Benoît BRAÏDA*

2016 Virtual Winterschool on Computational Chemistry

Basics of Valence Bond theory

Laboratoire de Chimie Théorique

Université Pierre et Marie Curie

* benoit.braida@upmc.fr

VB lectures

- Purpose and History
- Basics of VB theory and VB formalism
- *If time remains:* Qualitative VB
- *If time remains:* VB diagrams for reactivity

Motivation and history

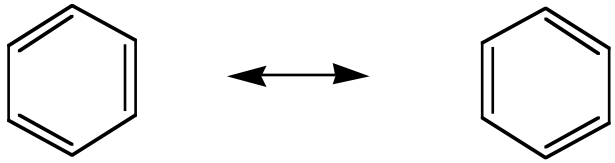
Heuristic models

- Lewis' model :
  - Lewis (1916) : **electron pairing**
  - Langmuir (1919) : **octet rule**

Heuristic models

- Lewis' model :
  - Lewis (1916) : **electron pairing**
  - Langmuir (1919) : **octet rule**

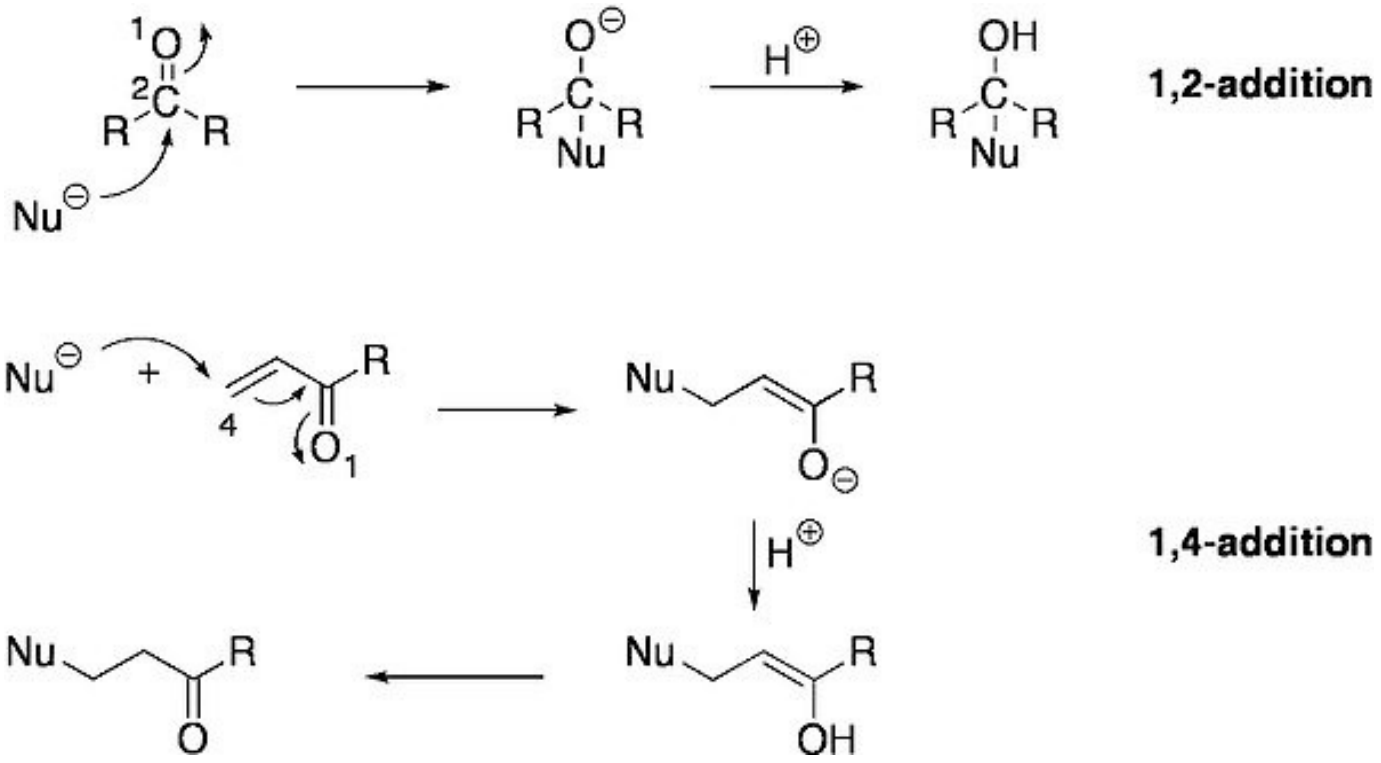
- Mesomery / resonance :



  - Arndt, Robinson, Ingold (1924) : mesomery

Heuristic models

- Arrow-pushing language :



➡ describe the rearrangement of electrons during a reaction (mechanisms)

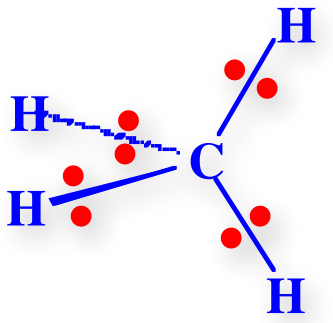
Heuristic models

Chemist's models:

- Have **shaped chemist's mind**
- Now form the **chemist's basic language**
- Allow to **organize** and **rationalize** a incredibly large quantity of **chemical facts**

Chemists' «schizophrenia»

- **Concepts and heuristic models** based on a localized vision :



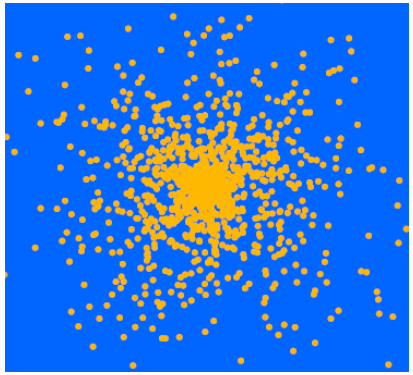
Lewis model, arrow-pushing language, VSEPR, hybridization,...

- Localized electron pairs

- Chemical bond concept

- **Quantitative theory** based on a delocalized particles vision :

$$\hat{H}\Psi = E\Psi$$

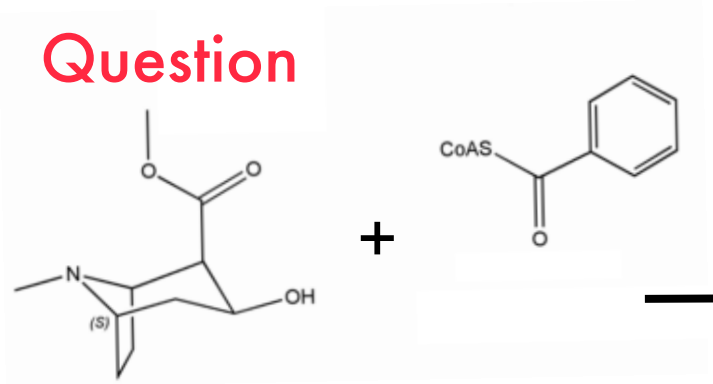


- delocalized particles (e^-, n^+)

- indistinguishable and all-interacting (no chemical bond)

Chemists' «schizophrenia»

Chemical Question



Quantum Calculations

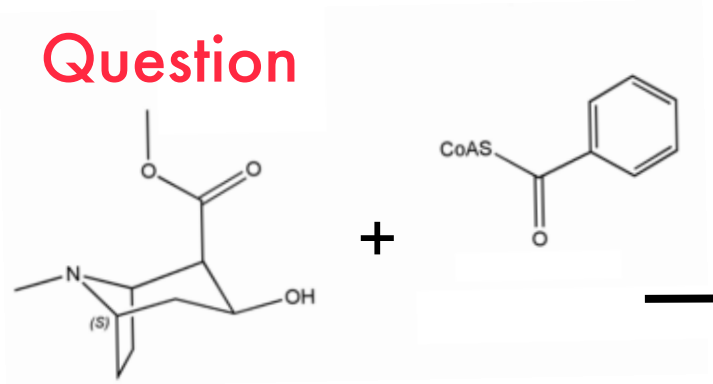
ΔH_{rnx}

$\Delta H^{\ddagger}$

etc.

Chemists' «schizophrenia»

Chemical Question



Quantum Calculations

ΔH_{rnx}

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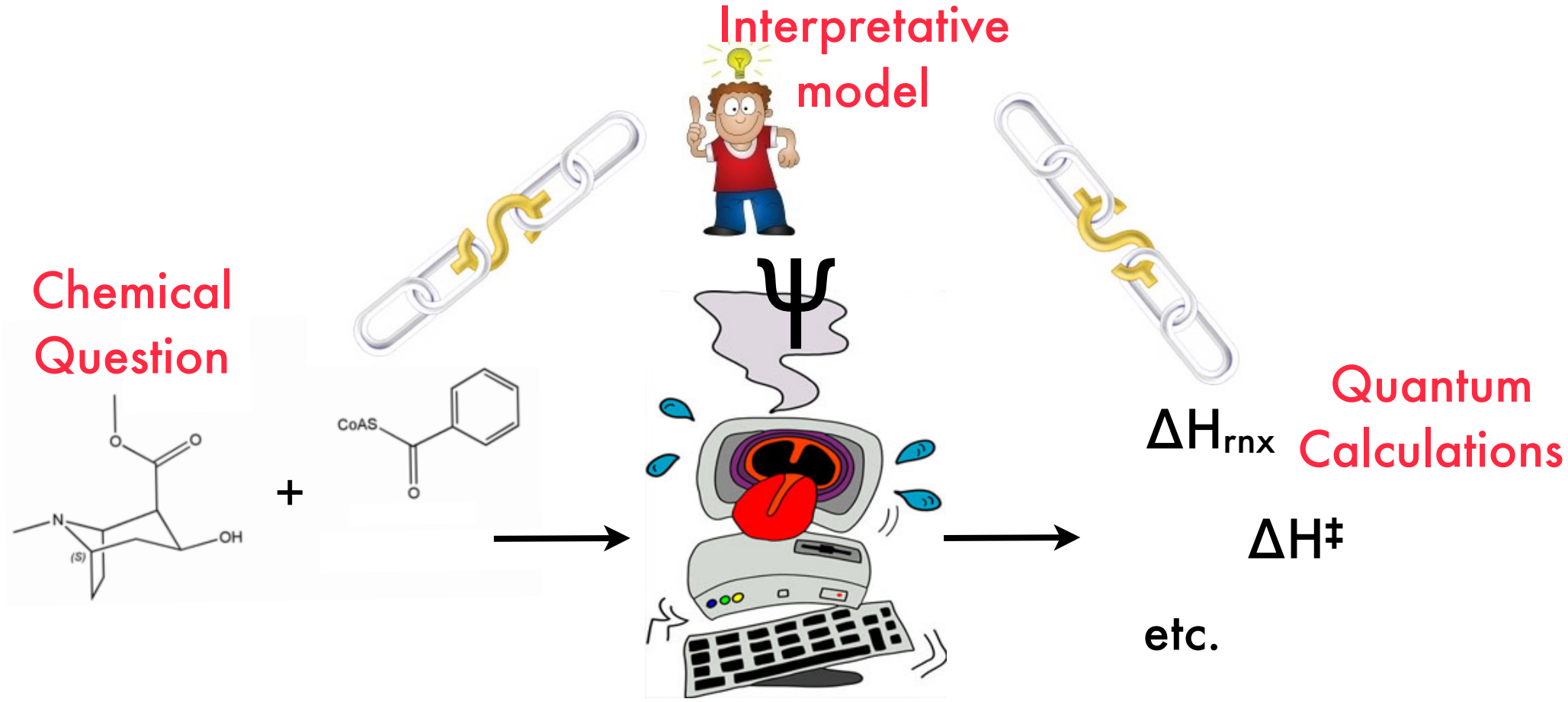
etc.

«I am very glad the computer understands this.
But I would like to understand it too» (Eugene Wigner)

Chemists' «schizophrenia»



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Chemists' «schizophrenia»

The challenges :

- How to **build a bridge** between quantum mechanics and chemists' vision ?

- How to to **organize** and **rationalize** the enormous and ever-increasing quantity of data produced ?

Chemists' «schizophrenia»

The challenges :

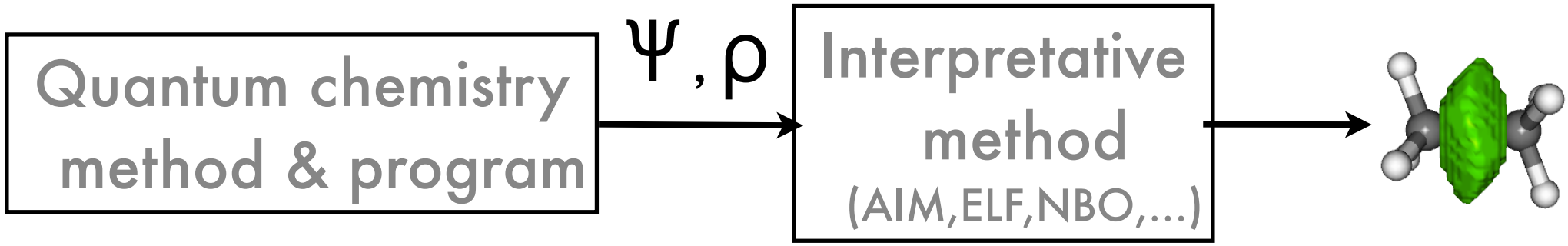
- How to **build a bridge** between quantum mechanics and chimists' vision ?

- How to to **organize** and **rationalize** the enormous and ever-increasing quantity of datas produced ?

➡ Need for interpretative methods to act as **interface** between experiments and computations, to **create order**, and by doing this to **open new thoughts**

Interpretative methods

- « Standard » interpretative method:



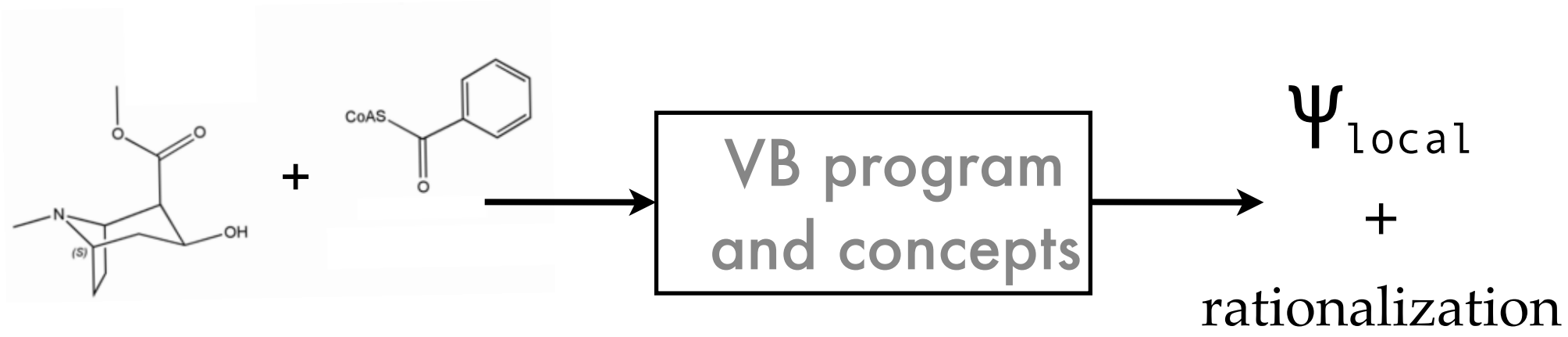
➡ Definition and **meaning** of localized regions not straightforward

➡ Link with the **energy** absent of qualitative (NBO)

➡ Does not directly provide general **laws** (create order)

Interpretative methods

- Valence bond theory :



➡ VB provides **wavefunction** (QC) methods and **«built-in» interpretative tools** at the same time

- Birth and origins:

1916

G.N. Lewis

1927-34

L. Pauling

VB: a quantum dressing of Lewis model

- ~1930-1950s: Rise and glory

L. Pauling

VB dominated the mental map of chemistry

- ~1940-1960: The MO-VB rivalry

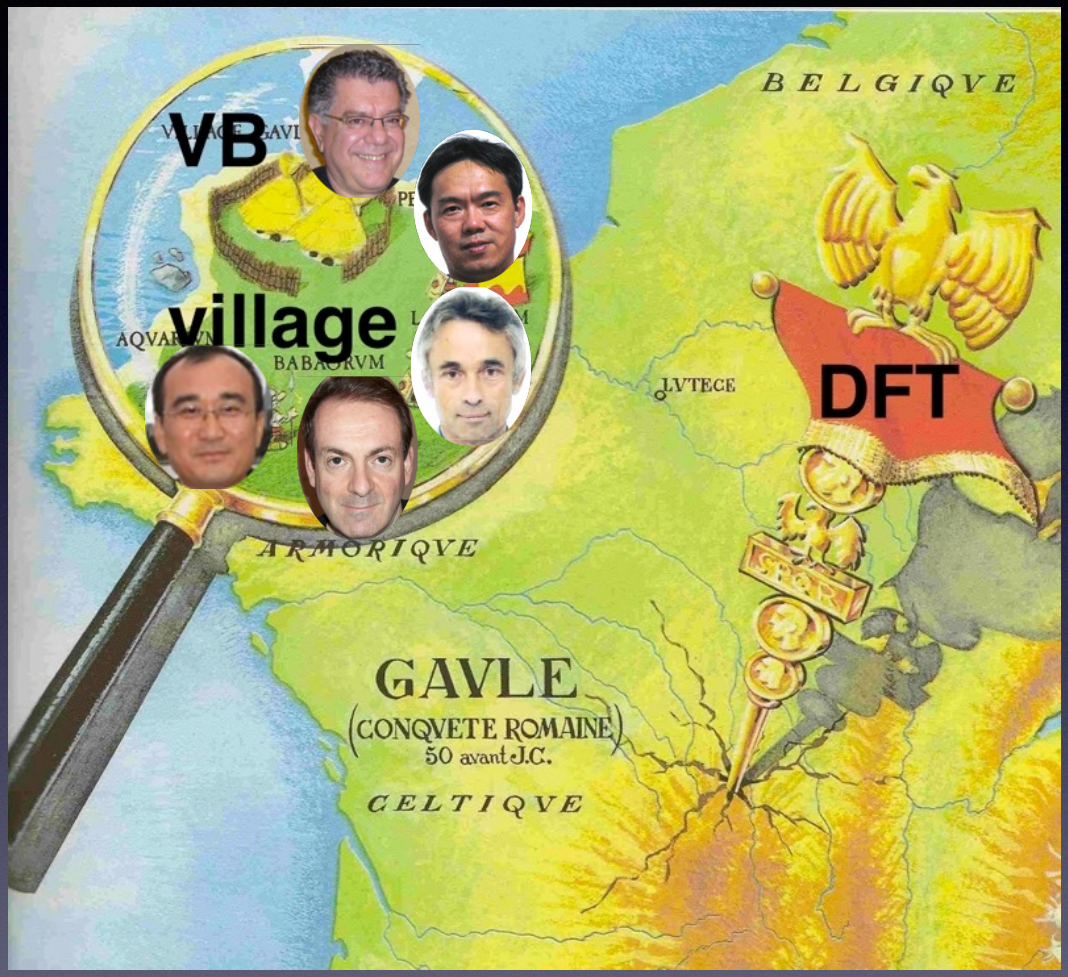
Successes of MO theory vs. VB «failures»

- ~1960-1980: The downfall

Sir John A. Pople

MO programs are developed, VB had nothing

- ~1980-2010: small but active community

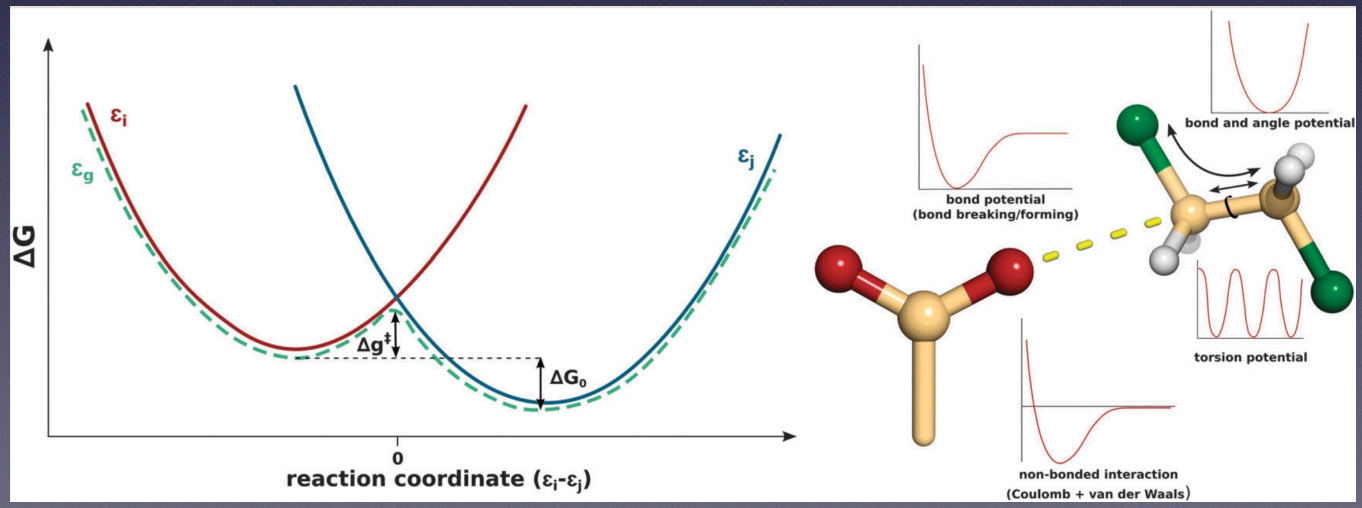


New models, methods, programs, applications

- 1992+2013: Two nobel prices

Rudolph A. Marcus
ET theory

Ariel Warshel
EVB



Developments of VB theory

- 201x-...: awakening of the sleeping beauty?

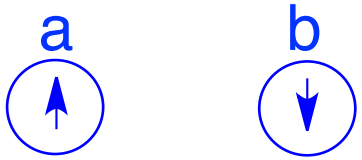
All elements for a Valence Bond revival are ready

Basics of VB theory

Heitler-London

- Notations :

Dihydrogen molecule H_2 : H_a——H_b



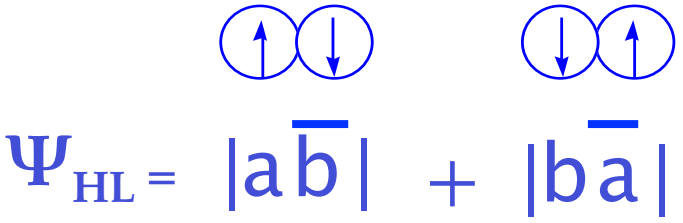
$$\left|a\bar{b}\right| = \begin{matrix}(1,s_1)\\(2,s_2)\end{matrix}\begin{vmatrix} a(1)\otimes\alpha(s_1) & b(1)\otimes\beta(s_1) \\ a(2)\otimes\alpha(s_2) & b(2)\otimes\beta(s_2)\end{vmatrix}$$

$$\begin{cases} 1 = (x_1, y_1, z_1) : \text{spatial coordinates for electron 1} \\ s_1 : \text{spin coordinate for electron 1}\end{cases}$$

Heitler-London

Dihydrogen molecule H_2 : H_a——H_b

- Heitler-London (1927) :



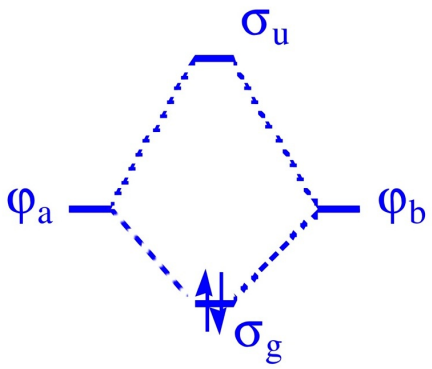
- Electrons in atomic orbitals
- Shared electron pair (covalent bond)

➡ **basis of VB theory**

Heitler-London

Dihydrogen molecule H_2 : H_a——H_b

- Hund-Mulliken (1927) :



$$\sigma_u \propto a - b$$

$$\sigma_g \propto a + b$$

$$\Psi_{HM} = |\sigma_g \overline{\sigma_g}|$$

➡ **basis of MO theory**
(HF wave function)

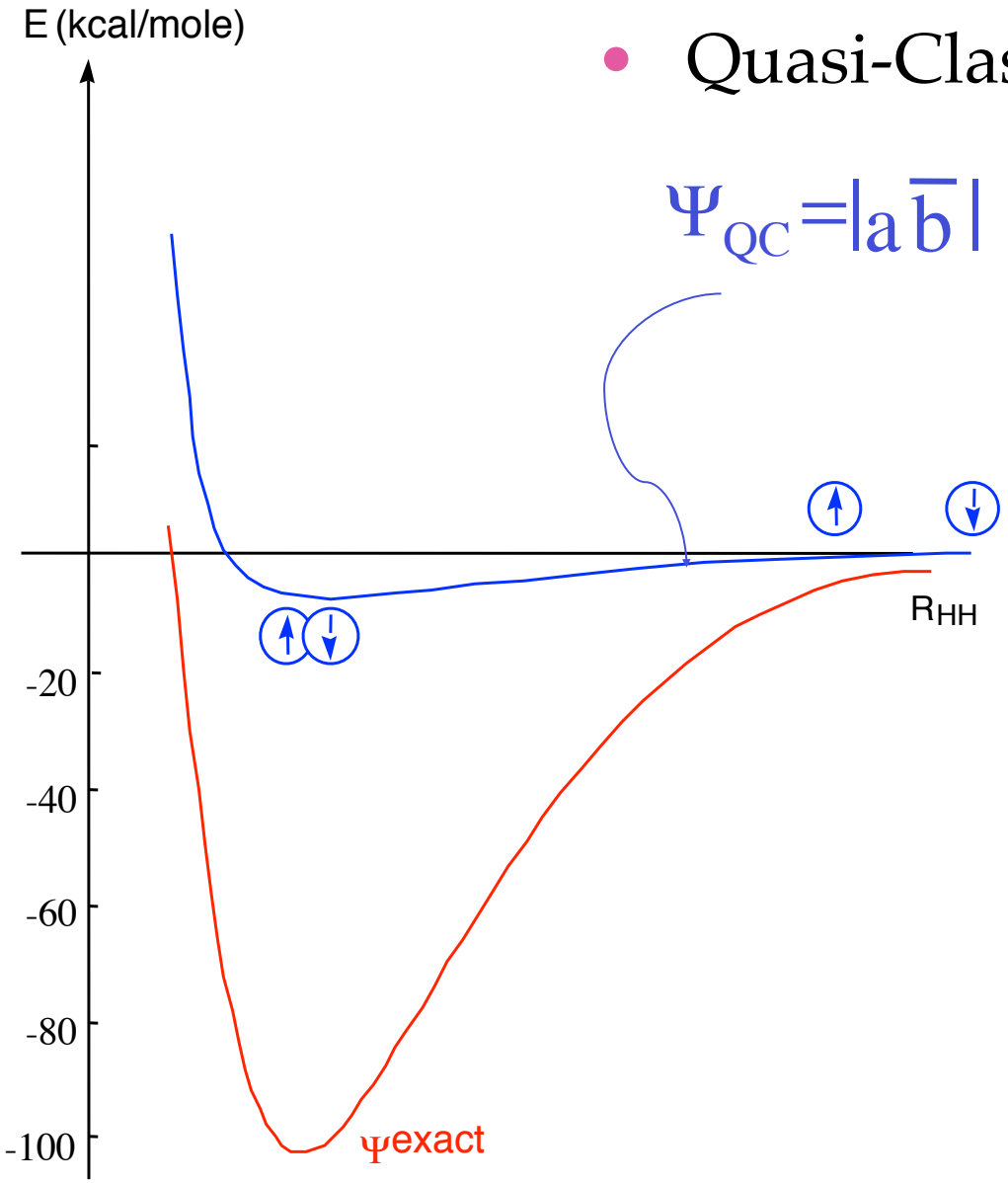
- Heitler-London (1927) :

$$\Psi_{HL} = |a\overline{b}| + |b\overline{a}|$$

- Electrons in atomic orbitals
- Shared electron pair (covalent bond)

➡ **basis of VB theory**

Heitler-London



- Quasi-Classical (QC) state :

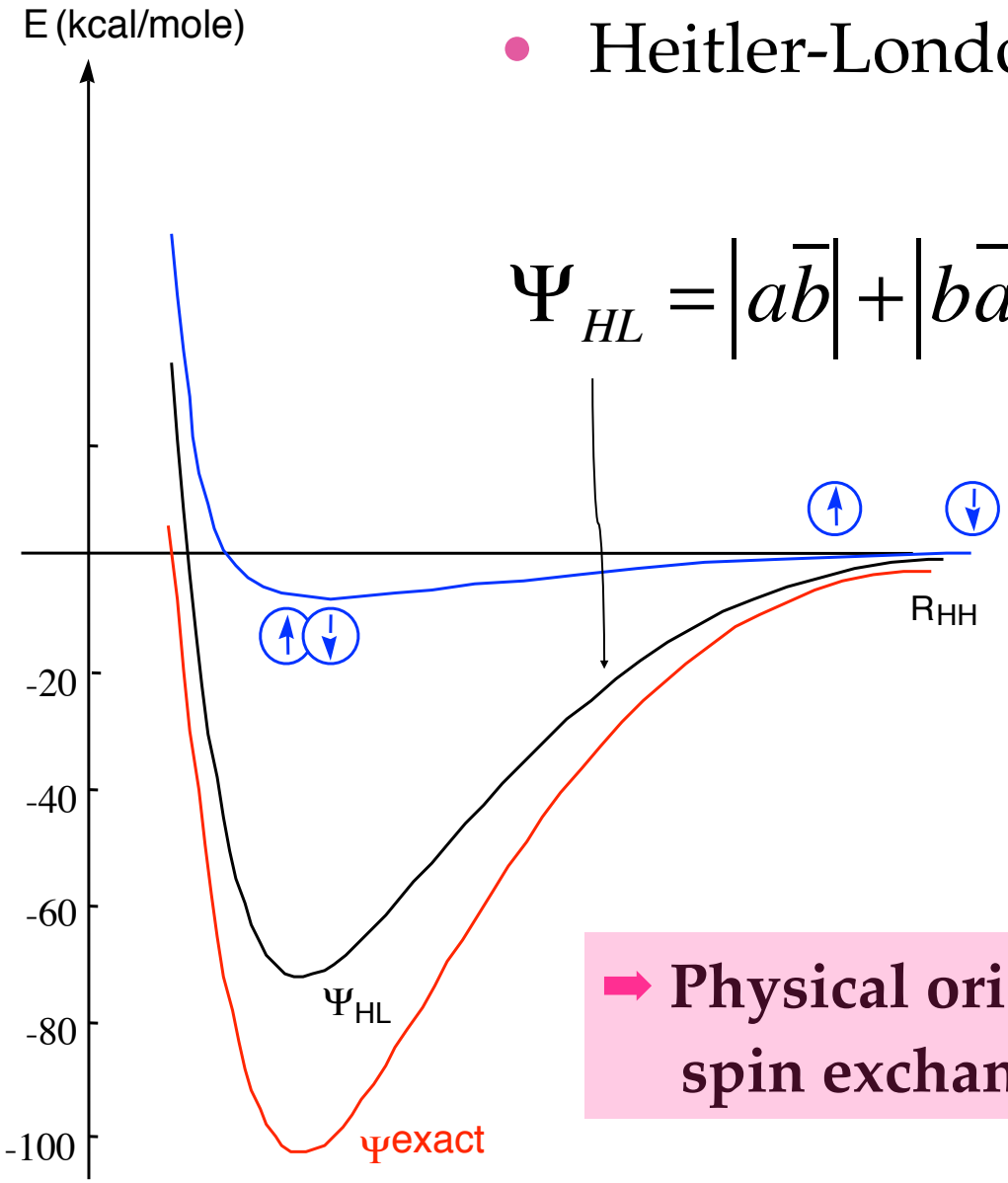
$$\Psi_{QC} = |a\,\bar{b}|$$

$$E_{QC} = \frac{\left\langle \left| a\bar{b} \right| \right| H^{\acute{e}l} \left| \left| a\bar{b} \right| \right\rangle}{\left\langle \left| a\bar{b} \right| \right| \left| a\bar{b} \right| \right\rangle} = h_{aa} + h_{bb} + J_{ab}$$

E_{QC} ~ cte along the dissociation curve

➡ **no spin exchange ⇨ no bonding**

Heitler-London



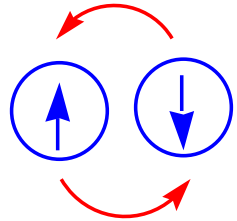
- Heitler-London (HF) wf :

$$\Psi_{HL} = |a\bar{b}| + |b\bar{a}|$$

$$E_{HL} = (\underbrace{h_{aa} + h_{bb} + J_{ab}}_{E_{QC}} + \underbrace{2h_{ab}S_{ab} + K_{ab}}_{<0})$$

Overlap (distance) dependant

➡ **Physical origin of the chemical bond : spin exchange between AOs**



Heitler-London

$$\Psi_S = \frac{|a\bar{b}| + |b\bar{a}|}{\sqrt{2(1+S_{ab}^2)}} \propto [a(1)b(2) + a(2)\,b(1)] \otimes [\alpha(s_1)\,\beta(s_2) - \alpha(s_2)\,\beta(s_1)],$$

antisymetric $\Rightarrow$ **Singlet**

$$\Psi_T = \frac{|a\bar{b}| - |b\bar{a}|}{\sqrt{2(1-S_{ab}^2)}} \propto [a(1)b(2) - a(2)\,b(1)] \otimes [\alpha(s_1)\,\beta(s_2) + \alpha(s_2)\,\beta(s_1)],$$

symetric $\Rightarrow$ **Triplet (M_S=0)**

Heitler-London

$$\Psi_S = \frac{|a\bar{b}| + |b\bar{a}|}{\sqrt{2(1+S_{ab}^2)}} \propto [a(1)b(2) + a(2)\,b(1)] \otimes [\alpha(s_1)\,\beta(s_2) - \alpha(s_2)\,\beta(s_1)],$$

antisymetric $\Rightarrow$ **Singlet**

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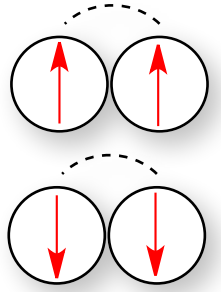
symetric $\Rightarrow$ **Triplet (M_S=0)**

Note that :

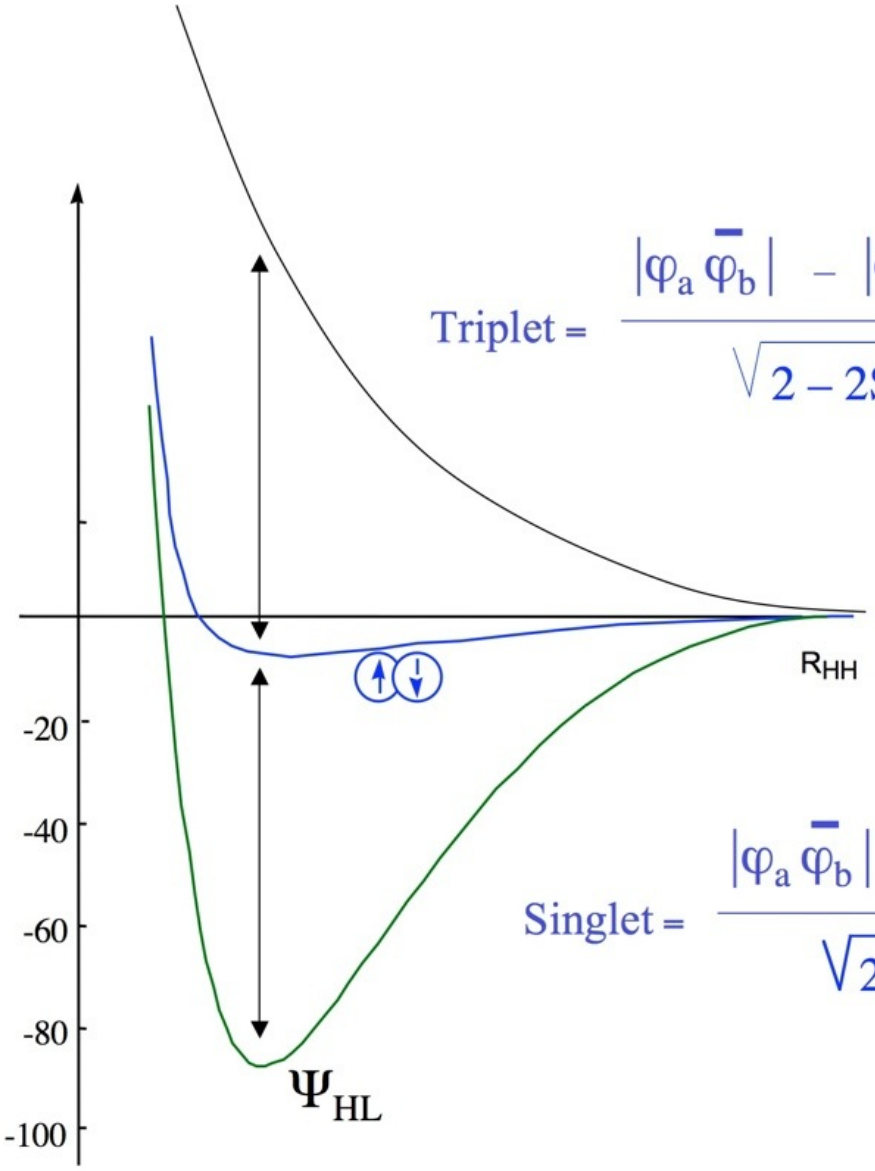
$$\Psi_T \propto |ab| = [a(1)b(2) - a(2)\,b(1)] \otimes [\alpha(s_1)\,\alpha(s_2)] \Rightarrow M_S = +1$$

$$\Psi_T \propto |\bar{a}\bar{b}| = [a(1)b(2) - a(2)\,b(1)] \otimes [\beta(s_1)\,\beta(s_2)] \Rightarrow M_S = -1$$



*... **all triplets have the same energy** as* $\hat{H}$ *is spin-independent*

Heitler-London



$$\text{Triplet} = \frac{|\varphi_a \bar{\varphi}_b| - |\varphi_b \bar{\varphi}_a|}{\sqrt{2-2S^2}}$$

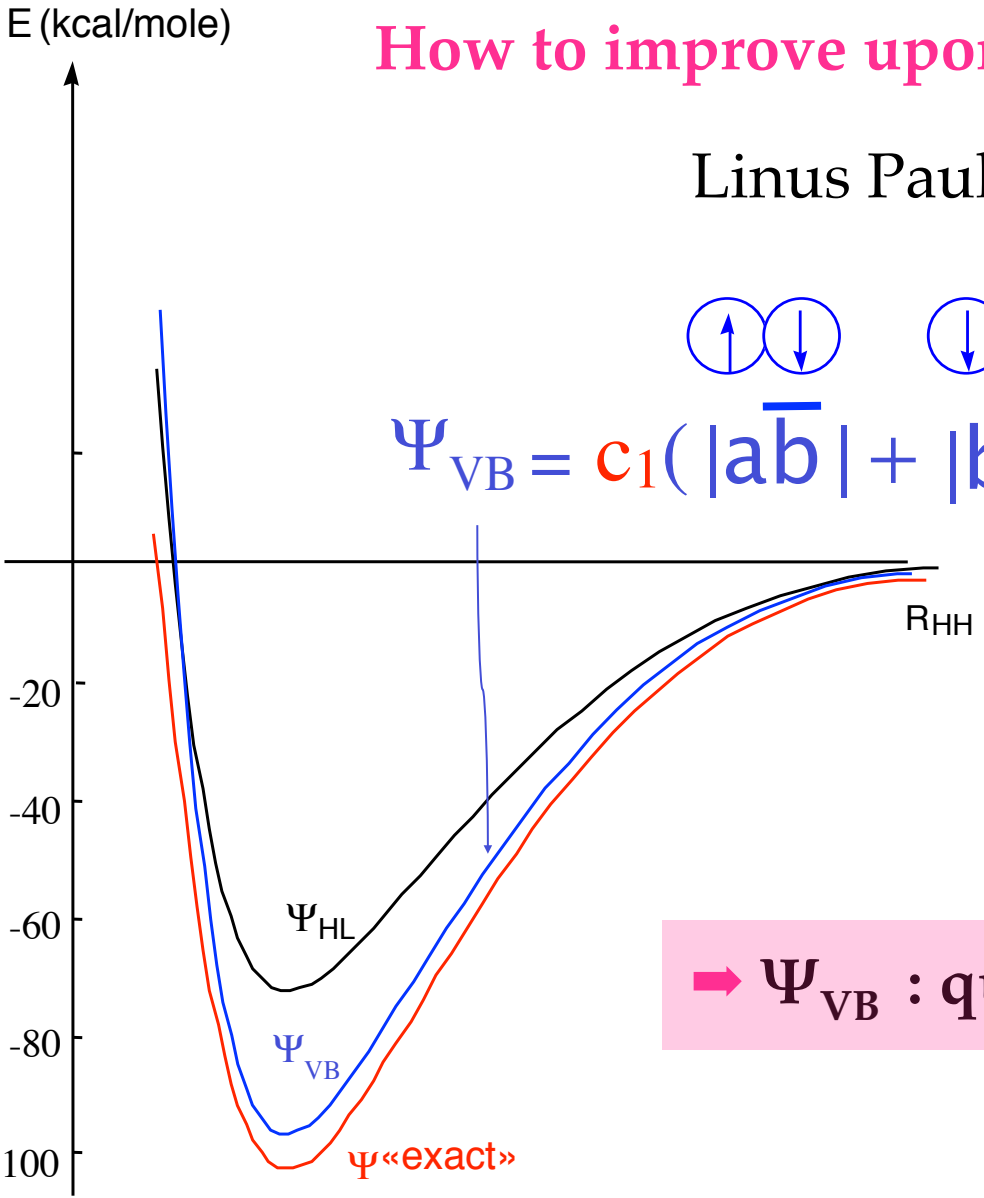
$$\text{Singlet} = \frac{|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|}{\sqrt{2+2S^2}}$$

$$E(T) = \frac{1}{\sqrt{(1-S_{ab}^2)}}(\underbrace{h_{aa} + h_{bb} + J_{ab}}_{E_{QC} \approx E(R_{HH} \to \infty)} \underbrace{- 2h_{ab}S_{ab} - K_{ab}}_{>0})$$

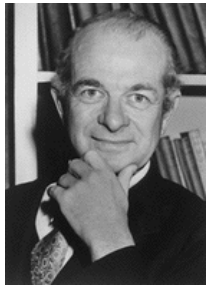
$$E(S) = \frac{1}{\sqrt{(1+S_{ab}^2)}}(\underbrace{h_{aa} + h_{bb} + J_{ab}}_{E_{QC} \approx E(R_{HH} \to \infty)} \underbrace{+ 2h_{ab}S_{ab} + K_{ab}}_{<0})$$

$S \to T$ gap $\approx 2De$

The VB wave function



How to improve upon the HL wave function ?



Linus Pauling (1931) :

$$\Psi_{VB} = c_1(|a\bar{b}| + |b\bar{a}|) + c_2(|a\bar{a}| + |b\bar{b}|)$$

Covalent + ionic superposition

➡ **Ψ_{VB} : quantum dressing of Lewis' model**

VB vs. MO

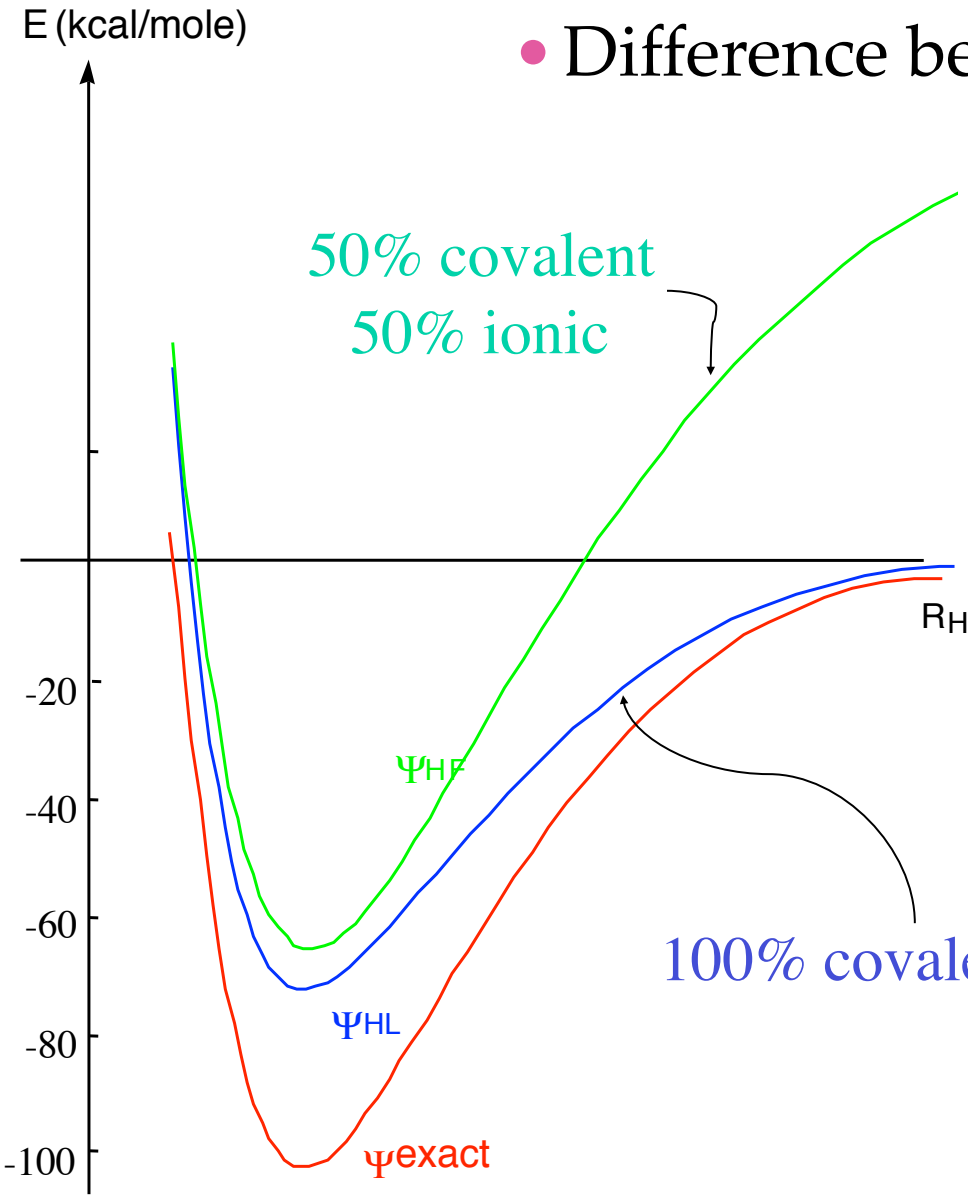
➡ Exercise 1 :

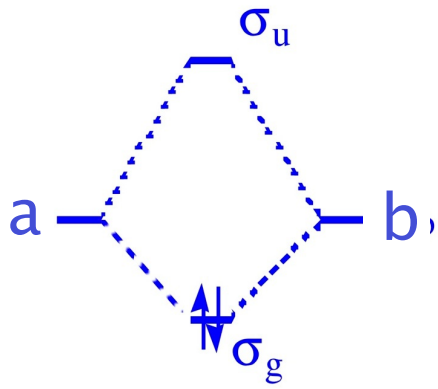
Expand the Hartree-Fock wave-function for H_2 (Hund-Mulliken) : $\Psi_{HF} = \frac{1}{\sqrt{2}}\left|\sigma_g \overline{\sigma_g}\right|$ in in the basis of VB determinants (built on atomic orbital). We will use : $\sigma_g = N'(a+b)$.

Make the correspondance with Pauling's VB wave-function for H_2.

VB vs. MO

- Difference between HL and HF ?





$$\sigma_u = \frac{1}{\sqrt{2(1+S)}}(a-b) =$$

$$\sigma_g = \frac{1}{\sqrt{2(1+S)}}(a+b) =$$

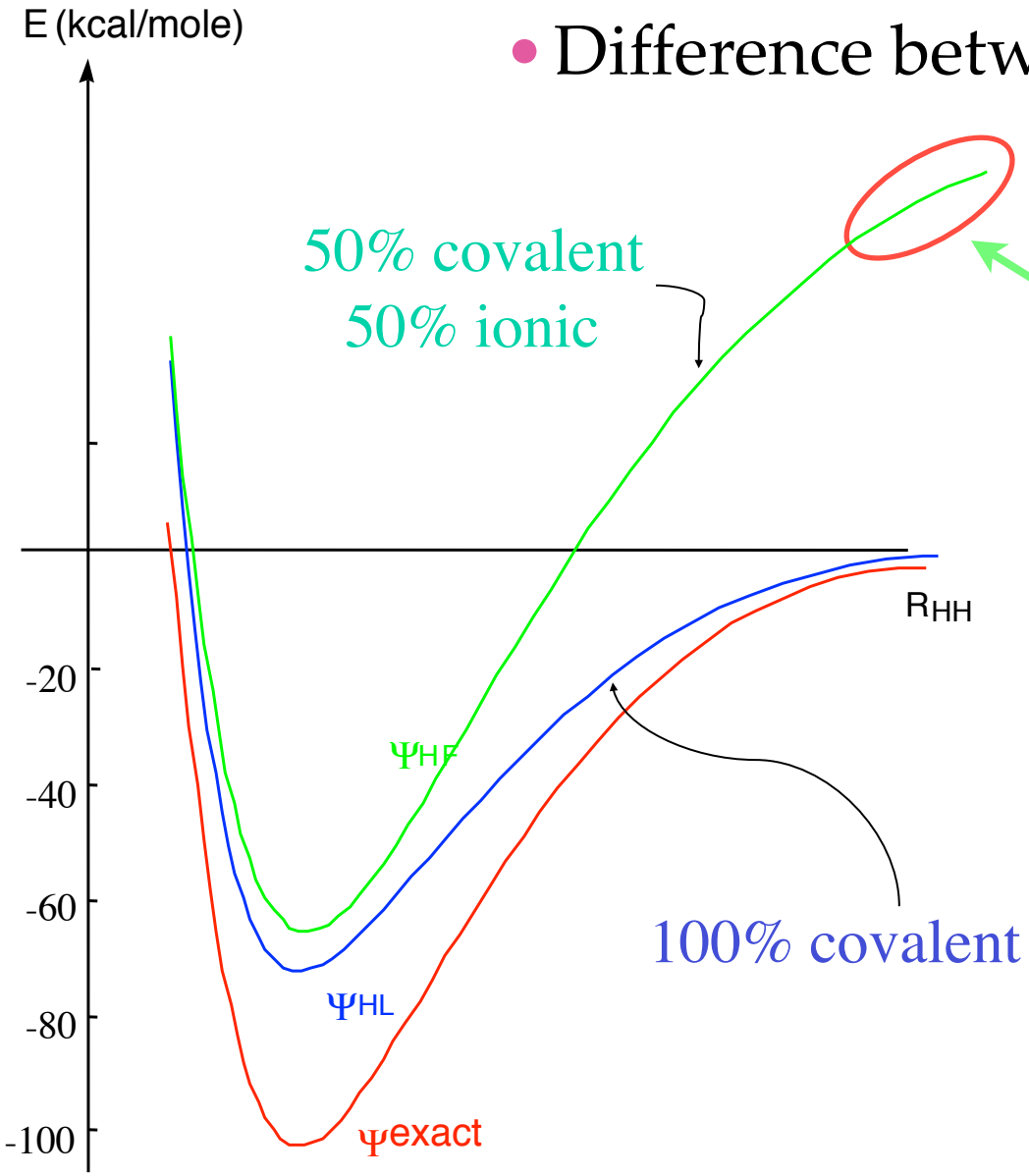
$$\Psi_{HF} = |\sigma_g \bar{\sigma}_g|$$

$$= \underbrace{|a\bar{b}| + |b\bar{a}|}_{\mathbf{H\bullet\!-\!\!-\!\bullet H}} + \underbrace{|a\bar{a}| + |b\bar{b}|}_{\mathbf{H^-H^+ + H^+H^-}}$$

50% covalent 50% ionic

VB vs. MO

- Difference between HL and HF ?

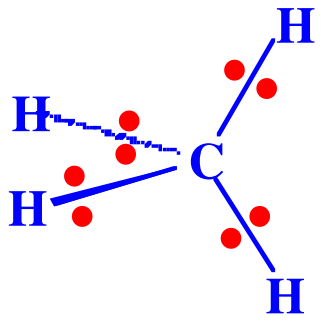


Optimal ≈ 80% covalent
20% ionic

Writing VB wave functions

- Extension to the general case :

Lewis :

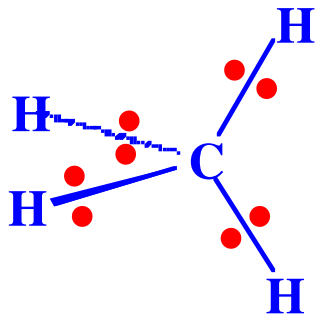


- We want to construct a VB w.f. which corresponds to Lewis' picture
- Which orbitals to use ?

Writing VB wave functions

- Extension to the general case / **1) general localized orbital:**

Lewis :



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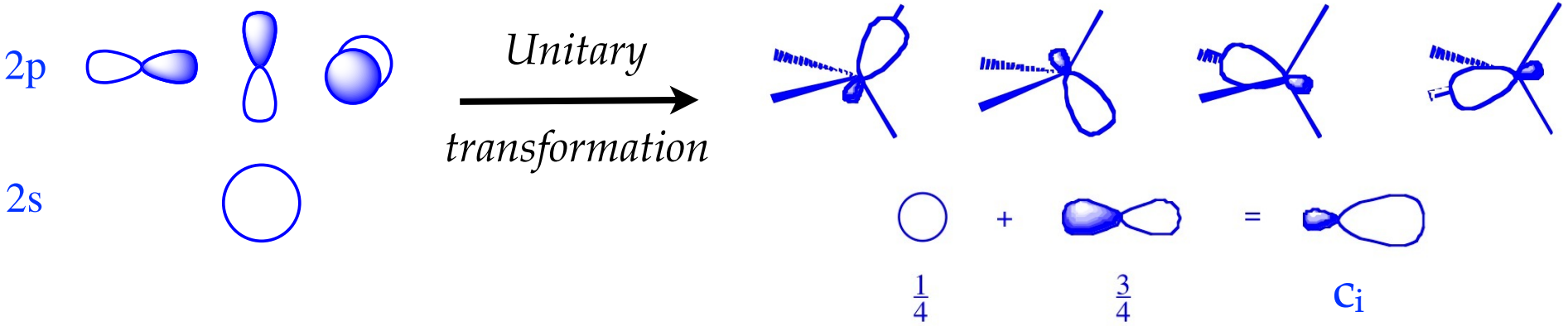
Atomic Orbitals **Hybrid Orbitals**

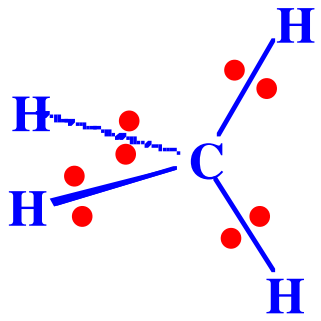


Four equivalent directional sp^3 orbitals

Writing VB wave functions

- Extension to the general case / **1) general localized orbital:**

Lewis :



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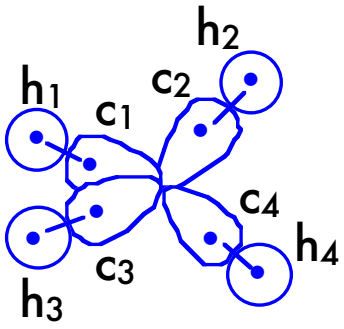
HL :



$$\Psi_{HL} = \left|(c_1\overline{h_1} + h_1\overline{c_1})(c_2\overline{h_2} + h_2\overline{c_2})(c_3\overline{h_3} + h_3\overline{c_3})(c_4\overline{h_4} + h_4\overline{c_4})\right|$$

Electrons occupy **localized** orbitals (atomics, hybrids,...)

A **bond** = two singlet-coupled electrons in two orbitals (+minor ionics)

Writing VB wave functions

- Extension to the general case / **2) active electrons/orbitals:**

Not all electrons are treated at the VB level : **inactive** / **active** separation

$$\psi_{VB} = \mathcal{A}\left[\{inactives\} \bullet \{actives\}\right]$$

Writing VB wave functions

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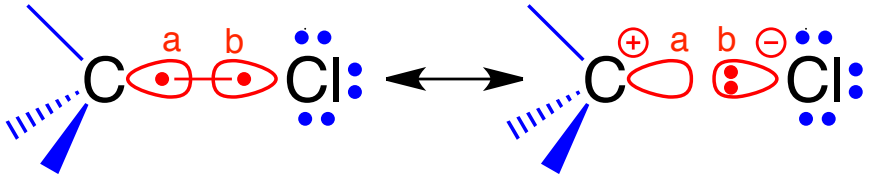

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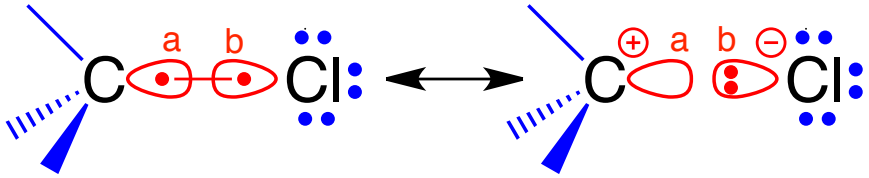


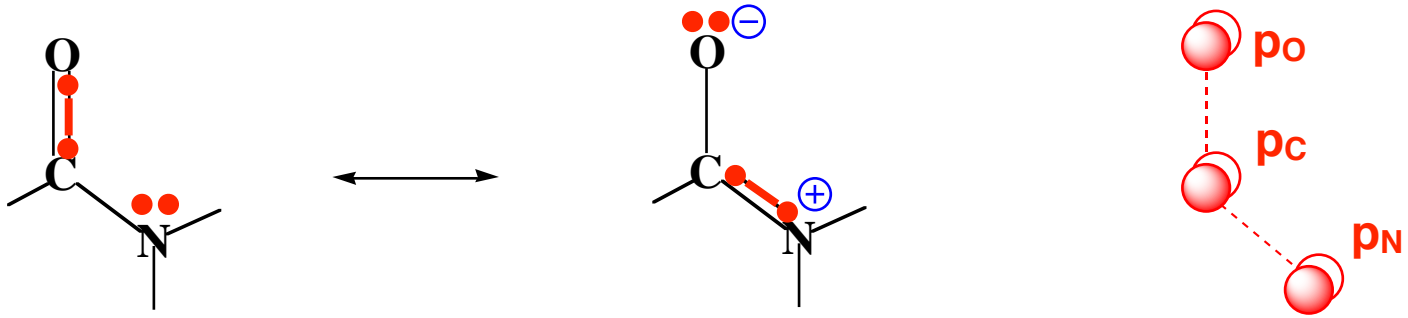
$$\psi_{VB} = \left| \underbrace{\sigma_1\sigma_2\ldots\sigma_n}_{\text{delocalized MOs}} \left(a\bar{b} - \bar{a}b\right) \right| + \left| \underbrace{\sigma_1\sigma_2\ldots\sigma_n}_{\text{delocalized MOs}} b\bar{b} \right|$$

- an **active space** of electrons / orbitals treated at the **VB level**
- **the rest** (called inactive or «spectators») at the **MO level**

- The active space chosen depending on the chemical problem

Writing VB wave functions

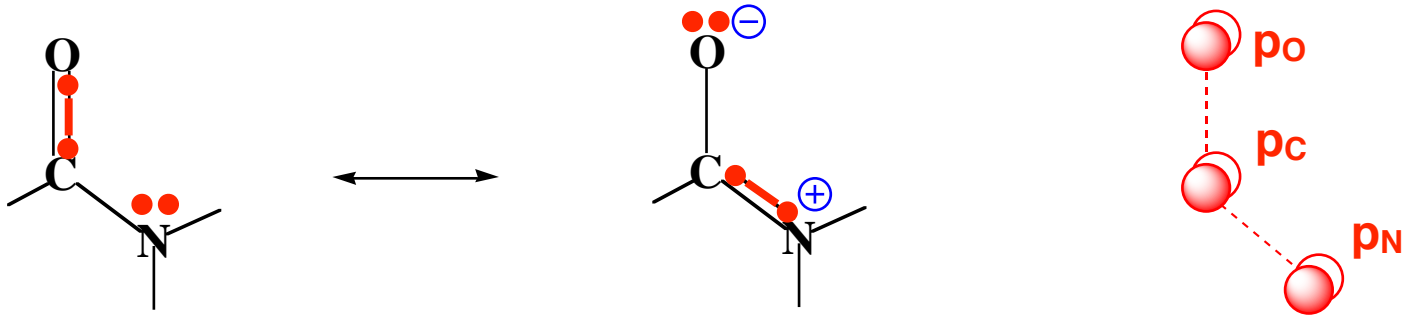
- Extension to the general case / **3) multi-structure:**



1 **2**

Writing VB wave functions

- Extension to the general case / **3) multi-structure:**



1 **2**

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

$$= C_1\left|p_N\,\overline{p_N}\,(p_O\,\overline{p_C} + p_C\,\overline{p_O})\right| + C_2\left|p_O\,\overline{p_O}\,(p_C\,\overline{p_N} + p_N\,\overline{p_C})\right|$$

➡ VB wave function : two **resonating** components,
each one corresponding to one of the **2 structures**

Writing VB wave functions

➡ Exercise 2 :

We want to study the SN2 reaction using VB theory.

1. How many active electron and orbitals do we have to consider?
2. Write a complete basis of Lewis structure for this problem.
3. Write the mathematical expression of the corresponding VB structures
4. What structures describe the reactant electronic structure ? The product electronic structure ?
5. What will be the major structure(s) at the transition state geometry, for the SN2 reaction on the carbon? On the silicium?

Writing VB wave functions

➡ **Exercise 2 :**

It is a 4e in 3 orbitals problem:

Writing VB wave functions

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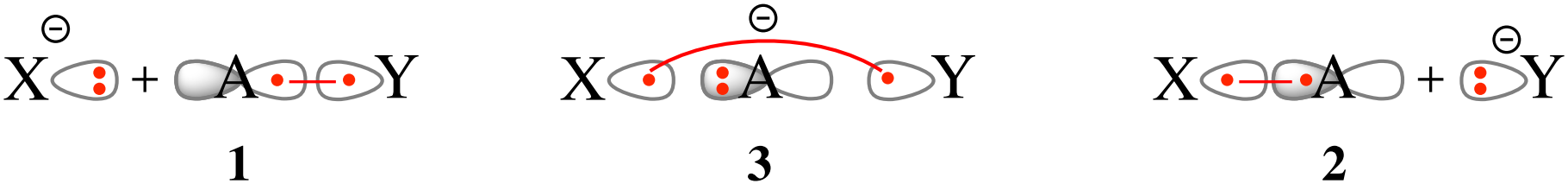
It is a 4e in 3 orbitals problem:

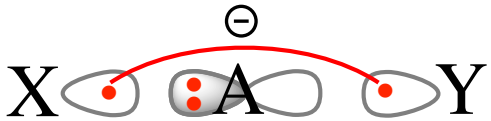


Writing VB wave functions

➡ Exercise 2 :

It is a 4e in 3 orbitals problem:

1



3

2

6

4

5

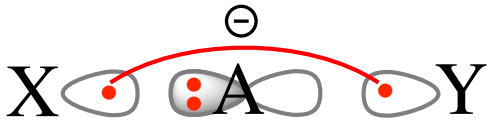
Writing VB wave functions

➡ Exercise 2 :

It is a 4e in 3 orbitals problem:

1

$$|x\bar{x}(a\bar{y}+\bar{a}y)|$$



3

$$|a\bar{a}(x\bar{y}+\bar{x}y)|$$

2

$$|y\bar{y}(x\bar{a}+a\bar{x})|$$

6

$$|x\bar{x}a\bar{a}|$$

4

$$|x\bar{x}y\bar{y}|$$

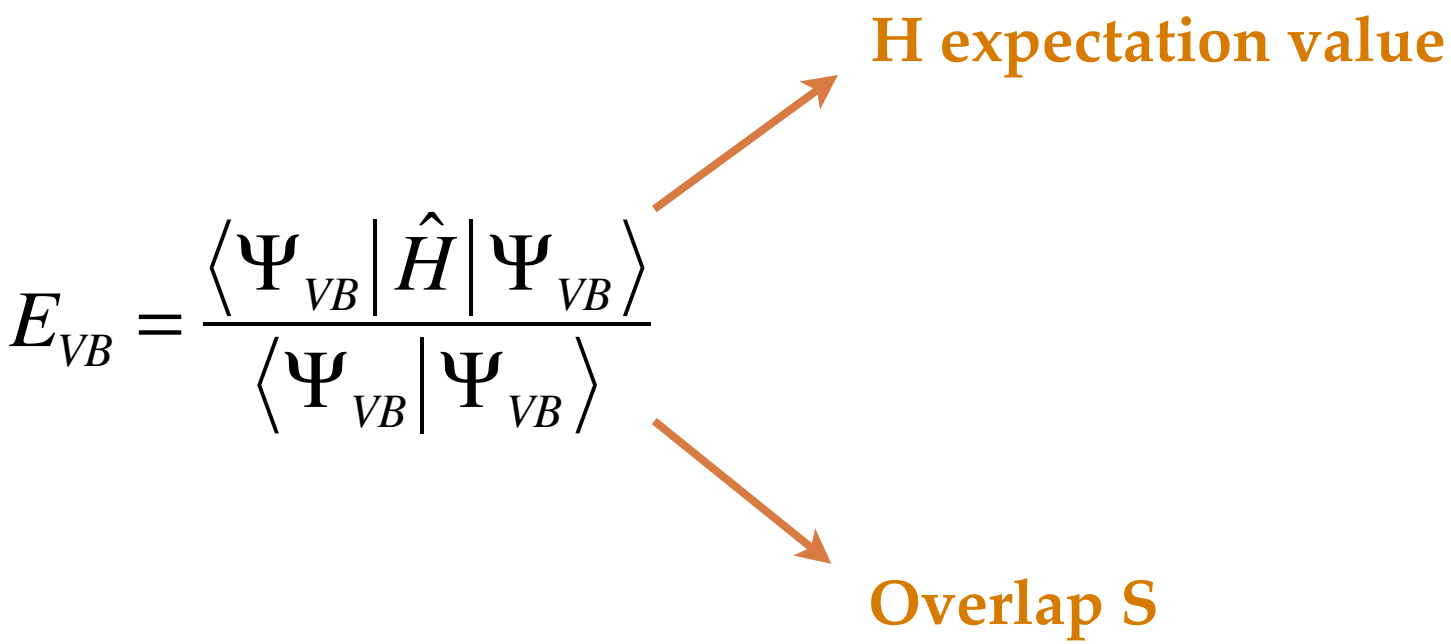
5

$$|a\bar{a}y\bar{y}|$$

Qualitative Valence Bond

Qualitative VB

What we wan't to calculate simple expressions for:



…for a specific $\mathbf{\Psi}_{VB}$ corresponding to

n electrons in N orbitals and a given spin state

Qualitative VB

$\Rightarrow$ **This is a « Hückel-type » version of VB theory**

- **Basic ingredients :**

  1) Effective Hamiltonian : $\mathbf{H^{eff} = h^{eff}(1) + h^{eff}(2) + h^{eff}(3) + \ldots}$

$$with: h^{eff}(i) = -\frac{1}{2}\nabla_{r_i}^2 - \frac{Z}{r_i} + \underbrace{\mathrm{Rep}(i)}_{\substack{averaged \\ repulsion}}$$

Qualitative VB

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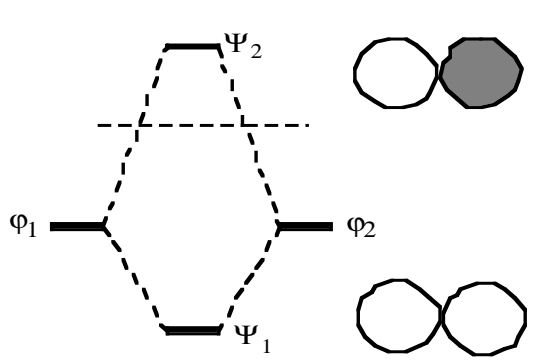
2) Parametrization : ε, β, **S**

Same as in Hückel theory :

$$\begin{cases} \varepsilon_i : \text{orbital i self-energy} & = \int a(1)h(1)a(1)d\tau_1 \\ \beta : \text{resonance integral} & = \int a(1)h(1)b(1)d\tau_1 \\ S : \text{overlap integral} & = \int a(1)b(1)d\tau_1 \end{cases}$$



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

$\frac{\varepsilon+\beta}{(1+S)}$

Qualitative VB

- **Basic ingredients :**

  1) Effective Hamiltonian : $\mathbf{H^{eff} = h^{eff}}(1) + \mathbf{h^{eff}}(2) + \mathbf{h^{eff}}(3) + \ldots$

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Qualitative VB

- **Basic ingredients :**

  1) Effective Hamiltonian : $\mathbf{H^{eff} = h^{eff}(1) + h^{eff}(2) + h^{eff}(3) + \ldots}$

  2) Parametrization : **ε, β, S**

  3) Choice of an **origin of energies (shift)**:

$$\begin{cases} \varepsilon_a = h_{aa} - \dfrac{1}{2}(h_{aa} + h_{bb}) \\ \beta_{ab} = h_{ab} - \dfrac{1}{2}(h_{aa} + h_{bb}) \end{cases}$$

  $\Rightarrow$ new energy scale where : $\varepsilon_a + \varepsilon_b = 0$

Qualitative VB

- **Basic ingredients :**

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$\Rightarrow$ new energy scale where : $\varepsilon_a + \varepsilon_b = 0$

4) « **Nearest neighbors** » **approximation**:

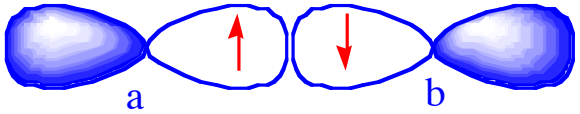
Neglect S_{ac} and h_{ac} if **a** and **c** are not nearest neighbors

=> We'll restrict to the **two orbital case**

Qualitative VB

- **Elementary interactions energies :**

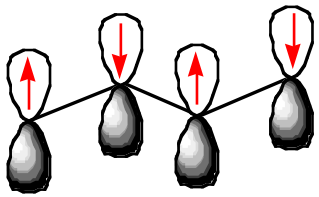
1) The QC state :



$$\Psi_{QC} = \left|a\bar{b}\right|$$

$$\left\langle \Psi_{QC} \left| \hat{H}^{eff} \right| \Psi_{QC} \right\rangle = \left\langle \left(\left|a\bar{b}\right|\right) \left| \hat{h}_1 + \hat{h}_2 \right| \left(\left|a\bar{b}\right|\right) \right\rangle \propto \varepsilon_1 + \varepsilon_2 = 0$$

Same for all **spin-alternant determinants** (choice of energy reference) :

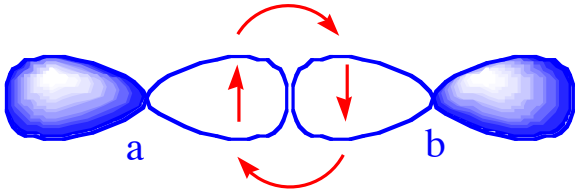


$E_{QC}=0$

Qualitative VB

- **Elementary interactions energies :**

  2) The two electron bond :

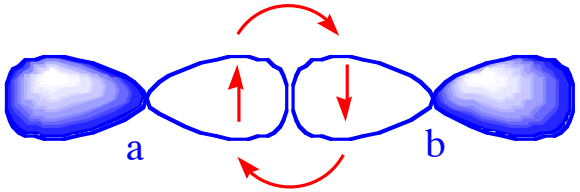


$$\Psi_{2e} \propto \left|a\bar{b}\right| + \left|b\bar{a}\right|$$

Qualitative VB

- **Elementary interactions energies :**

  2) The two electron bond :



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$$\langle\Psi|\hat{H}^{eff}|\Psi\rangle \Rightarrow \begin{cases} \text{Symmetric terms (two)} : \left\langle \left(\left|a\bar{b}\right|\right) \middle| \hat{h}_1 + \hat{h}_2 \middle| \left(\left|a\bar{b}\right|\right) \right\rangle = \varepsilon_1 + \varepsilon_2 = 0 \\ \text{Dissymmetric terms (two)} : \left\langle \left(\left|a\bar{b}\right|\right) \middle| \hat{h}_1 + \hat{h}_2 \middle| \left(\left|b\bar{a}\right|\right) \right\rangle = +2\beta_{ab}S_{ab} \end{cases}$$

Qualitative VB

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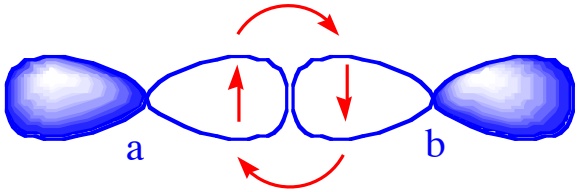

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$$\Rightarrow E(2e) = \frac{+2\beta S}{1+S^2} = D_e(2e)$$

Qualitative VB

- **Elementary interactions energies :**

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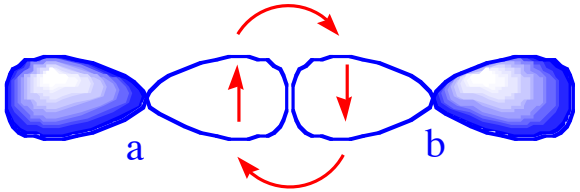

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Qualitative VB

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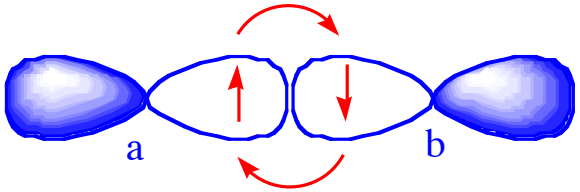

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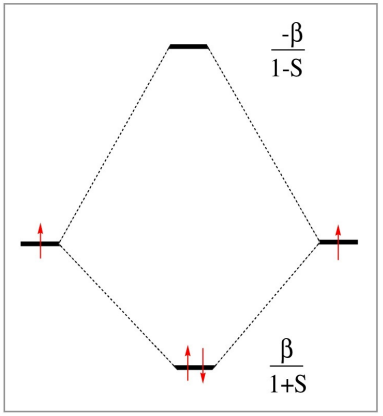


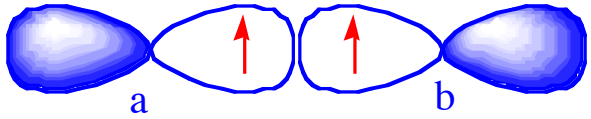
Different in MO-Hückel theory :

$D_e = 2\beta/(1+S)$

Qualitative VB

- **Elementary interactions energies :**

  3) The triplet repulsion :

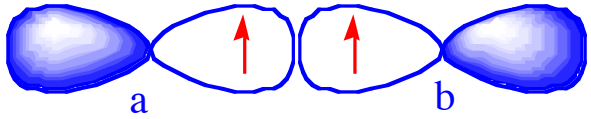


$$\Psi_T \propto \left|a\bar{b}\right| - \left|b\bar{a}\right|$$

Qualitative VB

- **Elementary interactions energies :**

3) The triplet repulsion :



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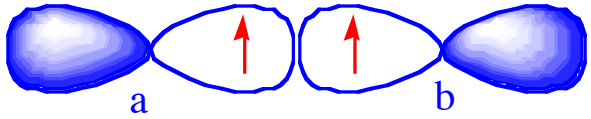
$$\Rightarrow E(T) = \frac{-2\beta S}{1-S^2}$$

Qualitative VB

- **Elementary interactions energies :**

3) The triplet repulsion :



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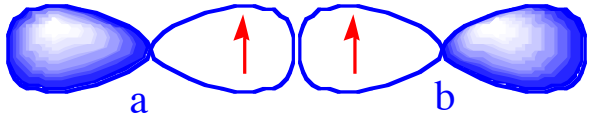
$$\Rightarrow E(T) = \frac{-2\beta S}{1-S^2} \approx -2\beta S$$

Qualitative VB

- **Elementary interactions energies :**

3) The triplet repulsion :



$$\Psi_T \propto \left|a\bar{b}\right| - \left|b\bar{a}\right|$$

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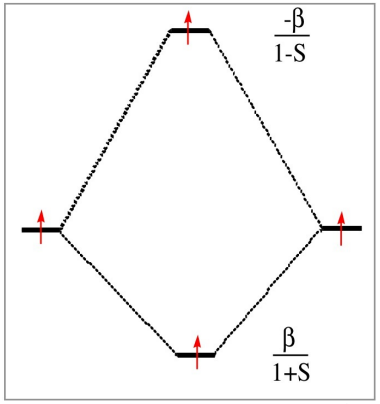
$$\Rightarrow E(T) = \frac{-2\beta S}{1-S^2} \approx -2\beta S$$

Same in MO-Hückel theory :



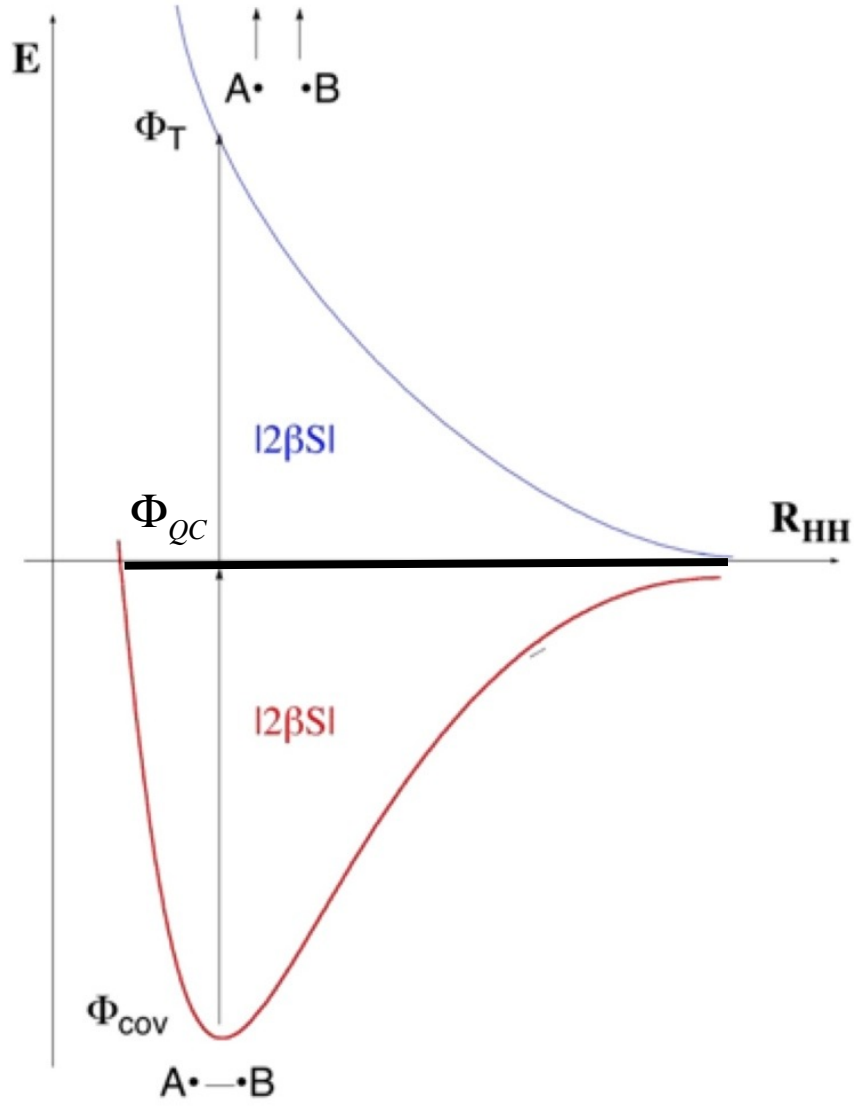
$$E = \frac{\beta}{1+S} + \frac{-\beta}{1-S} = \frac{-2\beta S}{1-S^2}$$

Qualitative VB

- **Elementary interactions energies :**

- Part 1 :

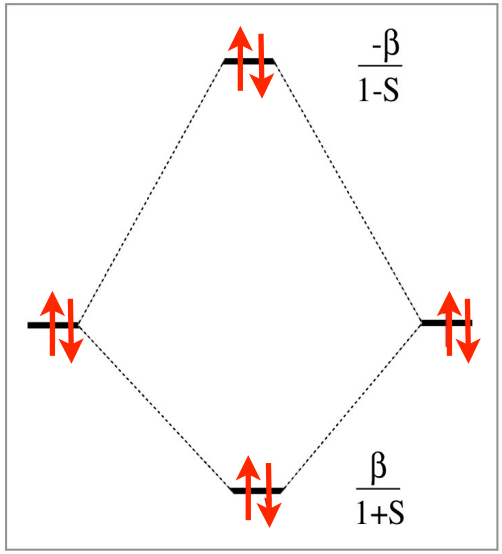
$\Delta E_{ST} \approx 2De$



Qualitative VB

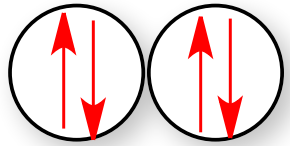
4) The 4e repulsion (two electron pairs) :

MO



$$E(4e_{rep}) = \frac{2\beta}{1+S} - \frac{2\beta}{1-S} = \ldots = \frac{-4\beta S}{1-S^2}$$

VB



$$\Psi(4e_{rep}) = \frac{|ab\bar{a}\bar{b}|}{1-S^2}$$

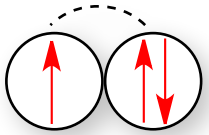
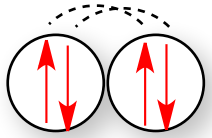
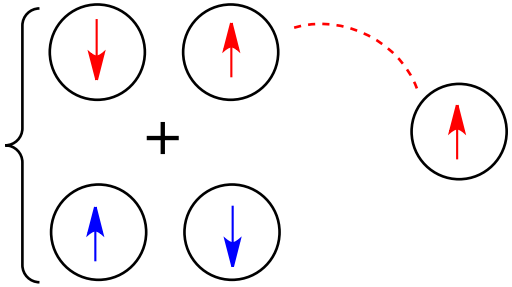
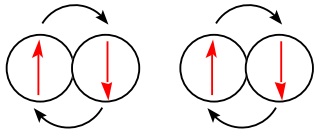
$$E(4e_{rep}) = \frac{-4\beta S}{1-S^2} \approx -4\beta S$$

$\Rightarrow$ **Twice the triplet repulsion**

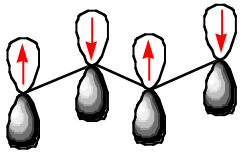
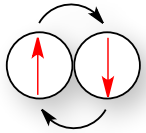
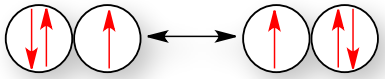
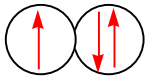
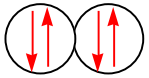
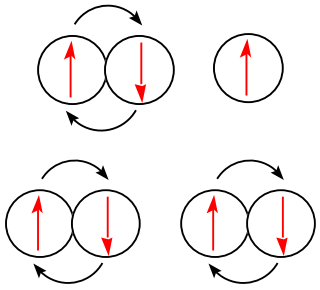
Qualitative VB

- **Elementary interactions energies :**

4) All repulsions :

		VB	MO
• 3e repulsion : **same** as triplet :		≈ –2ßS	Same
• 4e repulsion : **two times** triplet :		≈ –4ßS	Same
• NCI : **half time** triplet :			
bond… single electron		≈ –ßS	/
bond… bond		≈ –ßS	/

Qualitative VB

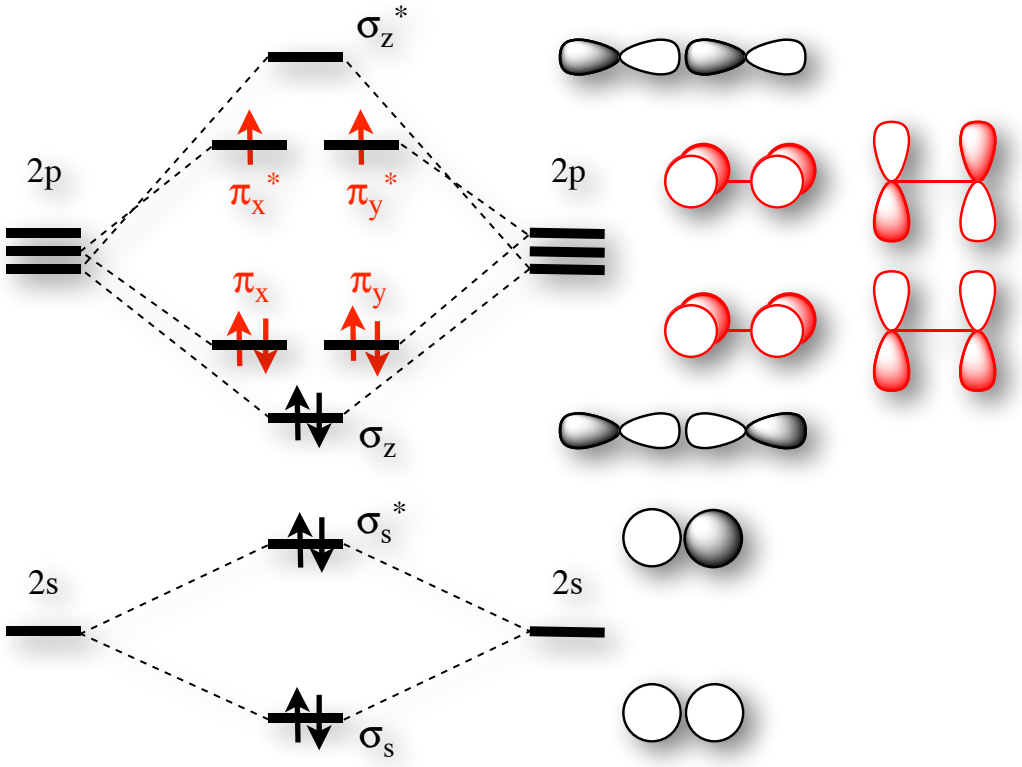
		VB	MO
spin-alternated det.		0	(VB only)
2-e bond (A–B) =		$2ßS/(1+S^2)$	$2ß/(1+S)$
3-e bond(A∴B) =		$ß(1-3S)/(1-S^2)$	Same as VB
triplet=3-e repulsion		$-2ßS/(1-S^2)$	Same as VB
4-e repulsion		$-4ßS/(1-S^2)$	Same as VB
bond…single e⁻ and bond...bond		$-ßS/(1-S^2)$	(VB only)

Qualitative VB

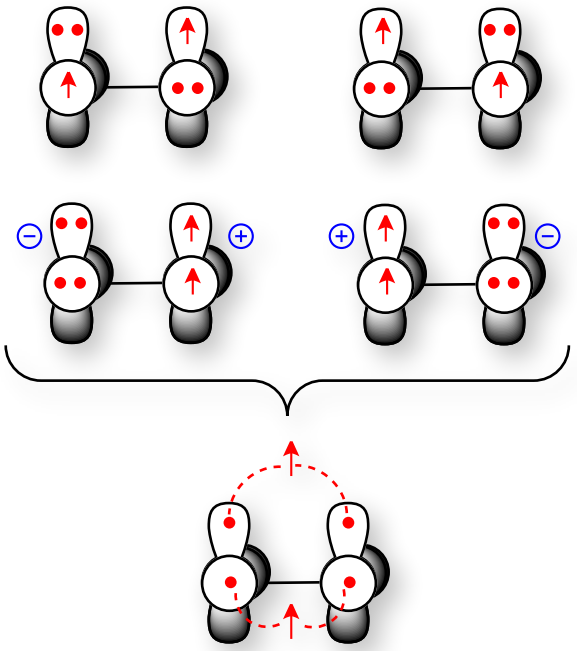
➡ **Exercise 4 : ground state of O_2 :**

Dioxygen triplet ground state : two π-type 3e-bonds :

MO



VB



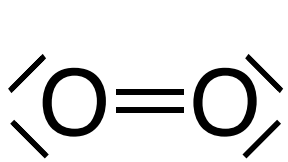
Qualitative VB

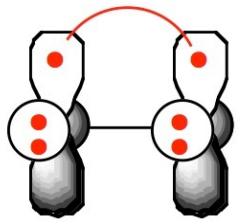
➡ Exercise 3 : ground state of O_2 :

1) Calculate the energy expression for the π system of the lowest triplet state of the dioxygen molecule, at the qualitative VB level (using the complete expressions with denominators)

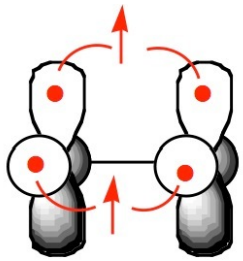
2) Same question for the closed-shell singlet state, corresponding to the usual Lewis structure used for this molecule.

3) Take the difference, and conclude which state is predicted to be the lowest at the qualitative VB level of theory.





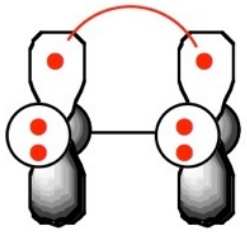
Singlet



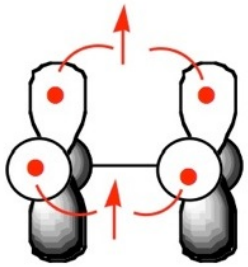
Triplet

Qualitative VB

➡ **Exercise 4 : ground state of O2 (answer) :**



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



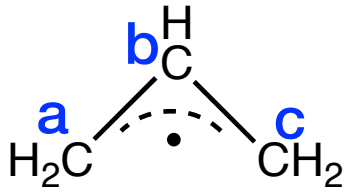
$$E(T) = 2\beta\,(1 - 3S)/(1-S^2)$$

$$E(S) - E(T) = -2\beta\,(1-S)^2/(1-S^4) > 0$$

➡ *The triplet state is always the lower*

Qualitative VB

➡ Exercise 4 : spin polarization in allyl radical :



The allyl radical is a planar molecule with three electrons in its π system (in 3 p_C orbitals).

1) What are the three possible covalent structures for the allyl radical ? Express their energy at the qualitative VB level, and show that two of them are degenerate.

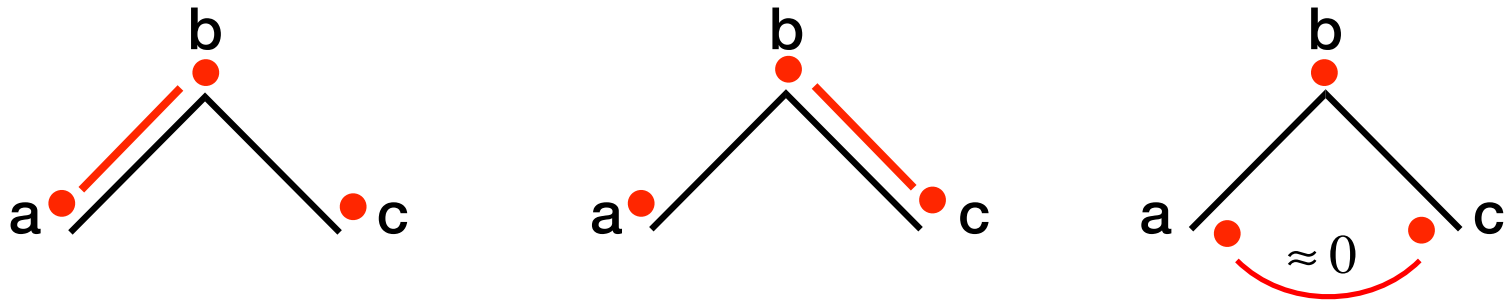
2) Show that the third structure can be expressed as a linear combination of the first two structures, and thus that only two of the three covalent structures form a complete basis of non-redundant structures (Rumer basis).

3) EPR measurements show that the spin density on the central atom is –0.2 (ie : excess of down spin electron), whereas –1. value of is predicted at the UHF level. Express the HL w.f. corresponding to the ground state, and calculate the predicted spin density.

Continuation of the exercise : https://wiki.lct.jussieu.fr/workshop/index.php/VBTutorial2

Qualitative VB

➡ **Exercise 4 : spin polarization in allyl radical :**



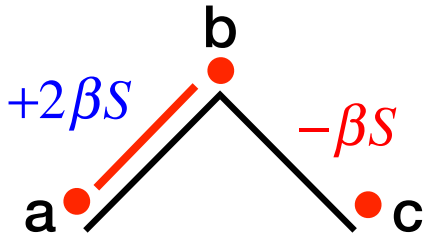
$$\psi(I) = \frac{1}{\sqrt{2}}(|a\bar{b}c| + |b\bar{a}c|)$$

$$\psi(II) = \frac{1}{\sqrt{2}}(|ab\bar{c}| + |ac\bar{b}|)$$

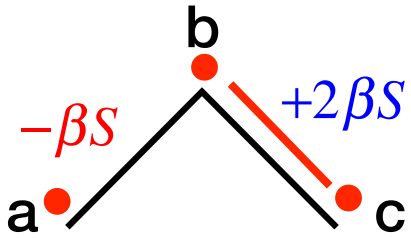
$$\psi(III) = \frac{1}{\sqrt{2}}(|ab\bar{c}| + |cb\bar{a}|) = \psi(I) + \psi(II)$$

Qualitative VB

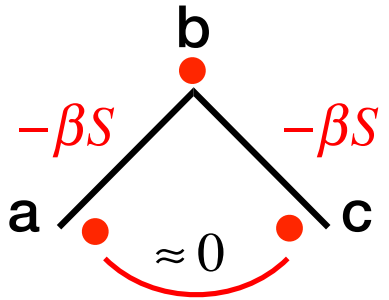
➡ **Exercise 4 : spin polarization in allyl radical :**



$$\Rightarrow E(I) = +\beta S < 0$$



$$\Rightarrow E(II) = +\beta S < 0$$

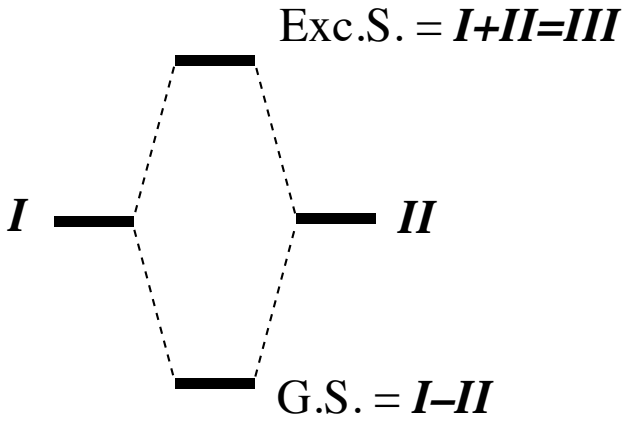


$$\Rightarrow E(III) = -2\beta S$$

$$\psi(I) = \frac{1}{\sqrt{2}}(|a\bar{b}c| + |b\bar{a}c|)$$

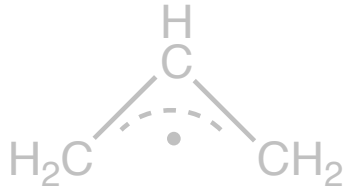
$$\psi(II) = \frac{1}{\sqrt{2}}(|ab\bar{c}| + |ac\bar{b}|)$$

$$\psi(III) = \frac{1}{\sqrt{2}}(|ab\bar{c}| + |cb\bar{a}|) = \psi(I) + \psi(II)$$



Qualitative VB

➡ Exercise 4 : spin polarization in allyl radical :



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1) What are the three possible covalent structures for the allyl radical ? Express their energy at the qualitative VB level, and show that two of them are degenerate.

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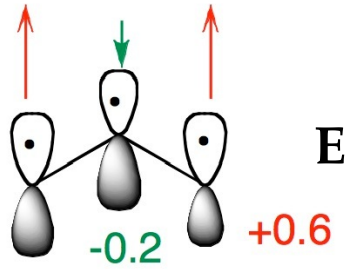
Continuation of the exercise : https://wiki.lct.jussieu.fr/workshop/index.php/VBTutorial2

Qualitative VB

➡ Exercise 4 : spin polarization in allyl radical :

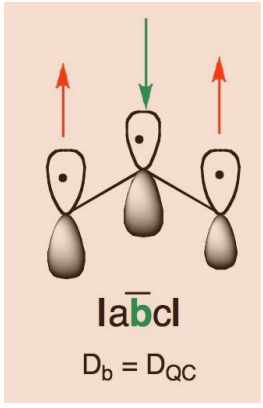
$$\psi_{GS} = \frac{1}{\sqrt{6}}(2|a\bar{b}c| + |b\bar{a}c| + |a\bar{c}b|)$$

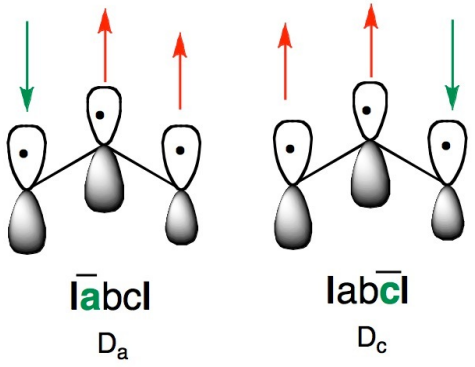
Spin density on center b : $\rho_b = \frac{1}{6}(\underbrace{c_2^2 + c_3^2}_{\text{alpha spin on b}} - \underbrace{c_1^2}_{\text{beta spin on b}}) = -0.33$

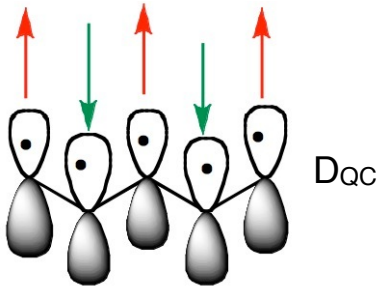


EPR

⇒ much closer to experiment than UHF (–0.8 on central C)







☞ The spin alternant determinant D_{QC}, having the lowest energy, control the spin density pattern

☞ General rule, works for all polyenes

VB diagrams

VB diagrams by Shaik and Pross

- A powerful VB model for rationalizing reactivity :

J. Am. Chem. Soc. **1981**, *103*, 3692–3701

What Happens to Molecules as They React? A Valence Bond Approach to Reactivity

Sason S. Shaik

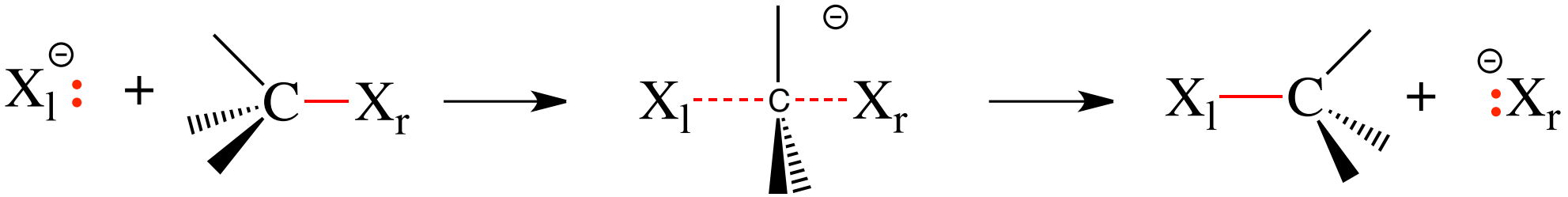
Contribution from the Department of Chemistry, Ben-Gurion University of the Negev, P.O.B. 653, Beer Sheva, 84120, Israel. *Received June 12, 1980*

• Developed and applied since then to a huge number of organic chemical reactions, inorganic reactions, clusters and metalloenzymes

• Reviews : https://wiki.lct.jussieu.fr/workshop/index.php/VB_tutorial

Principles

- VB diagram for the S_N2 reaction :



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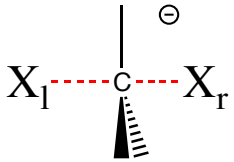
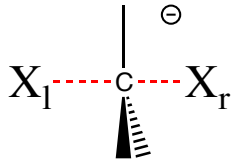
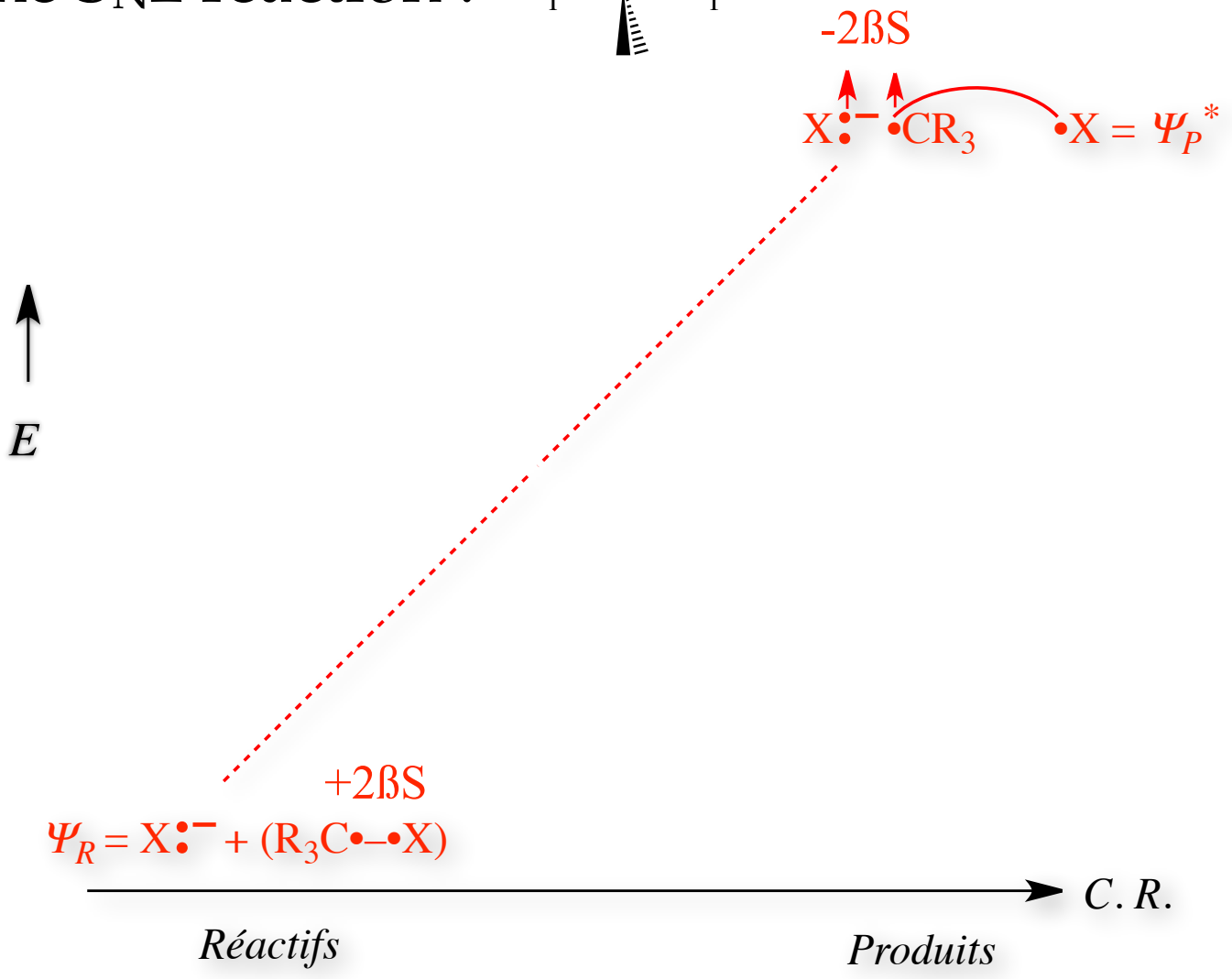
- VB diagram for the S_N2 reaction : 

$$\Psi_R \propto \left| x_l \overline{x_l} (c \overline{x_r} + x_r \overline{c}) \right|$$

$$\Psi_R = X:^- + (R_3C\bullet\text{–}\bullet X) \quad (+2\beta S)$$

Principles

- VB diagram for the S_N2 reaction : 



$$\Psi_R \propto \left| x_l \overline{x_l} (c \overline{x_r} + x_r \overline{c}) \right|$$

Principles

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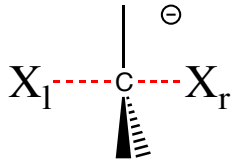
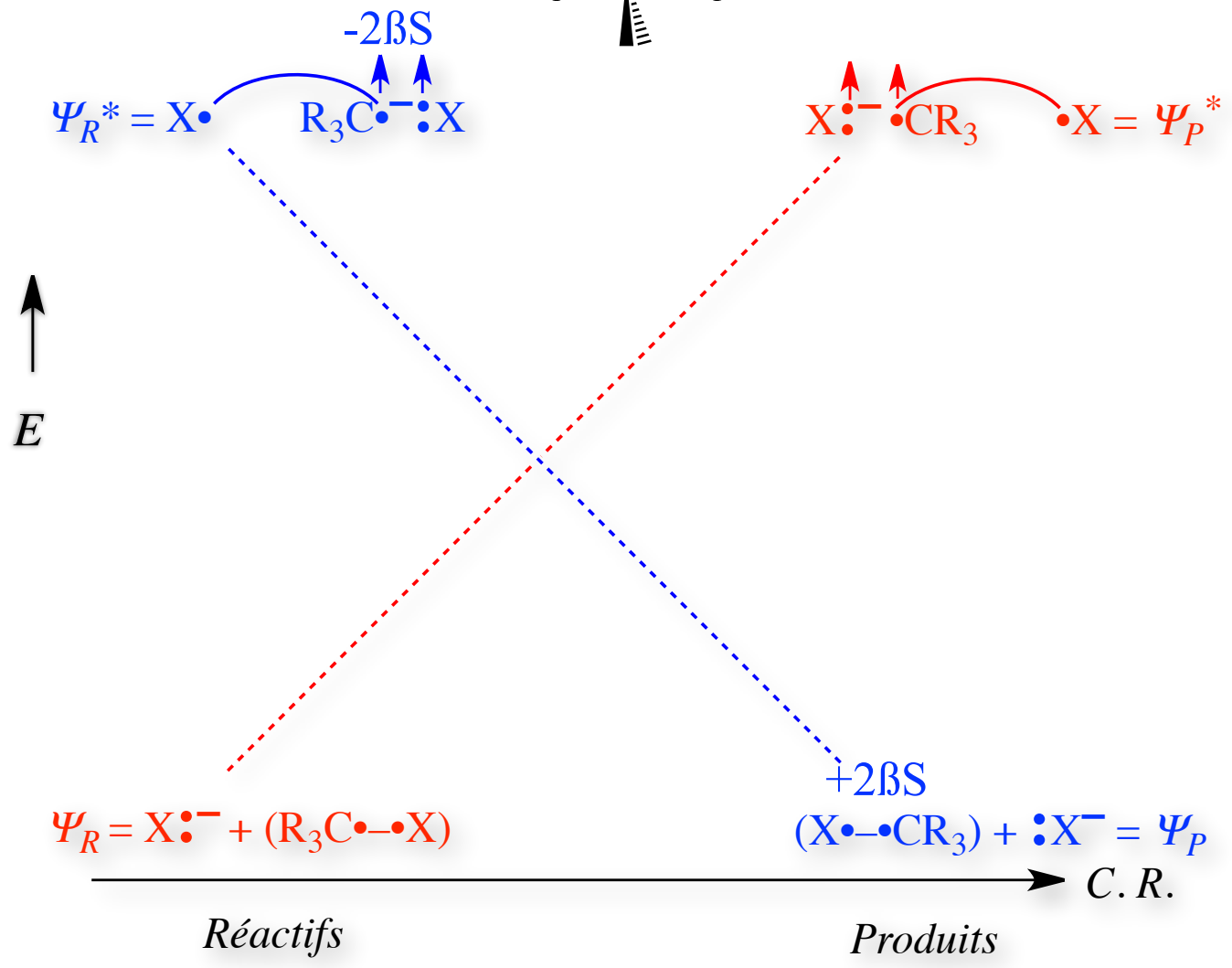
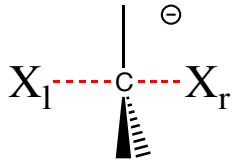


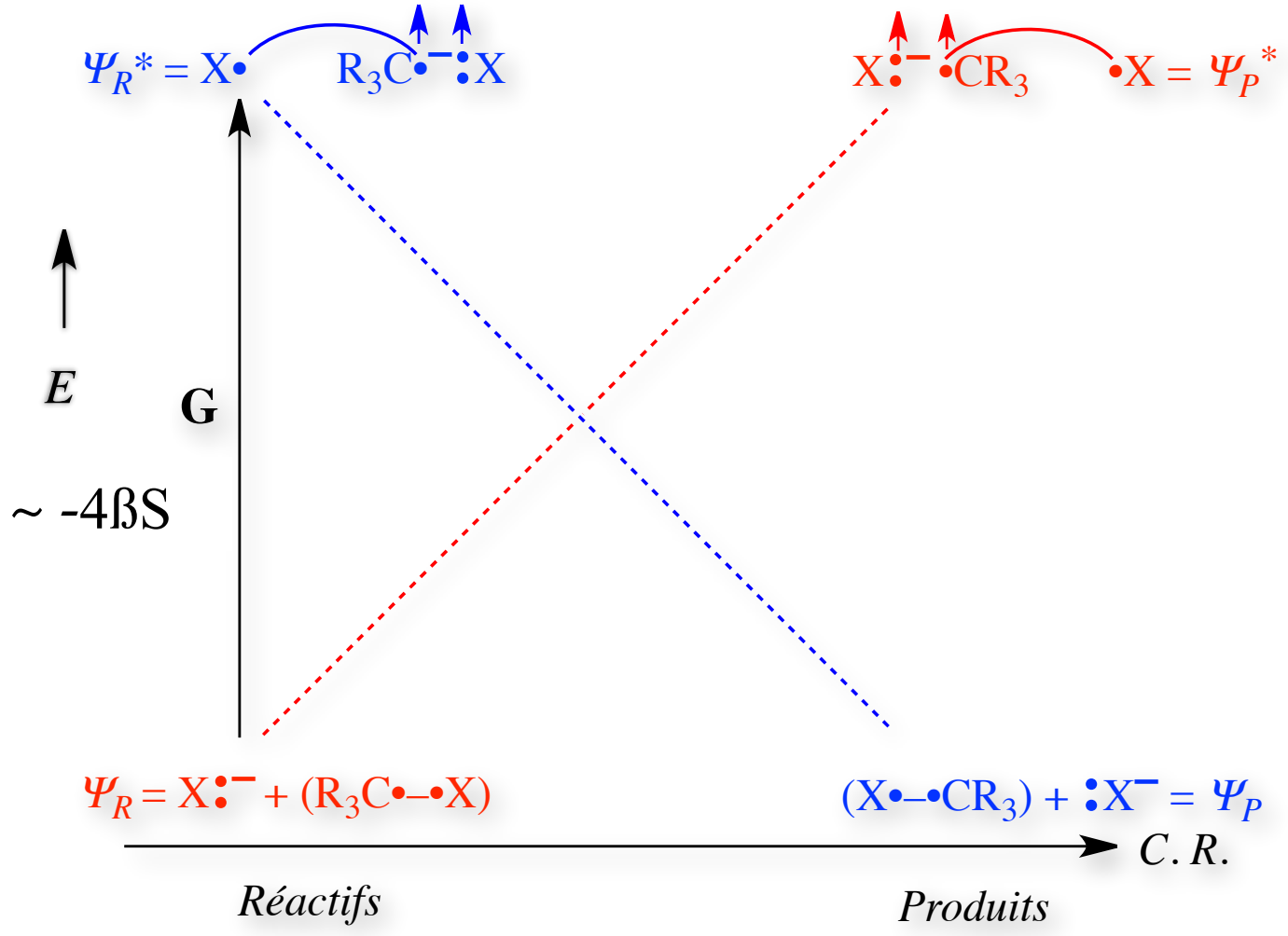


$$\Psi_P \propto \left| (c\overline{x_l} + x_l\overline{c})x_r\overline{x_r} \right|$$

Principles

- VB diagram for the S_N2 reaction :





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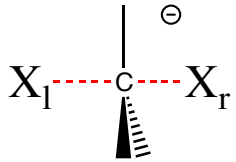
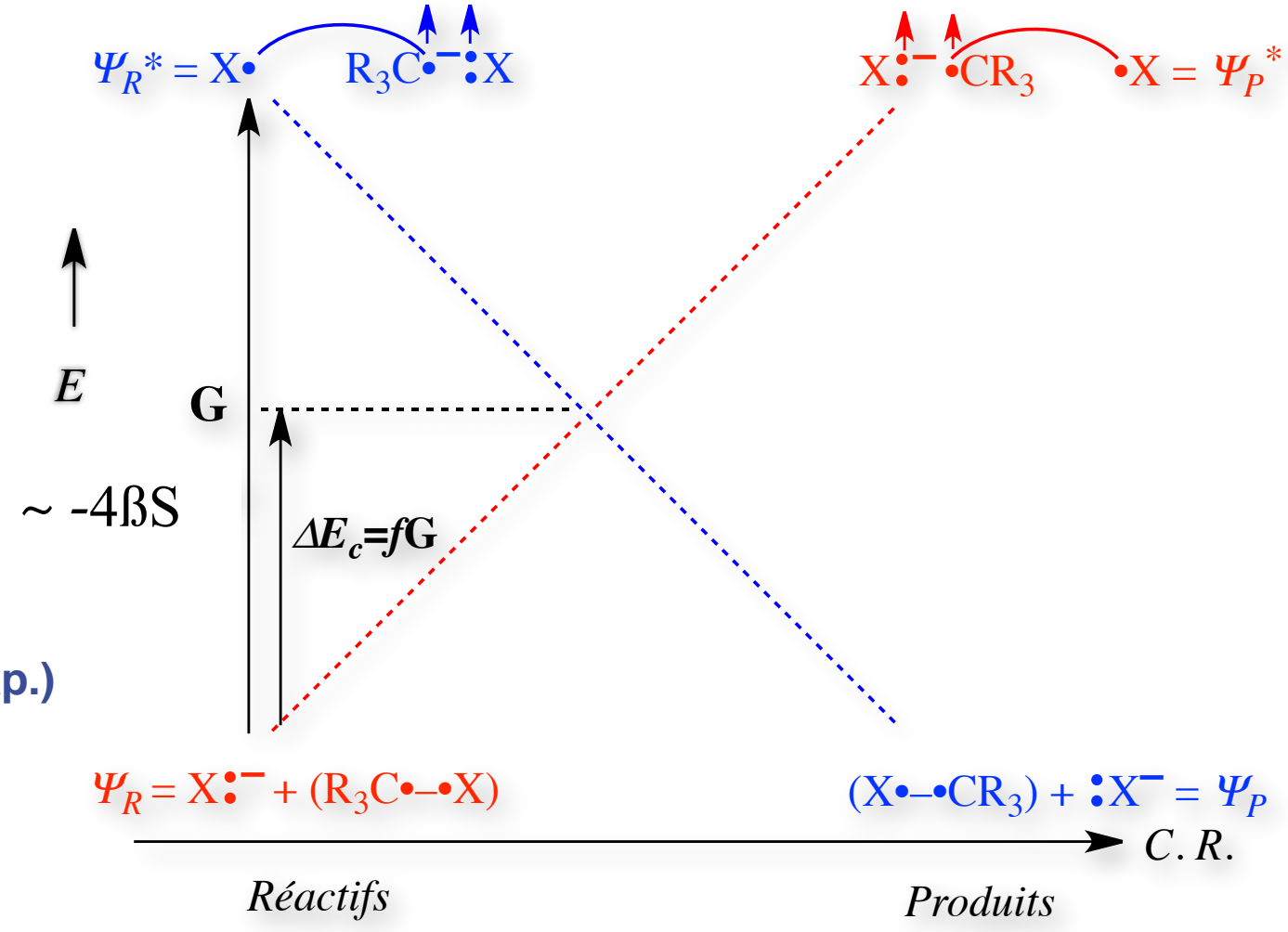
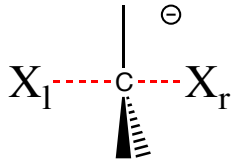
- VB diagram for the S_N2 reaction : 



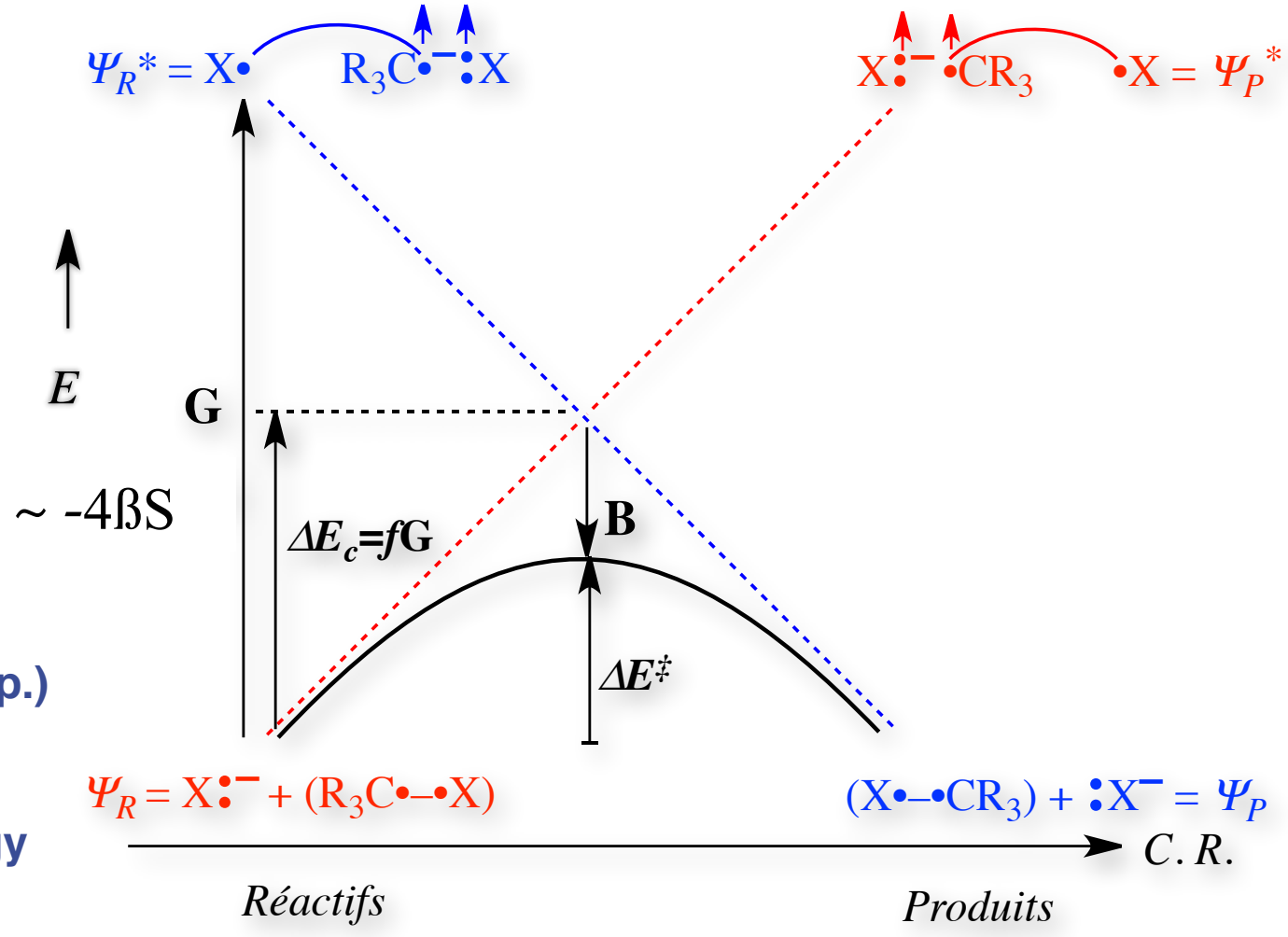
G : reactants' property (exp.)

f : curvature factor

Principles

- VB diagram for the S_N2 reaction : 

$$\Delta E^{\neq} = f\,G - B$$



G : reactants' property (exp.)

f : curvature factor

B : resonance energy

Principles

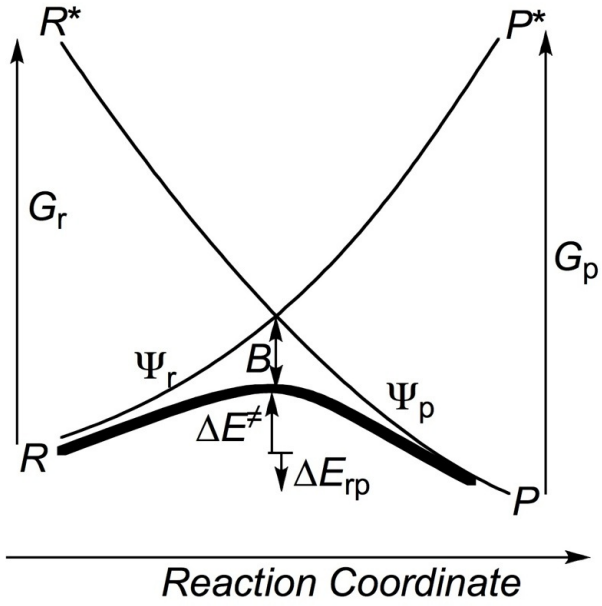
- Basic ingredients of the VB diagrams :

  - **G : promotion energy** : R→R* is an excited diabatic state which prepare the reactants ground state for the bonding changes from R to P.

  - ***f*** **:** measure the **intrinsic «smoothness»** of the electronic structure change in R and P

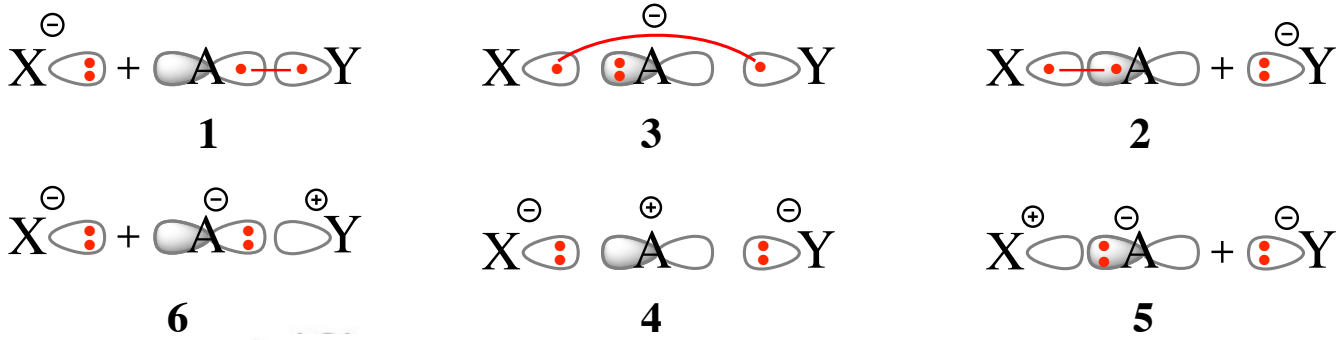
  ⇒ *f*G : gauges the total deformation and repulsive interactions R have to experience to achieve resonance with P

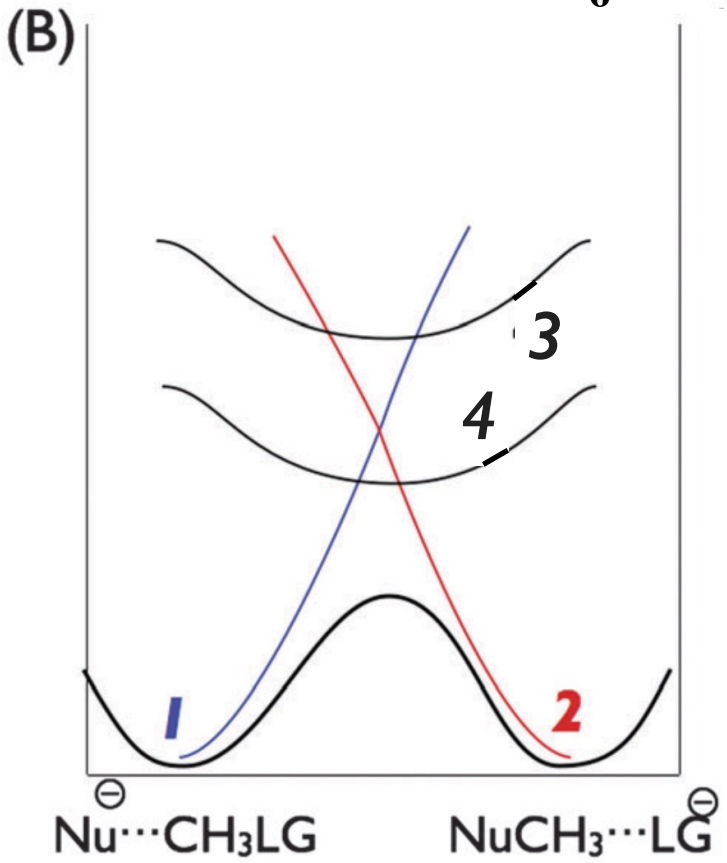
  - **B : resonance energy** of the TS due to VB mixing at the crossing point



Principles

- Exercice 2 (SN2):





Principles

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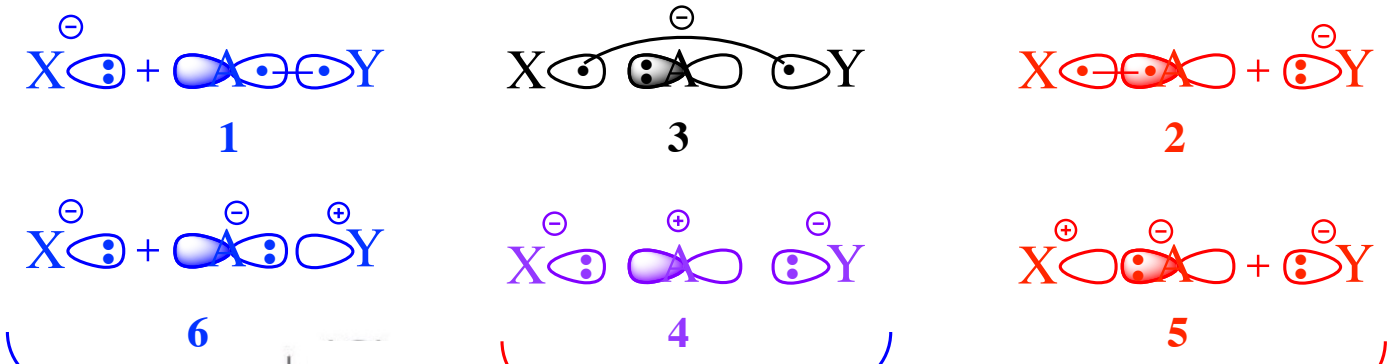

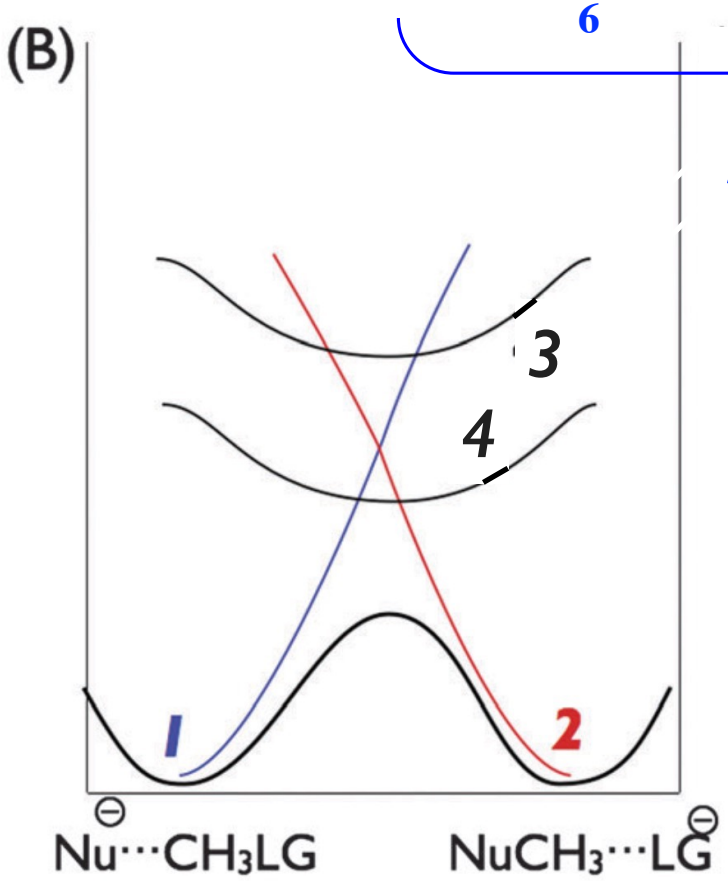

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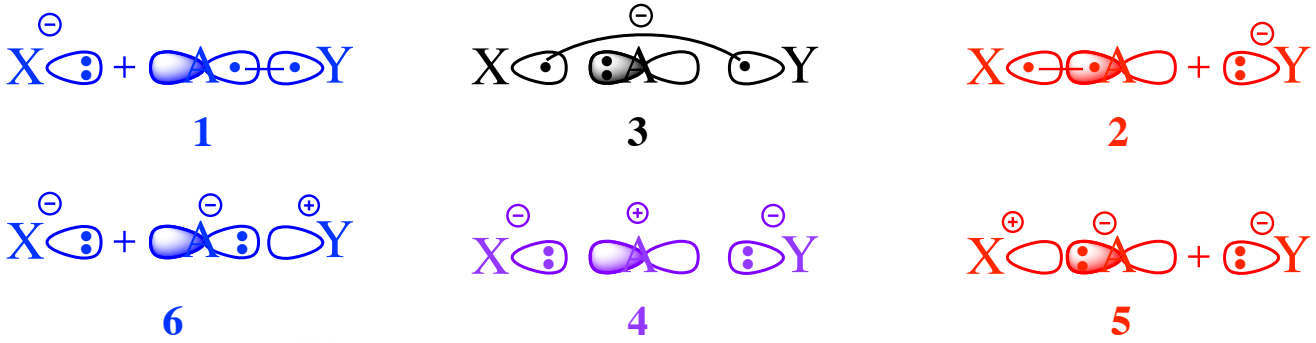
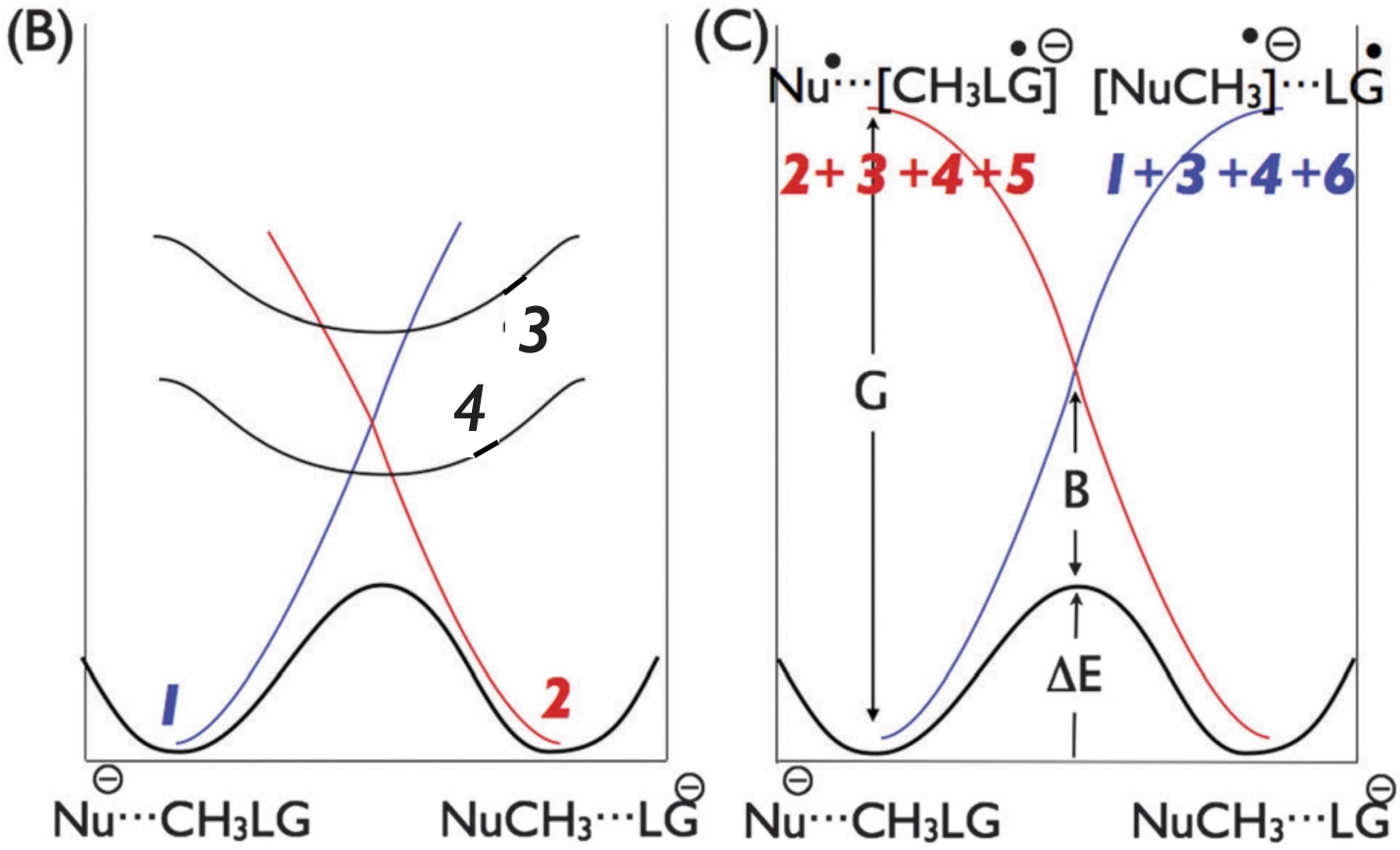
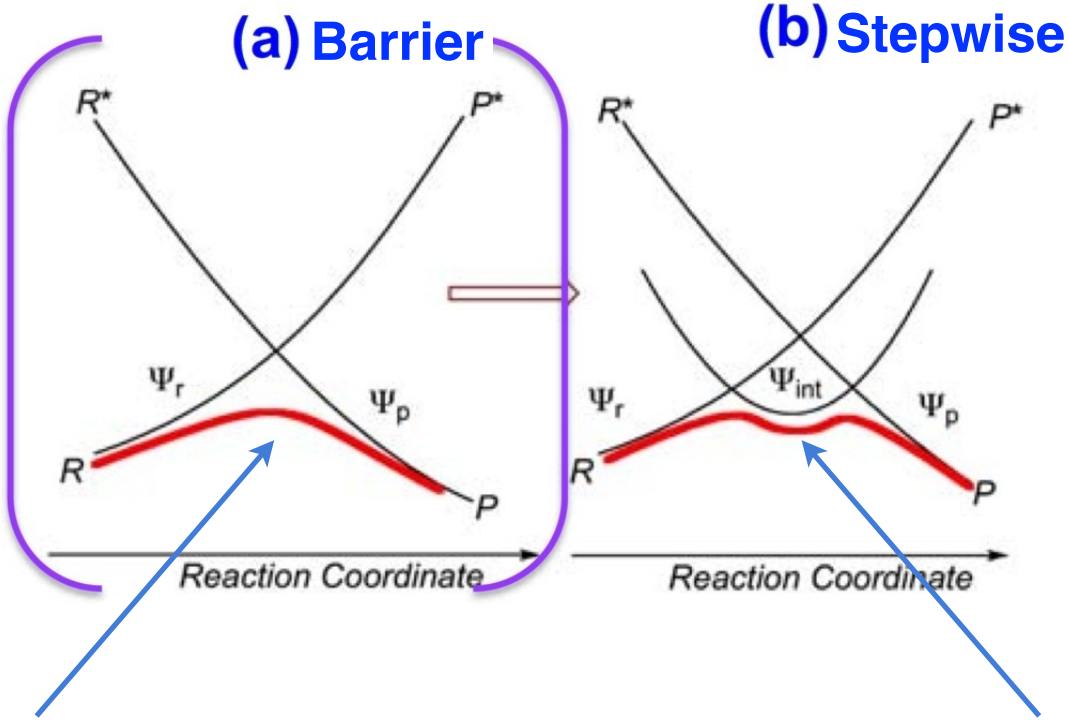
- Exercice 2 (SN2):





Principles

- Two-state (VBSCD) vs. multi-state diagrams (VBCMD) :



R and P mix to form the barrier and the TS for an elementary process

The intermediate has a different electronic structure than R and P («internal catalysis»)

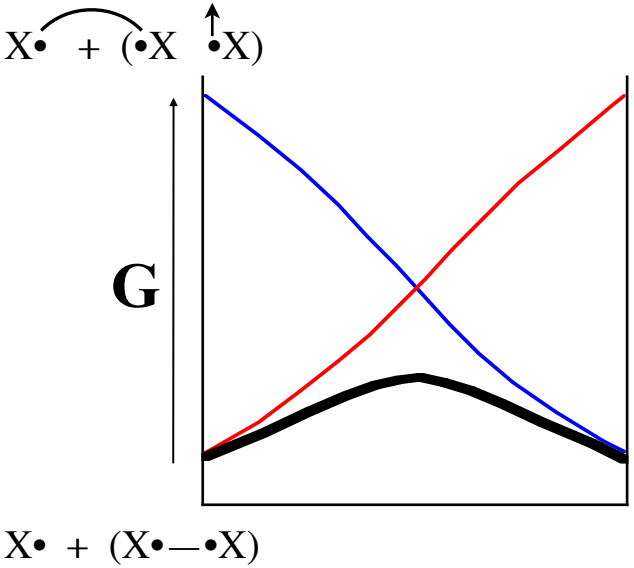
Illustrations

- **1)** Radical exchange reactions

Stability or unstability of X_3• clusters (X= H, F, Cl, Br, I, Li, Na, etc.)

X• + X-X → [X--X--X]• → X–X + X•

$$\text{Rule 1}: \Rightarrow G \approx \Delta E_{ST}(X-X) \propto 2D_e$$



Strong bonds (H_3):
Large barrier

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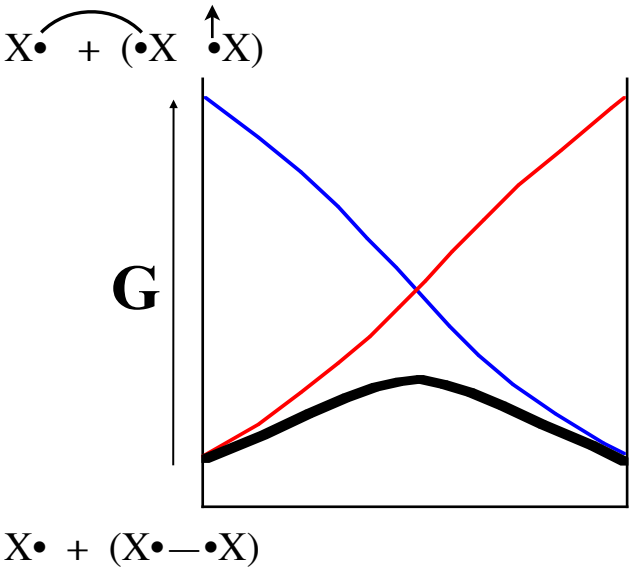

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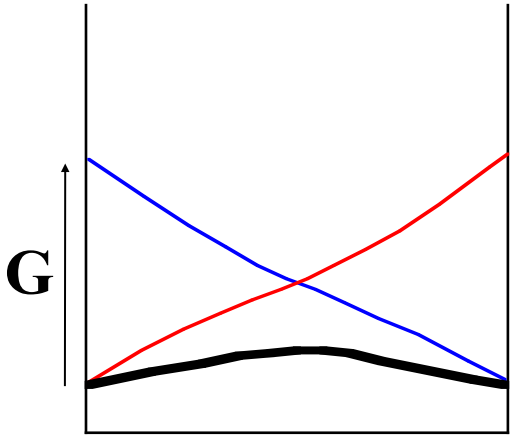

Weaker bonds (Cl_3):
Smaller barrier

Illustrations

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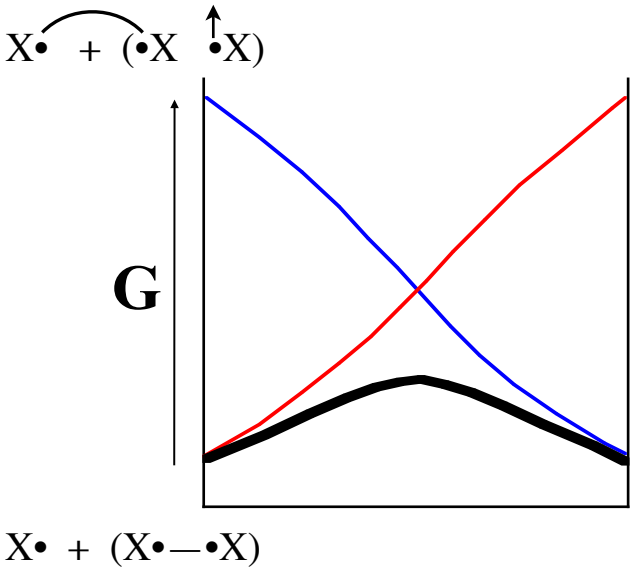

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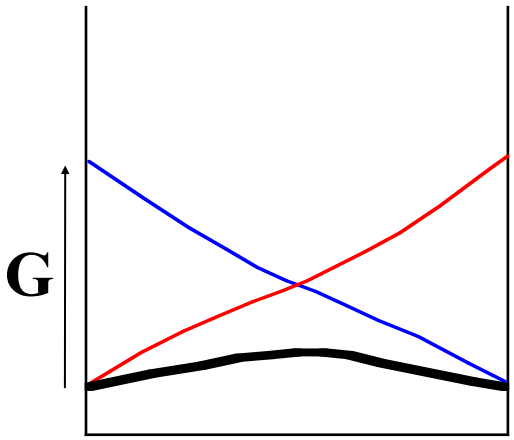

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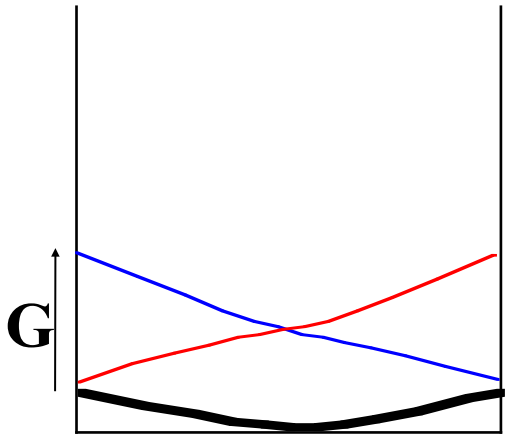
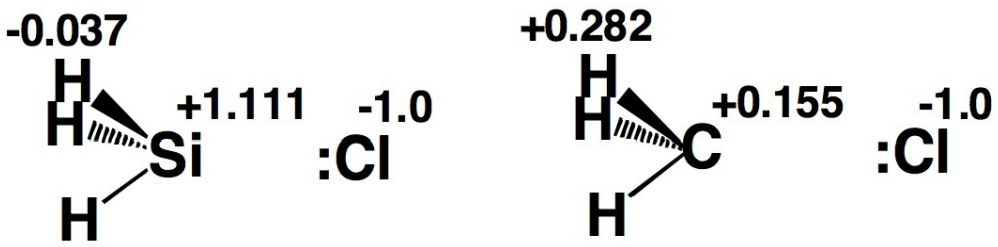


Weak bonds (Li_3):
Stable cluster

Illustrations

- **2)** SN2(C) vs. SN2(Si) - Origin of hypercoordination :

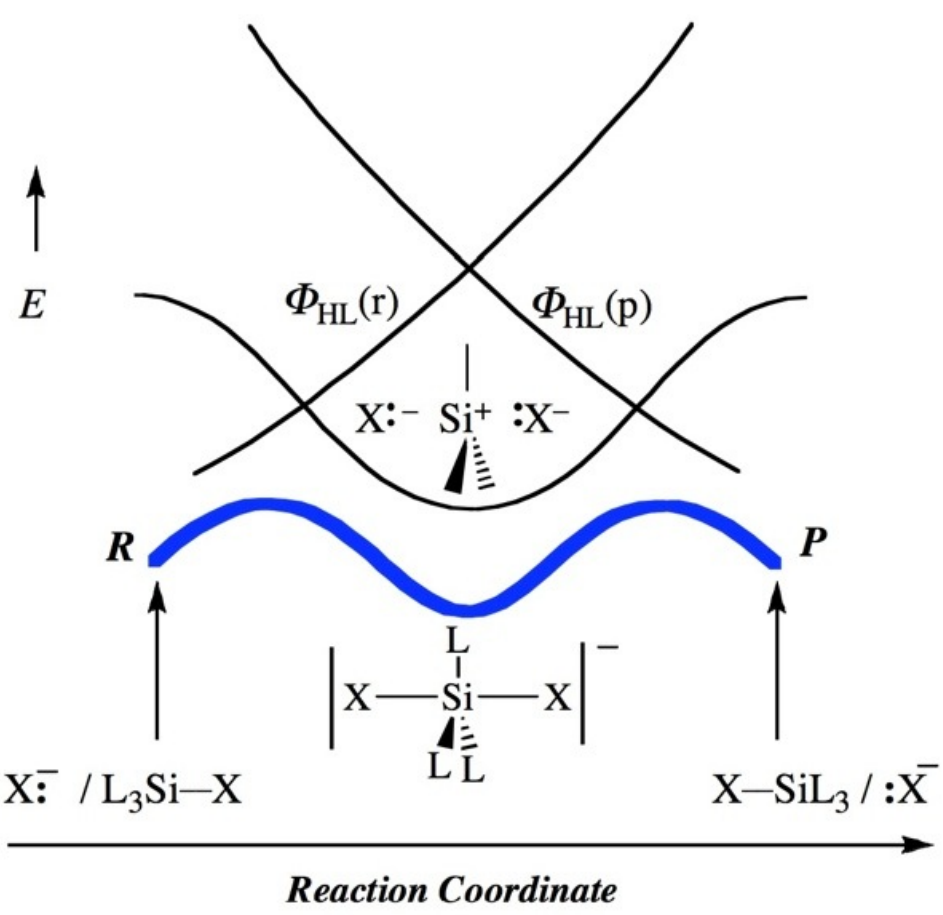


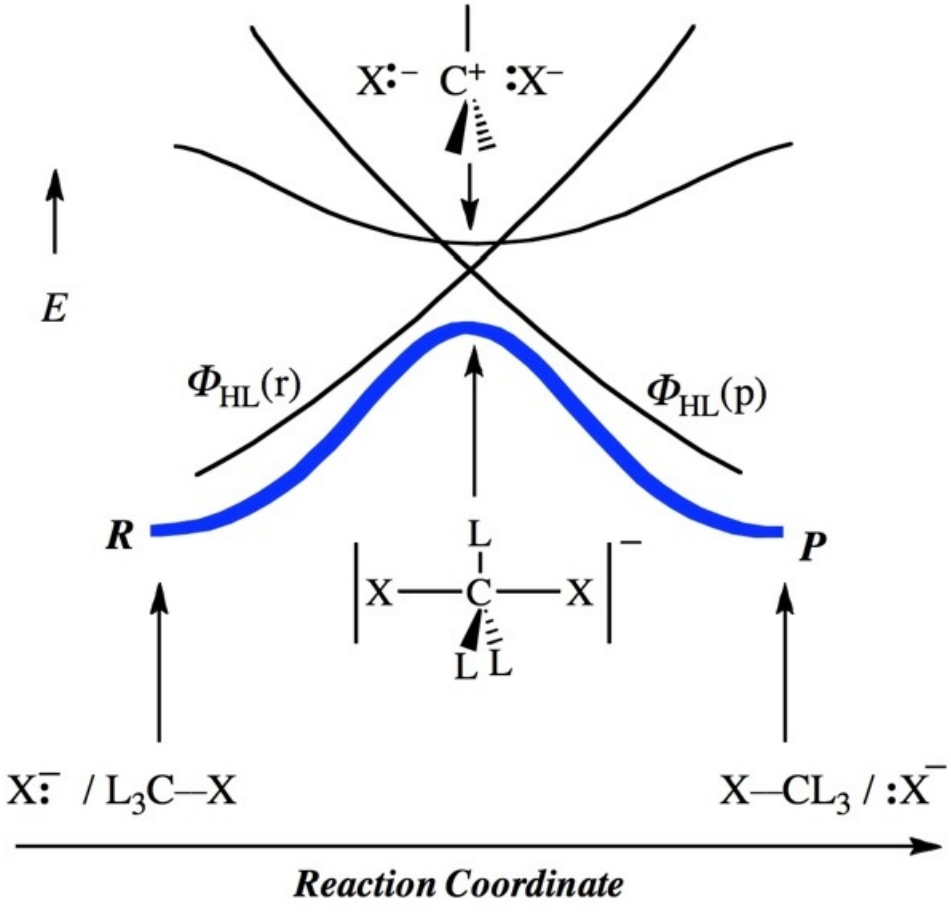
Positive charge localization on Si vs. delocalization on C

⇒ Si small ion allowing close approach of anions and a significant electrostatic stabilization of its ionic structure

Illustrations

- **2)** SN2(C) vs. SN2(Si) - Origin of hypercoordination :



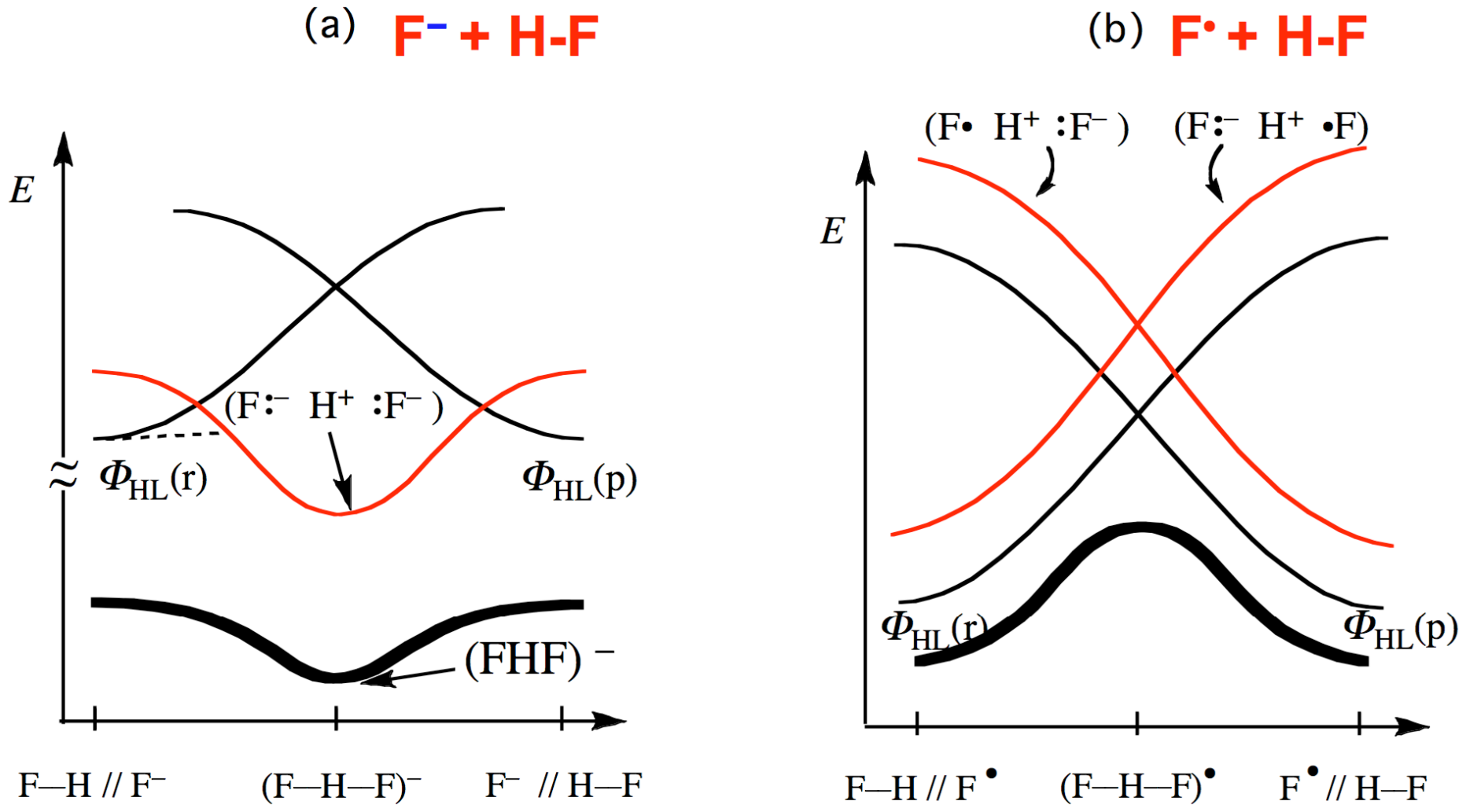


Illustrations

- **3)** F^- + HF vs. $F^\bullet$ + HF: impact of a single electron:

Illustrations

- **3)** F– + HF vs. F• + HF: impact of a single electron:



Conclusion

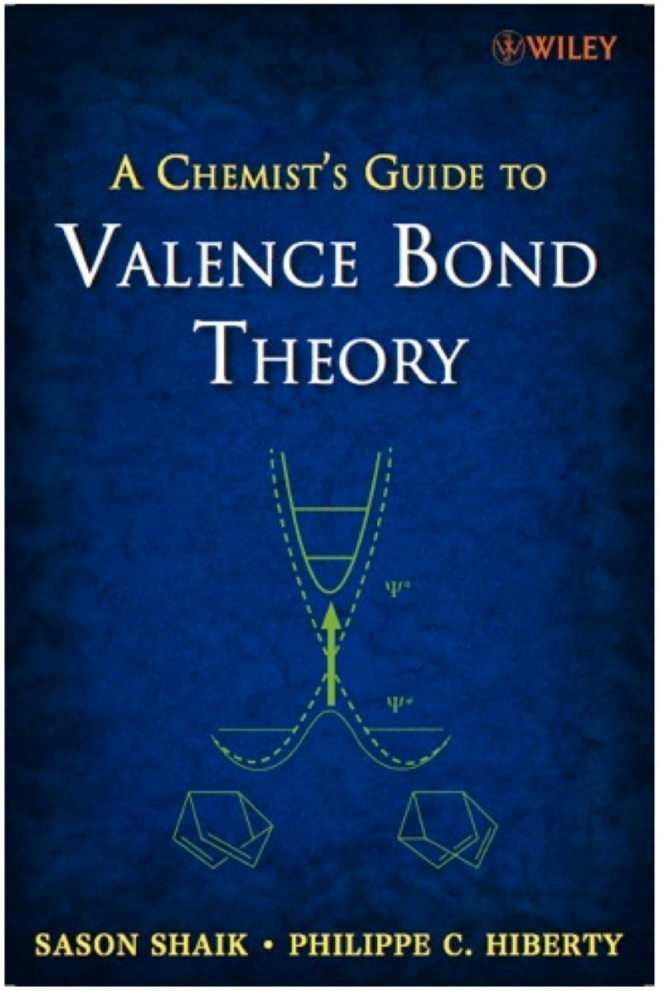
- A general and **powerful model for reactivity** :
  - Nucleophilic, electrophilic, radical, pericyclic…
  - Simple: could be applied «on the **back of en envelop**»
  - Insightful: allows to **create order** among great families of reactions
- Both interpretative and quantitative :
  - **qualitative reasonings** : a few rules and elementary interactions
  - **quantitive proof** : by high level VB calculations

VB theory

➡ VB theory :

- provides a **wave-function *ansatz*** which enables to compute high level wf that are quantum dressing of Lewis' model ;
- retrieves fundamental **chemical concepts**, such as : resonance / mesomery, hybridization, arrow-pushing language, and provides a theoretical support for them ;
- incorporates **interpretative tools** which are both directly connected to quantum mechanics and to the local vision of chemists' (VB weights, resonance energies, VB diagrams)

To go further…



https://wiki.lct.jussieu.fr/workshop/index.php/VB_tutorial