\beta S$$

$$E(R_2) = 2\beta S - \beta S - \beta S = 0$$

Application: ground state and 1^{rst} excited state of butadiene

Two covalent structures, R$_1$ and R$_2$:

$$R_1 = 0.5(\,|a\bar{b}c\bar{d}|+|\bar{a}b\bar{c}d|-|\bar{a}bc\bar{d}|-|a\bar{b}\bar{c}d|\,) \quad = $$

$$R_2 = 0.5(\,|ab\bar{c}\bar{d}|+|\bar{a}\bar{b}c d|-|a\bar{b}c\bar{d}|-|\bar{a}b\bar{c}d|\,) \quad = $$
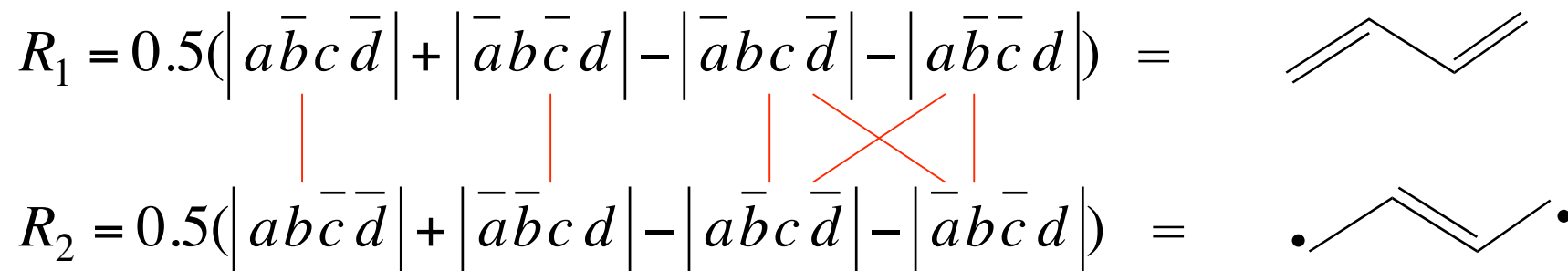
Overlap between R$_1$ and R$_2$

If we neglect the overlaps between different AOs,
only identical determinants overlap with each other

$$\Longrightarrow \quad \langle R_1 | R_2 \rangle = -0.5$$

Application: ground state and 1^{rst} excited state of butadiene

Two covalent structures, R$_1$ and R$_2$:

$$R_1 = 0.5(\,|a\bar{b}c\bar{d}| + |\bar{a}b\bar{c}d| - |\bar{a}bc\bar{d}| - |a\bar{b}\bar{c}d|\,) =$$

$$R_2 = 0.5(\,|ab\bar{c}\bar{d}| + |\bar{a}\bar{b}cd| - |\bar{a}bc\bar{d}| - |a\bar{b}\bar{c}d|\,) =$$

Hamiltonian matrix element between R$_1$ and R$_2$

2 determinants differin by spin exchange between
2 neighboring orbitals have a matrix element -2βS

$$\Longrightarrow \quad \langle R_1|H|R_2\rangle = -3\beta S$$

Application: ground state and 1ʳˢᵗ excited state of butadiene

$$\begin{vmatrix} 0 & -3\beta S \\ -3\beta S & -3\beta S \end{vmatrix} -E \begin{vmatrix} 1. & -0.5 \\ -0.5 & 1. \end{vmatrix} = 0$$
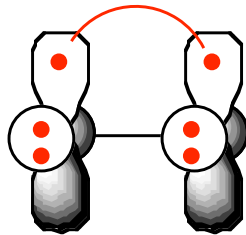
$\Psi^* = 0.82(\!\!\diagdown\!\!) + 1.12(\cdot\!\!\diagdown\!\!\cdot)$
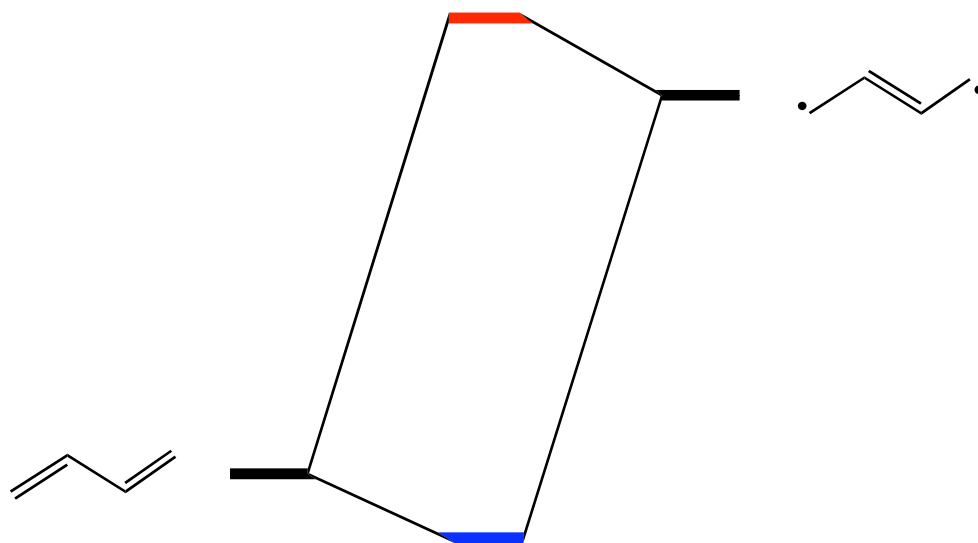
$\Psi_0 = 0.82(\!\!\diagdown\!\!) - 0.30(\cdot\!\!\diagdown\!\!\cdot)$

The alleged « failures » of valence bond theory

1) Dioxygen molecule: O=O or ↑O–O↑ ?
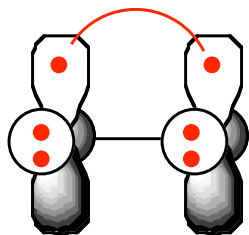

O=O, singlet state
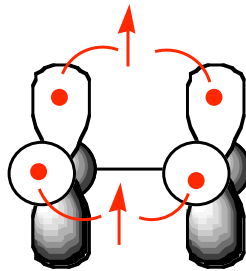
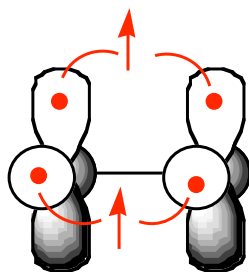↑O–O↑ , diradical displaying two 3-e bonds, triplet state

The alleged « failures » of valence bond theory

1) Dioxygen molecule: O=O or $^{\uparrow}$O–O$^{\uparrow}$?

$$E(S) = 2\beta S /(1+S^2) - 4\beta S /(1-S^2)$$

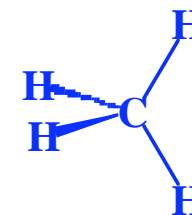$$E(T) = 2\beta (1 - 3S)/(1-S^2)$$

$$E(S) - E(T) = -2\beta (1-S)^2/(1-S^4) > 0$$
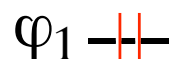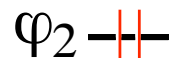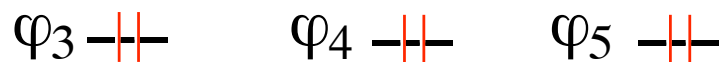
Qualitative VB predicts O$_2$ to be a triplet diradical
Pauling, 1931 (!)

The alleged « failures » of valence bond theory

2) The two ionization potentials of CH_4

- The MO model:

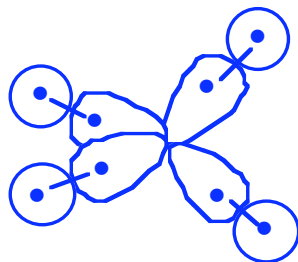φ_3 ⥮ φ_4 ⥮ φ_5 ⥮

φ_2 ⥮

φ_1 ⥮

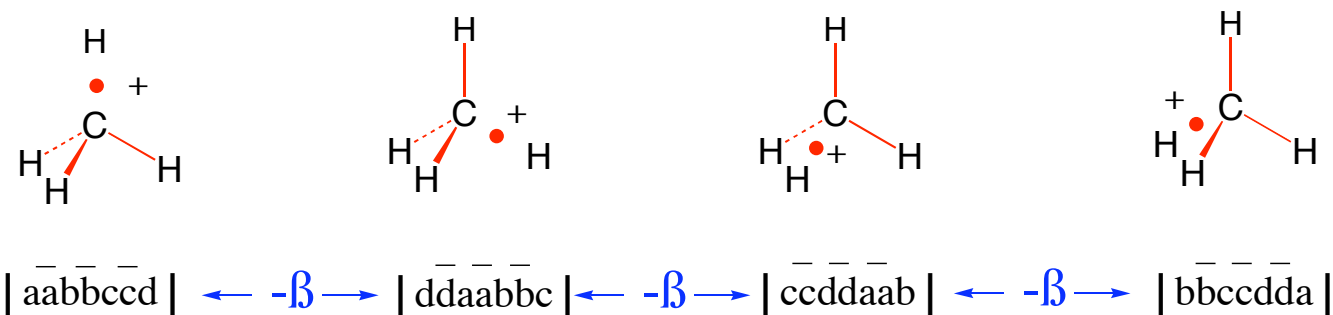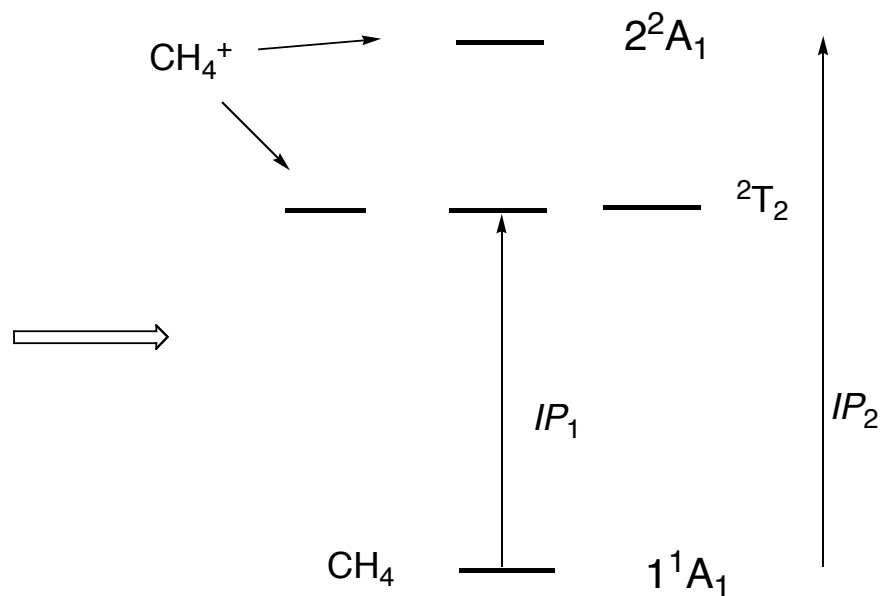Two valence MO energies => two IPs

- The VB model:

Four equivalent local bonds
=> only one IP **?**

The alleged « failures » of valence bond theory

2) The two ionization potentials of CH_4

$$|\,\overline{a}a\overline{b}b\overline{c}cd\,| \quad \xleftarrow{\;-\beta\;} \quad |\,\overline{d}d\overline{a}a\overline{b}bc\,| \quad \xleftarrow{\;-\beta\;} \quad |\,\overline{c}c\overline{d}d\overline{a}ab\,| \quad \xleftarrow{\;-\beta\;} \quad |\,\overline{b}b\overline{c}c\overline{d}da\,|$$

$$\begin{vmatrix} -E & -\beta & -\beta & -\beta \\ -\beta & -E & -\beta & -\beta \\ -\beta & -\beta & -E & -\beta \\ -\beta & -\beta & -\beta & -E \end{vmatrix} = 0$$

Qualitative VB predicts
CH_4 to have two IPs

Conclusions

- **VB and MO: two complementary theories.**

    - lower level: MO too much ionic, VB not enough

    - elaborate level: MO $\equiv$ VB

    - There are 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 (VB lecture VII, S. Shaik))

Some reading…

Thinking and Computing Valence Bond in Organic Chemistry, P.C. Hiberty, **J. Mol. Struc. (Theochem) 451**, 237 (1998).

BOVB - A Modern Valence Bond Method that Includes Dynamic Correlation, P.C. Hiberty et S. Shaik, **Theor. Chem. Acc. 108**, 255-272 (2002)

Valence Bond Theory. Its History, Fundamentals, and Applications. A Primer.
S. Shaik and P.C. Hiberty, **Reviews in Computational Chemistry 20**, 1-100 (2004)

A conversation on VB vs MO Theory: A Never-Ending Rivalry?
R. Hoffmann, S. Shaik and P.C. Hiberty, **Acc. Chem. Res. 36**, 750-756 (2003)