

Benoît BRAÏDA*

ICS Summer school 2013

Valence Bond theory

Laboratoire de Chimie Théorique
Université Pierre et Marie Curie - Paris6

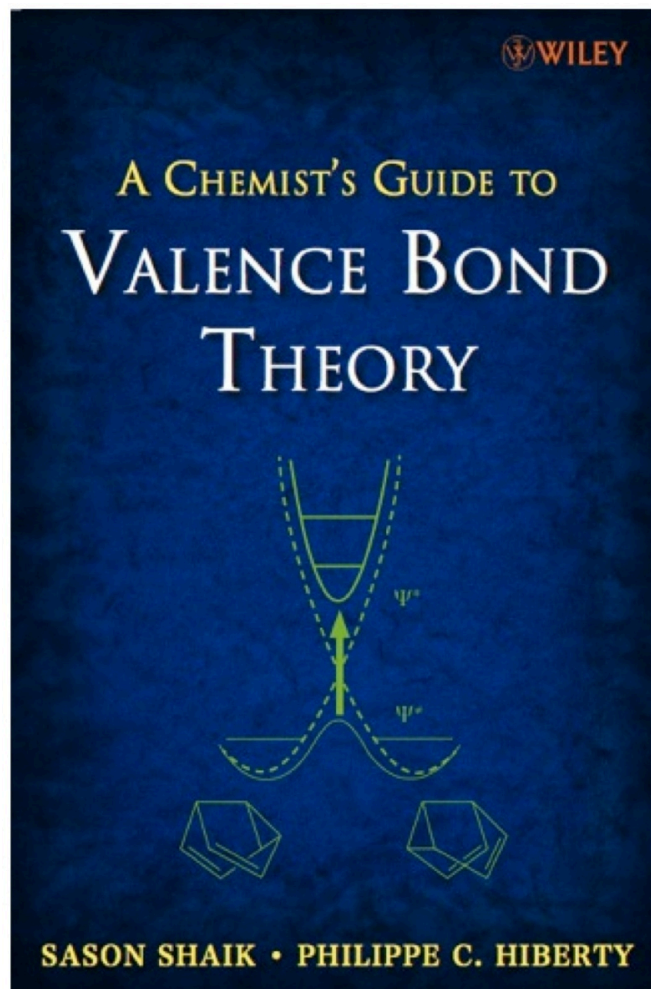
* benoit.braida@upmc.fr

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 exercises)

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

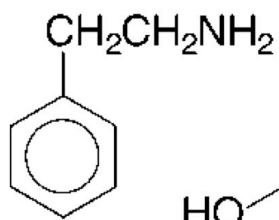
Chemistry

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

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

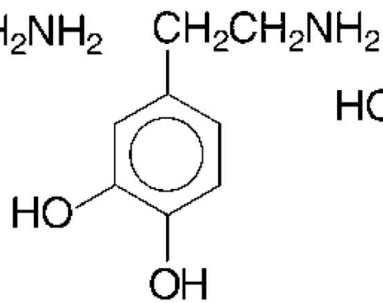
Chemistry

Genes → Chemicals → Emotions



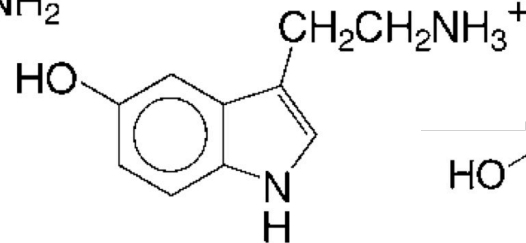
1, PEA

*Love
Well-being*



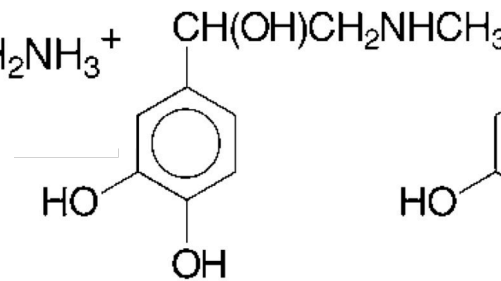
2, Dopamine

Reward



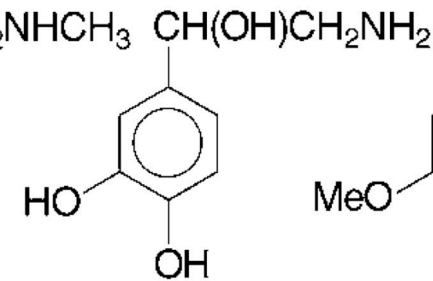
3, Serotonin

*«mood
molecule»*



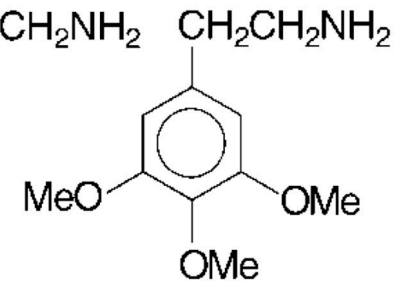
4, Adrenaline

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

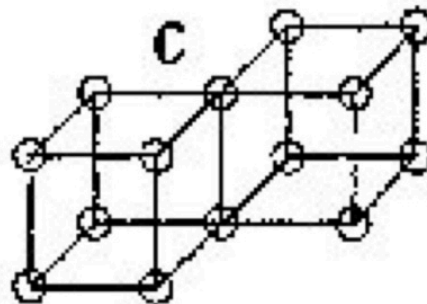
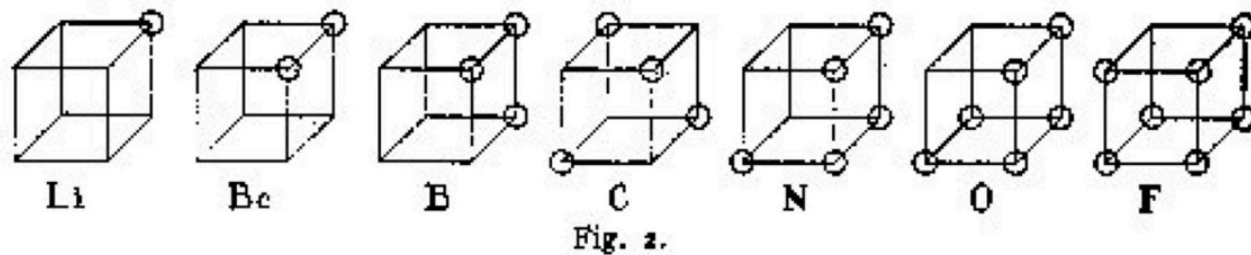
Heuristic models

- Lewis' model :

THE ATOM AND THE MOLECULE.

BY GILBERT N. LEWIS.

JACS 1916, 762

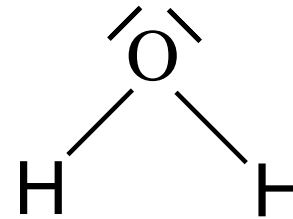


Heuristic models

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



Lewis' time

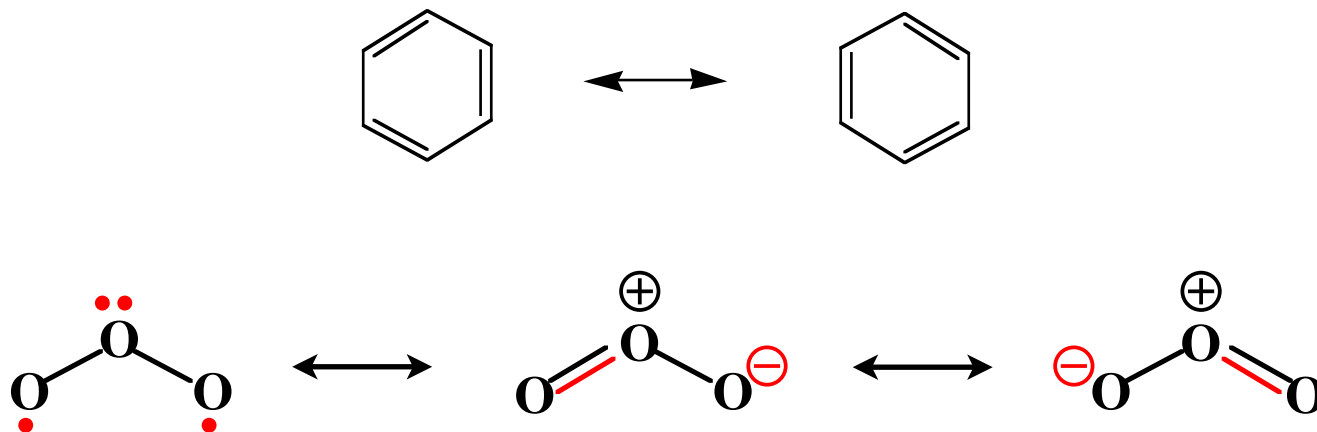


Today

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

Heuristic models

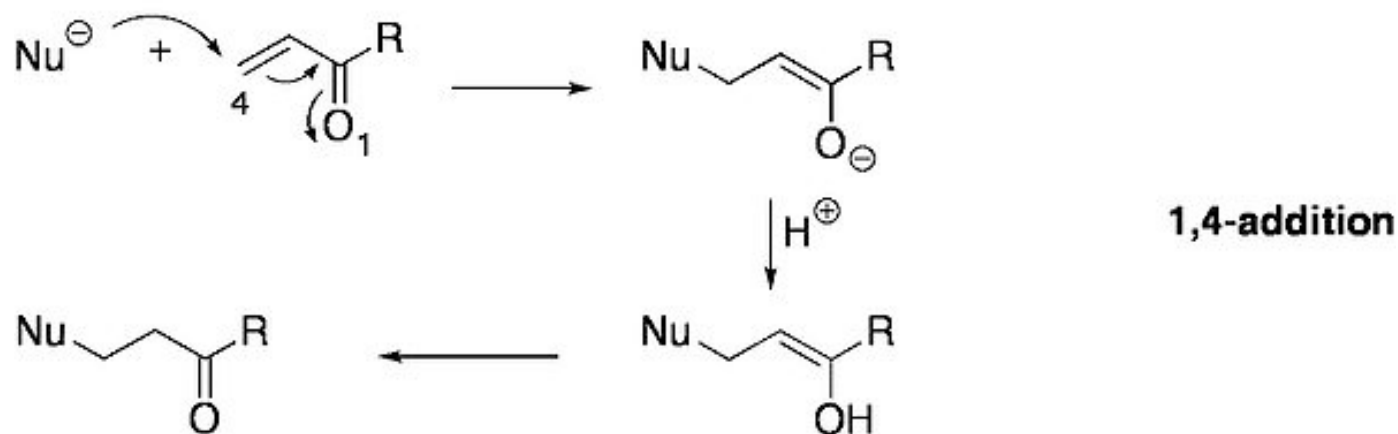
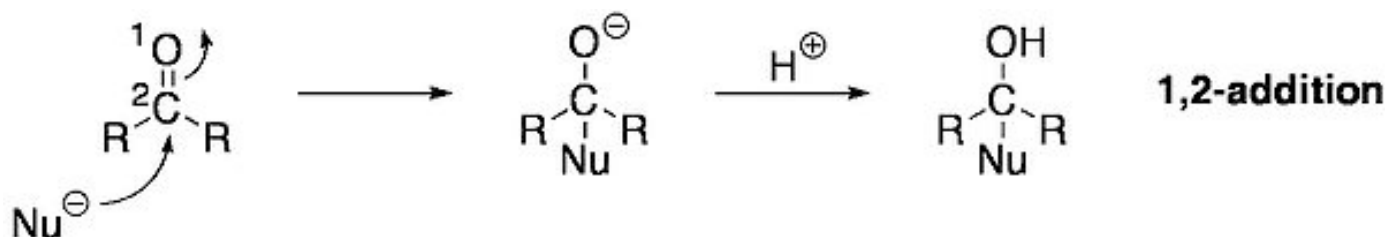
- Mesomery / resonance :
 - Arndt, Robinson, Ingold (1924-38) : mesomery
 - Pauling, Wheland (1928-33) : resonance theory



➔ when more than one Lewis structure is needed

Heuristic models

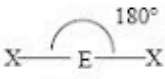
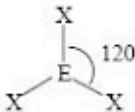
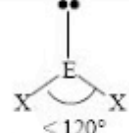
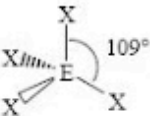
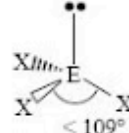

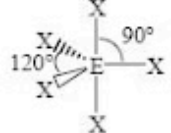
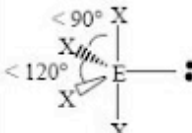
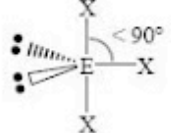
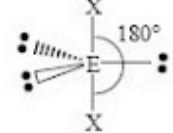

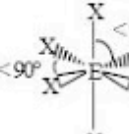
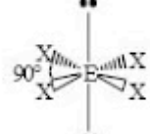

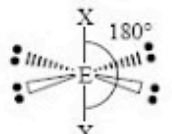
- Arrow-pushing language :



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

Heuristic models

- VSEPR model :

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

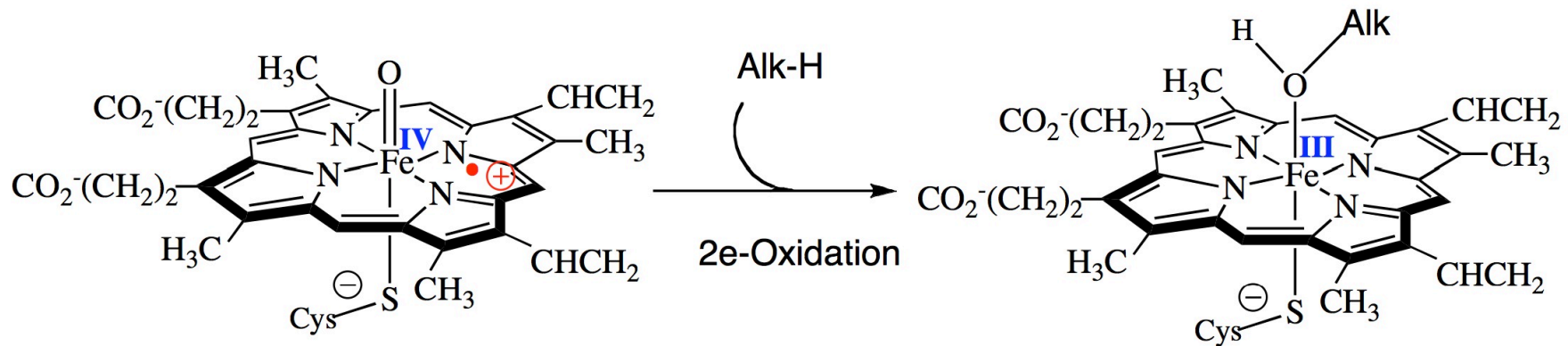
➔ rationalization of molecular geometries

Heuristic models

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

Quantum Chemistry

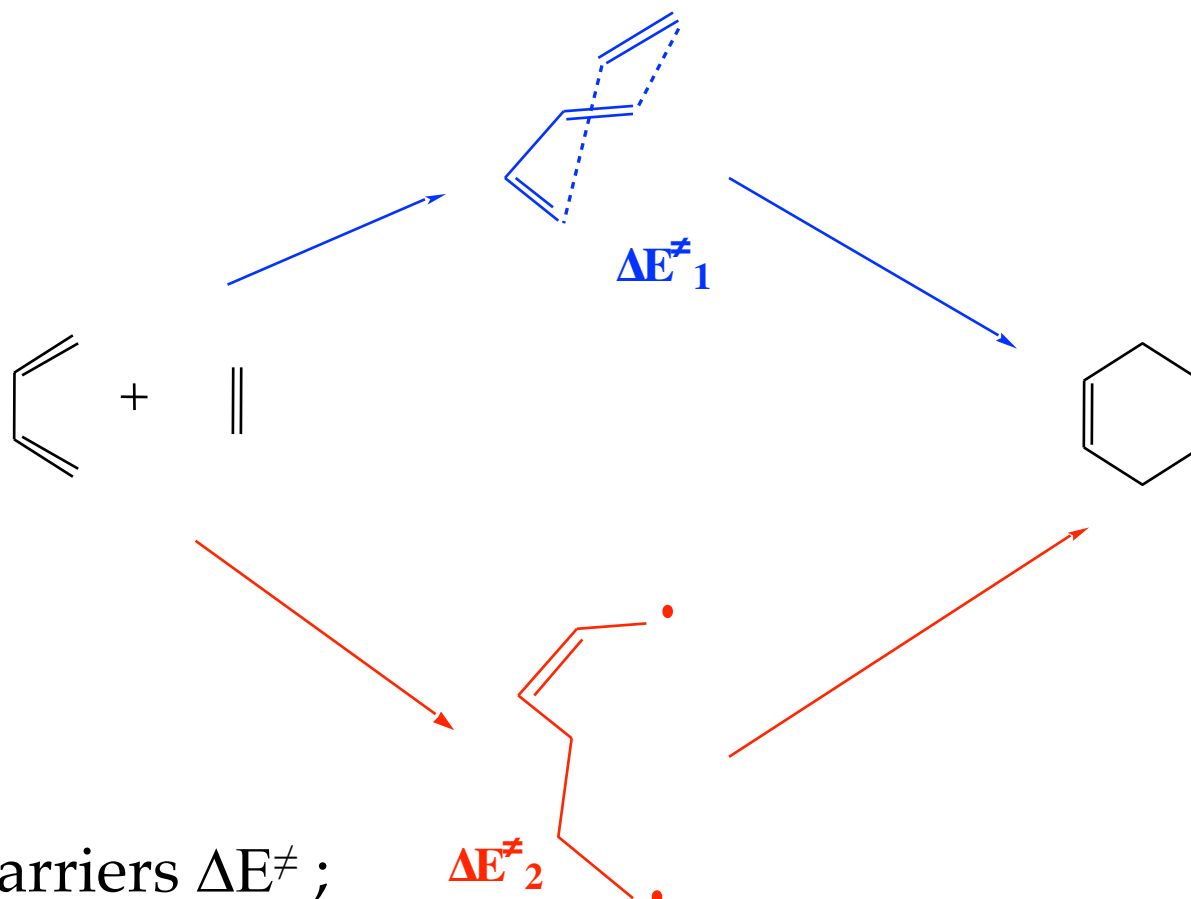
- Accurate quantum theory based calculations can provide :



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

Quantum Chemistry

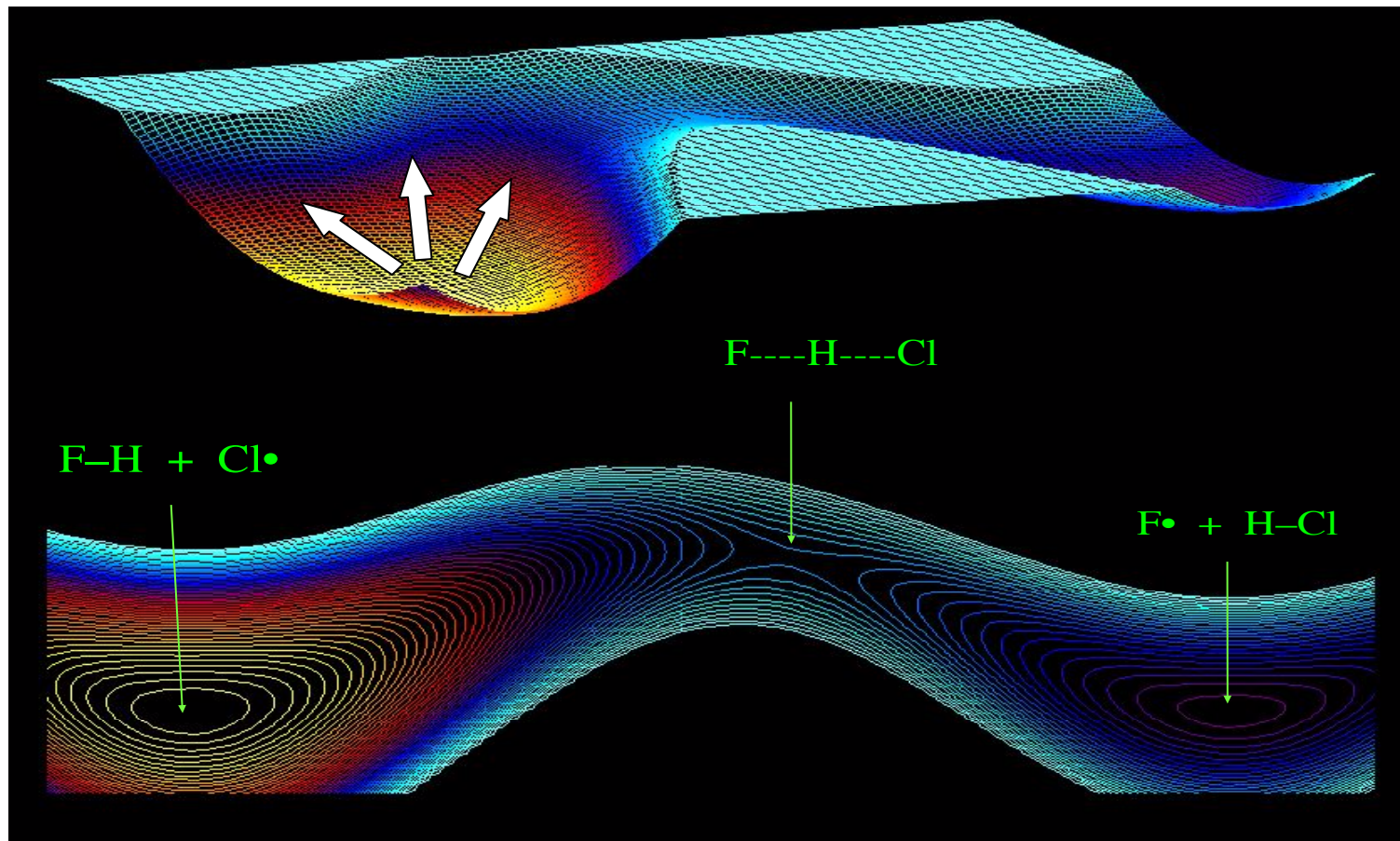
- Accurate quantum theory based calculations can provide :



- accurate barriers ΔE^\ddagger ;
- 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**



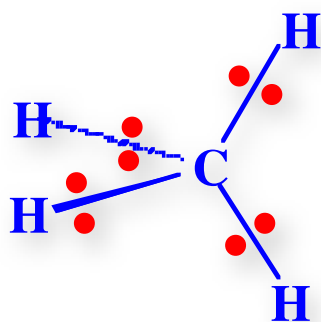
$\Delta E^\ddagger = 22 \text{ kcal.mol}^{-1}$
 \Rightarrow low barrier, easy



?
have to do the computation...

Chemists' «schizophrenia»

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

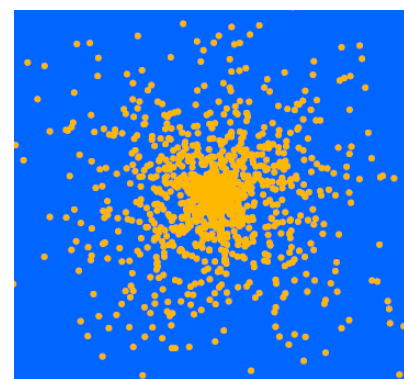


Lewis model, arrow-pushing language, VSEPR, hybridization,...

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

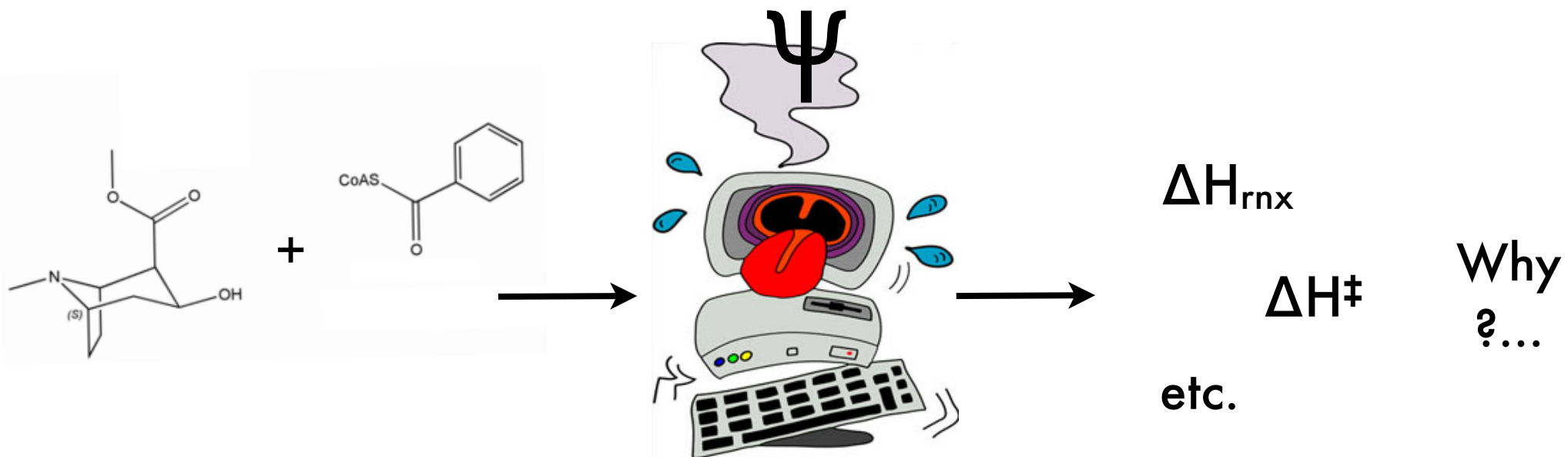
- **Quantitative theory** based on a delocalized particles vision :

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

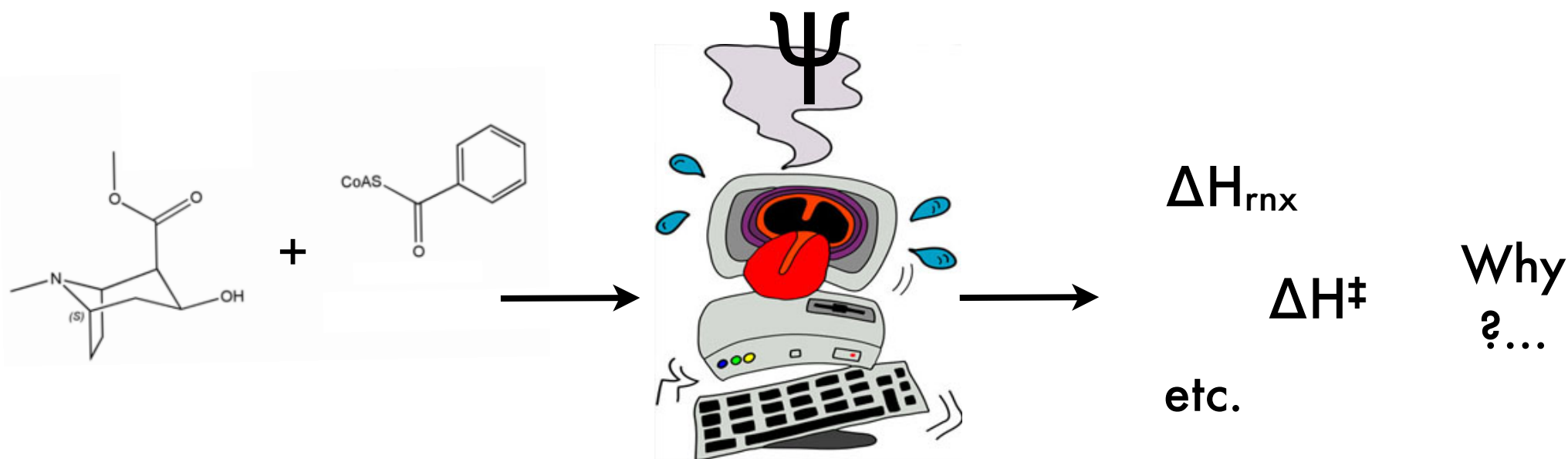


- **delocalized** particles (e^- , n^+)
- **indistinguishable** and all-interacting (no chemical bond)

Chemists' «schizophrenia»

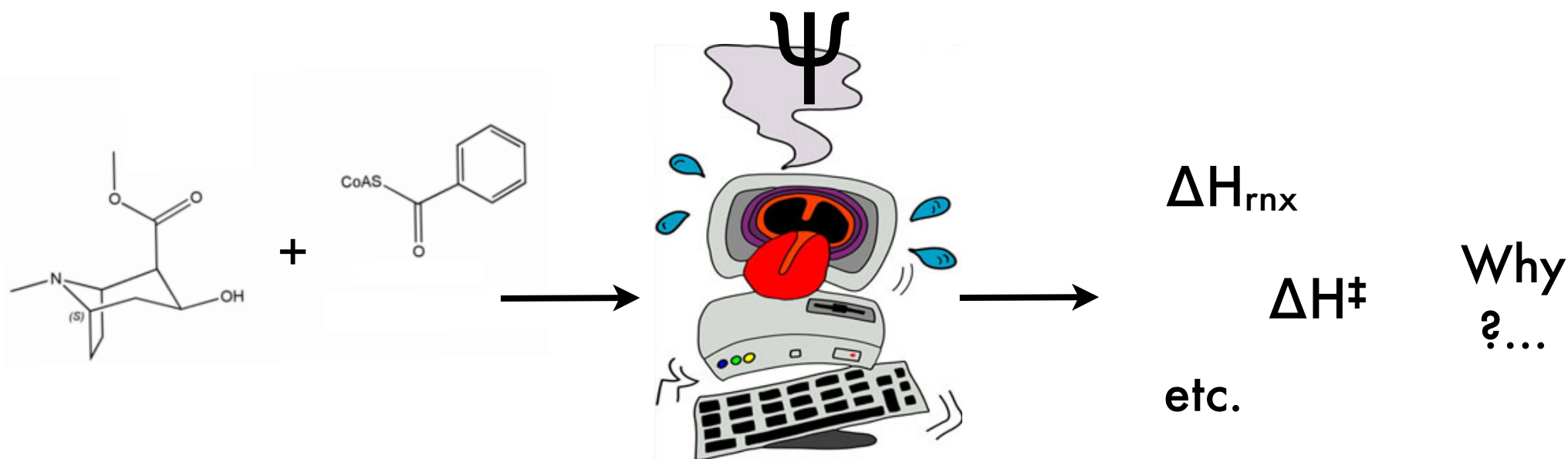


Chemists' «schizophrenia»



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

Chemists' «schizophrenia»



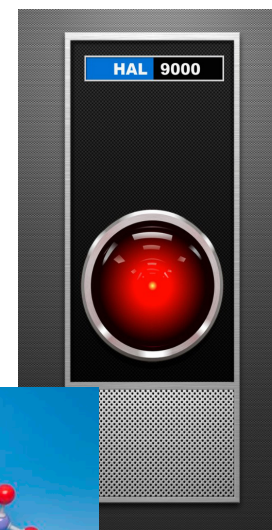
*«I am very glad the computer understands this.
But I would like to understand it too» (Eugene Wigner)*

Chemists' «schizophrenia»

The challenges :

- How to **build a bridge** between quantum mechanics and chemists' vision ?
- How to **organize** and **rationalize** the enormous and ever-increasing quantity of data produced ?

Interpretative methods

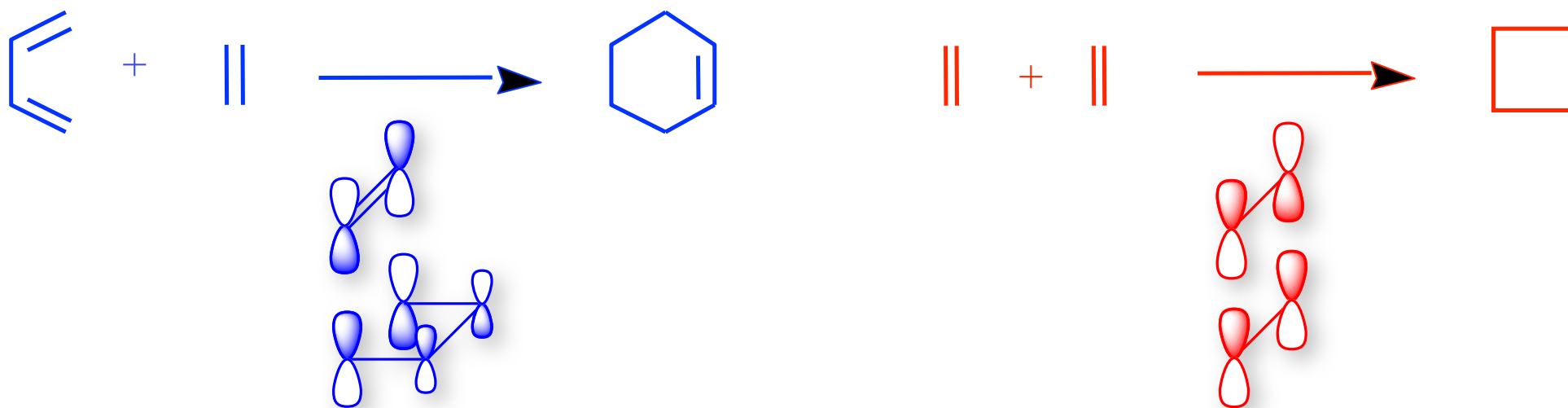


➔ Need for interpretative methods to act as **interface** between experiments and computations, to **create order**, and by doing this to **open new thoughts**

Interpretative methods

- Qualitative MO-based models :

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



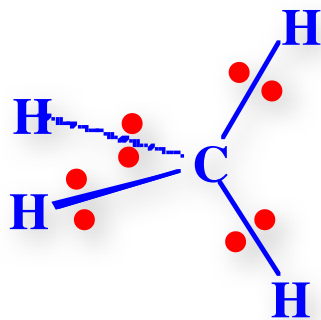
➔ Not quantitative (*a posteriori* rationalization)

Interpretative methods

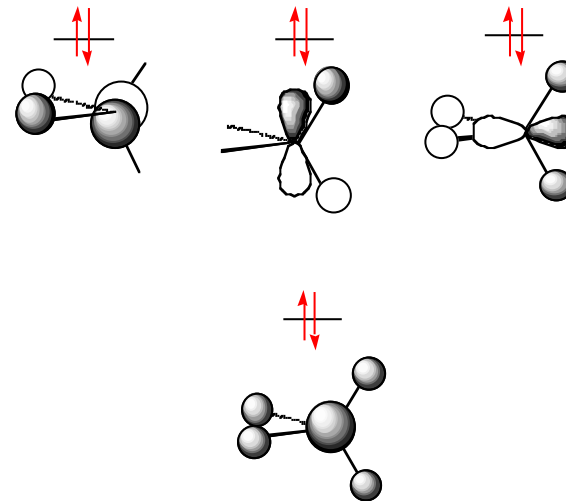
- Qualitative MO-based models :

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

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



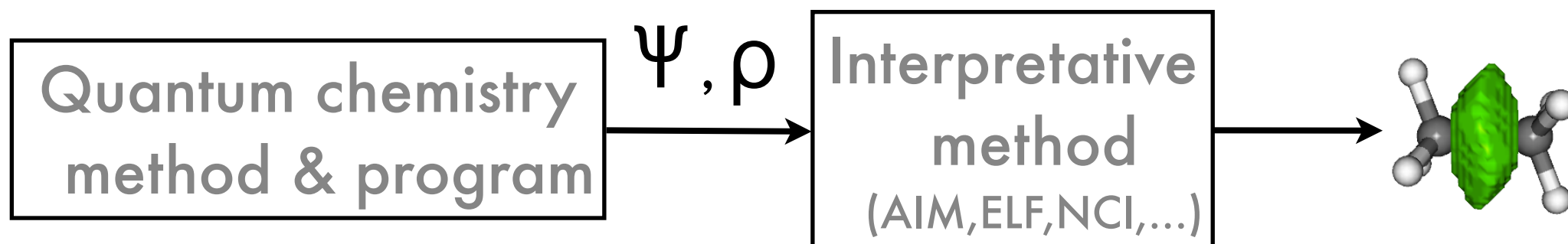
*Which one
to choose ?...*



➔ No direct link with chemists' local vision

Interpretative methods

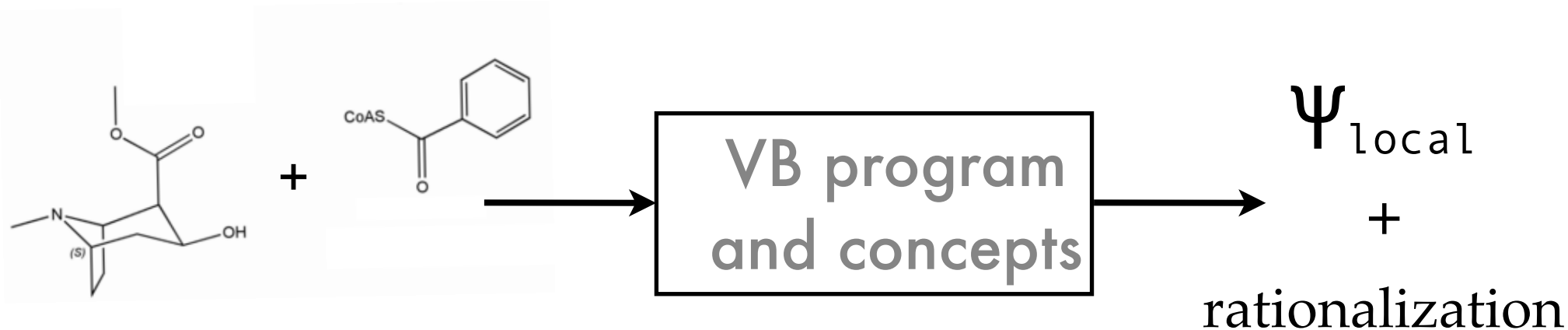
- Real space «topological» methods :



- ➔ 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

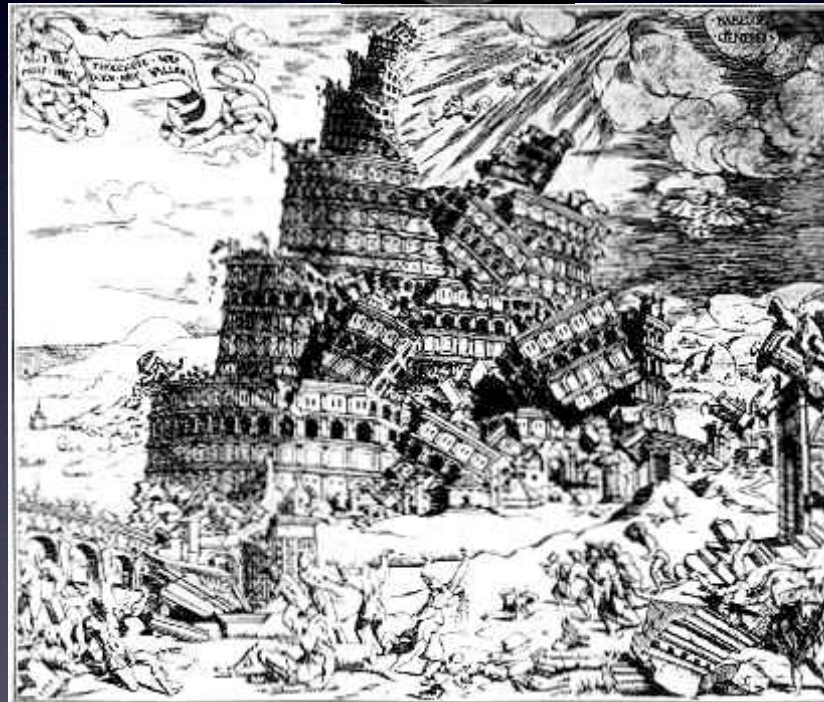


Successes of MO theory vs. VB «failures»

- ~1960-1980: The downfall

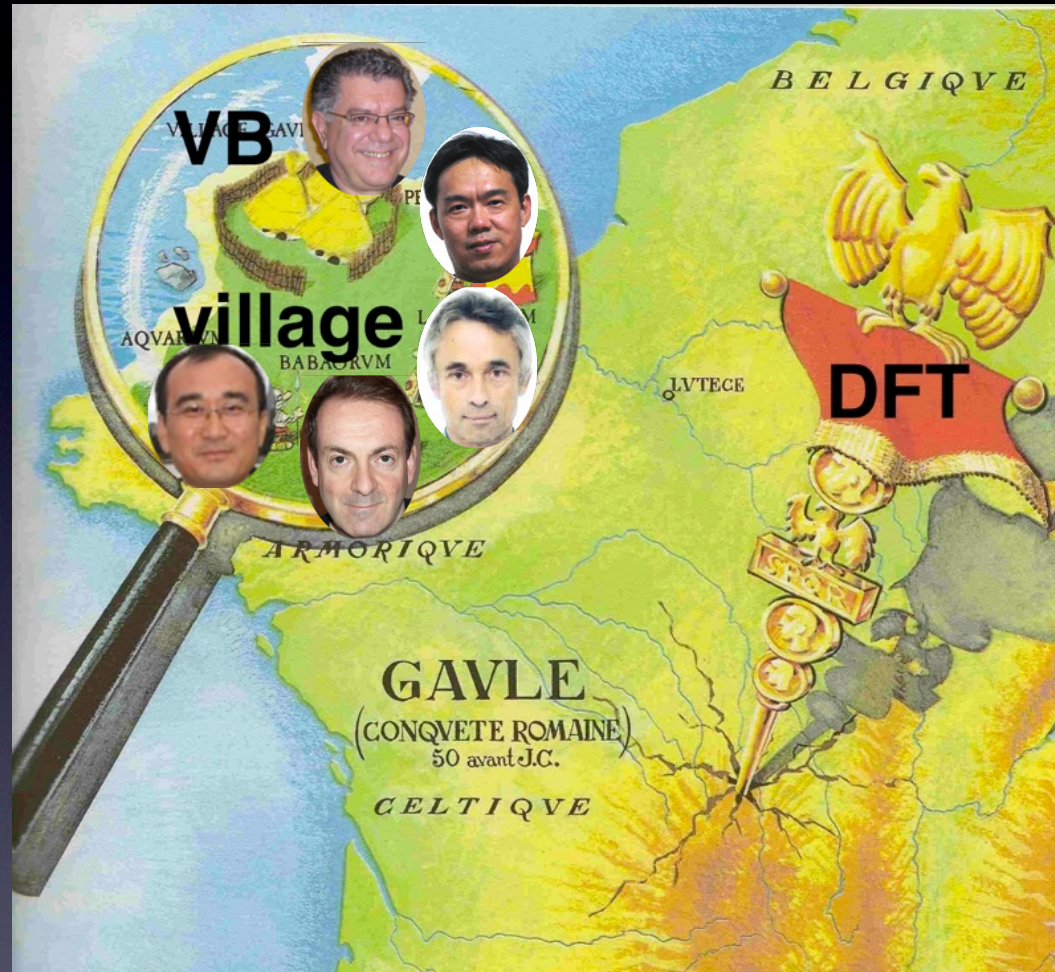


Sir John A. Pople



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 : $H_a \text{---} H_b$

- Heitler-London (1927) :

$$\Psi_{HL} = \overset{\begin{matrix} \uparrow & \downarrow \\ \circ & \circ \end{matrix}}{|a\bar{b}|} - \overset{\begin{matrix} \downarrow & \uparrow \\ \circ & \circ \end{matrix}}{|\bar{b}a|}$$

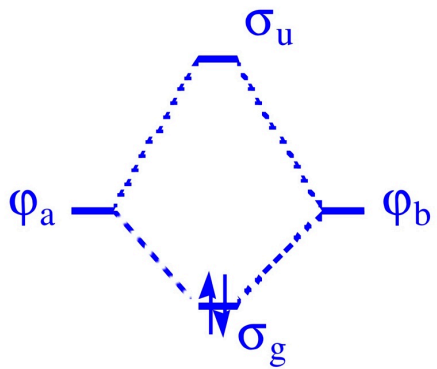
- Electrons in atomic orbitals
- Shared electron pair
(covalent bond)

➔ basis of **VB** theory

Heitler-London

Dihydrogen molecule H_2 : H_a — H_b

- Hund-Mulliken (1927) :



$$\sigma_u \propto a - b \quad \text{○●}$$

$$\sigma_g \propto a + b \quad \text{○○}$$

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

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

- Heitler-London (1927) :

A diagram showing two atomic orbitals, a and b , on the left and right respectively. Above them are two molecular orbitals: a bonding \overline{ab} orbital and an antibonding \overline{ba} orbital. The \overline{ab} orbital contains a pair of electrons, represented by two arrows pointing in opposite directions. The \overline{ba} orbital also contains a pair of electrons, represented by two arrows pointing in opposite directions.

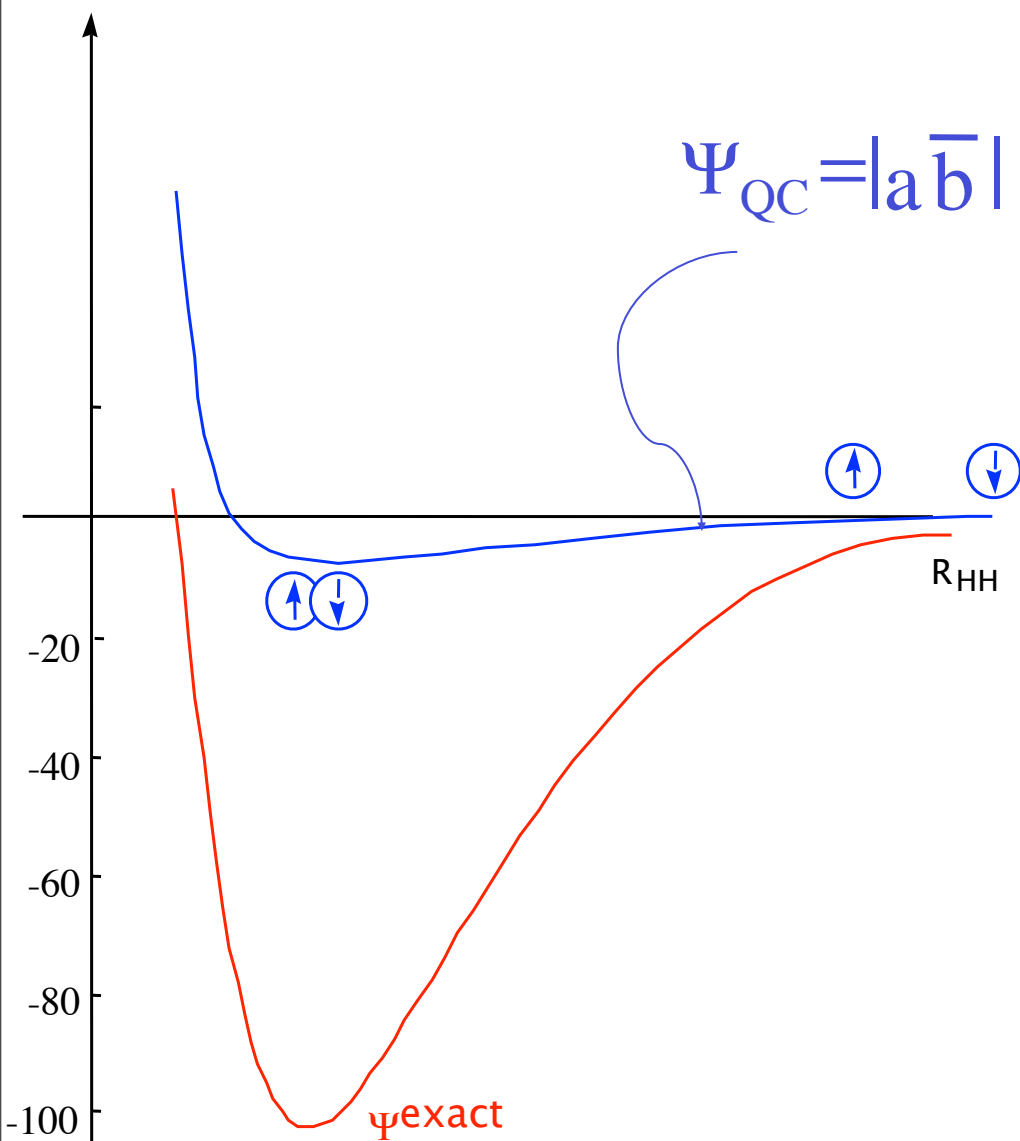
$$\Psi_{HL} = |\overline{ab}| - |\overline{ba}|$$

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

→ basis of **VB** theory

Heitler-London

E (kcal/mole)

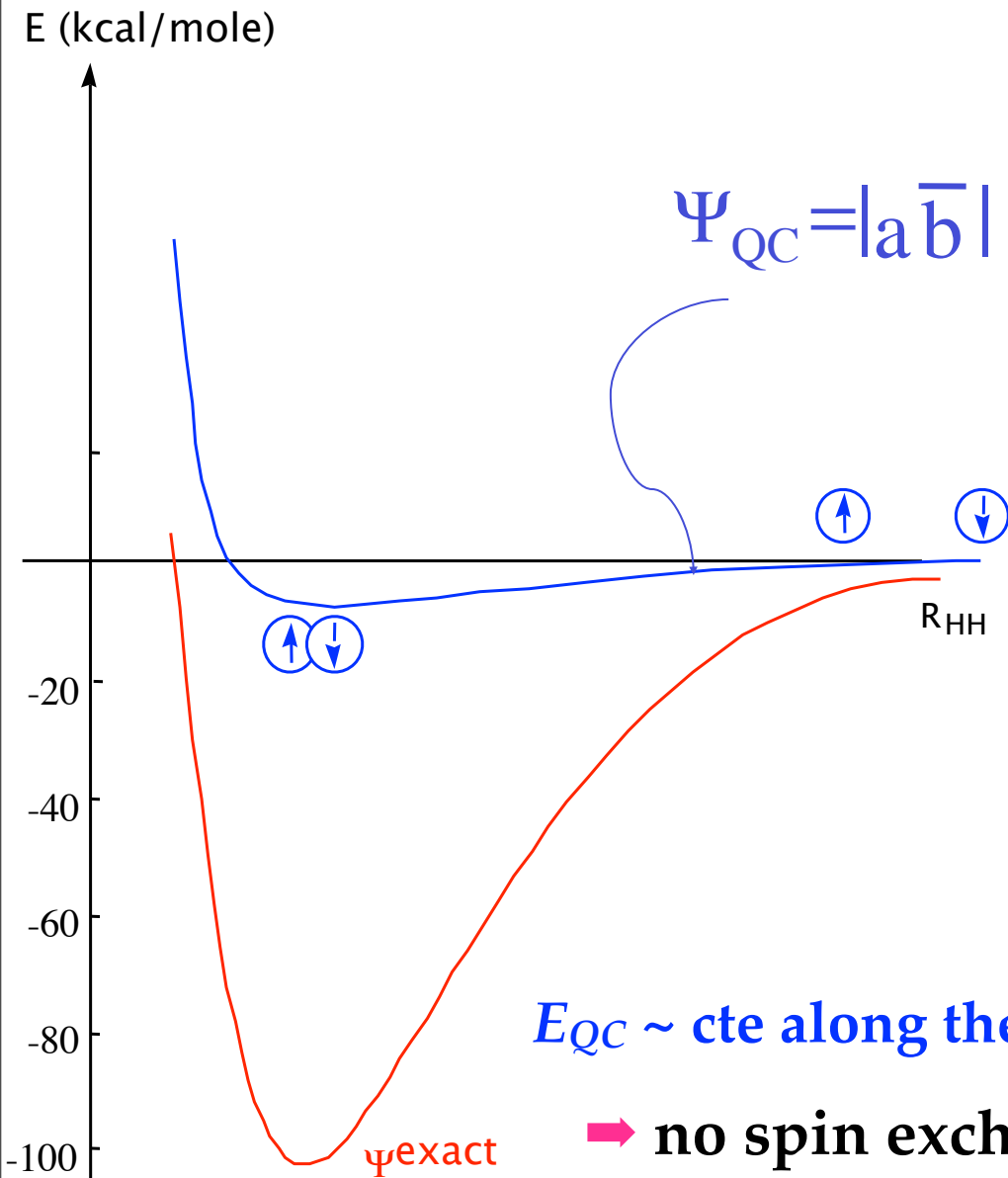


- Quasi-Classical (QC) state :

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

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

Heitler-London



- Quasi-Classical (QC) state :

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

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

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

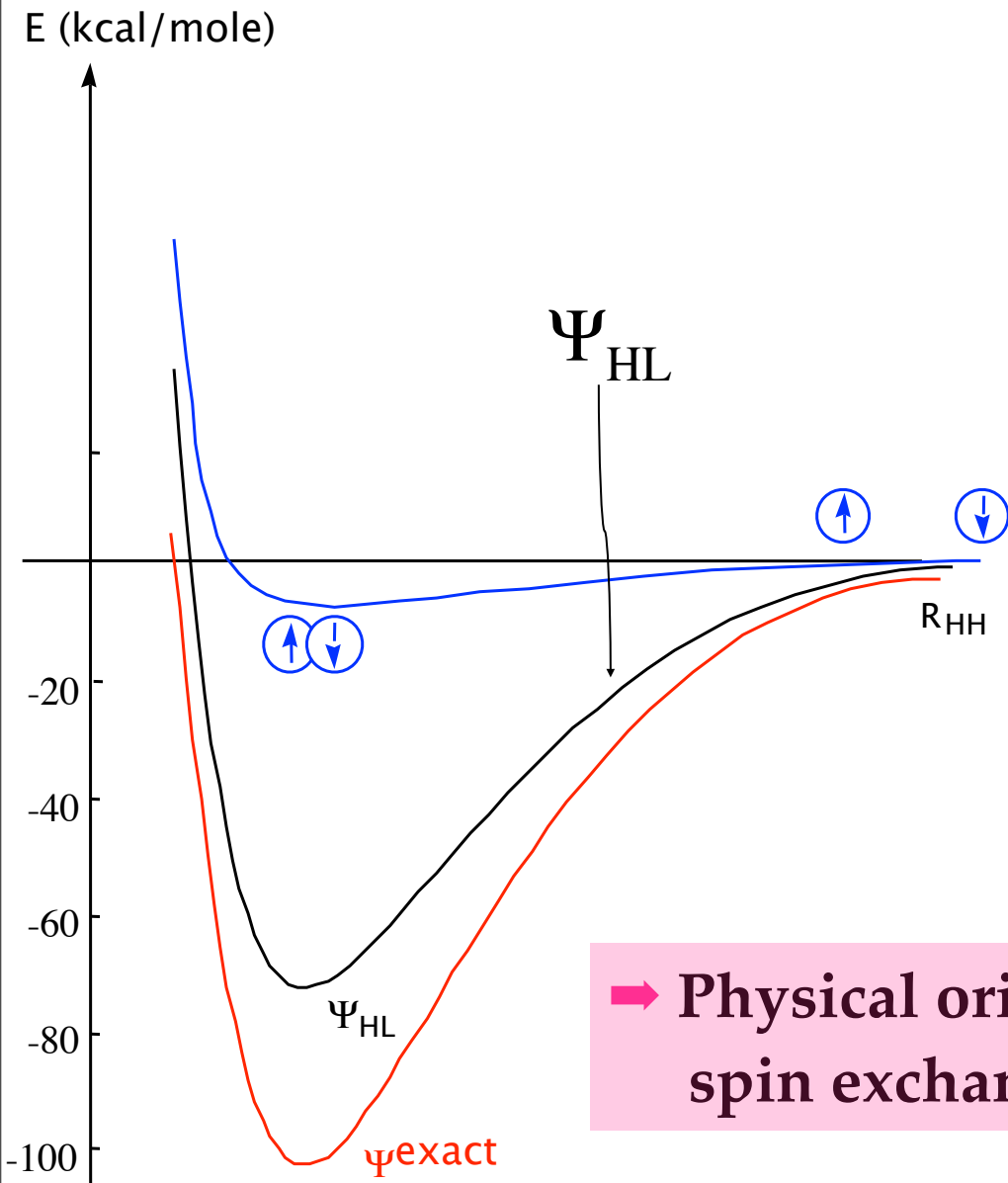
$$\text{with : } \begin{cases} h_{ii} = \int i^*(1) i(1) h(1) d\tau_1 \\ J_{ab} = \iint a^*(1) a(1) \frac{1}{r_{12}} b^*(2) b(2) d\tau_1 d\tau_2 \end{cases}$$

$$\text{and : } d\tau_i = dx_i dy_i dz_i d\sigma_i$$

$E_{QC} \sim \text{cte}$ along the dissociation curve

→ no spin exchange \Rightarrow no bonding

Heitler-London



- Heitler-London (HF) wf :

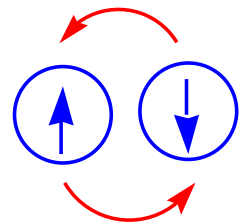
$$\Psi_{HL} \propto |a\bar{b}| + |b\bar{a}|$$

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

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

$$\text{with: } \begin{cases} h_{ab} = \int a^*(1)b(1)h(1)d\tau_1 \\ K_{ab} = \iint a^*(1)b(1)\frac{1}{r_{12}}b^*(2)a(2)d\tau_1d\tau_2 \end{cases}$$

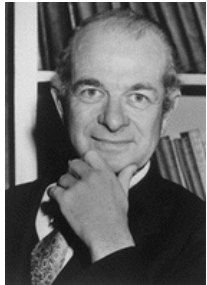
→ Physical origin of the chemical bond : spin exchange between AOs



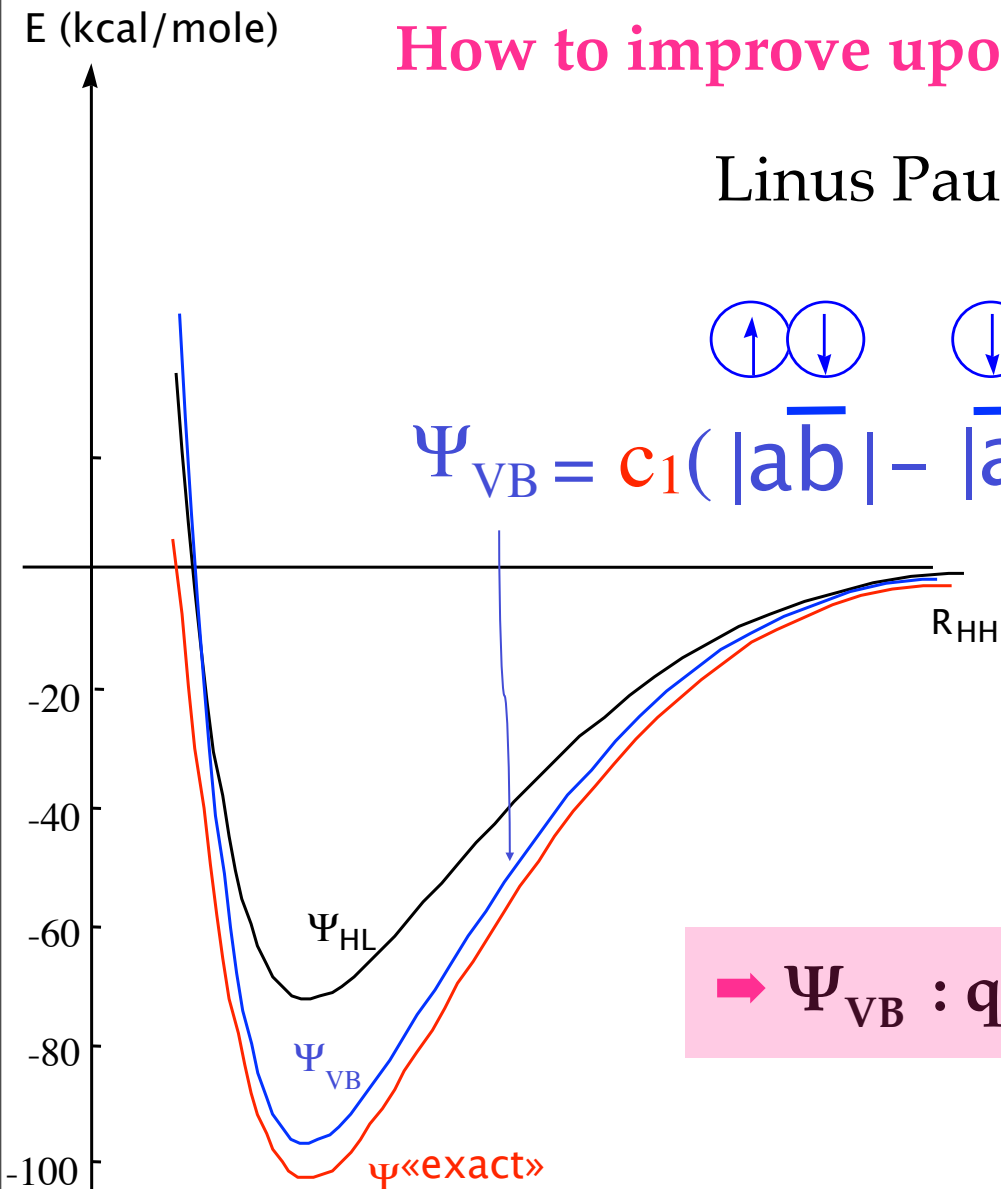
The VB wave function

How to improve upon the HL wave function ?

Linus Pauling (1930-33) :



$$\Psi_{VB} = c_1 (|\overset{\uparrow}{a}\overset{\downarrow}{b}| - |\overset{\downarrow}{a}\overset{\uparrow}{b}|) + c_2 (|\overset{\uparrow\downarrow}{a}\overset{\cdot}{a}| + |\overset{\cdot}{b}\overset{\uparrow\downarrow}{b}|)$$



Covalent + ionic superposition

→ Ψ_{VB} : quantum dressing of Lewis' model

Heitler-London

→ Exercise 1 :

1. Expand the Heitler-London wave-function for H_2 : $\Psi_{HL} = N(|a\bar{b}\rangle + |b\bar{a}\rangle)$, 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 function 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) : $\Psi_{HF} = \frac{1}{\sqrt{2}}|\sigma_g \bar{\sigma}_g\rangle$ 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

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

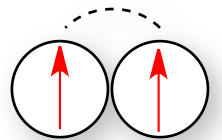
antisymmetric \Rightarrow **Singlet**

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

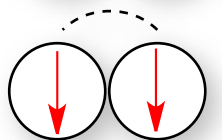
symmetric \Rightarrow **Triplet ($M_S=0$)**

Note that :

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

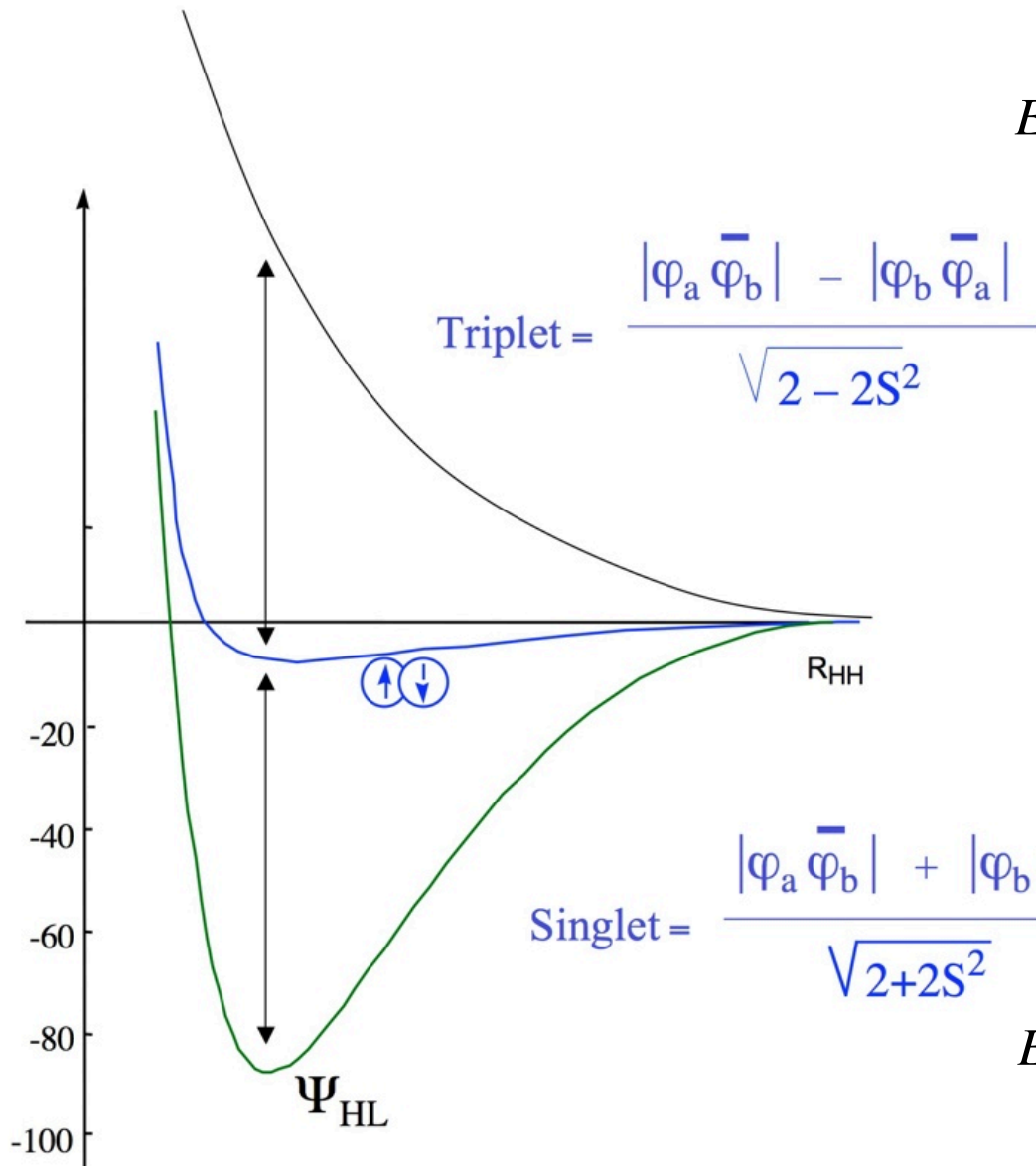


$$\Psi_T \propto |a\bar{b}| = [a(1)b(2) - a(2)b(1)] \otimes [\beta(1)\beta(2)] \Rightarrow M_S = -1$$



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

Heitler-London



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

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



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

VB vs. MO

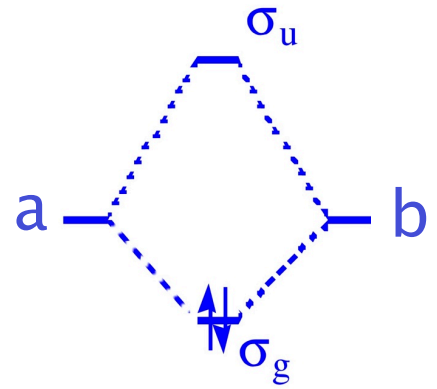
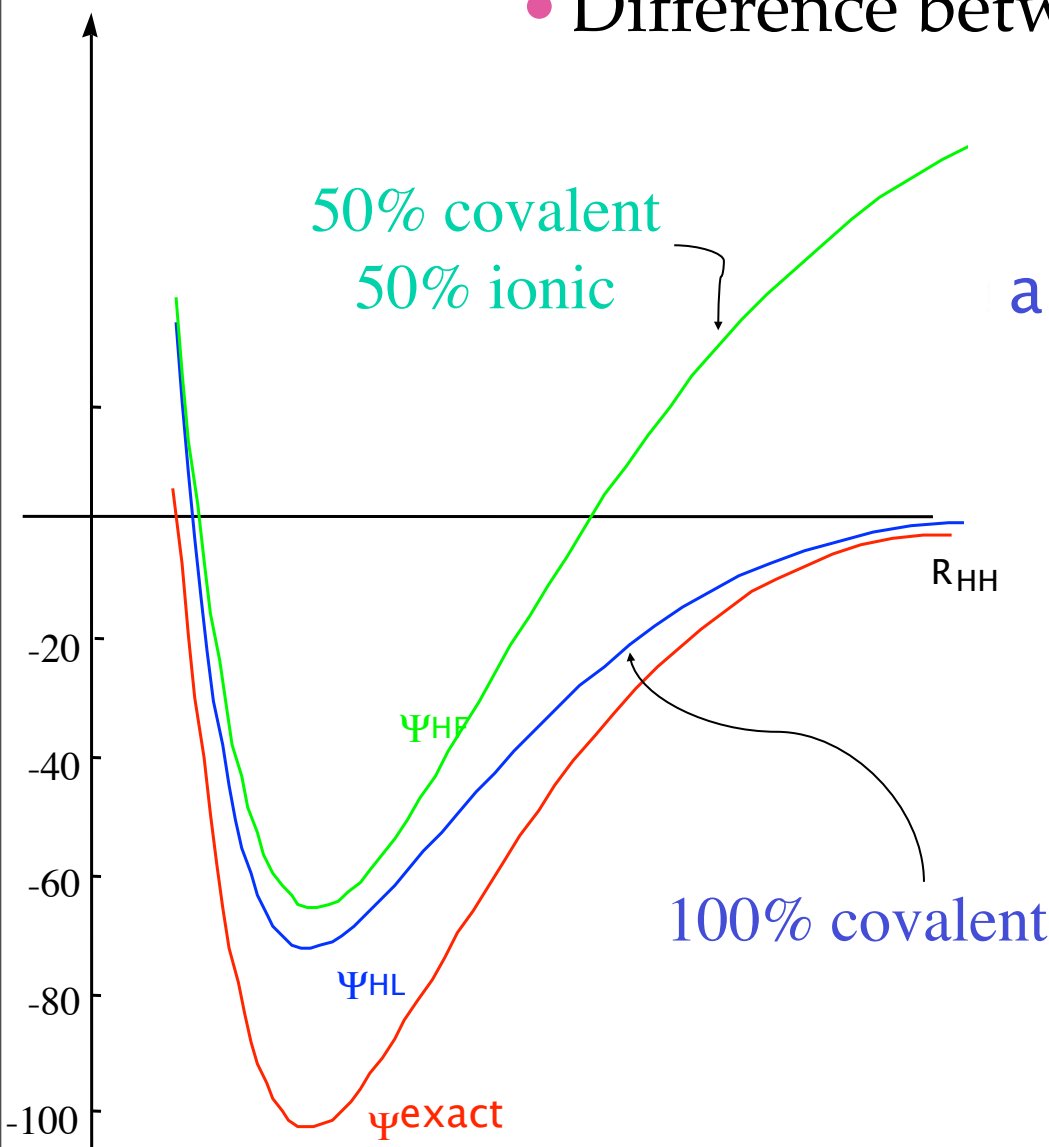
→ Exercise 1 :

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) : $\Psi_{HM} = \frac{1}{\sqrt{2}}|\sigma_g \bar{\sigma}_g|$ 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 ?

E (kcal/mole)



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

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

$$\Psi_{HF} = |\sigma_g^- \sigma_g^-|$$

$$= \underbrace{|a\bar{b}| + |b\bar{a}|}_{\text{50\% covalent}} + \underbrace{|a\bar{a}| + |b\bar{b}|}_{\text{50\% ionic}}$$



50% covalent

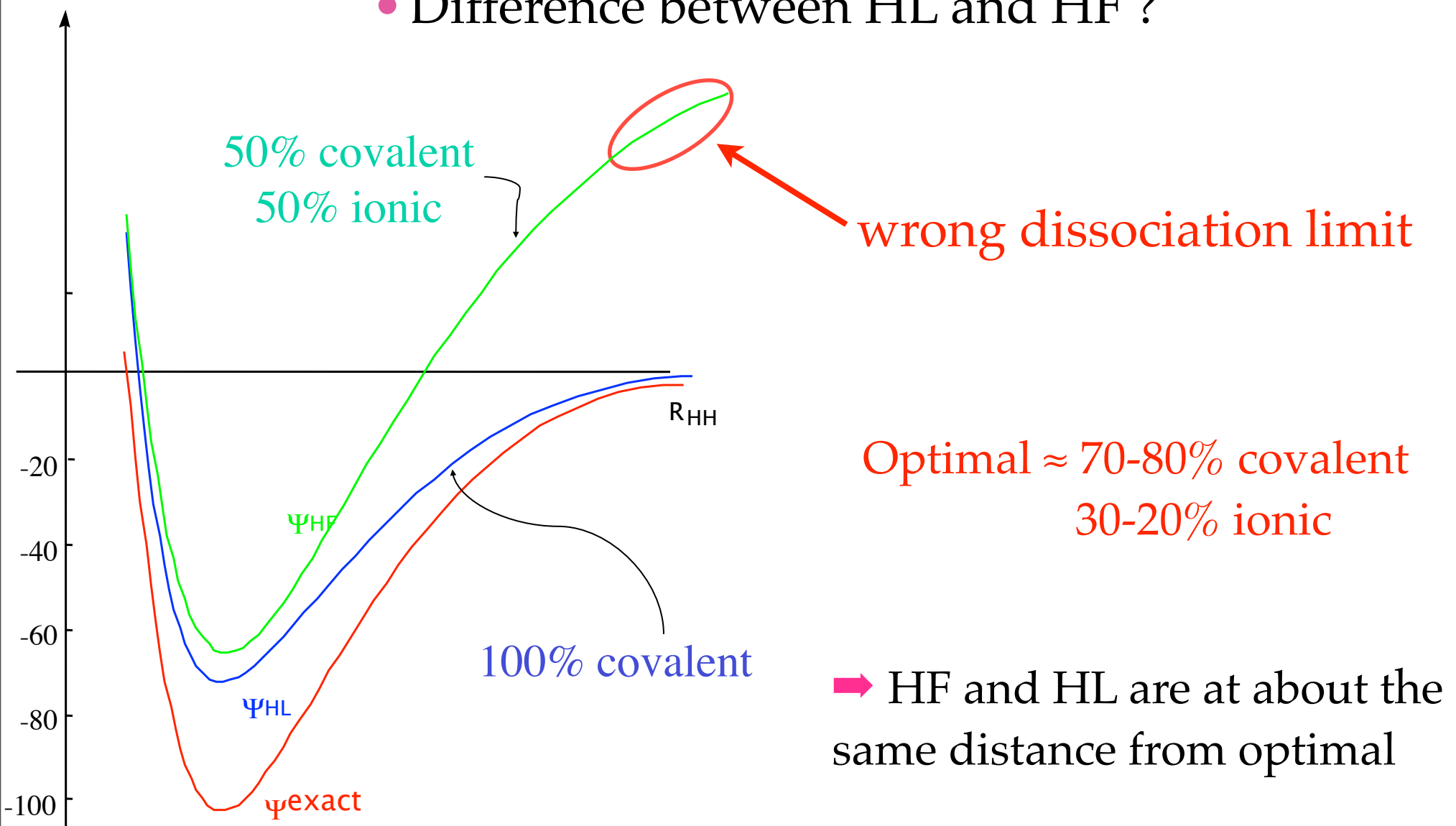


50% ionic

VB vs. MO

- Difference between HL and HF ?

E (kcal/mole)



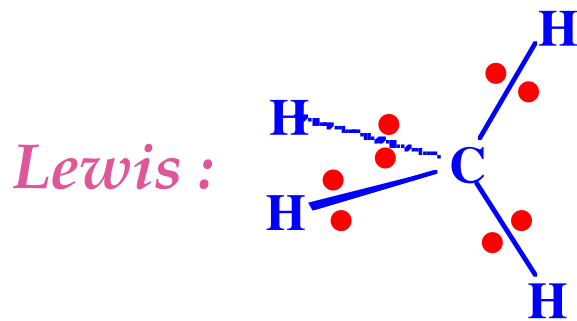
wrong dissociation limit

Optimal \approx 70-80% covalent
30-20% ionic

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

The VB wave function

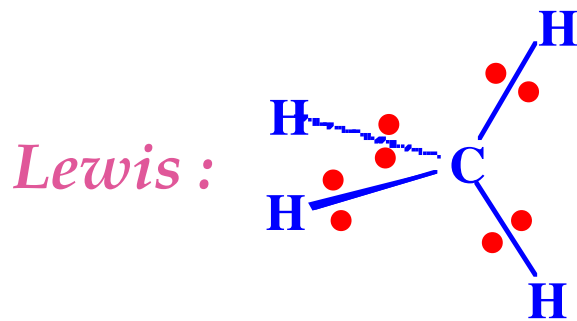
- Extension to the general case :



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

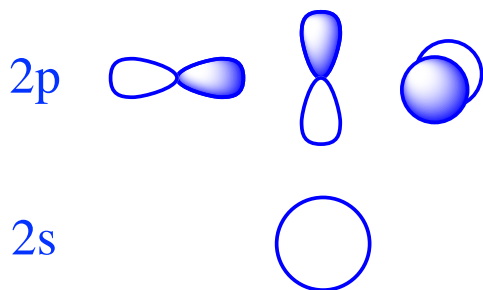
The VB wave function

- Extension to the general case / **1)** hybridization :



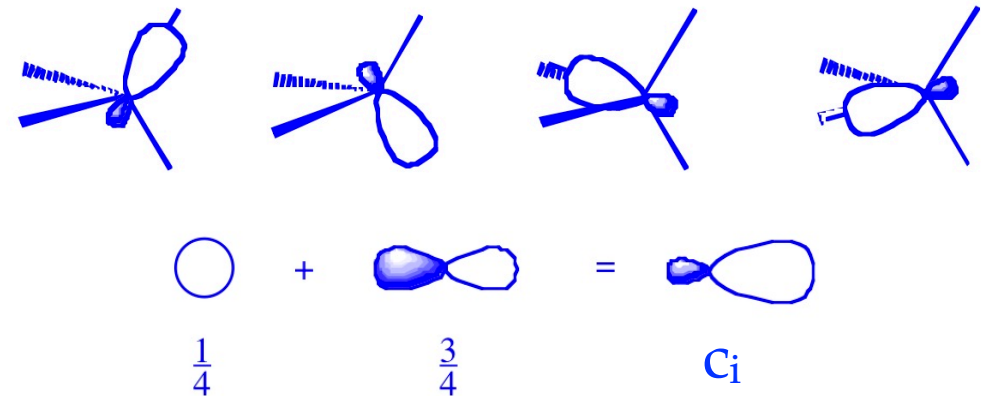
- We want to construct a VB w.f. which corresponds to Lewis' picture
- Which orbitals to use ?

Atomic Orbitals



Unitary
transformation

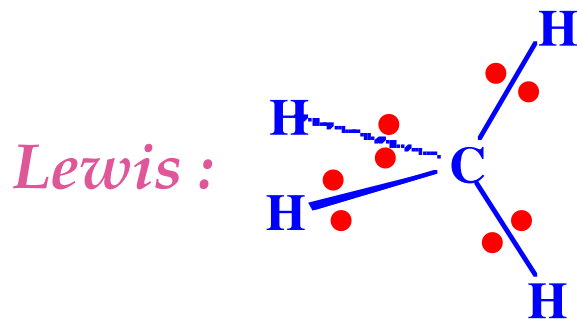
Hybrid Orbitals



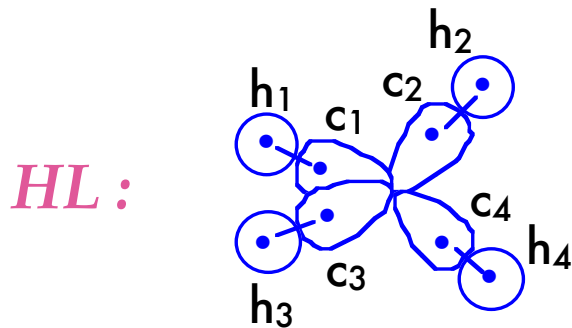
Four equivalent directional sp^3 orbitals

The VB wave function

- Extension to the general case / **1)** hybridization :



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



$$\Psi_{HL} = \left| (c_1 \bar{h}_1 + h_1 \bar{c}_1)(c_2 \bar{h}_2 + h_2 \bar{c}_2)(c_3 \bar{h}_3 + h_3 \bar{c}_3)(c_4 \bar{h}_4 + h_4 \bar{c}_4) \right|$$

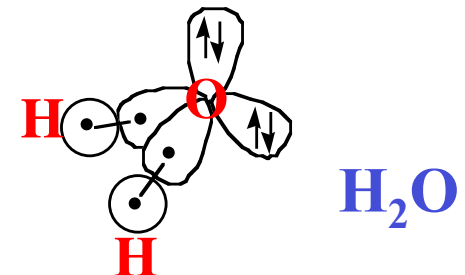
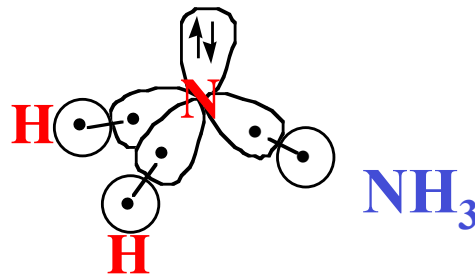
Electrons occupy **localized** orbitals (atomics, hybrids,...)

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

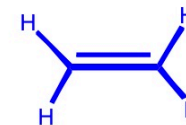
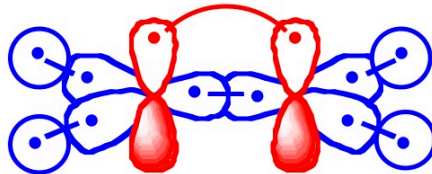
The VB wave function

- Extension to the general case / 1) hybridization :

« sp^3 »

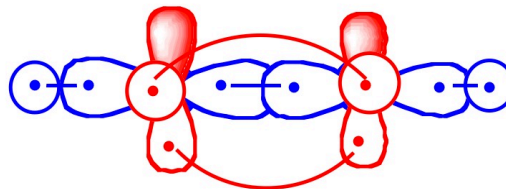


Three « sp^2 » hybrids
+ $2p_z$ (unchanged)



Ethylen

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



The VB wave function

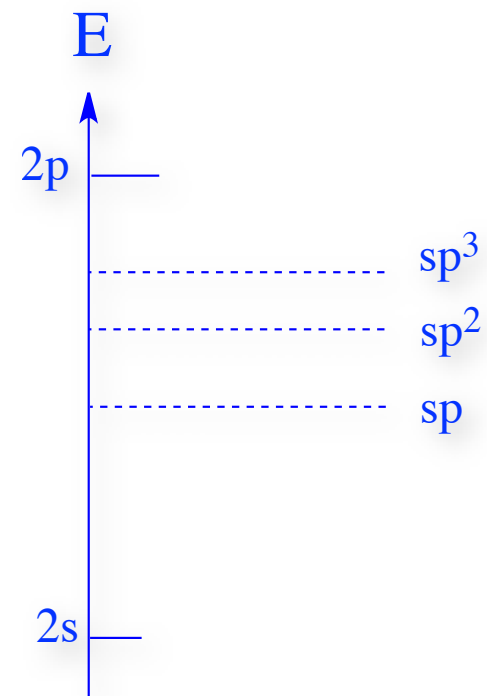
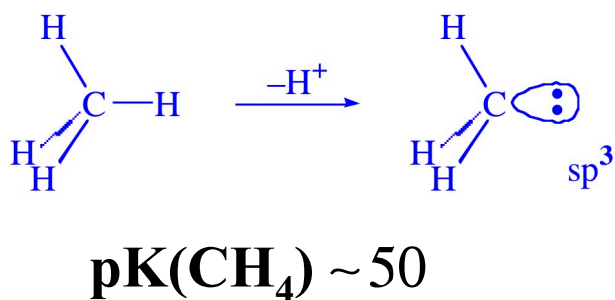
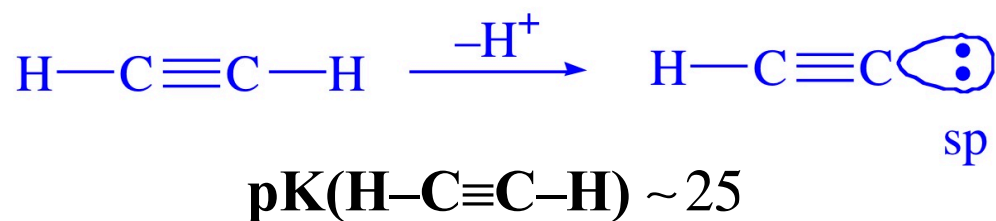
- Hybridization, a legitimate and useful concept :
 - Three categories of C–C bonds :

	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

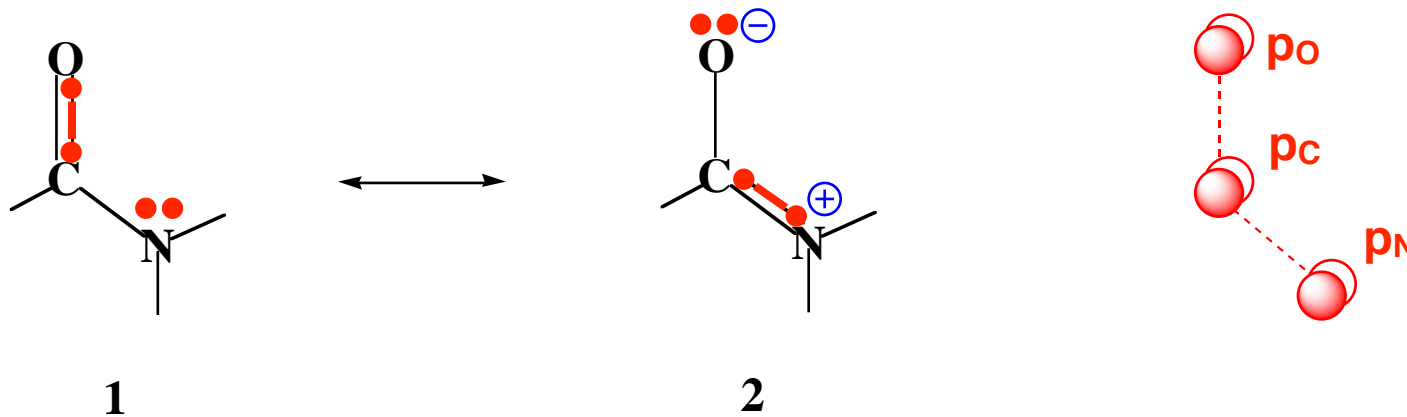
- Hybridization, a legitimate and useful concept :
 - Relative acidities of hydrocarbons :



→ $E(\text{sp}) < E(\text{sp}^3) \Rightarrow \text{H}-\text{C}\equiv\text{C}^-$ more stable than H_3C^-

The VB wave function

- Extension to the general case / 2) mesomerism :



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

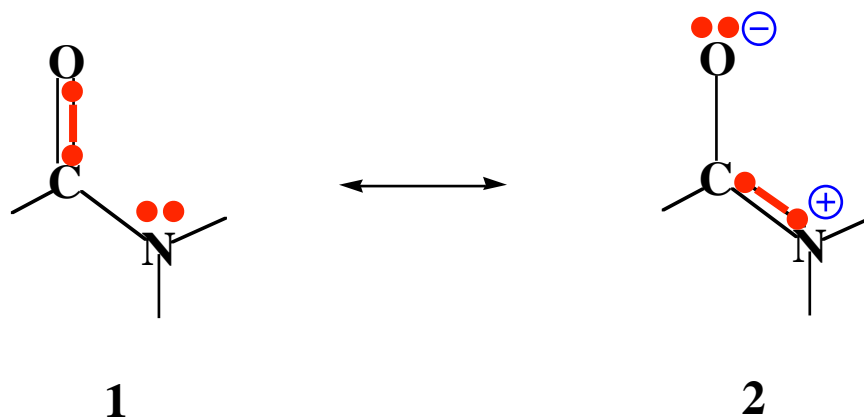
$$= C_1 | p_N \bar{p}_N (p_O \bar{p}_C + p_C \bar{p}_O) | + C_2 | p_O \bar{p}_O (p_C \bar{p}_N + p_N \bar{p}_C) |$$

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

The VB wave function

- Resonance concept :

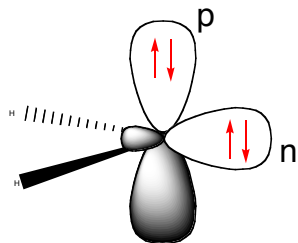
$$\Psi_{\text{VB}} = c_1 \left(\begin{array}{c} \uparrow \downarrow \\ |a\bar{b}| \\ \downarrow \uparrow \\ |\bar{a}b| \end{array} \right) - \begin{array}{c} \downarrow \uparrow \\ |\bar{a}b| \\ \downarrow \uparrow \\ |a\bar{b}| \end{array} + c_2 \left(\begin{array}{c} \uparrow \downarrow \\ |a\bar{a}| \\ \uparrow \downarrow \\ |b\bar{b}| \end{array} \right) + \begin{array}{c} \uparrow \downarrow \\ |b\bar{b}| \\ \uparrow \downarrow \\ |a\bar{a}| \end{array}$$



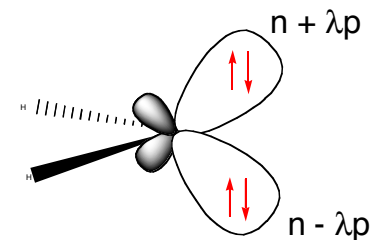
➔ The resonance concept is a central pillar of VB theory

VB vs. MO

→ Exercise 2 :



Ψ_{MO}



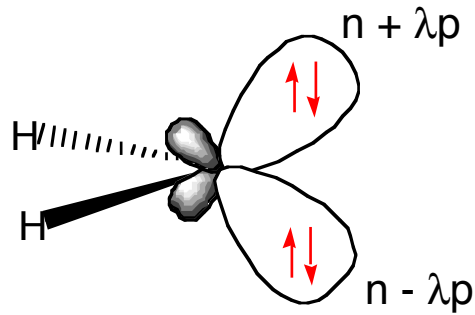
Ψ_{VB}

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} .

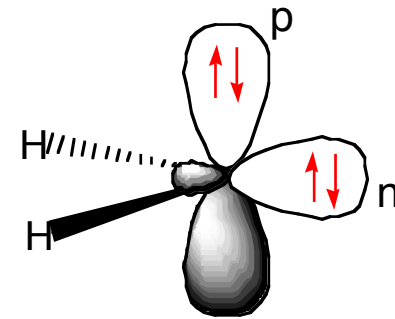
Continuation of the exercise : <https://wiki.lct.jussieu.fr/workshop/index.php/VBTutorial1>

VB vs. MO

→ Exercise 2 (answer) :



2 equivalent lone pairs



2 non-equivalent lone pairs

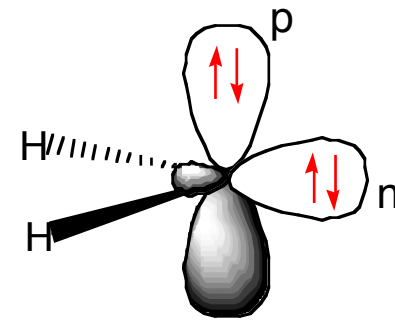
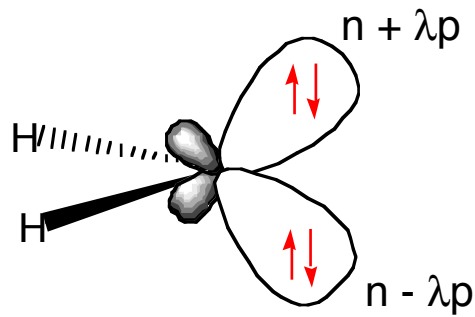
1) What is the difference between Ψ_{VB} and Ψ_{MO} ?

$$\begin{aligned} \Psi_{VB} &= |(n+\lambda p)(\bar{n}+\lambda\bar{p})(n-\lambda p)(\bar{n}-\lambda\bar{p})| \\ &= \lambda^2 |n\bar{n}p\bar{p}| - \lambda^2 |n\bar{p}p\bar{n}| - \lambda^2 |p\bar{n}n\bar{p}| + \lambda^2 |p\bar{p}n\bar{n}| + \dots |n\bar{n}n\bar{p}| + \dots \\ &= |n\bar{n}p\bar{p}| = \Psi_{MO} \end{aligned}$$

No difference!

VB vs. MO

→ Exercise 2 (answer) :

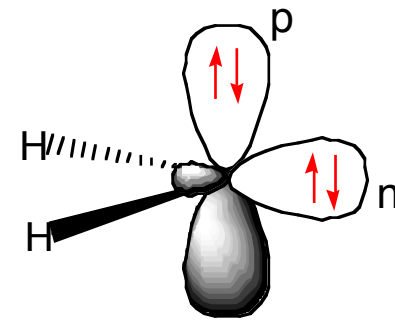
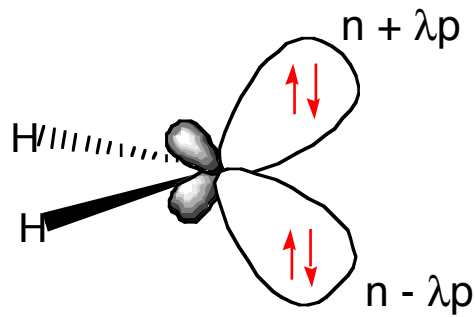


So why do we get two different images ?

⇒ one is more handy than the other depending on what you want to look for !

VB vs. MO

→ Exercise 2 (answer) :



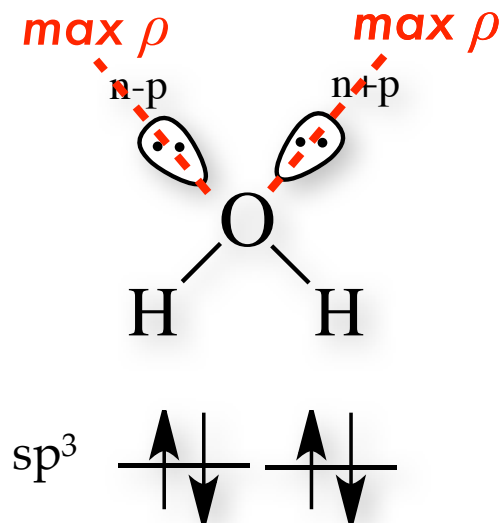
So why do we get two different images ?

⇒ one is more handy than the other depending on what you want to look for !

VB vs. MO

→ Exercise 2 (extra) :

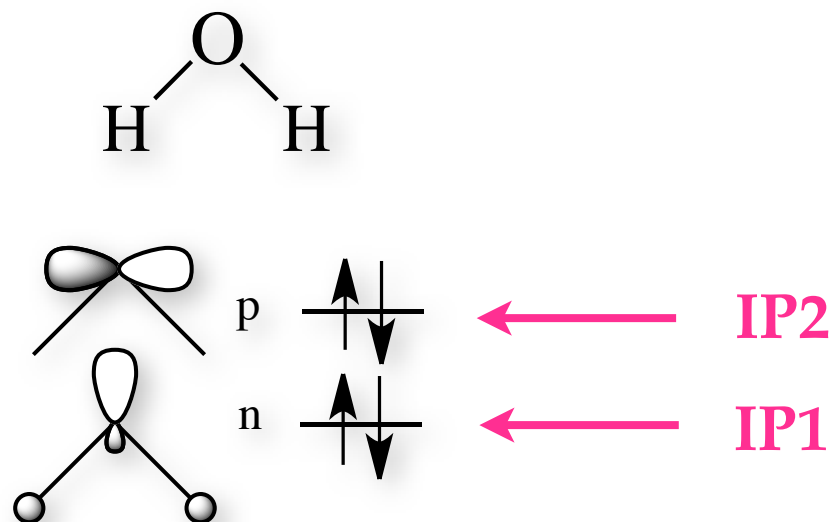
- The «rabbit-ear» image is a faithful representation of the electron density in the isolated molecule :



VB vs. MO

→ Exercise 2 (extra) :

- The MO image more readily account the two different IP in the water molecule :

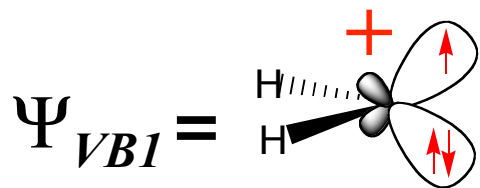
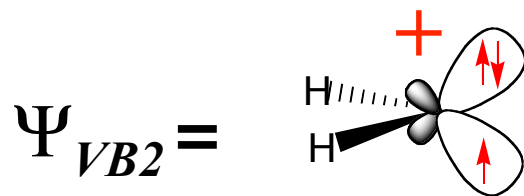


⇒ Canonical MOs allows to account to what will happen to a molecule when a perturbed (Koopman's theorem, FO theory)

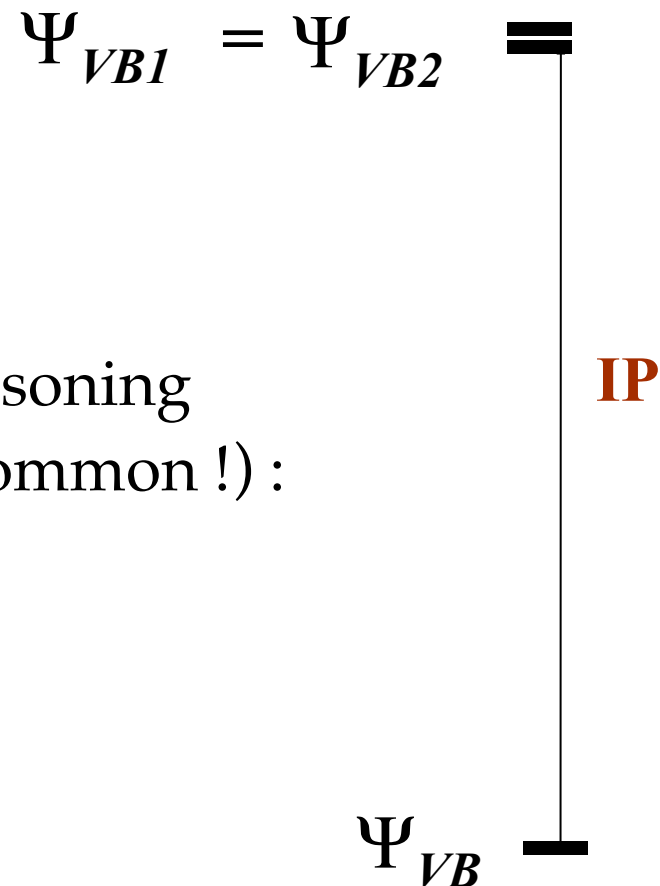
VB vs. MO

→ Exercise 2 (extra) :

- Can VB predict two IPs for the water molecule ?

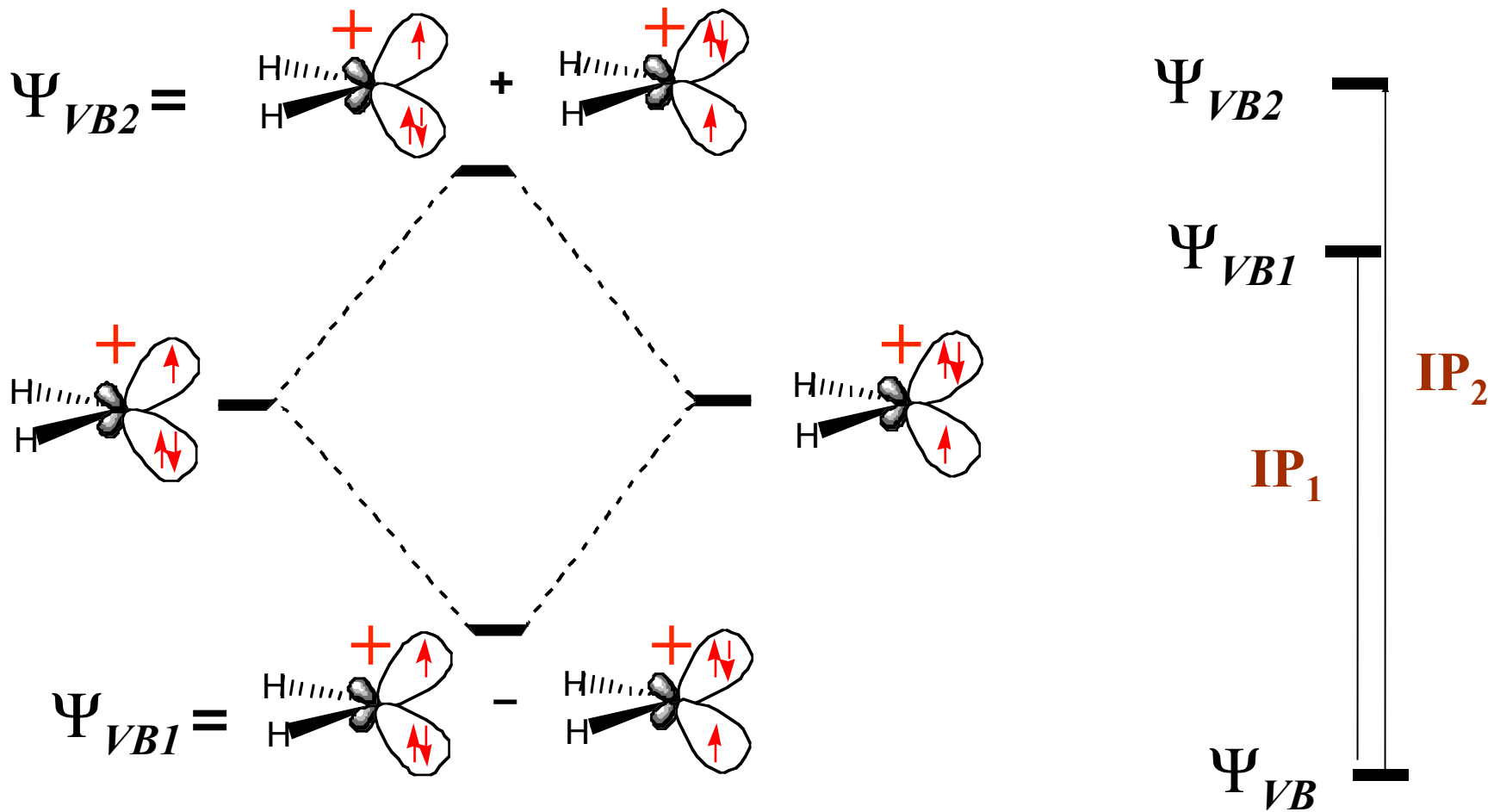


easy reasoning
(very common !):



VB vs. MO

- Correct reasoning :



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 / mesomerism, 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)