Benoît BRAÏDA*

ICS Summer school 2013

Valence Bond theory

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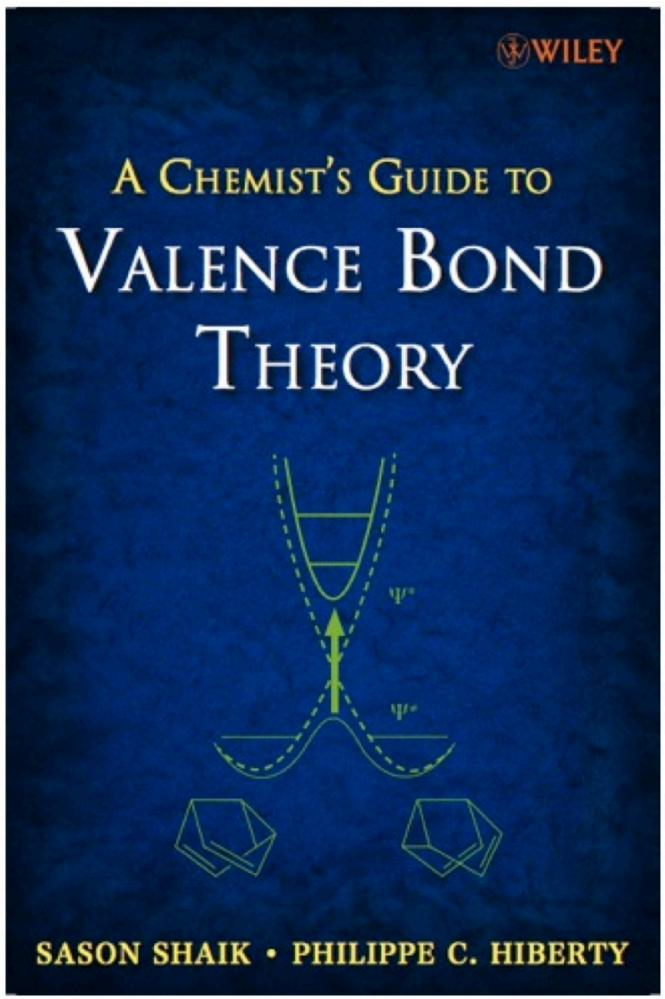
VB lectures

- Part. 1 (Tues. 10h45-12h15) - Basics of VB theory
- Part. 2 (Wed. 10h45-12h15) - *Ab initio* VB methods
- Part. 3 (Fri. 09h00-10h30) - Qualitative VB
- Part. 4 (Fri. 10h45-12h15) - VB diagrams for reactivity

(including paper exercices)

VB references

- Book :



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

Motivation

Short story about the purpose of chemistry, heuristic models, the chemists' «schizophrenia», and brief history of VB theory from birth to present

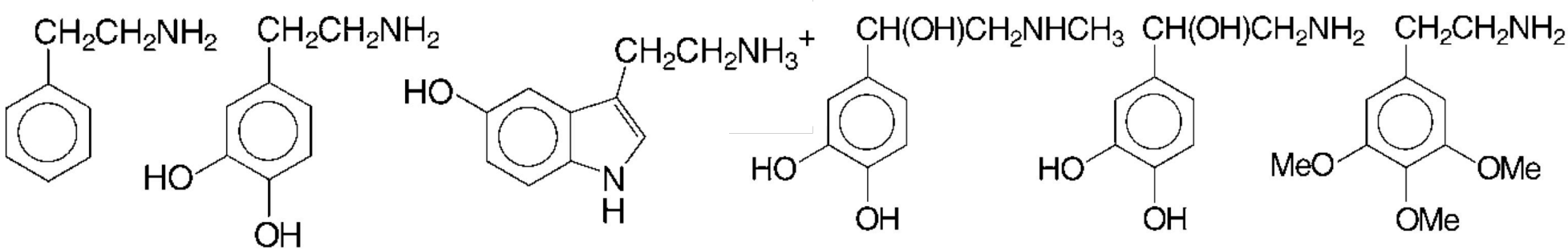
Chemistry

Why are we doing chemistry ? What is chemistry all about ?

Chemistry is the window given to us
to penetrate into our material essence

Chemistry

Genes → Chemicals → Emotions



1, PEA — *Love Well-being*

2, Dopamine — *Reward*

3, Serotonin — *«mood molecule»*

4, Adrenaline — *Energy*

5, Noradrenaline — *Vitality and focus*

6, Mescaline — *Psychedelic*

Our emotional life is orchestrated by specific brain chemicals

Chemistry

Chemistry in central to mankind

➡ We, and the world, are made of matter

➡ The purpose of chemistry is to explore and master this material dimension of our own

Chemistry

Chemistry lean on a few central paradigms

1) There exists atoms which can bond together

2) Bonds determines the molecular architecture, interactions, and reactivity of molecules

3) This in turn determines properties of matter

Chemistry

Chemistry aims to develop a world viewpoint via an organization of our knowledge, and an extension of it, based on these central paradigms

Heuristic models

- Lewis' model :

THE ATOM AND THE MOLECULE.

By Gilbert N. Lewis.

JACS 1916, 762

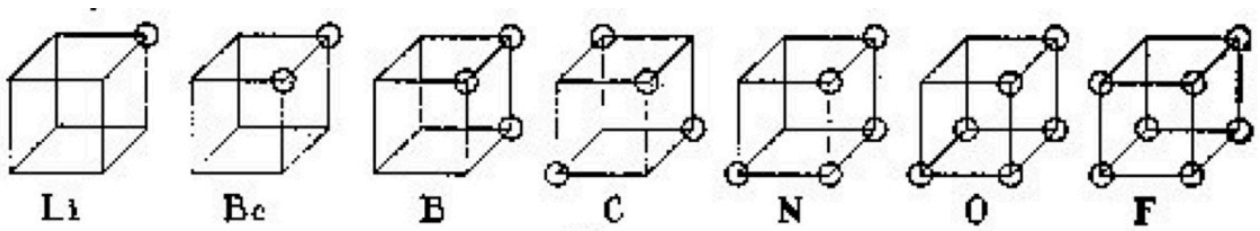
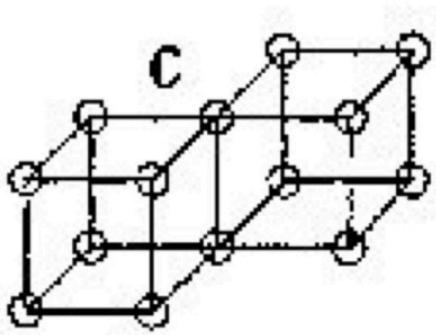


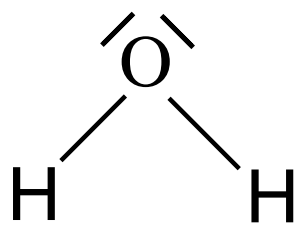
Fig. 2.



Heuristic models

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

Lewis' time

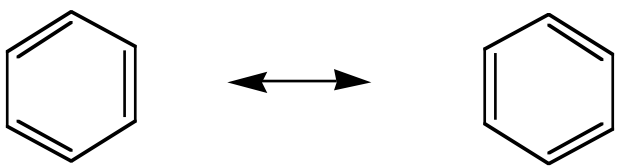


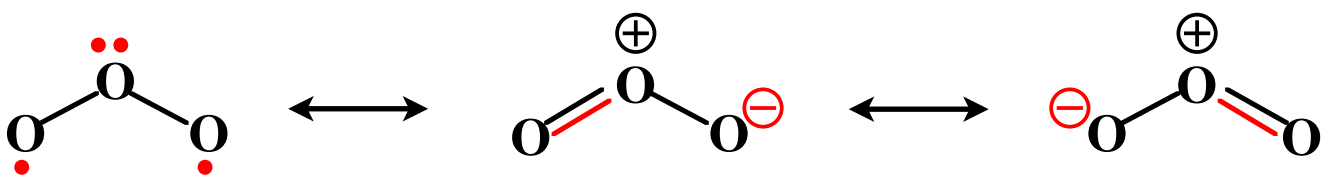
Today

➡ at the basis of chemists' language («solfège»)

Heuristic models

- Mesomery / resonance :
  - Arndt, Robinson, Ingold (1924-38) : mesomery
  - Pauling, Wheland (1928-33) : resonance theory

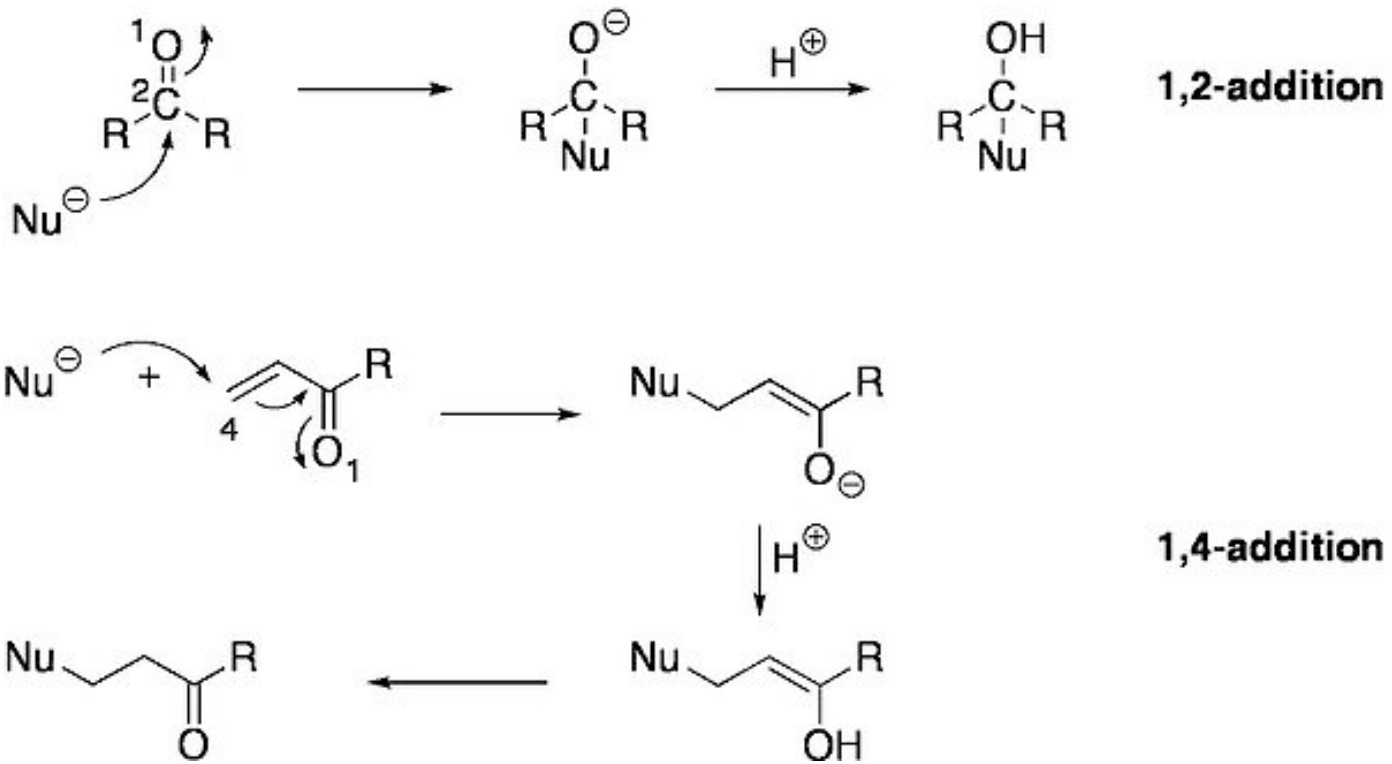




➡ when more than one Lewis structure is needed

Heuristic models

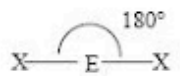
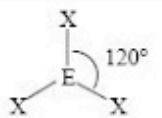
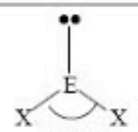
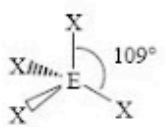
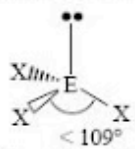
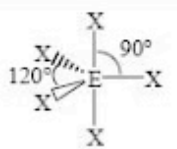
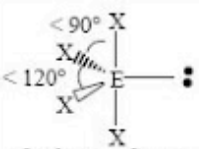
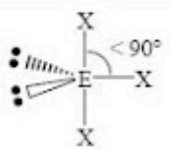
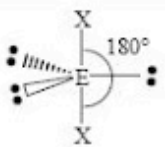
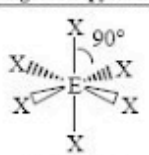
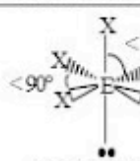
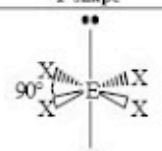
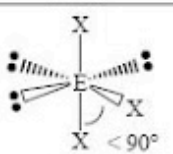
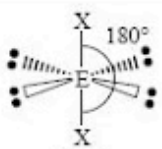
- Arrow-pushing language :



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

Heuristic models

- VSEPR model :

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

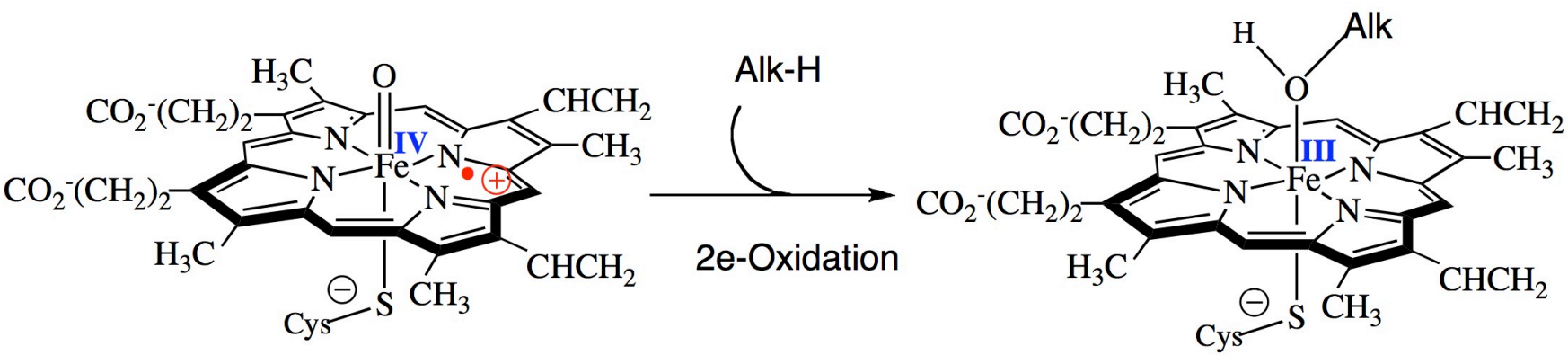
➡ rationalization of molecular geometries

Heuristic models

Heuristic models encodes the central paradigms of the chemical science and form the basic language of chemistry

Quantum Chemistry

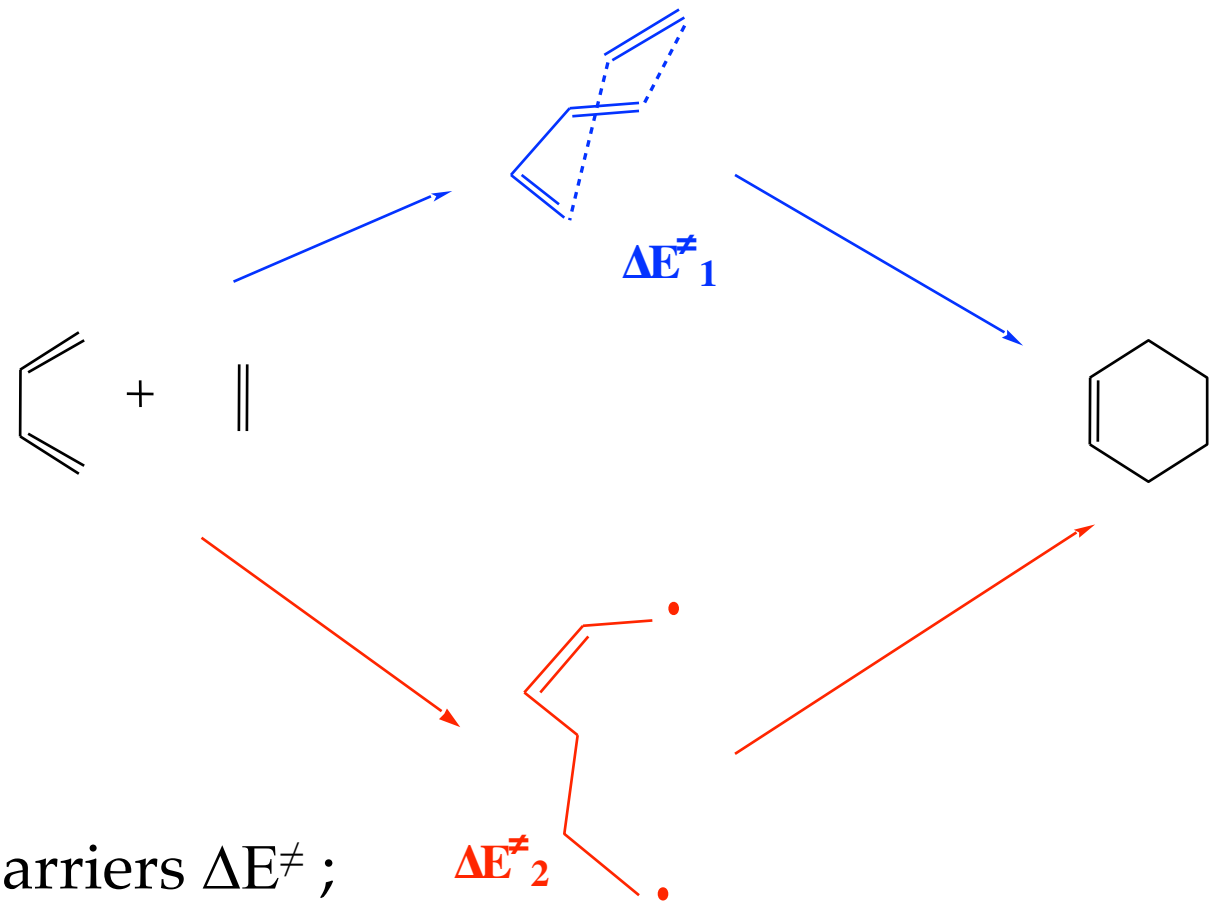
- Accurate quantum theory based calculations can provide :



- geometries ;
- energy differences (=> reaction barriers, different conformers...) ;
- many over observables (dipole moments, densities, NMR shifts...)

Quantum Chemistry

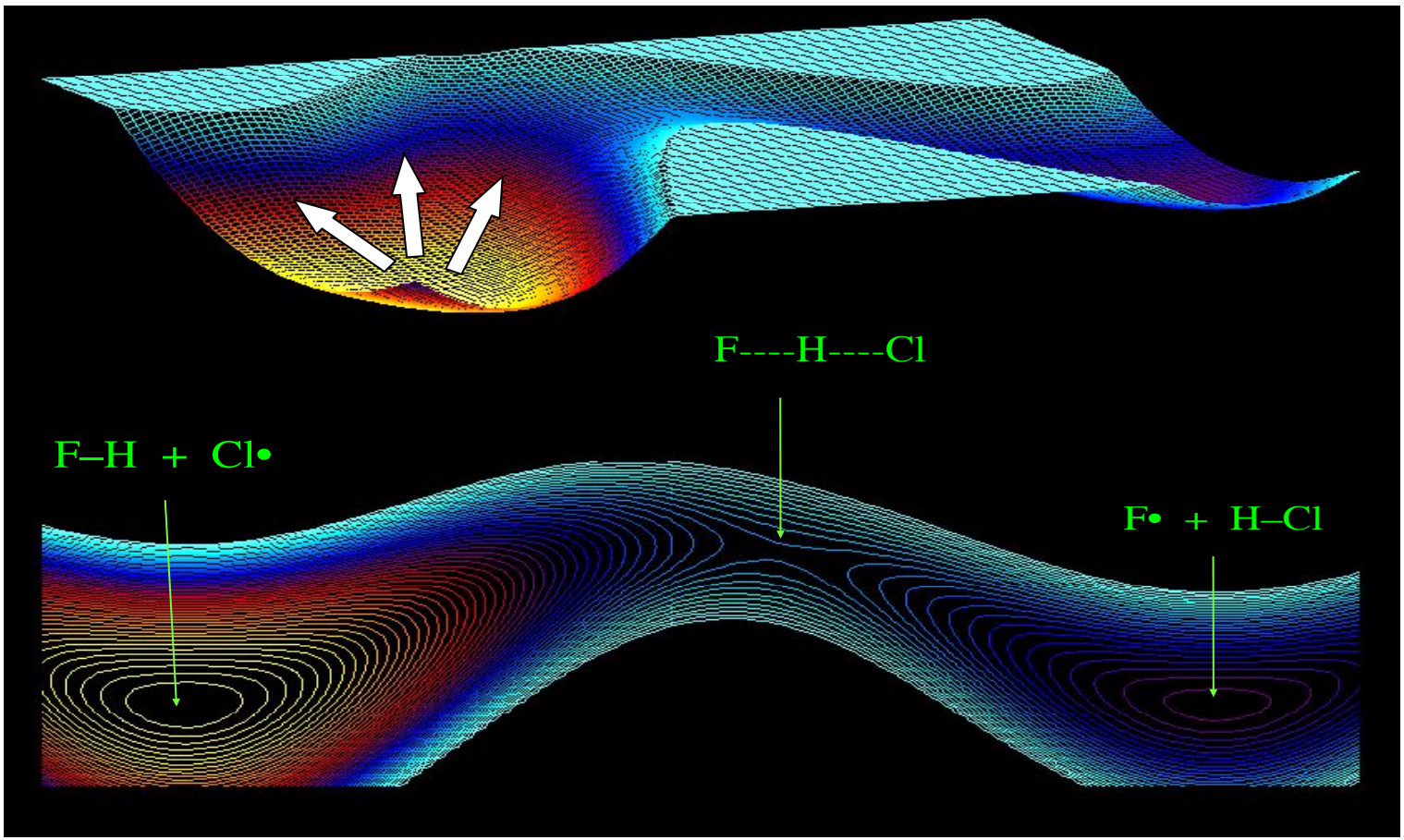
- Accurate quantum theory based calculations can provide :



- accurate barriers $\Delta E^{\neq}$;
- details about reaction mechanisms

Quantum Chemistry

- Accurate quantum theory based calculations can provide :



- complete exploration of the PES and reaction dynamics

Quantum Chemistry

- ... but it does not (directly) provide :

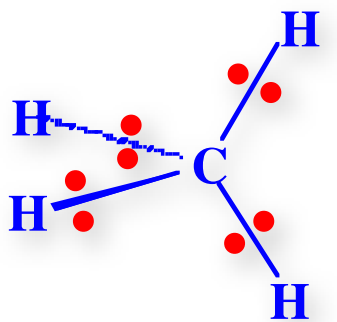
  - human type **comprehension** of the computation outcome
  - general **laws** and trends over a family of compounds/reactions
  - description in terms of chemists' **local picture**

$\Delta E^{\neq} = 22$ kcal.mol^{-1}
⇨ low barrier, easy

?
have to do the computation...

Chemists' «schizophrenia»

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

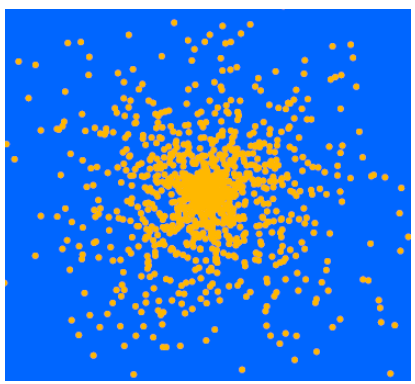


Lewis model, arrow-pushing language, VSEPR, hybridization,...

- **Localized** electron pairs
- **Chemical bond** concept

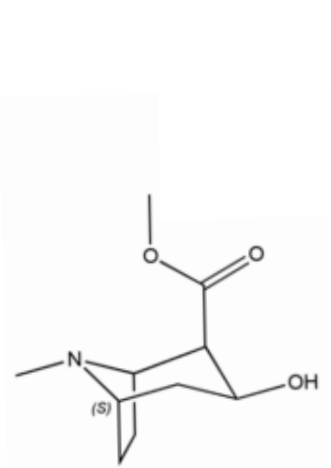
- **Quantitative theory** based on a delocalized particles vision :

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



- **delocalized** particles (e^-, n^+)
- **indistinguishable** and all-interacting (no chemical bond)

Chemists' «schizophrenia»



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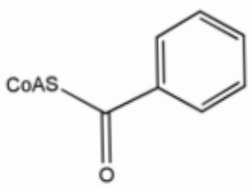


ΔH_{rnx}

$\Delta H^{\ddagger}$

etc.

Why ?...

Chemists' «schizophrenia»

«Chemists would like to have the computer in their heads» (Enerst R. Davidson)

Chemists' «schizophrenia»

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

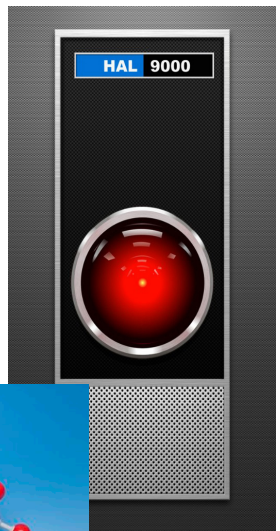
Chemists' «schizophrenia»

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 ?

Interpretative methods

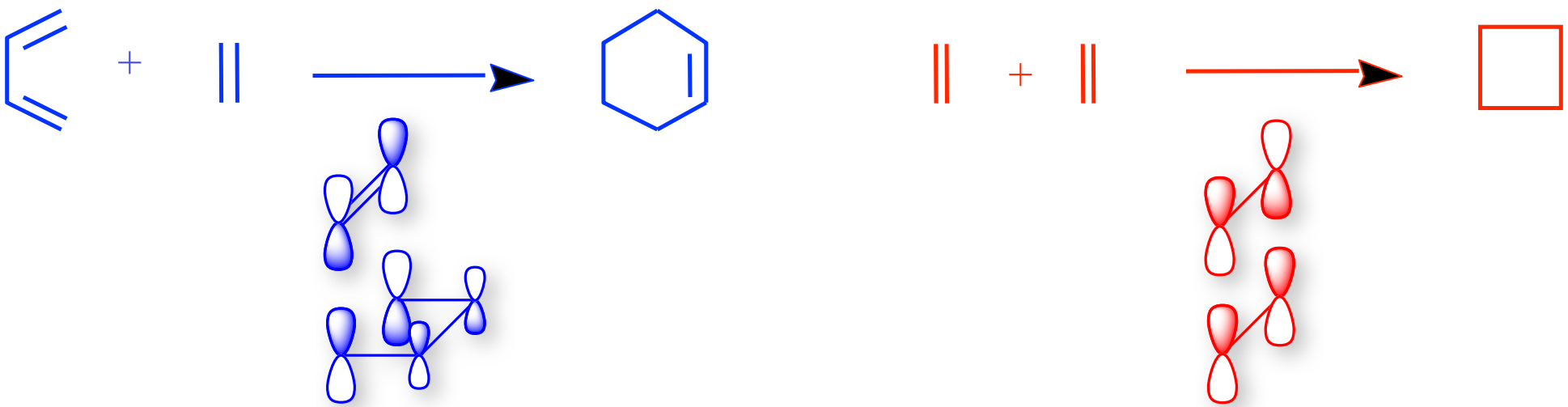


➡ Need for interpretative methods to act as **interface** between experiments and computations, to **create order**, and by doing this to **open new thoughts**

Interpretative methods

- Qualitative MO-based models :

  Hückel method, Frontier Molecular Orbitals, Woodward-Hoffman rules,...



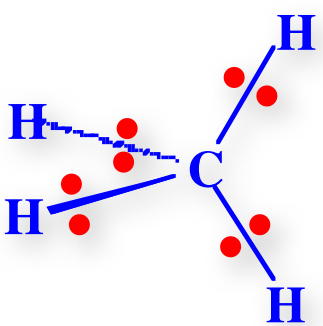
➡ Not quantitative (*a posteriori* rationalization)

Interpretative methods

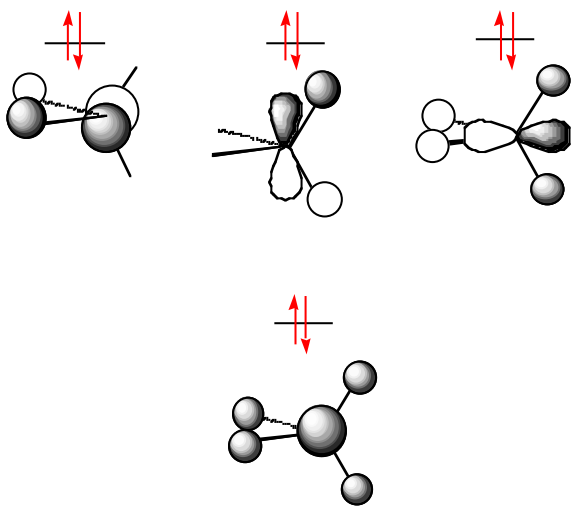
- Qualitative MO-based models :

- **Localized** electron pairs
- **Chemical bond** concept

- **delocalized** picture
- **Indirect chemical bonding**



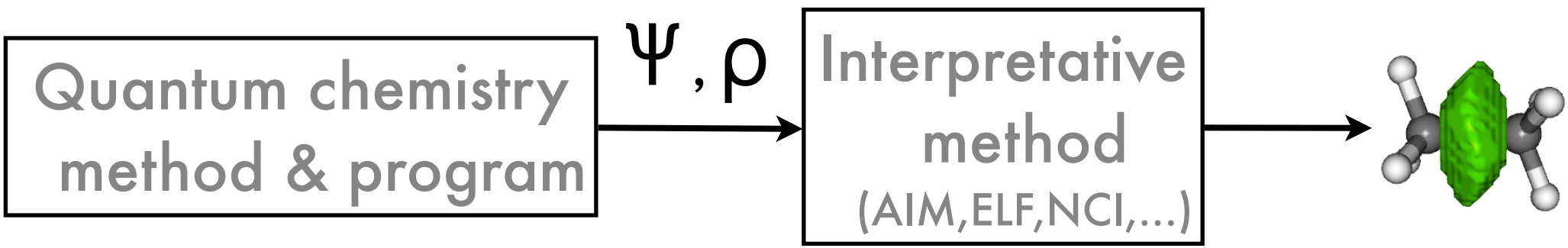
Which one to choose ?...



➡ No direct link with chemists' local vision

Interpretative methods

- Real space «topological» methods :



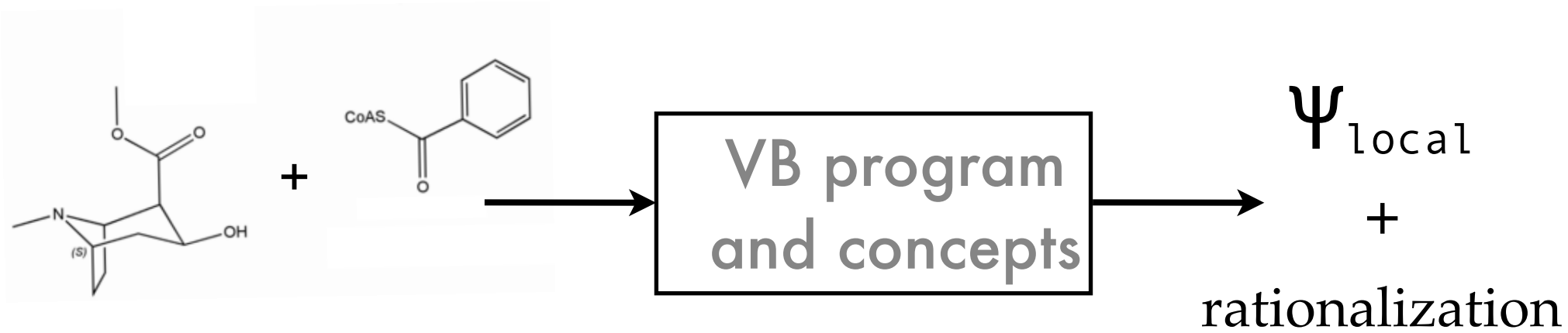
➡ Definition and **meaning** of localized regions not straightforward

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

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

Interpretative methods

- Valence bond theory :



➡ A wavefunction (QC) method and «built-in» interpretative method at the same time

- Birth and origins:

1916

G.N. Lewis

1928-34

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

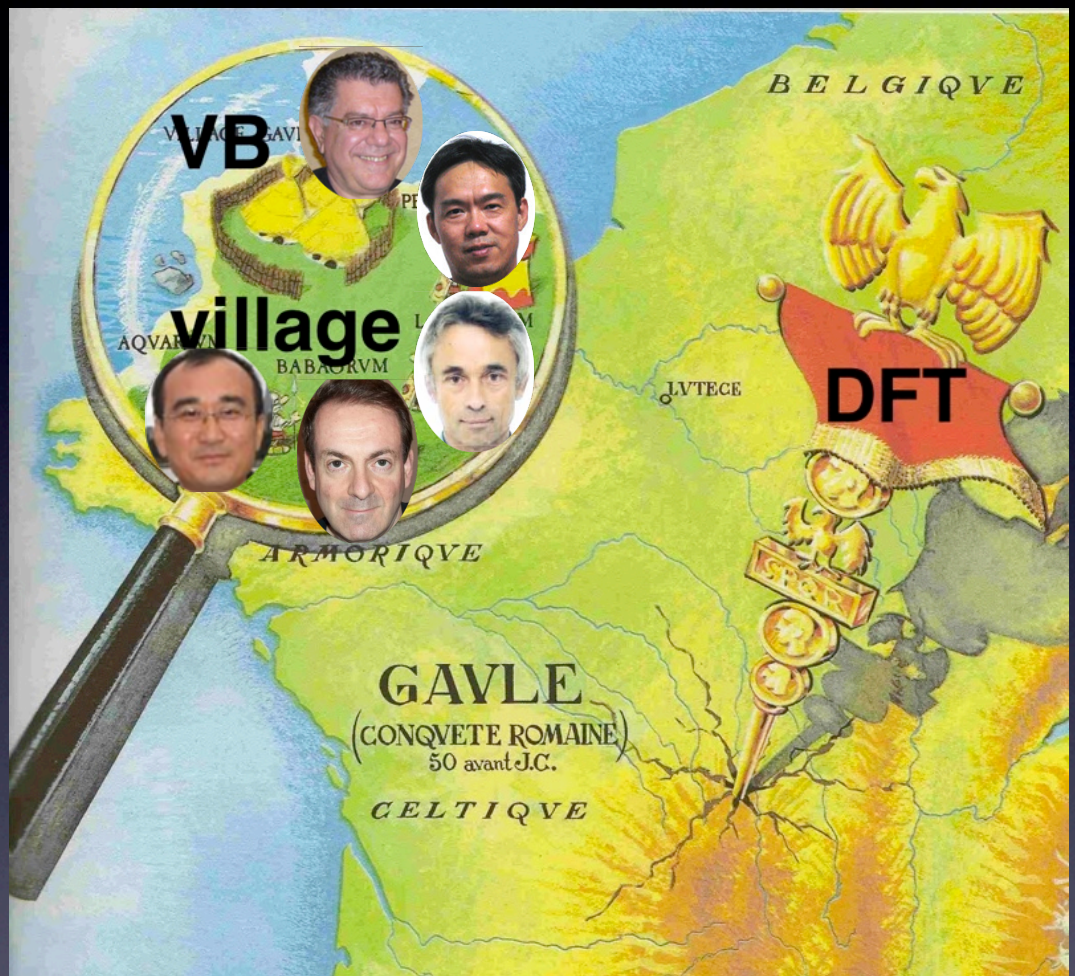
Successes of MO theory vs. VB «failures»

- ~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

- 2012-....: awakening of the sleeping beauty?

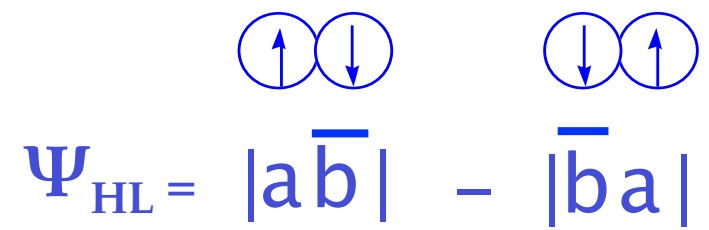
All elements for a Valence Bond revival are ready

Part 1. Basics of VB theory

Heitler-London

Dihydrogen molecule H_2 : H_a——H_b

- Heitler-London (1927) :



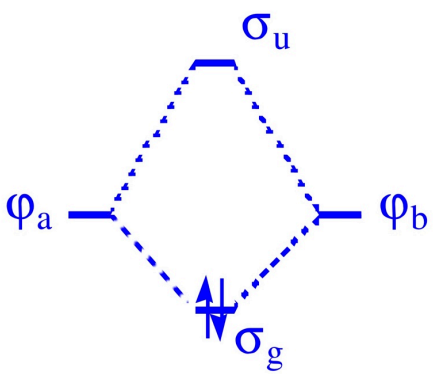
- Electrons in atomic orbitals
- Shaired electron pair (covalent bond)

➡ **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)

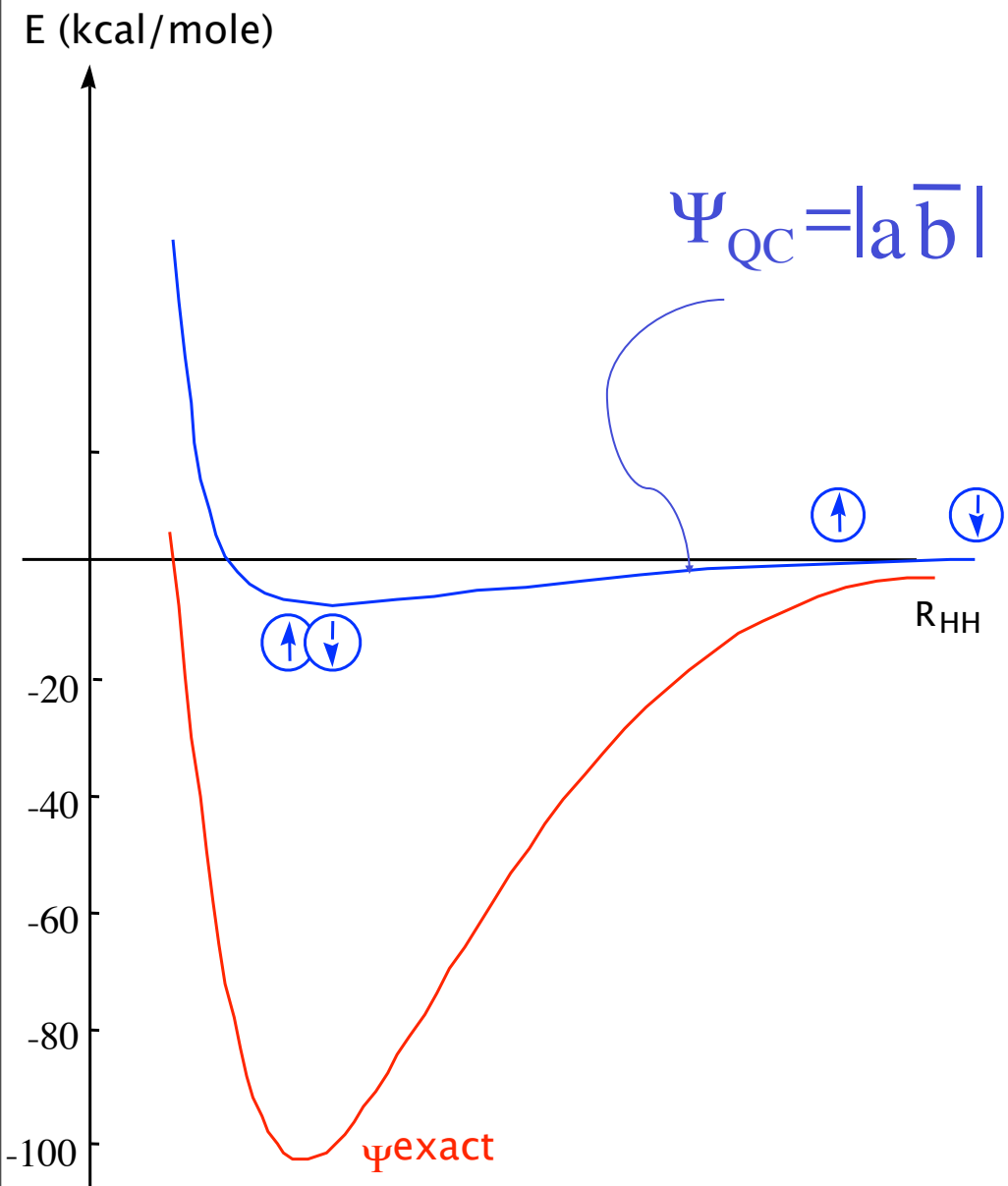
- Heitler-London (1927) :

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

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

➡ **basis of VB theory**

Heitler-London

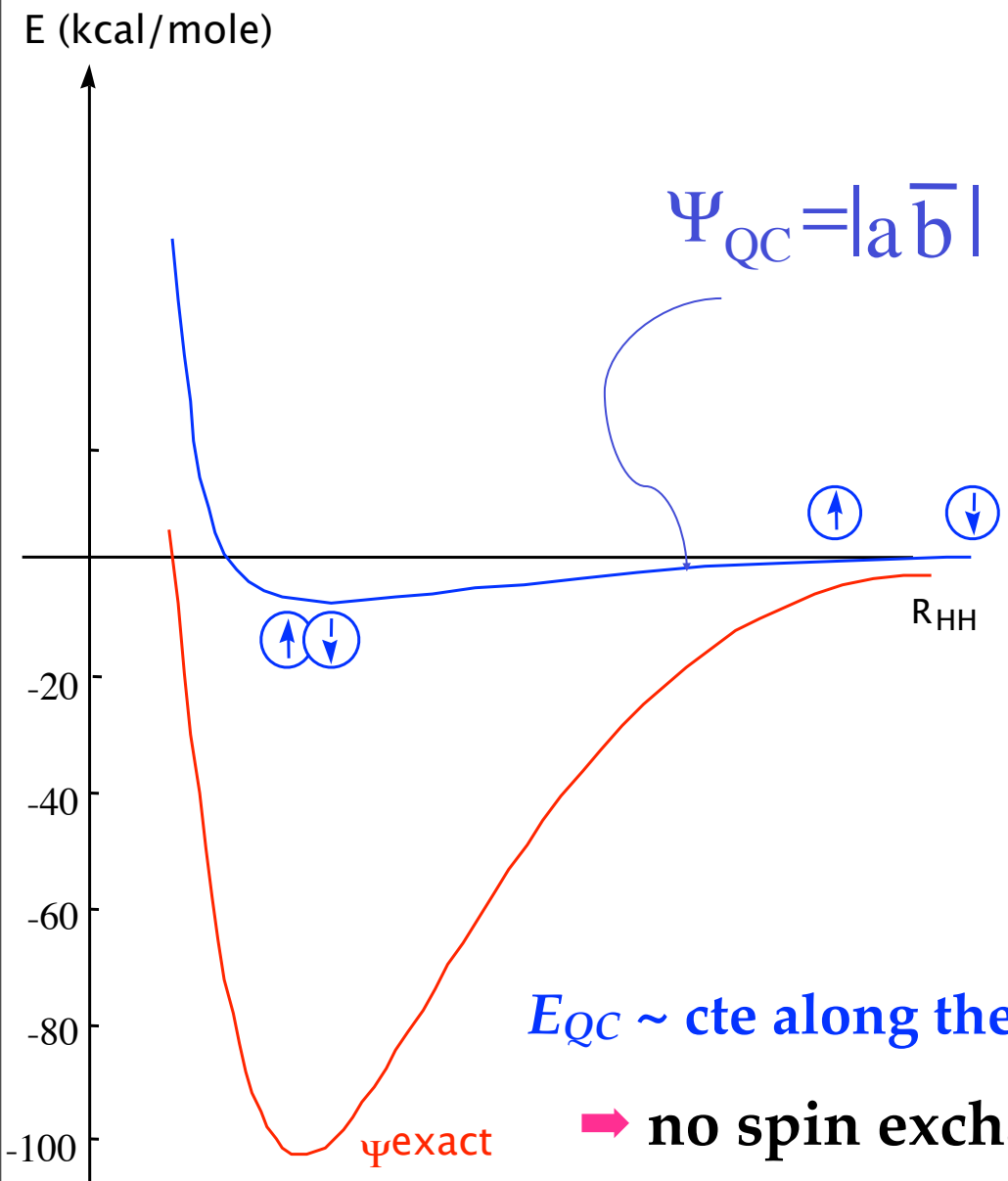


- Quasi-Classical (QC) state :

$$\hat{H}^{él} = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}$$

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

Heitler-London



- Quasi-Classical (QC) state :

$$\hat{H}^{él} = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}$$

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

$$E_{QC} = \frac{\langle |a\bar{b}| \, H^{él} \, |a\bar{b}| \rangle}{\langle |a\bar{b}| \, |a\bar{b}| \rangle} = h_{aa} + h_{bb} + J_{ab}$$

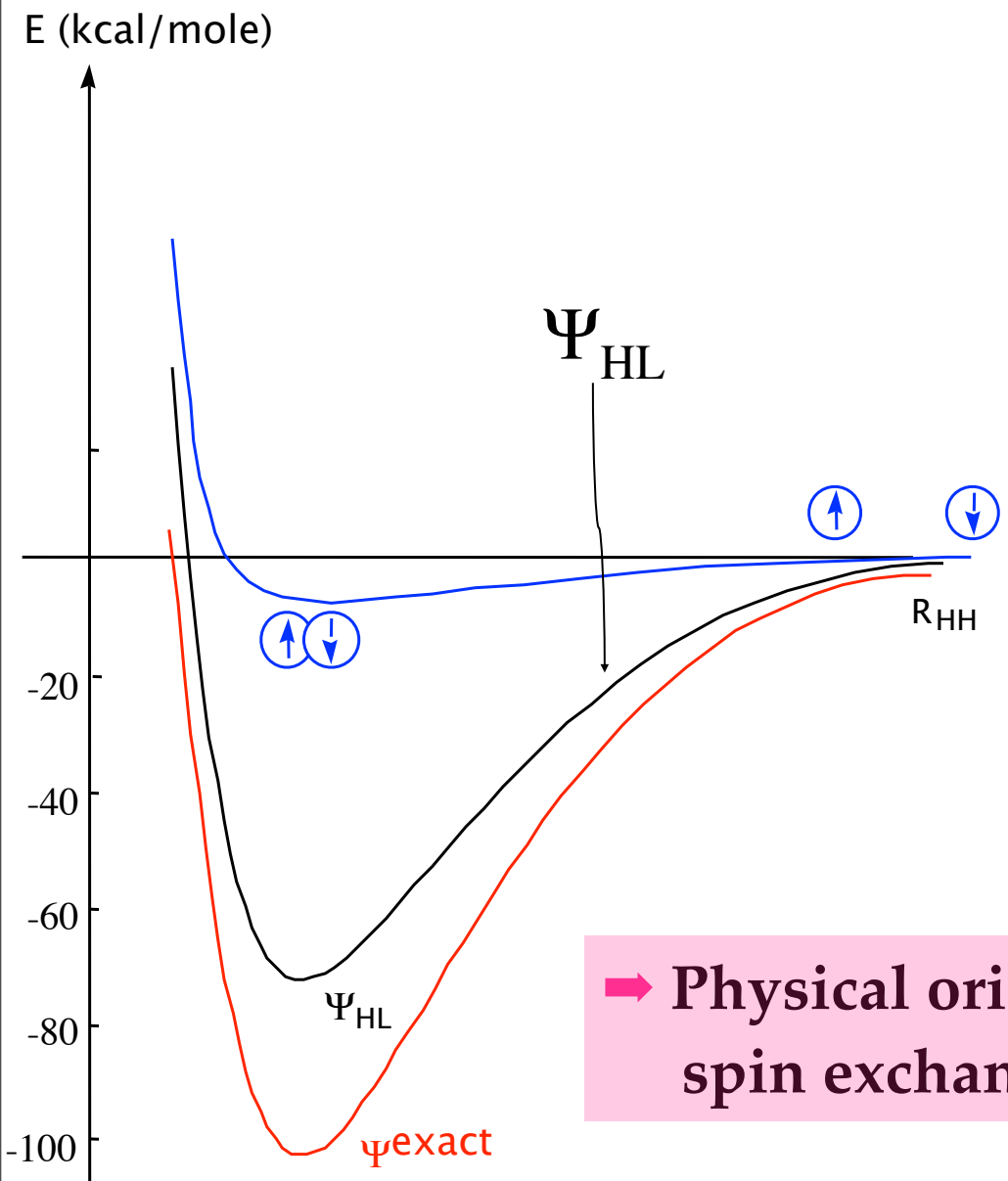
$$with : \begin{cases} h_{ii} = \int i^*(1) i(1) h(1) d\tau_1 \\ J_{ab} = \iint a^*(1) a(1) \frac{1}{r_{12}} b^*(2) b(2) d\tau_1 d\tau_2 \end{cases}$$

$$and : d\tau_i = dx_i dy_i dz_i d\sigma_i$$

E_{QC} ~ cte along the dissociation curve

➡ **no spin exchange ⇨ no bonding**

Heitler-London



- Heitler-London (HF) wf :

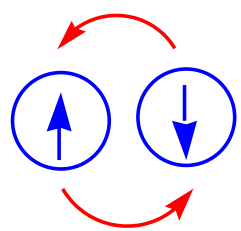
$$\Psi_{HL} \propto |a\bar{b}| + |b\bar{a}|$$

$$E_{HL} = \frac{\langle (|a\bar{b}| + |b\bar{a}|) | H^{él} | (|a\bar{b}| + |b\bar{a}|) \rangle}{\langle (|a\bar{b}| + |b\bar{a}|) | (|a\bar{b}| + |b\bar{a}|) \rangle}$$

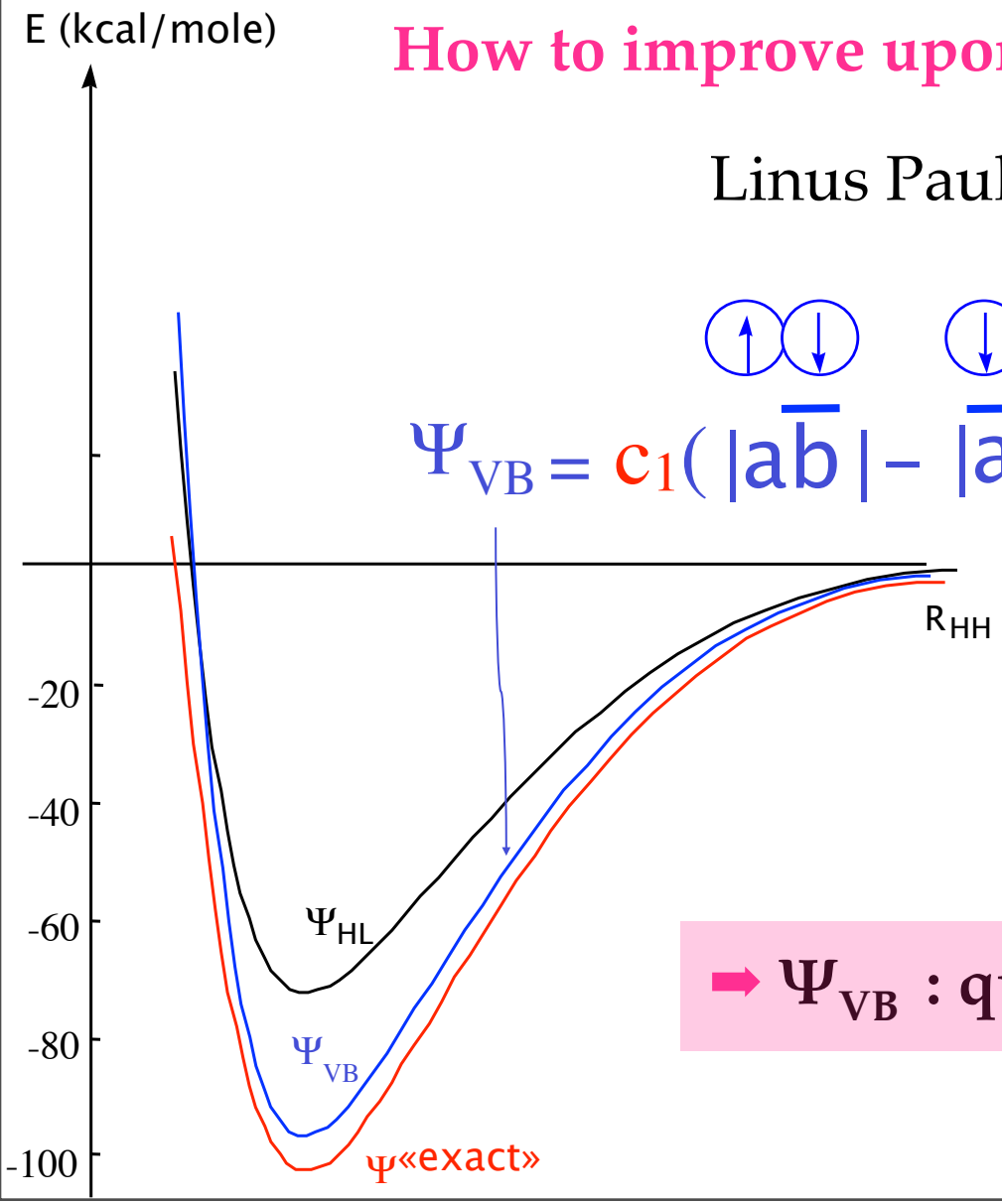
$$\Leftrightarrow E_{HL} = \frac{1}{\sqrt{(1+S_{ab}^2)}} (\underbrace{h_{aa} + h_{bb} + J_{ab}}_{E_{QC}} + \underbrace{2h_{ab}S_{ab} + K_{ab}}_{<0})$$

$$with : \begin{cases} h_{ab} = \int a^*(1) b(1) h(1) d\tau_1 \\ K_{ab} = \iint a^*(1) b(1) \frac{1}{r_{12}} b^*(2) a(2) d\tau_1 d\tau_2 \end{cases}$$

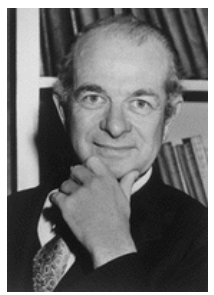
➡ **Physical origin of the chemical bond : spin exchange between AOs**



The VB wave function



How to improve upon the HL wave function ?



Linus Pauling (1930-33) :

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

Covalent + ionic superposition

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

Heitler-London

➡ Exercise 1 :

1. Expand the Heitler-London wave-function for H_2 : $\Psi_{HL} = N(|a\bar{b}| + |b\bar{a}|)$, and factorize it in terms of spatial and spin part, to show that it corresponds to a singlet state.
2. Express the normalization factor N as a fonction of the Atomic Orbitals overlap S_{ab}.
3. Propose a similar VB wave function for the triplet state. Express its energy. Deduce an approximate value for the singlet-triplet gap.
4. Develop the Hartree-Fock wave-function for H_2 (Hund-Mulliken) : $\Psi_{HF} = \frac{1}{\sqrt{2}}|\sigma_g \overline{\sigma_g}|$ in order to express it in the atomic orbital basis. We will use : $\sigma_g = N'(a+b)$, where N' it to be precised. Make the correspondance with Pauling's VB wave-function for H_2.

Heitler-London

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

antisymetric $\Rightarrow$ **Singlet**

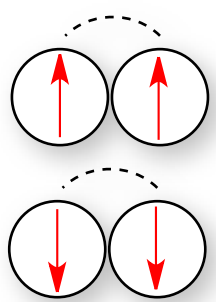
$$\Psi_T = \frac{|a\bar{b}| - |b\bar{a}|}{\sqrt{2(1-S_{ab}^2)}} \propto [a(1)b(2) - a(2)\,b(1)] \otimes [\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)],$$

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

Note that :

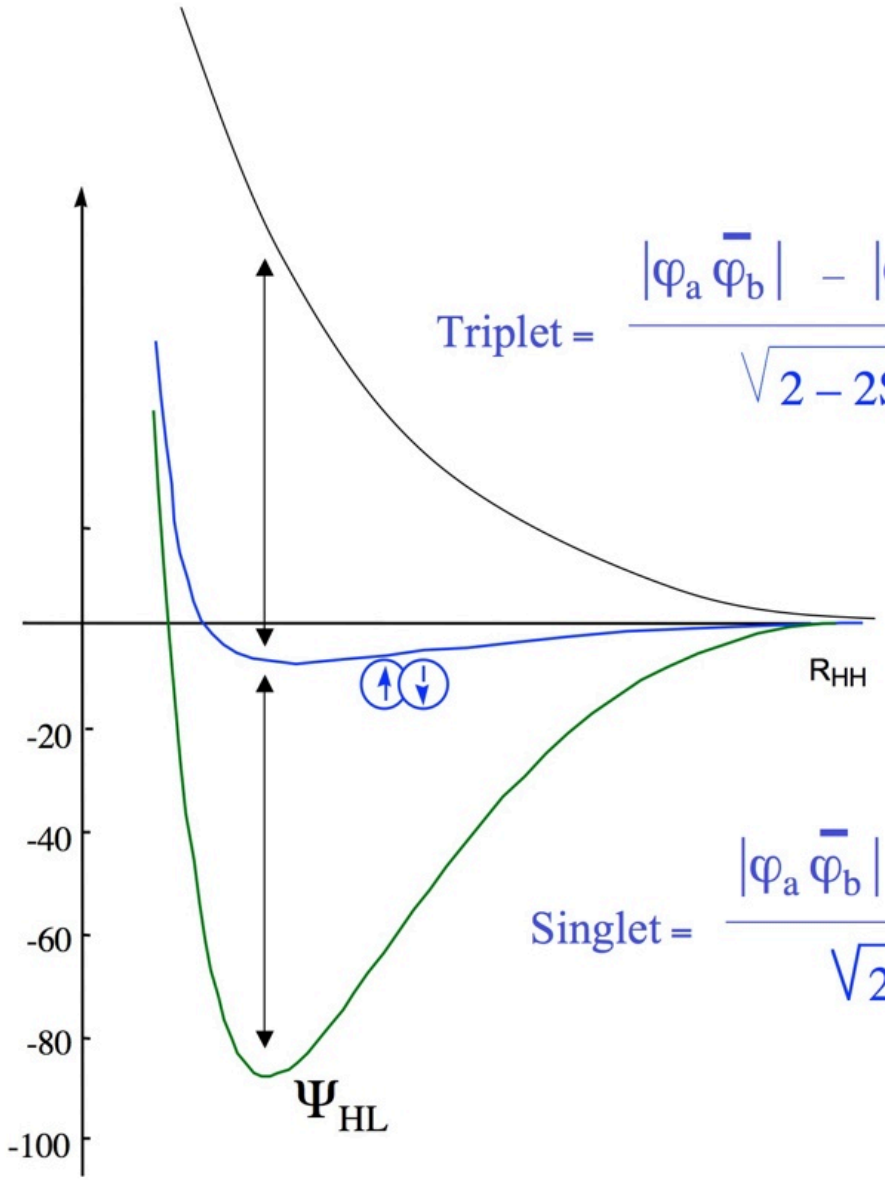
$$\Psi_T \propto |ab| = [a(1)b(2) - a(2)\,b(1)] \otimes [\alpha(1)\,\alpha(2)] \Rightarrow M_S = +1$$

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



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

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 $\approx 2De$

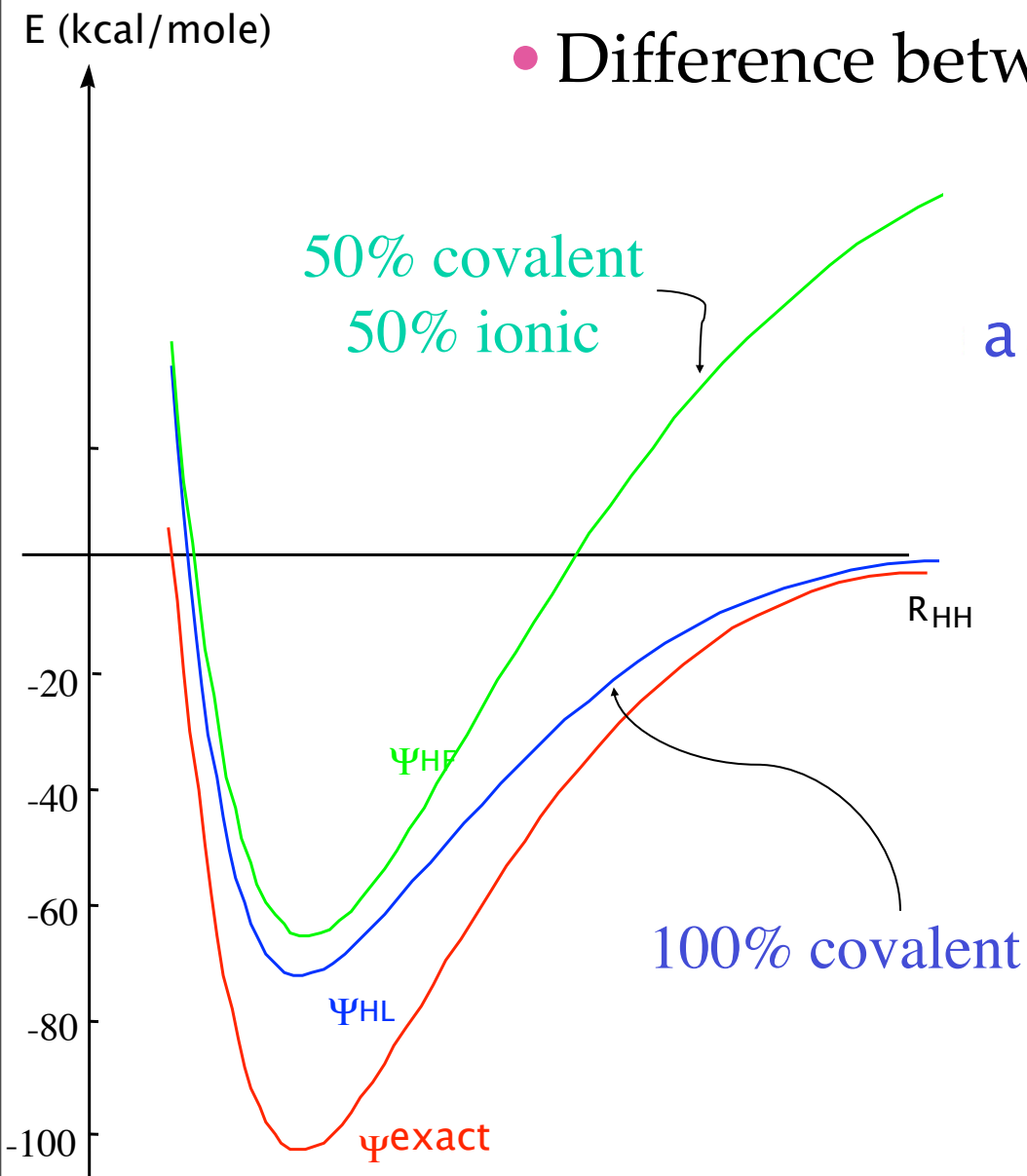
VB vs. MO

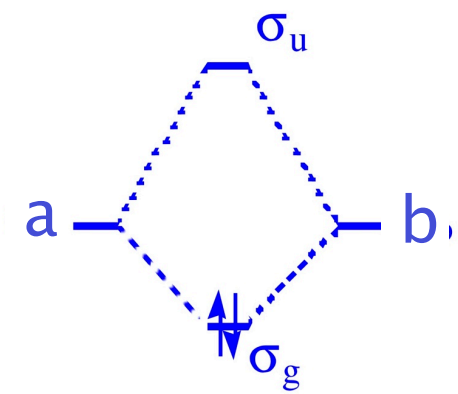
➡ Exercise 1 :

1. Expand the Heitler-London wave-function for H_2 : $\Psi_{HL} = N(|a\bar{b}| + |b\bar{a}|)$, and factorize it in terms of spatial and spin part, to show that it corresponds to a singlet state.
2. Express the normalization factor N.
3. Propose a similar VB wave function for the triplet state. Express its energy. Deduce an approximate value for the singlet-triplet gap.
4. Develop the Hartree-Fock wave-function for H_2 (Hund-Mulliken) : $\Psi_{HM} = \frac{1}{\sqrt{2}}|\sigma_g \overline{\sigma_g}|$ in order to express it in the atomic orbital basis. We will use : $\sigma_g = N'(a+b)$, where N' it to be precised. Make the correspondance with Pauling's VB wave-function for H_2.

VB vs. MO

- Difference between HL and HF ?





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

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

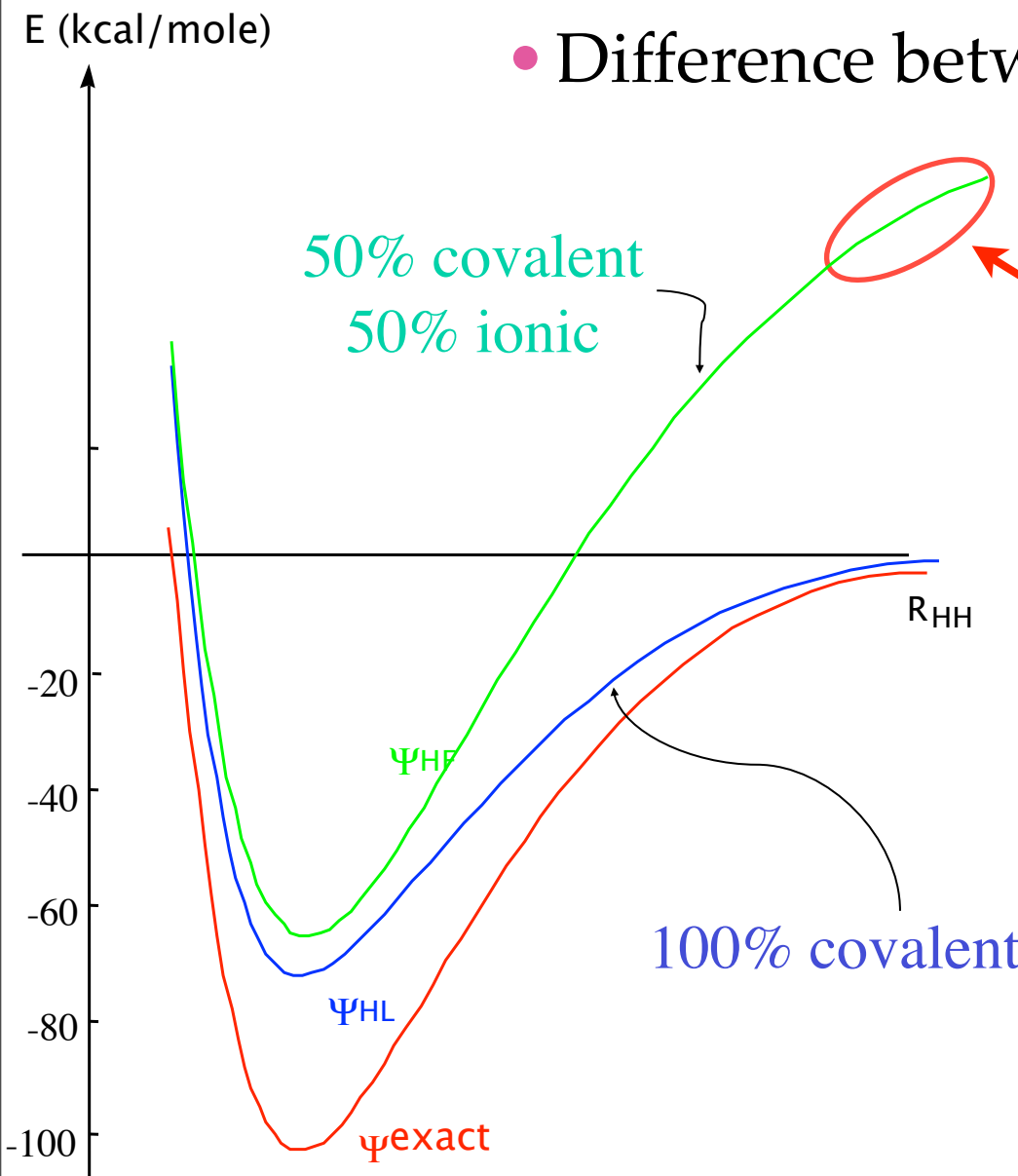
$$\Psi_{HF} = |\sigma_g \bar{\sigma}_g|$$

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

50% covalent 50% ionic

VB vs. MO

- Difference between HL and HF ?



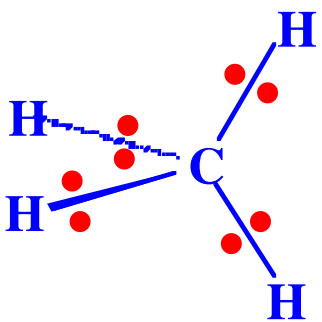
Optimal ≈ 70-80% covalent
30-20% ionic

➡ HF and HL are at about the same distance from optimal

The VB wave function

- Extension to the general case :

Lewis :

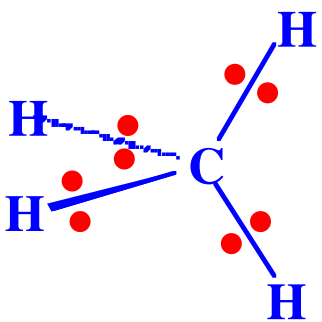


- We want to construct a VB w.f. which corresponds to Lewis' picture
- Which orbitals to use ?

The VB wave function

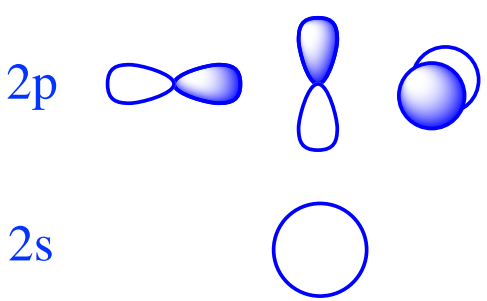
- Extension to the general case / 1) hybridization :

Lewis :



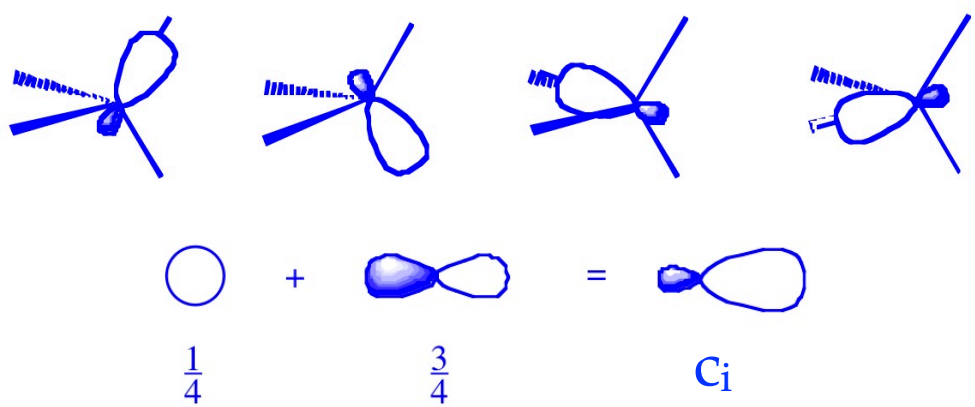
- We want to construct a VB w.f. which corresponds to Lewis' picture
- Which orbitals to use ?

Atomic Orbitals



Unitary transformation

Hybrid Orbitals

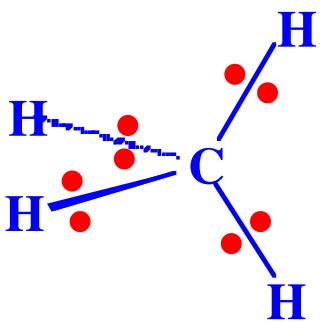


Four equivalent directional sp^3 orbitals

The VB wave function

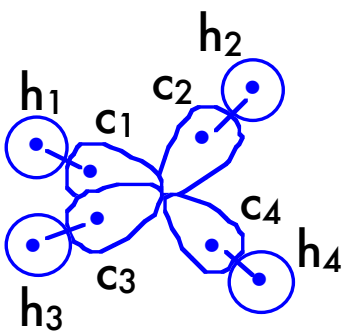
- Extension to the general case / 1) hybridization :

Lewis :



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

HL :



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

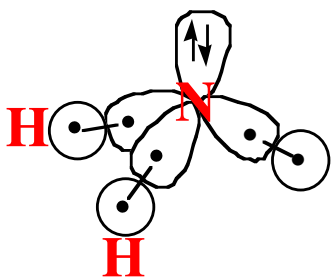
Electrons occupy **localized** orbitals (atomics, hybrids,...)

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

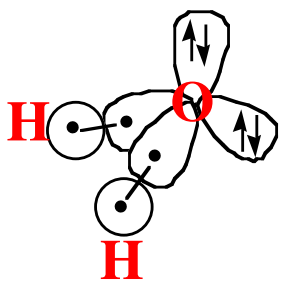
The VB wave function

- Extension to the general case / 1) hybridization :

« sp^3 »

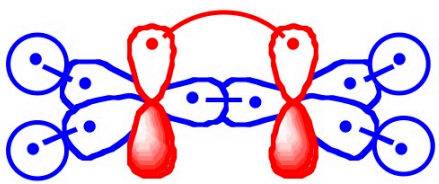


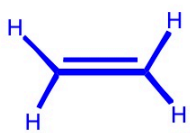
NH_3



H_2O

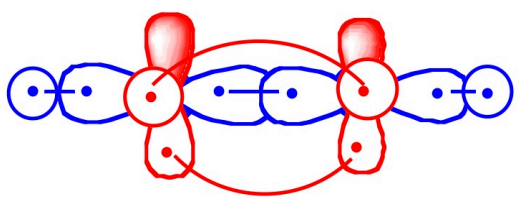
Three « sp^2 » hybrids
+ $2p_z$ (unchanged)





Ethylen

Two « sp » hybrids
+ $2p_x$ + $2p_y$ (unchanged)



The VB wave function

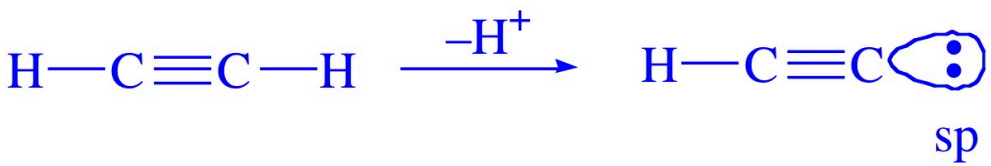
- Hybridization, a legitimate and useful concept :
  - Three categories of C–C bonds :

	alkanes	alkenes	alkynes
R (Å)	**1.09**	**1.08**	**1.06**
D_e (kcal)	**100**	**110**	**132**
ω (cm^{-1})	**2900**	**3100**	**3300**
Hybridation	sp^3	sp^2	sp

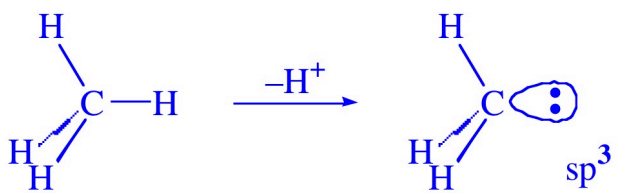
➡ Bond properties transferability

The VB wave function

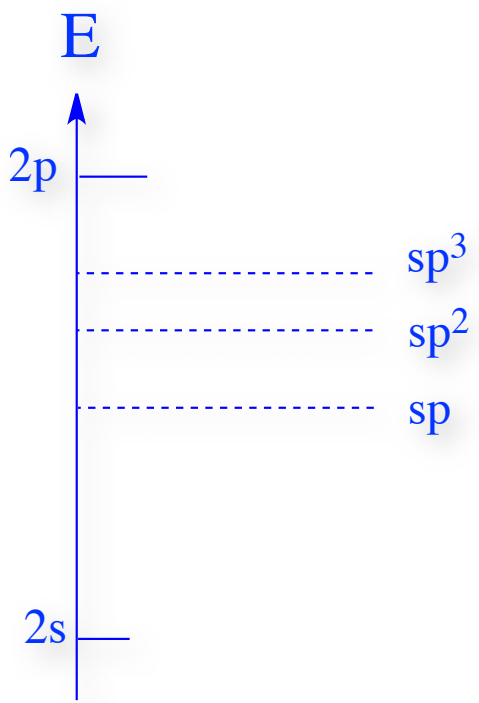
- Hybridization, a legitimate and useful concept :
  - Relative acidities of hydrocarbons :



pK(H–C≡C–H) ~ 25



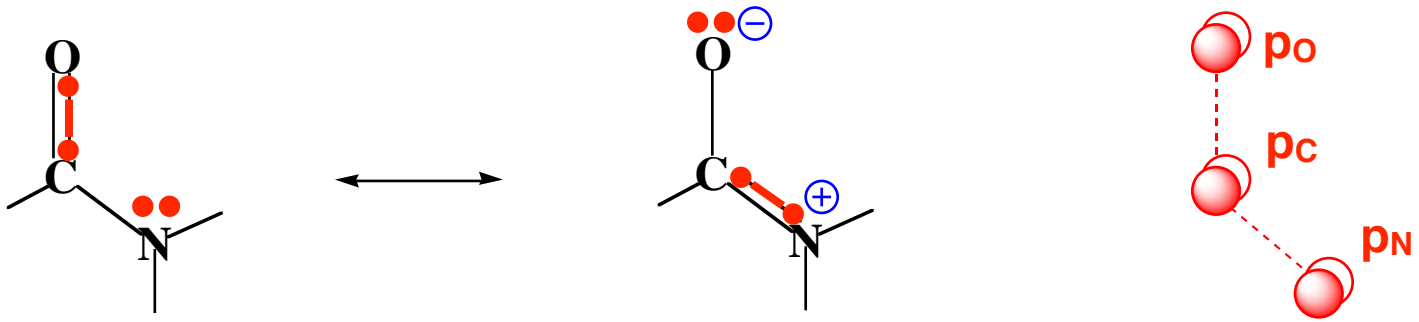
pK(CH_4) ~ 50



➡ $E(sp) < E(sp^3) \Rightarrow H–C\equiv C^-$ more stable than H_3C^-

The VB wave function

- Extension to the general case / 2) mesomery :



1 **2**

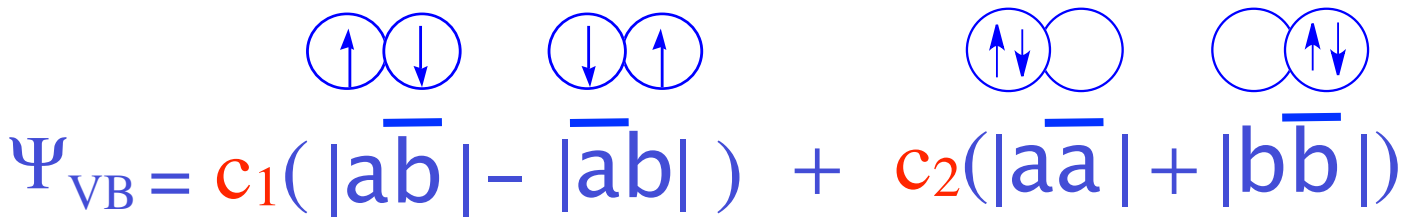
$$\Psi(\mathbf{1}\leftrightarrow\mathbf{2}) = C_1(\Psi_1) + C_2(\Psi_2)$$

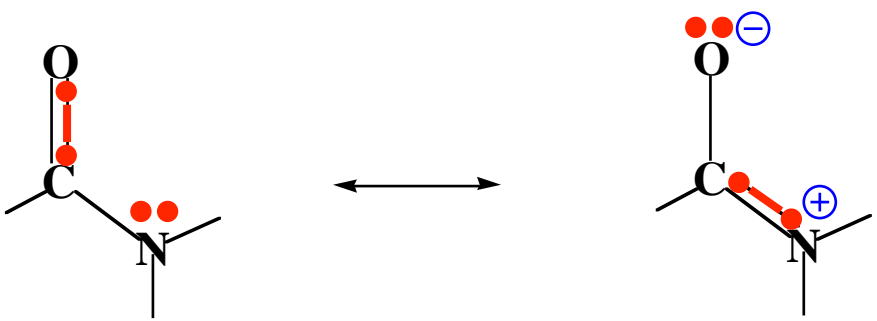
$$= C_1\left|p_N\overline{p_N}(p_O\overline{p_C} + p_C\overline{p_O})\right| + C_2\left|p_O\overline{p_O}(p_C\overline{p_N} + p_N\overline{p_C})\right|$$

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

The VB wave function

- Resonance concept :



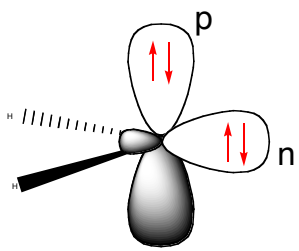


1 **2**

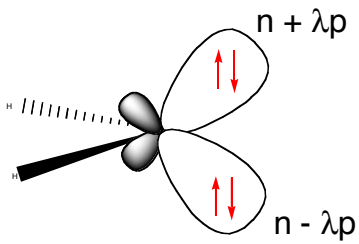
➡ The resonance concept is a central pillar of VB theory

VB vs. MO

➡ Exercise 2 :



ψ_{MO}



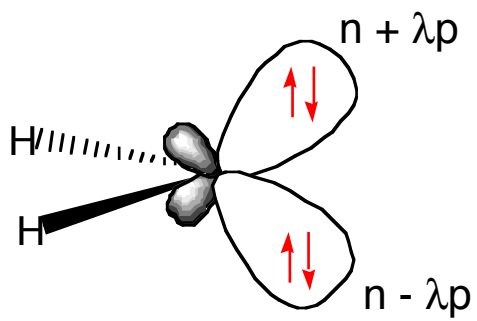
ψ_{VB}

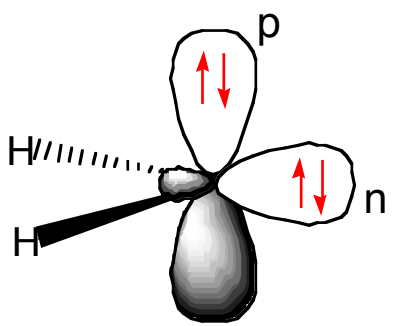
1. Focusing on the lone pairs only, write the four-electron single-determinants Ψ_{MO} and Ψ_{VB}.
2. Expand Ψ_{VB} into elementary determinants containing only n and p orbitals, eliminate determinants having two identical spinorbitals, and show the equivalence between Ψ_{VB} and Ψ_{MO}.

Continuation of the exercise : https://wiki.lct.jussieu.fr/workshop/index.php/VBTutorial1

VB vs. MO

➡ Exercise 2 (answer) :





2 equivalent lone pairs

2 non-equivalent lone pairs

1) What is the difference between Ψ_{VB} and Ψ_{MO} ?

$$\Psi_{VB} = |(n+\lambda p)(\bar{n}+\lambda\bar{p})(n-\lambda p)(\bar{n}-\lambda\bar{p})|$$

$$= \lambda^2|n\bar{n}p\bar{p}| - \lambda^2|n\bar{p}p\bar{n}| - \lambda^2|p\bar{n}n\bar{p}| + \lambda^2|p\bar{p}n\bar{n}| + \cancel{\ldots|n\bar{n}n\bar{p}|} + \ldots$$

$$= |n\bar{n}p\bar{p}| = \Psi_{MO}$$

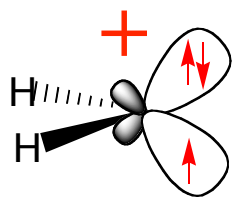
No difference!

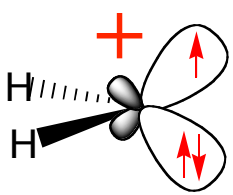
VB vs. MO

➡ **Extra :** Does VB predict 1 or 2 ionisation potentials ?

lasy reasoning
(very common !) :

$\Psi_{VB1} = \Psi_{VB2}$

$\Psi_{VB2} =$ 

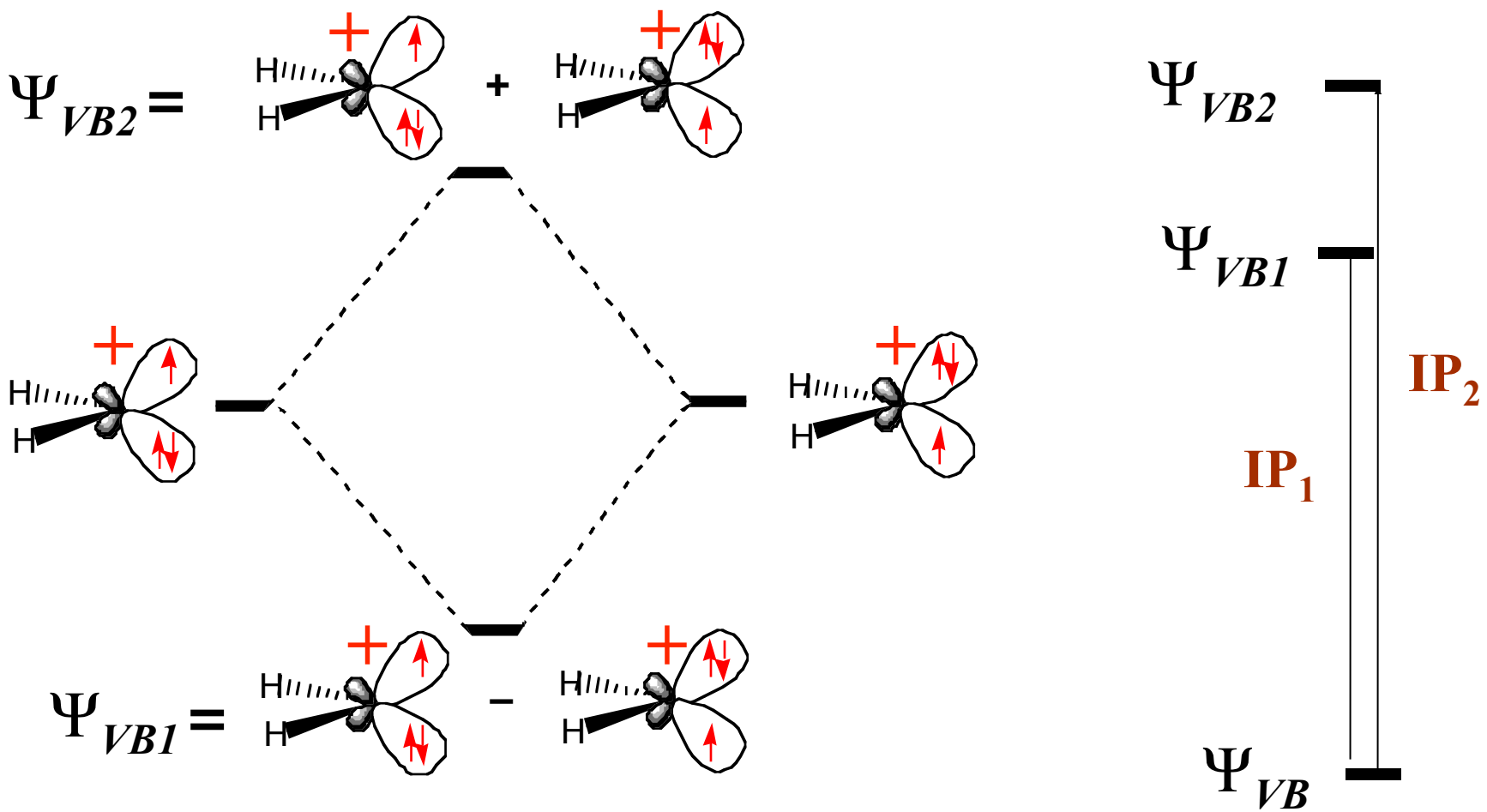
$\Psi_{VB1} =$ 

IP

Ψ_{VB}

VB vs. MO

➡ **Extra :** Does VB predict 1 or 2 ionisation potentials ?



In short

➡ VB theory :

VB theory lean on a few central paradigms

- electron and electron pairs are essentially localized in space
- spin exchange between two electrons as the essence of the chemical bond (covalent structures)
- resonance as a stabilizing factor (cov/ionic, multi-structures)

➡ The way VB to conciliate Chemists' vision and QM

In short

➡ 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)