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Label chimie théorique d'Ile de France 2016

Valence Bond theory

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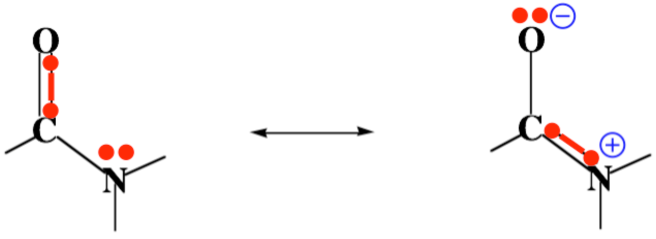
What is VB theory ?

Cours : Théorie Valence Bond - structure électronique et réactivité (Benoît Braïda)

- An **electronic structure theory** alternative to MO theory (Heitler-London 1927, Pauling 1931)
  - Wave function based on **localized atomic-like orbitals** => direct connexion with Lewis structures
  - Usual chemists' concept (resonance, hybridization, arrow-pushing language,…) are naturally retrieved



1 **2**

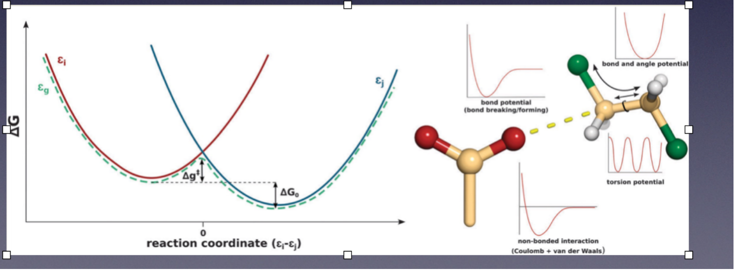
$$\Psi_{(1\leftrightarrow 2)} = C_1(\Psi_1) + C_2(\Psi_2)$$

- A set of **concepts** and **tools** for electronic **structure** and **reactivity**

Two recent Nobel prices for developments of VB theory

Rudolph A. Marcus
ET theory

Ariel Warshel
EVB



- Content of the lecture :

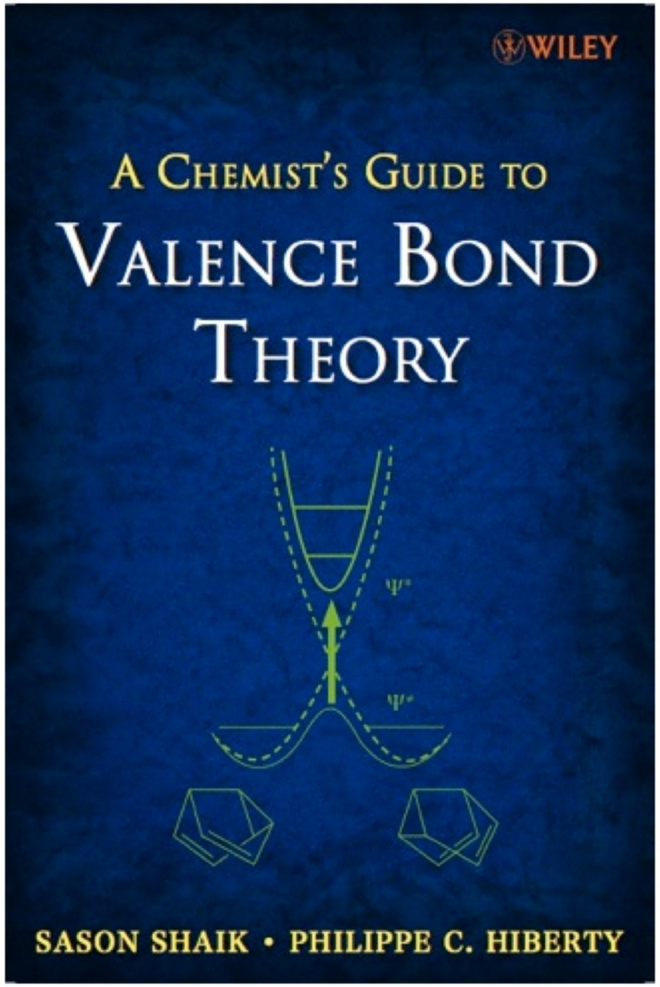
basics of VB theory, *ab initio* VB, application to electronic structure problems, the Valence Bond diagram model for reactivity

VB lectures

- Part. 0 - Purpose and History
- Part. 1 - Basics of VB theory and VB formalism
- Part. 2 - *Ab initio* VB
- Part. 3 - Qualitative VB
- Part. 4 - VB diagrams for reactivity

VB references

- Book :



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

Part 0. Motivation and history

Heuristic models

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

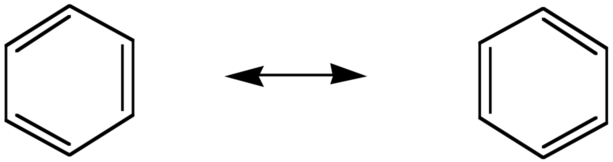
$$H:\underset{\cdot\cdot}{\ddot{O}}:H$$

Heuristic models

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

$\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}$

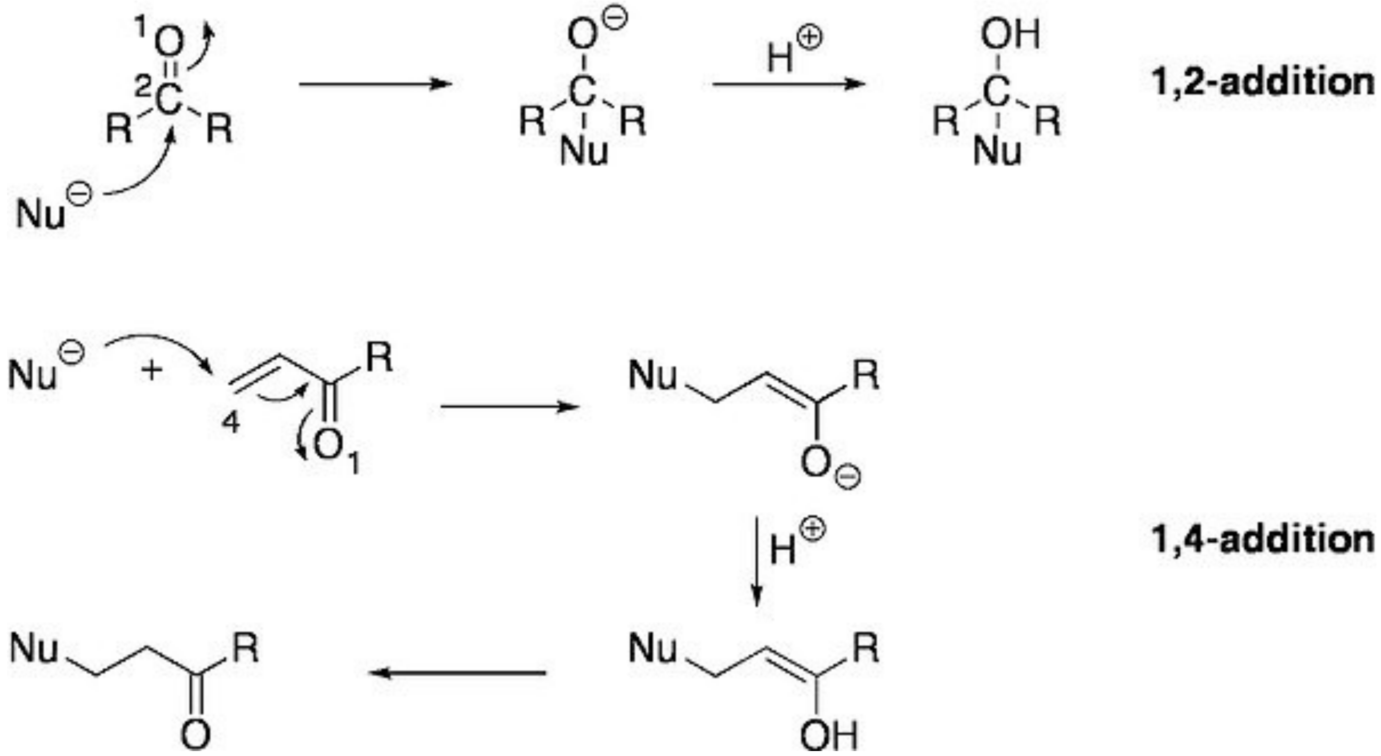
- Mesomery / resonance :



  - Arndt, Robinson, Ingold (1924) : mesomery

Heuristic models

- Arrow-pushing language :



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

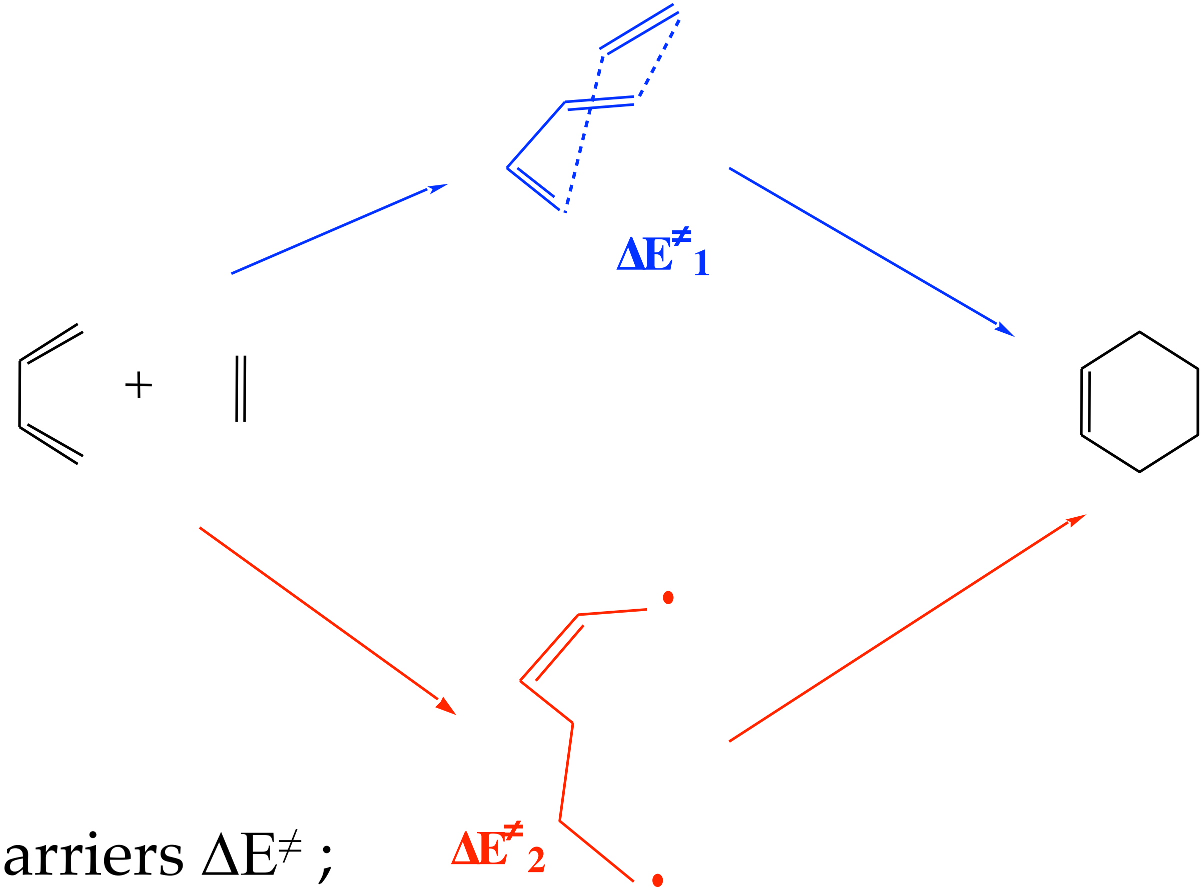
Heuristic models

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**

Quantum Chemistry

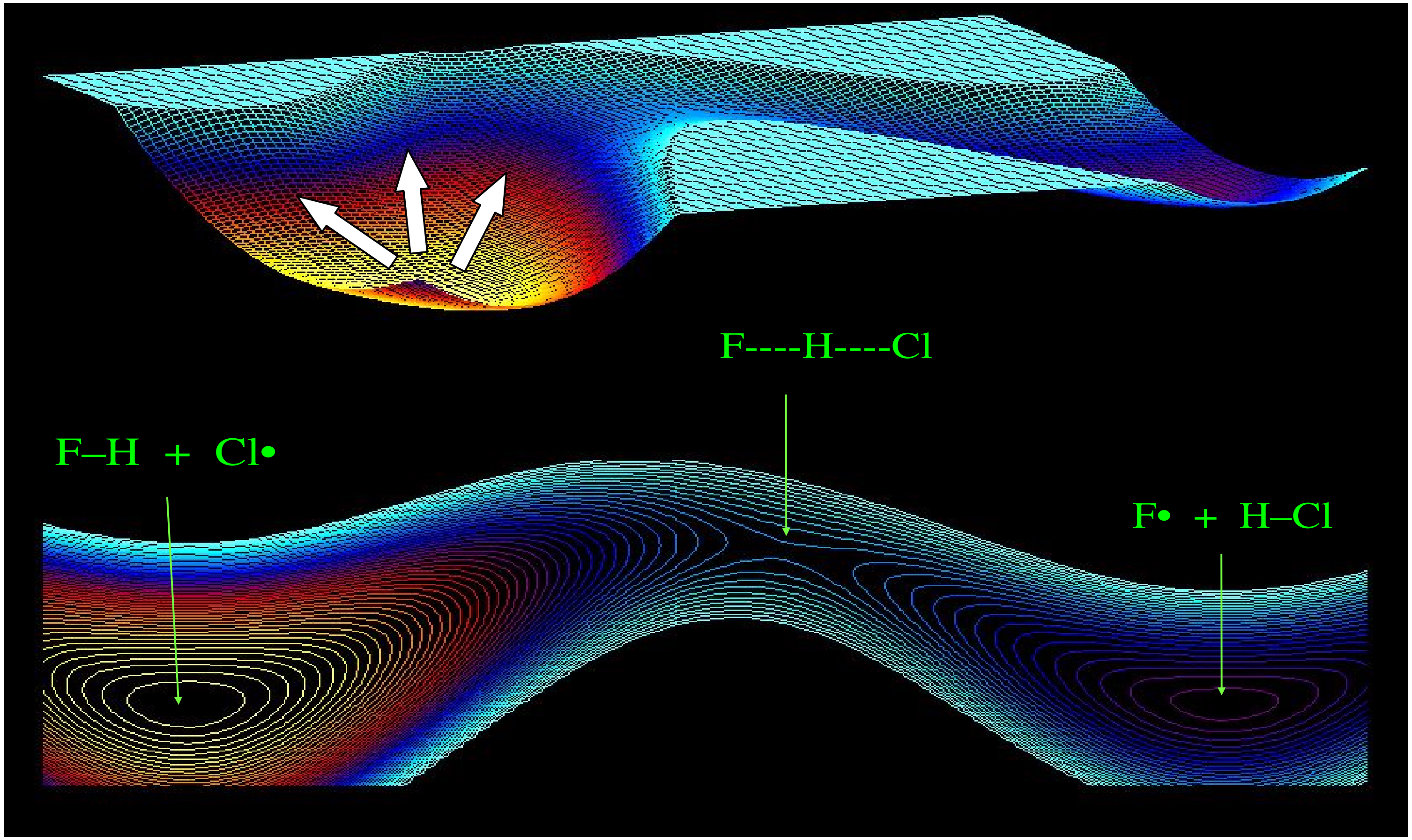
- Accurate quantum theory based calculations can provide :



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

Quantum Chemistry

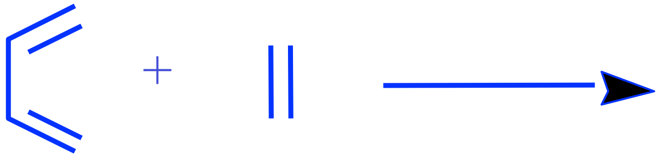
- Accurate quantum theory based calculations can provide :



  - 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}

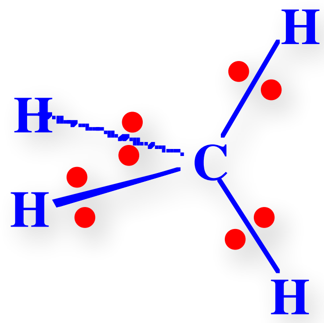
⇒ low barrier, easy

?

have to do the computation...

Chemists' «schizophrenia»

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

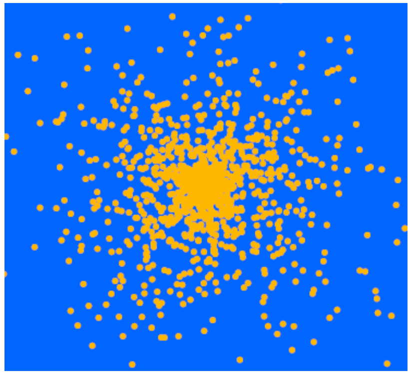


Lewis model, arrow-pushing language, VSEPR, hybridization,...

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

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

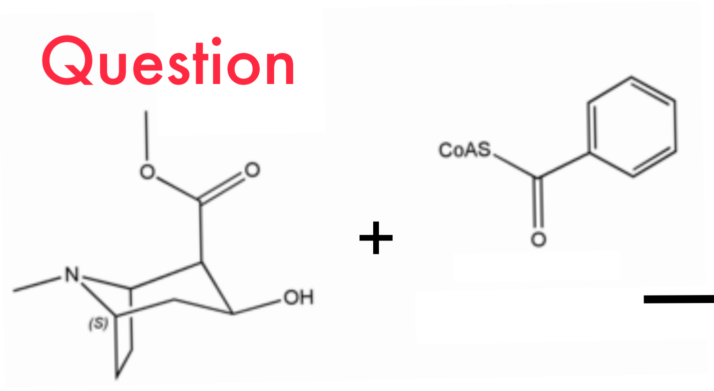
$$\hat{H}\Psi = E\Psi$$



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

Chemists' «schizophrenia»

Chemical Question



ΔH_{rnx}

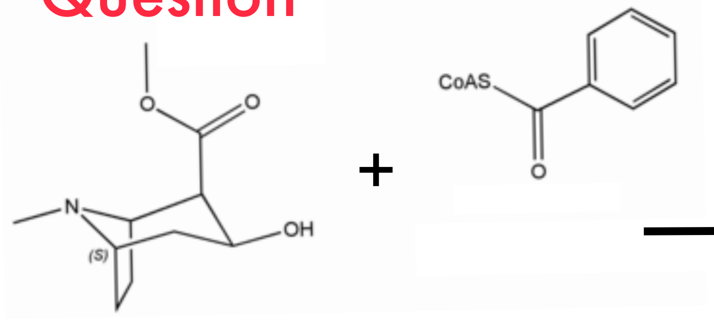
Quantum Calculations

$\Delta H^{\ddagger}$

etc.

Chemists' «schizophrenia»

Chemical Question



→

→

ΔH_{rnx}

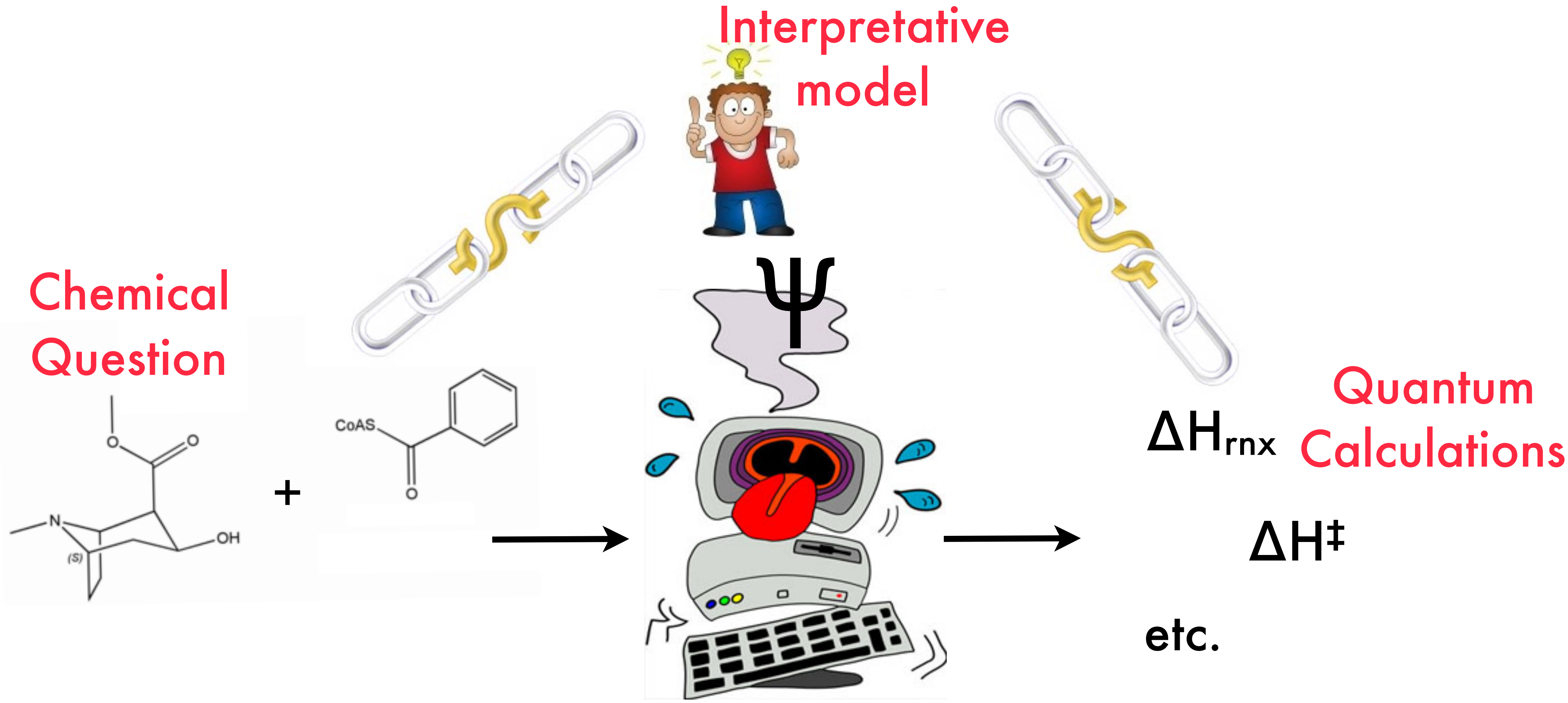
Quantum Calculations

$\Delta H^{\ddagger}$

etc.

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

Chemists' «schizophrenia»



Interpretative model

Chemical Question

Quantum Calculations

ΔH_{rnx}

$\Delta H^{\ddagger}$

etc.

«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 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**

- 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

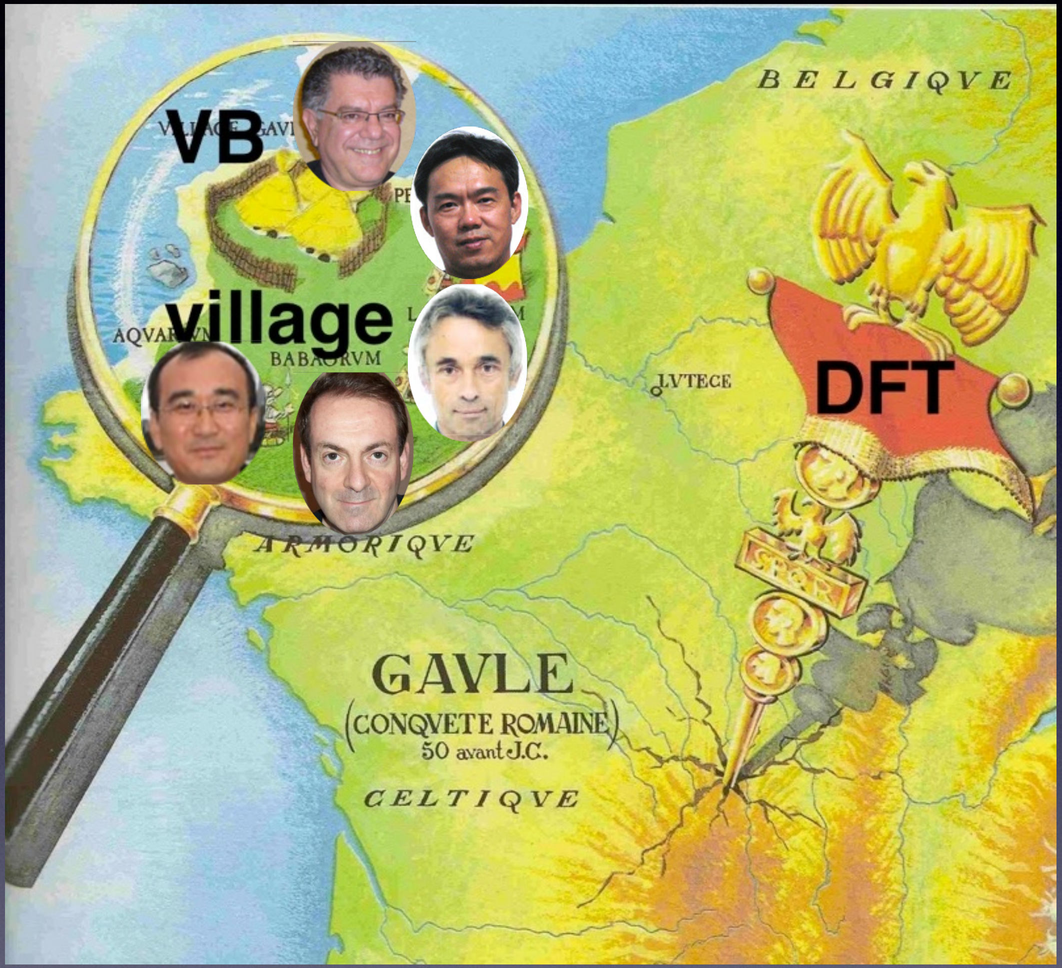
Successes of MO theory vs. VB «failures»

- ~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

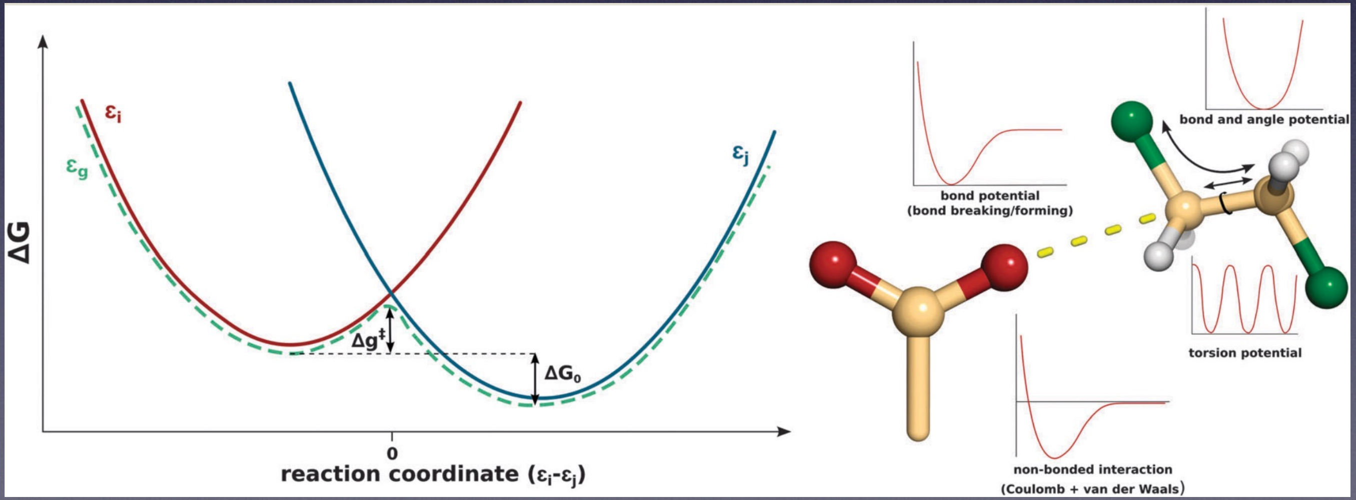
- 2012-...: awakening of the sleeping beauty?

All elements for a Valence Bond revival are ready

- 1992+2013: Two nobel prices

Rudolph A. Marcus
ET theory

Ariel Warshel
EVB



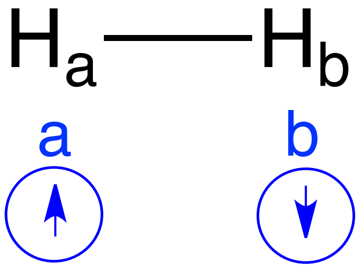
Developments of VB theory

Part 1. Basics of VB theory

Heitler-London

- Notations :

Dihydrogen molecule H_2 :



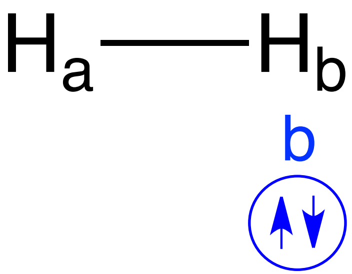
$$|a\bar{b}| = \begin{array}{c} (1,s_1) \\ (2,s_2) \end{array} \begin{vmatrix} a(1)\otimes\alpha(s_1) & b(1)\otimes\beta(s_1) \\ a(2)\otimes\alpha(s_2) & b(2)\otimes\beta(s_2) \end{vmatrix}$$

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

Heitler-London

- Notations :

Dihydrogen molecule H_2 :



$$\left|b\bar{b}\right| = \begin{array}{c|cc|} (1,s_1) & b(1)\otimes\alpha(s_1) & b(1)\otimes\beta(s_1) \\ (2,s_2) & b(2)\otimes\alpha(s_2) & b(2)\otimes\beta(s_2) \end{array}$$

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

Stop me at any time !

Heitler-London

Dihydrogen molecule H_2 : $H_a{-\!-\!-}H_b$

- Heitler-London (1927) :

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

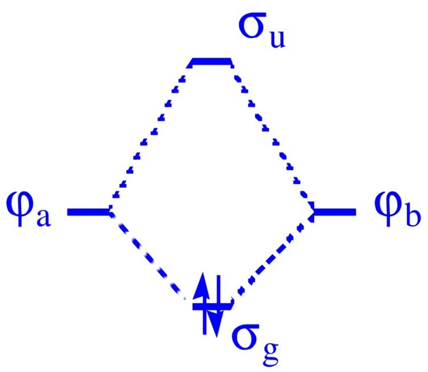
- Electrons in atomic orbitals
- Shared electron pair (covalent bond)

➡ **basis of VB theory**

Heitler-London

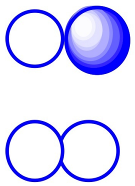
Dihydrogen molecule H_2 : H_a——H_b

- Hund-Mulliken (1927) :



$\sigma_u \propto a - b$

$\sigma_g \propto a + b$

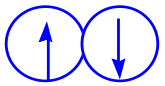


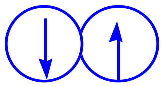
$$\Psi_{HM} = |\sigma_g \overline{\sigma_g}|$$

➡ **basis of MO theory**

(HF wave function)

- Heitler-London (1927) :





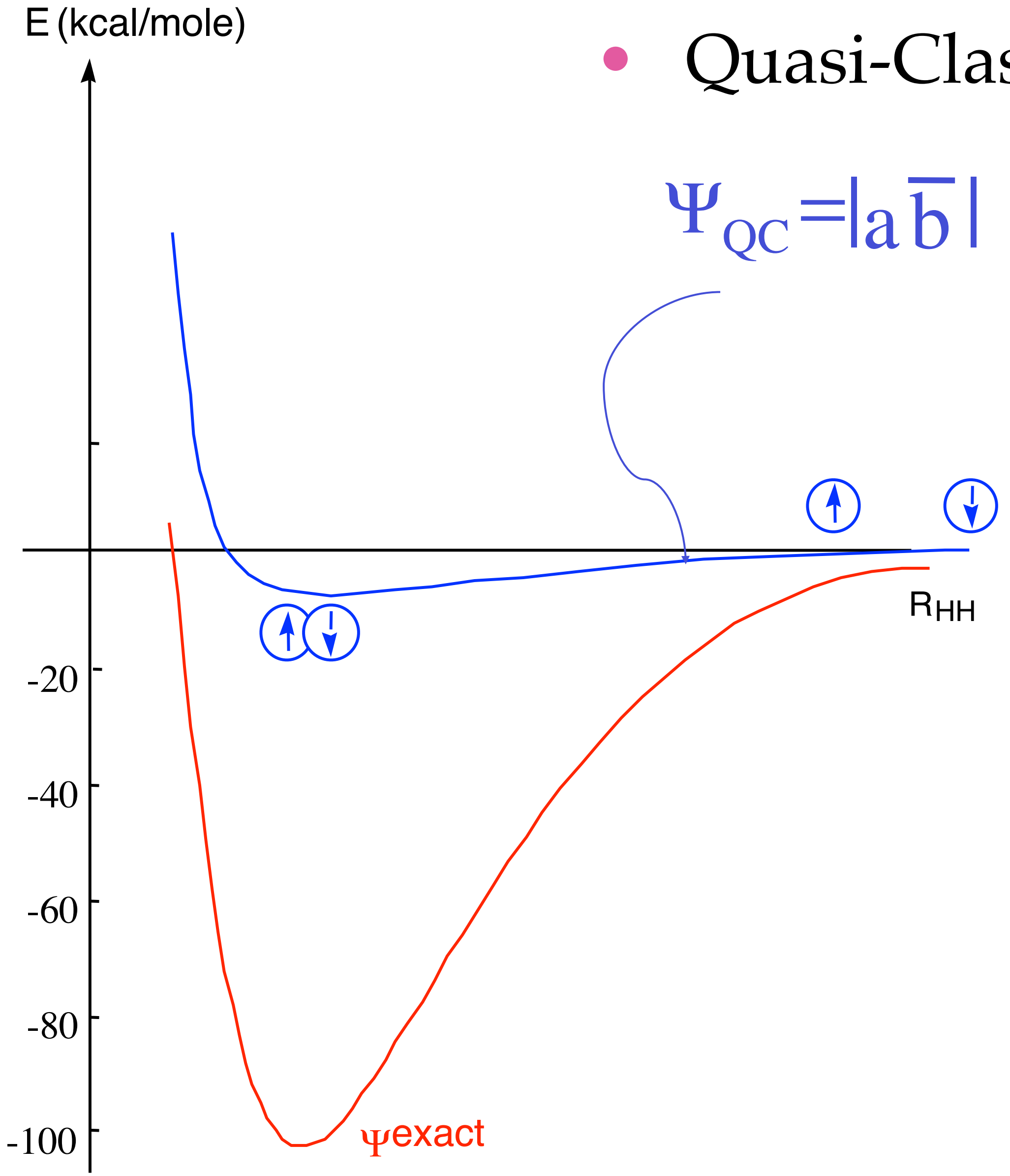
$$\Psi_{HL} = |a\overline{b}| + |b\overline{a}|$$

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

➡ **basis of VB theory**

Heitler-London

- Quasi-Classical (QC) state :



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

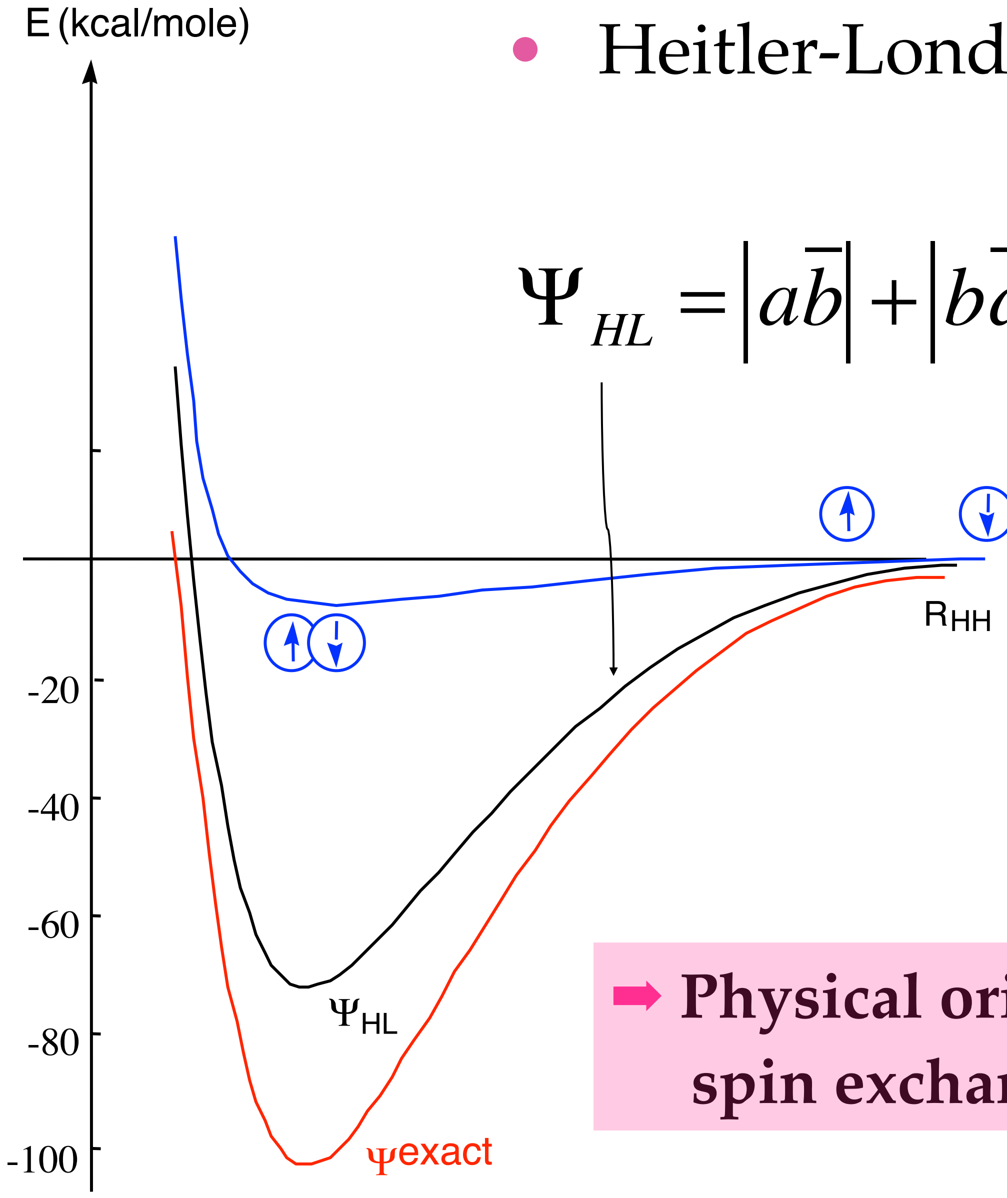
$$E_{QC} = \frac{\left\langle |a\bar{b}| \, H^{\acute{e}l} \, |a\bar{b}| \right\rangle}{\left\langle |a\bar{b}| |a\bar{b}| \right\rangle} = h_{aa} + h_{bb} + J_{ab}$$

E_{QC} ~ cte along the dissociation curve

➡ **no spin exchange ⇒ no bonding**

Heitler-London

- Heitler-London (HF) wf :

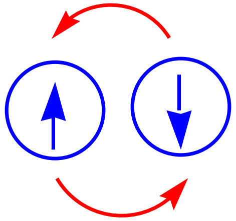


$$\Psi_{HL} = \left|a\bar{b}\right| + \left|b\bar{a}\right|$$

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

Overlap (distance) dependant

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



Heitler-London

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

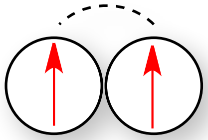
antisymetric ⇒ **Singlet**

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

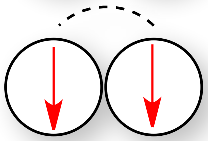
symetric ⇒ **Triplet (M_S=0)**

Note that :

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

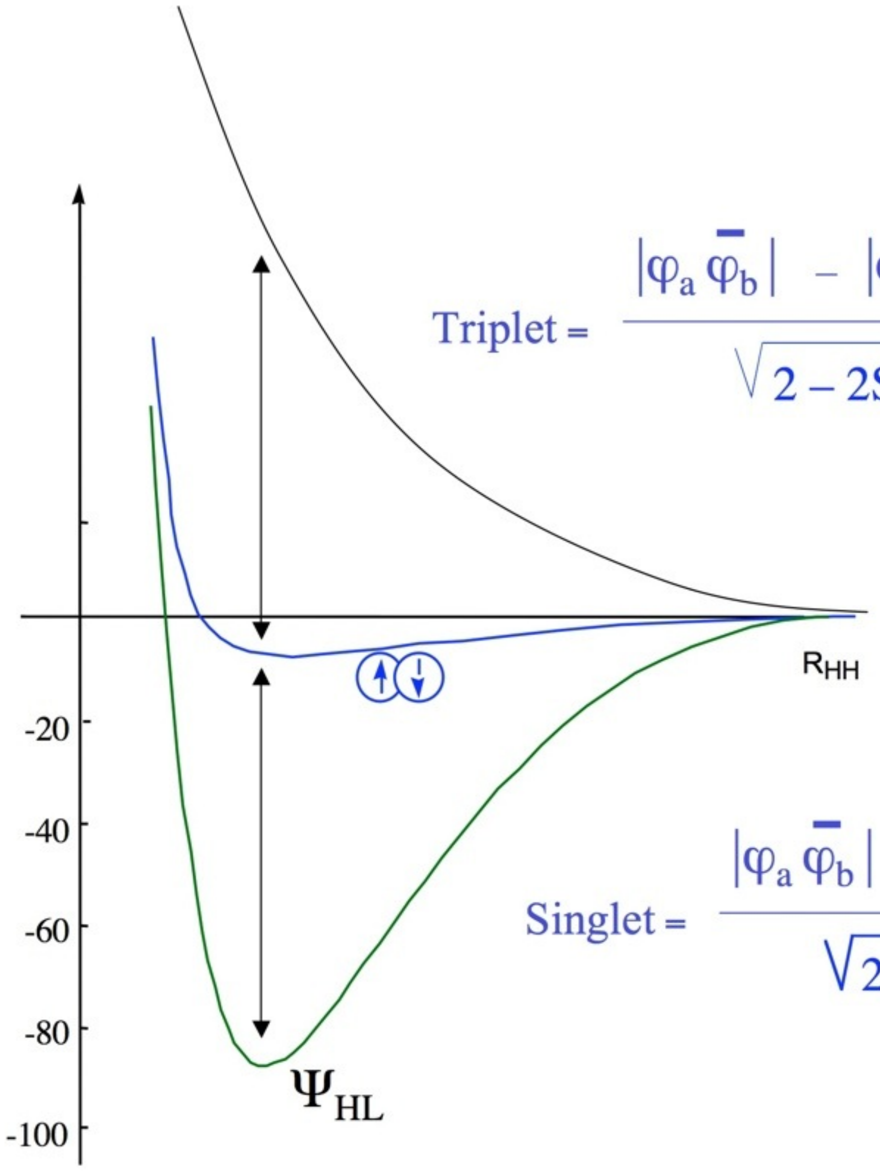


$$\Psi_T \propto |\bar{a}\bar{b}| = [a(1)b(2) - a(2)\,b(1)] \otimes [\beta(s_1)\,\beta(s_2)] \Rightarrow M_S = -1$$



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

Heitler-London



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

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

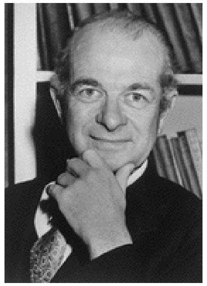
$$E(T) = \frac{1}{\sqrt{(1-S_{ab}^2)}}(\underbrace{h_{aa} + h_{bb} + J_{ab}}_{E_{QC} \approx E(R_{HH} \to \infty)} \underbrace{- 2h_{ab}S_{ab} - K_{ab}}_{>0})$$

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

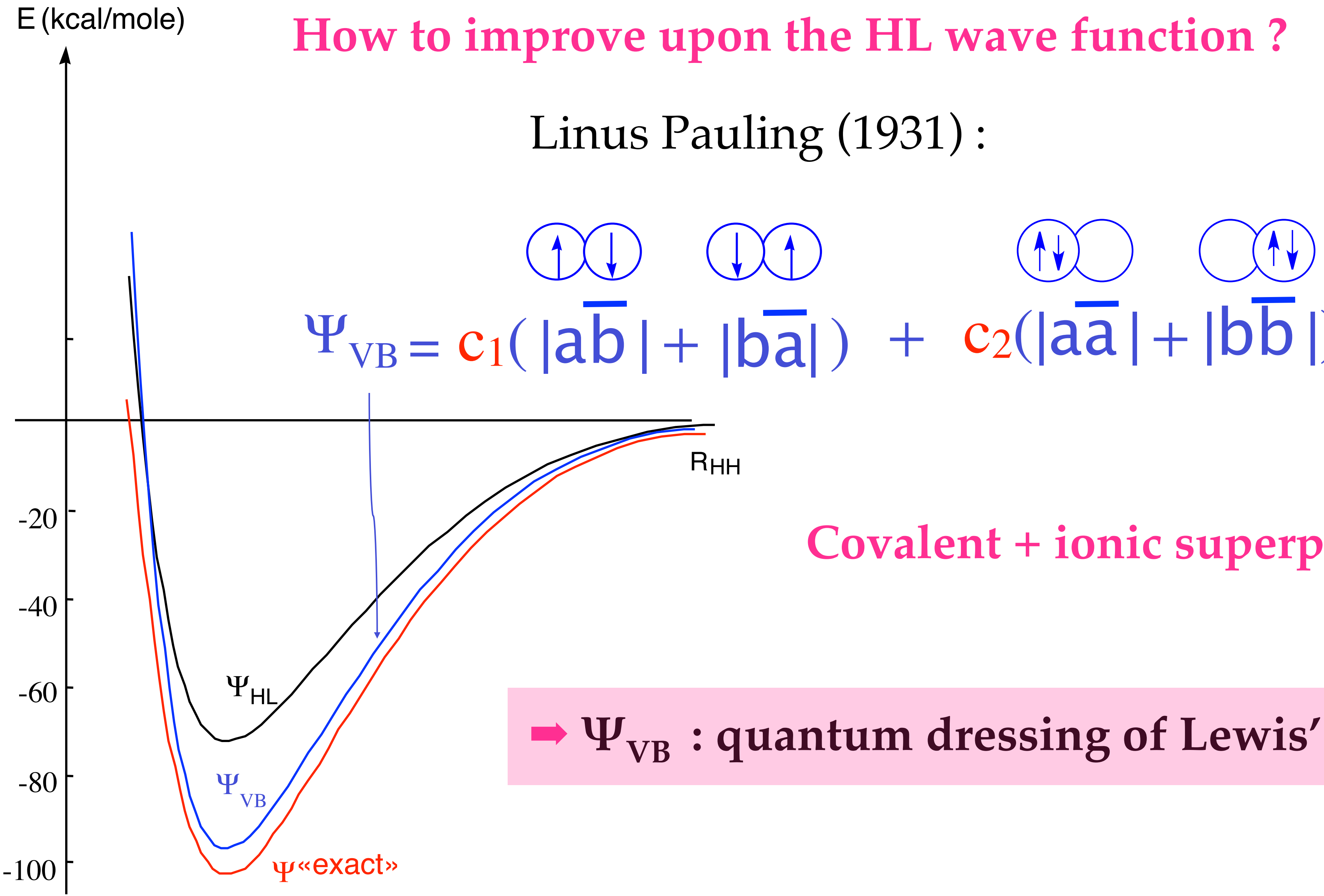
$$E(S) = \frac{1}{\sqrt{(1+S_{ab}^2)}}(\underbrace{h_{aa} + h_{bb} + J_{ab}}_{E_{QC} \approx E(R_{HH} \to \infty)} \underbrace{+ 2h_{ab}S_{ab} + K_{ab}}_{<0})$$

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

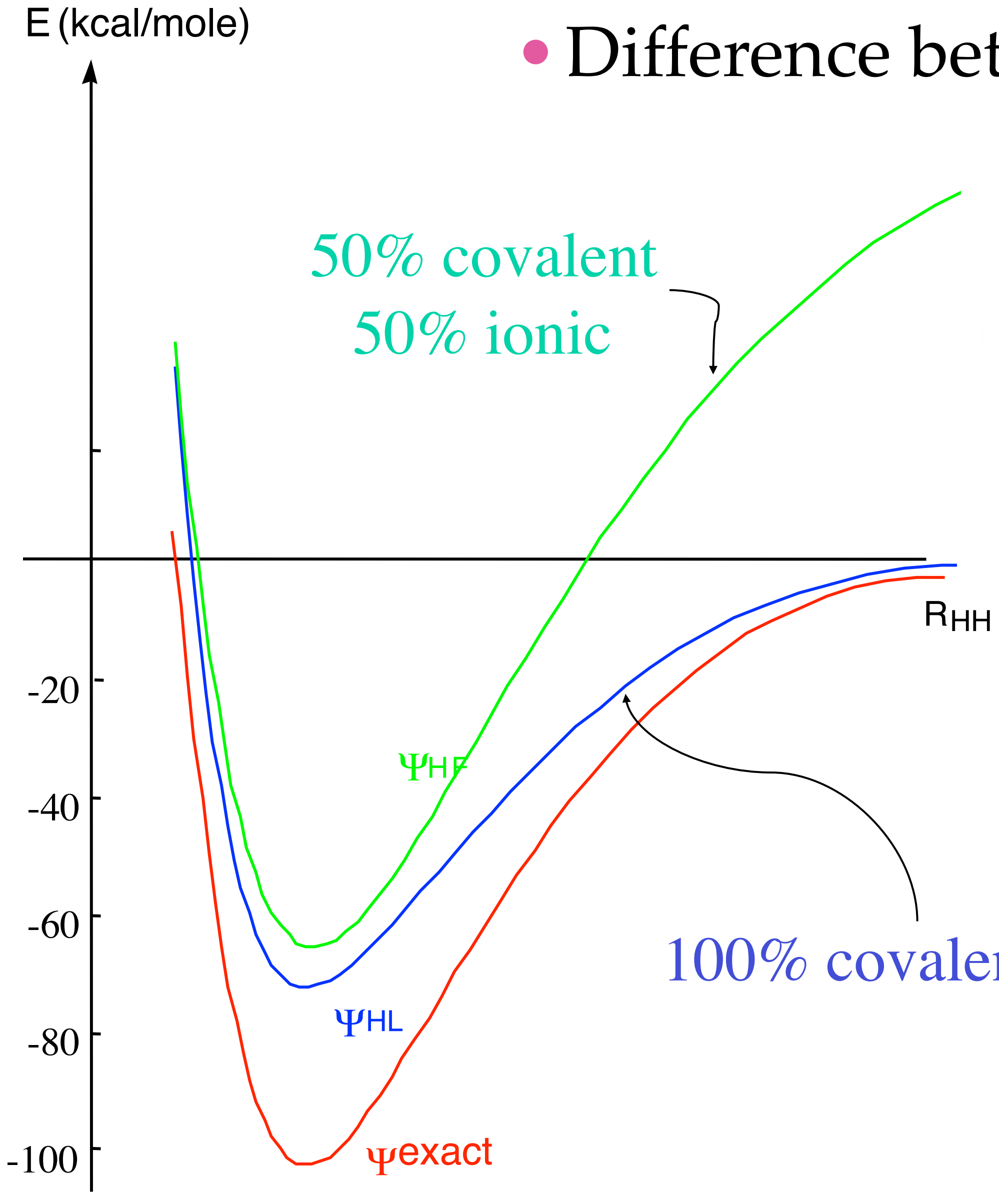
VB vs. MO

➡ 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.

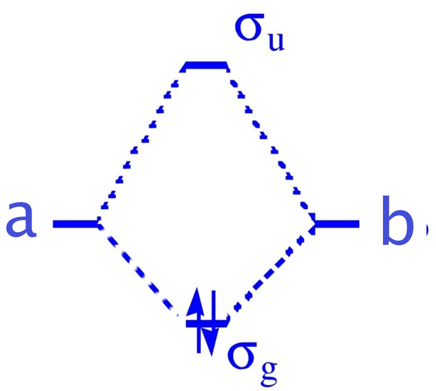
VB vs. MO

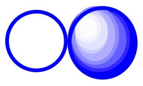
- Difference between HL and HF ?

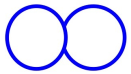


50% covalent
50% ionic

100% covalent



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

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

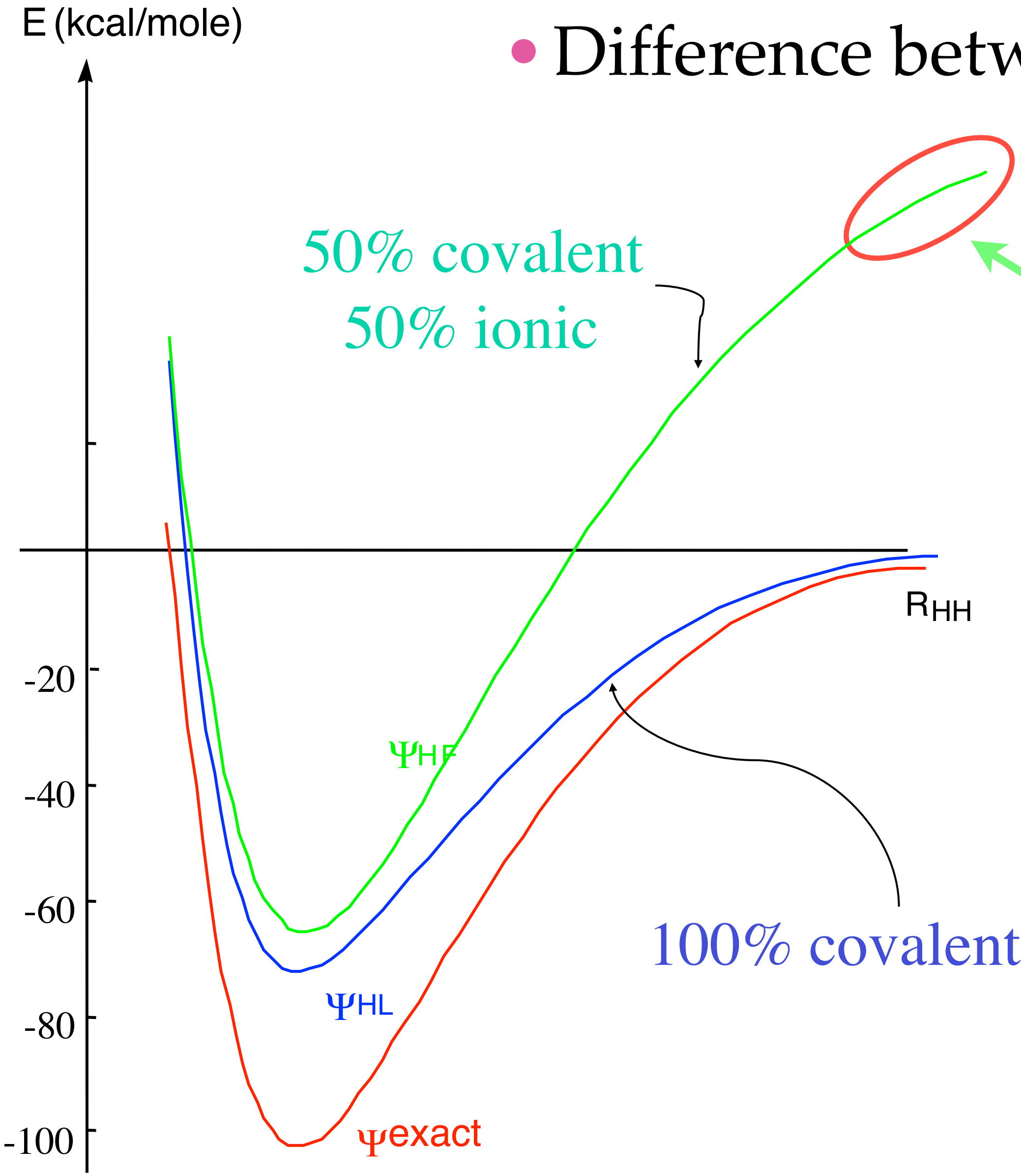
$$\Psi_{HF} = |\sigma_g \bar{\sigma}_g|$$

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

50% covalent　　50% ionic

VB vs. MO

- Difference between HL and HF ?



50% covalent
50% ionic

wrong dissociation limit

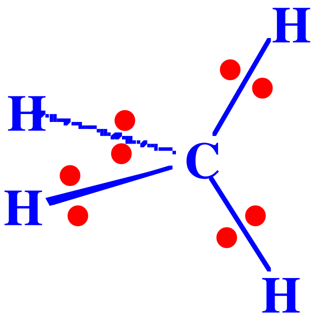
100% covalent

Optimal ≈ 80% covalent
20% ionic

Writing VB wave functions

- Extension to the general case :

Lewis :

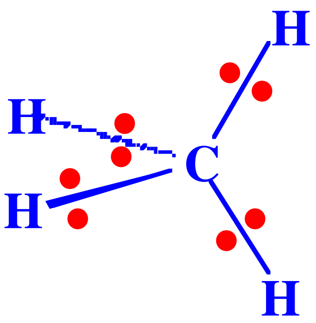


  - We want to construct a VB w.f. which corresponds to Lewis' picture
  - Which orbitals to use ?

Writing VB wave functions

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

Lewis :



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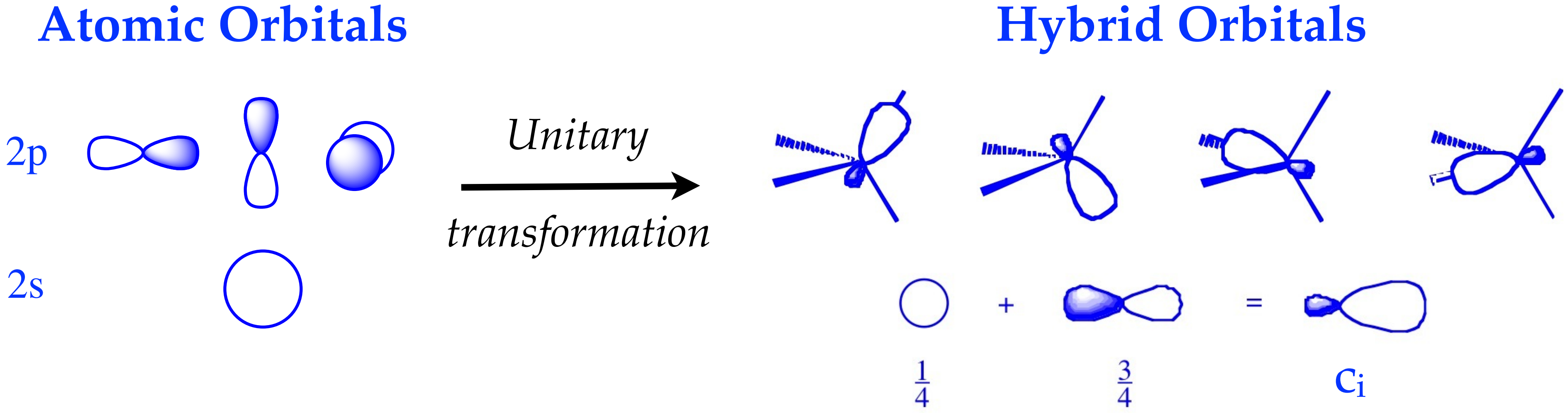
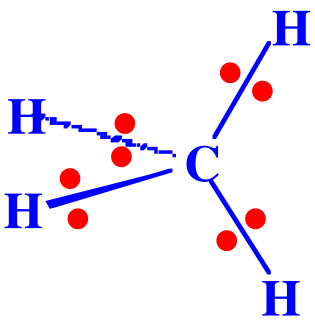


Four equivalent directional sp^3 orbitals

Writing VB wave functions

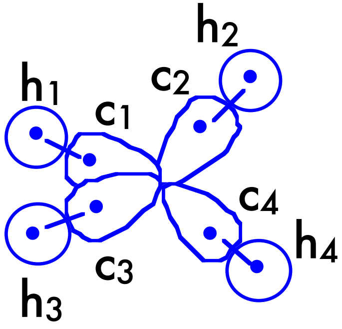
- Extension to the general case / **1) general localized orbital:**

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)

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

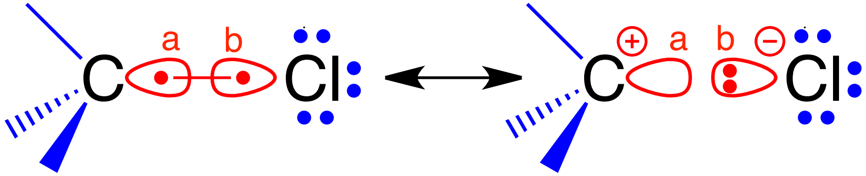
$$\psi_{VB} = \mathcal{A}\left[\{\mathit{inactives}\}\cdot\{\mathit{actives}\}\right]$$

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

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

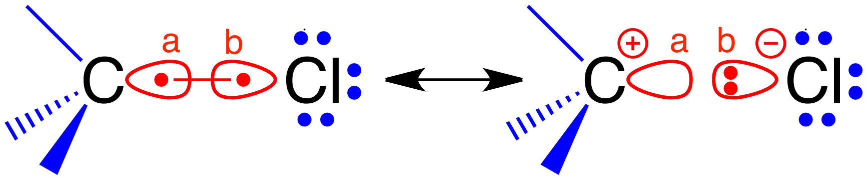


Writing VB wave functions

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

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

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



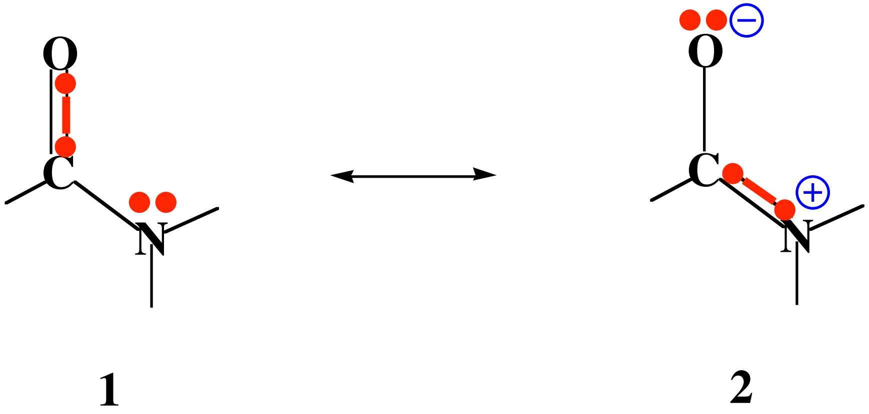
$$\psi_{VB} = \left|\underbrace{\sigma_1\sigma_2\ldots\sigma_n}_{\text{delocalized MOs}}\left(a\bar{b}-\bar{a}b\right)\right| + \left|\underbrace{\sigma_1\sigma_2\ldots\sigma_n}_{\text{delocalized MOs}}b\bar{b}\right|$$

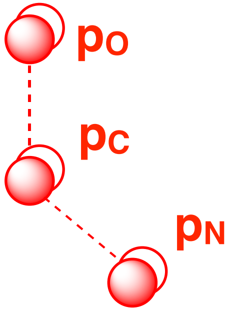
- an **active space** of electrons/orbitals treated at the **VB level**
- **the rest** (called inactive or «spectators») at the **MO level**

- The active space chosen depending on the chemical problem

Writing VB wave functions

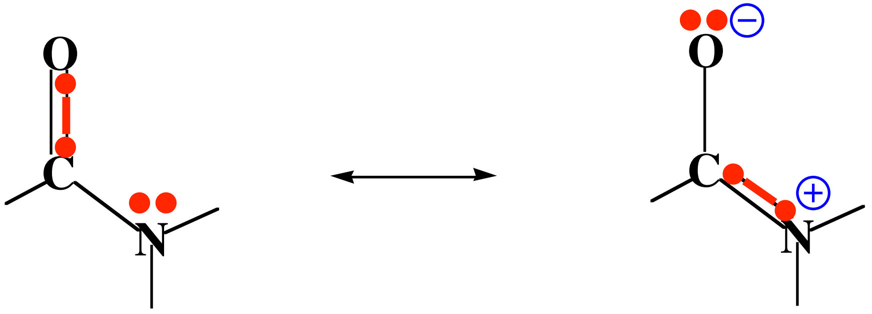
- Extension to the general case / **3) multi-structure:**



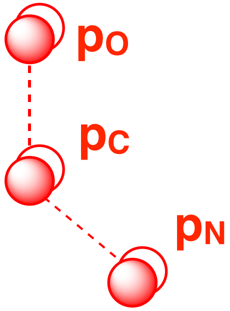


Writing VB wave functions

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



1 **2**



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

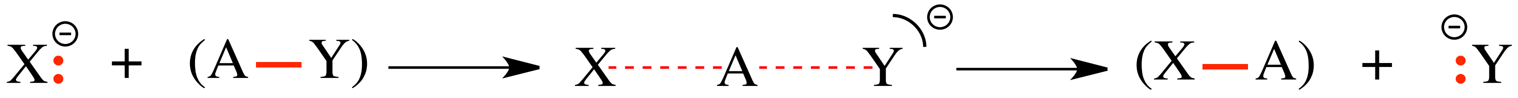
$$= C_1\left|p_N\overline{p_N}(p_O\overline{p_C} + p_C\overline{p_O})\right| + C_2\left|p_O\overline{p_O}(p_C\overline{p_N} + p_N\overline{p_C})\right|$$

➡ VB wave function : two **resonating** components,

each one corresponding to one of the **2 structures**

Writing VB wave functions

➡ Exercise 2 :

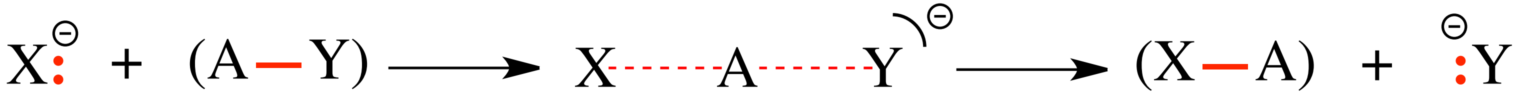


We want to study the SN2 reaction using VB theory.

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

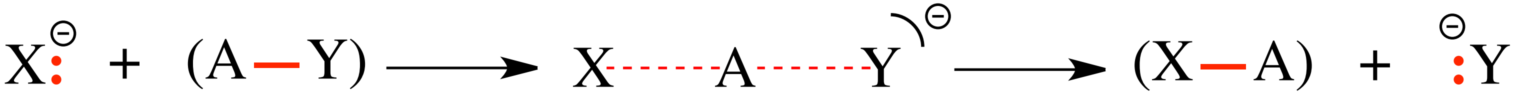
➡ Exercise 2 :



It is a 4e in 3 orbitals problem:

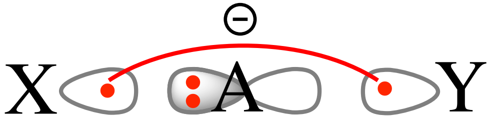
Writing VB wave functions

➡ **Exercise 2 :**



It is a 4e in 3 orbitals problem:

1

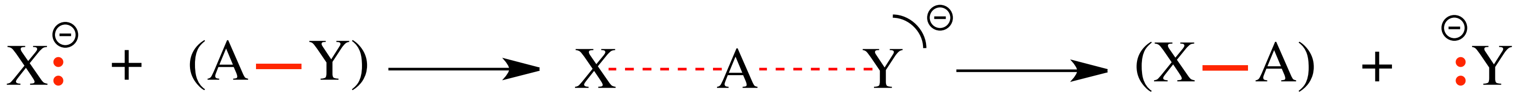


3

2

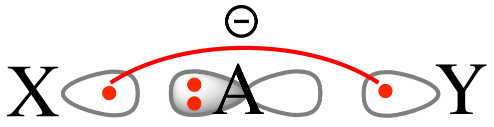
Writing VB wave functions

Exercise 2 :



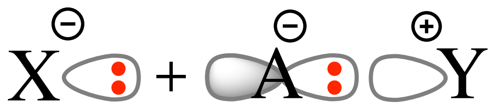
It is a 4e in 3 orbitals problem:

1



3

2



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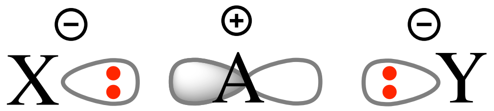
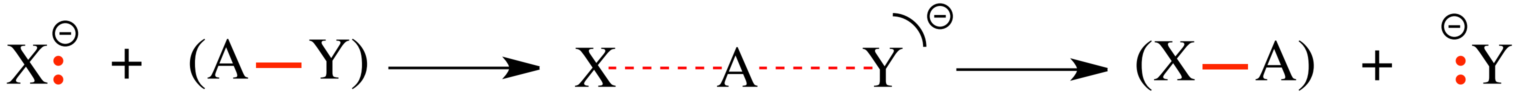


4

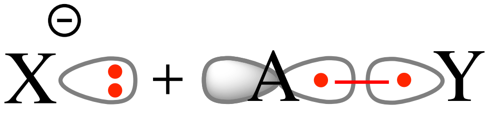
5

Writing VB wave functions

➡ Exercise 2 :

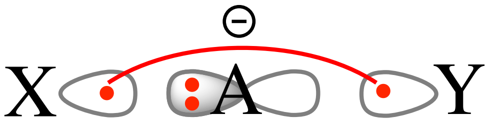


It is a 4e in 3 orbitals problem:



1

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

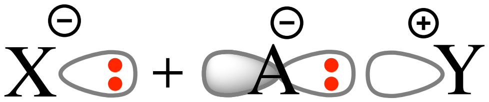


3

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

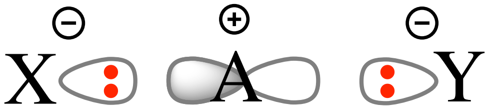
2

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



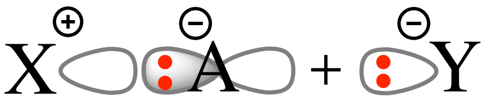
6

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



4

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



5

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

Part 2. *Ab initio* Valence Bond

VB methods including correlation

- **The VBSCF* method :**
  - Basically a MCSCF method with nonorthogonal orbitals :

$$\boxed{\Psi_{VBSCF} = \sum_K C_K \Phi_K} \quad \text{with :} \begin{cases} \Phi_K(1,\ldots,N) = \hat{A}\{\prod_{i=1}^{N} \varphi_i(1)\Theta_K\} : \text{VB structures} \\ \{\varphi_i\} : \text{set of non-orthogonal localized orbitals} \\ \qquad \text{expanded onto a set of basis functions } \{\chi_m\} : \varphi_i(1) = \sum_m d_m^i \chi_m(1) \\ \Theta_K \text{ spin function} \end{cases}$$

*van Lenthe; Balint-Kurti, J. Chem. Phys. 1983, 78, 5699

VB methods including correlation

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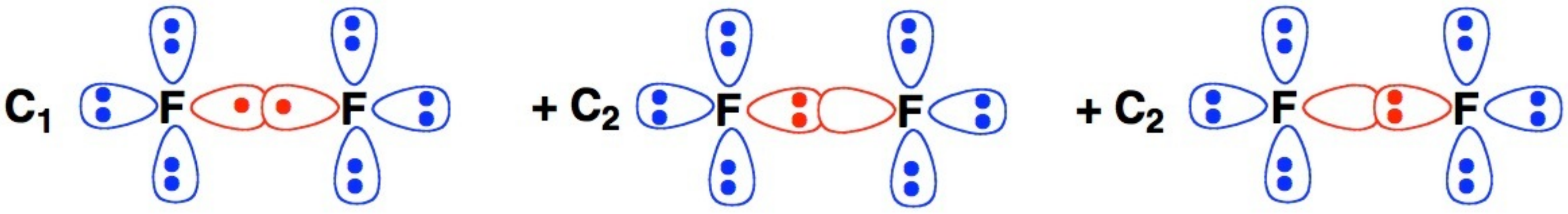
All w.f. parameters : structure coef. $\{C_K\}$ and orb. coef. $\{d^i_m\}$ are **optimized simultaneously** minimizing $\langle \Psi_{VBSCF} | \hat{H} | \Psi_{VBSCF} \rangle$

*van Lenthe; Balint-Kurti, J. Chem. Phys. 1983, 78, 5699

VB methods including correlation

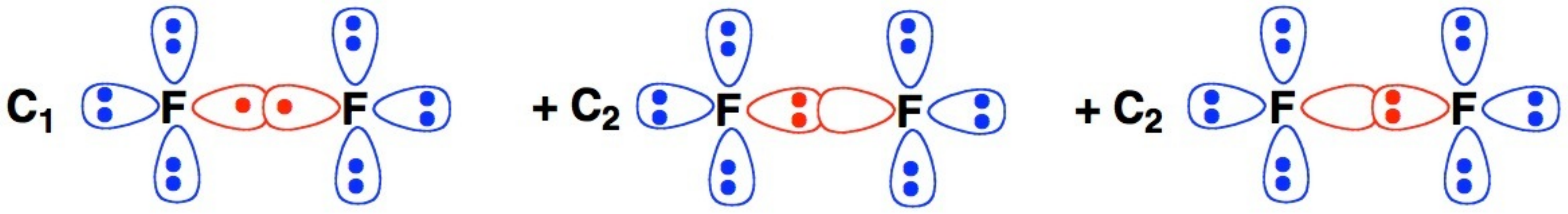
- **The VBSCF method :**



F•—•F F^-F^+ F^+F^-

VB methods including correlation

- **The VBSCF method :**



	F•—•F	F^-F^+	F^+F^-
HF :	50%	25%	25%
HL :	100%	0%	0%
VBSCF :	**80%**	**10%**	**10%**

➡ The VBSCF method ensures a correct balance beween covalent and ionic configurations («left-right» static correlation)

VB methods including correlation

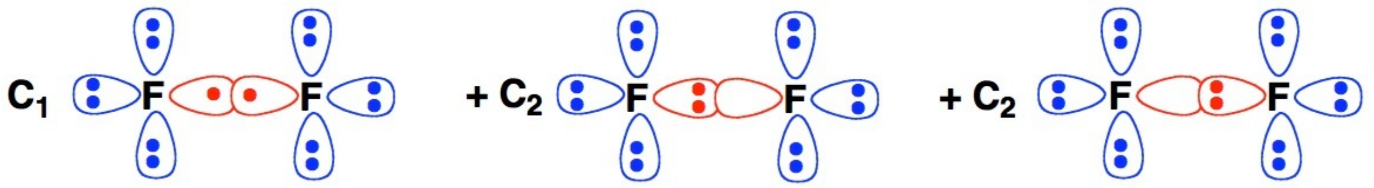
- **The VBSCF method :**
  - Accuracy : $\mathbf{F{-}F} \xrightarrow{\Delta E} \mathbf{F\bullet + F\bullet}$

	ΔE (kcal.mol^{-1})	
RHF	–37	←Too ionic
VBSCF	+15	←Why ???
Exact	*+39*	

Some important physical ingredient is missing...

VB methods including correlation

- **The VBSCF method :**
  - What the VBSCF method does :



F•——•F

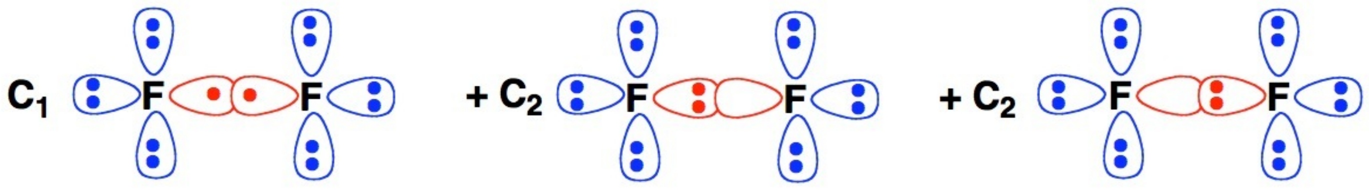
F^-F^+

F^+F^-

Same set of orbitals for all VB structures : optimized for a mean situation

VB methods including correlation

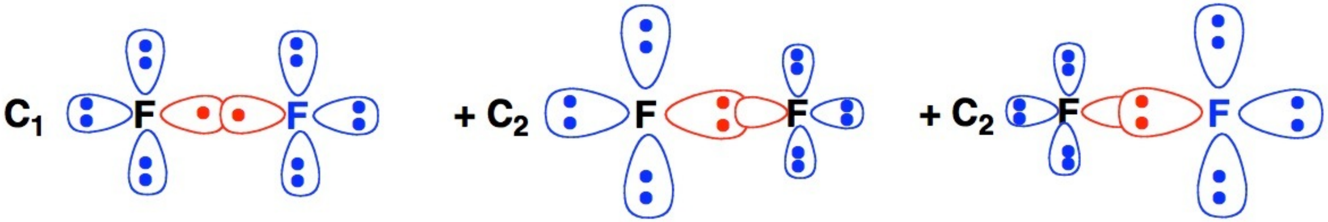
- **The VBSCF method :**
  - What the VBSCF method does :



F•—•F F^-F^+ F^+F^-

Same set of orbitals for all VB structures : optimized for **a mean** situation

  - A better wave function would be :



Each structure has its own specific set of orbitals optimized for **each** situation

VB methods including correlation

- **The BOVB* method :**

  - BOVB uses : same number of structures as VBSCF, but different orbitals for the different structures :

$$\boxed{\Psi_{BOVB} = \sum_K C_K \Phi_K^{BOVB}} \quad \text{with :} \begin{cases} \Phi_K^{BOVB}(1,\ldots,N) = \hat{A}\{\prod_{i=1}^{N} \varphi_i^K(1)\Theta_K\} \text{ : VB structures} \\ \{\varphi_i^K\} \text{ : set of non-orthogonal (del)localized orbitals for the structure K} \\ \qquad \text{expanded onto a set of basis functions } \{\chi_m\} \text{ : } \varphi_i^K(1) = \sum_m d_m^{i,K} \chi_m(1) \\ \Theta_K \text{ spin function} \end{cases}$$

All w.f. parameters : structure coef. $\{C_K\}$ and orb. coef. **sets** $\{d^i_m\}^K$ are optimized simultaneously minimizing $\langle \Psi_{BOVB} | \hat{H} | \Psi_{BOVB} \rangle$

* *Hiberty, P. C. ; Humbel, S. ; Byrman, C. P. ; van Lenthe J. H. J. Chem. Phys. 1994, 101, 5969*

VB methods including correlation

- **The BOVB method :**
  - Accuracy :

$$\text{F–F} \xrightarrow{\Delta E} \text{F}\bullet + \text{F}\bullet$$

	ΔE (kcal.mol^{-1})
RHF	–37
VBSCF	15
L-BOVB	28.2
SD-BOVB	33.6
Exact	*+39*

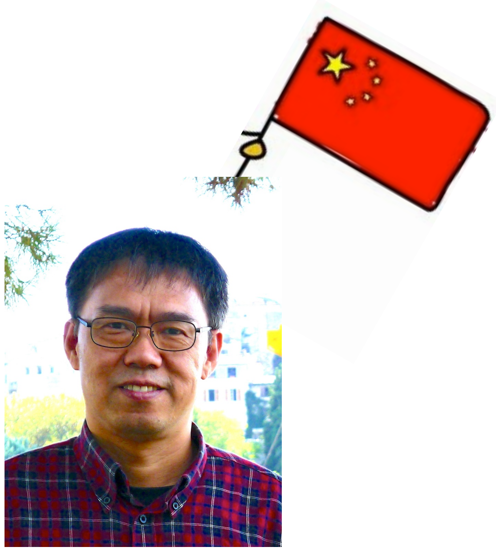
Basis set incompleteness

VB methods including correlation

- The **VBSCF** method

- The **BOVB** method

- The **VBCI** method



VB computations in practice

What do you get out of the calculation ?

VB computations in practice

(good) numbers...

VB computations in practice

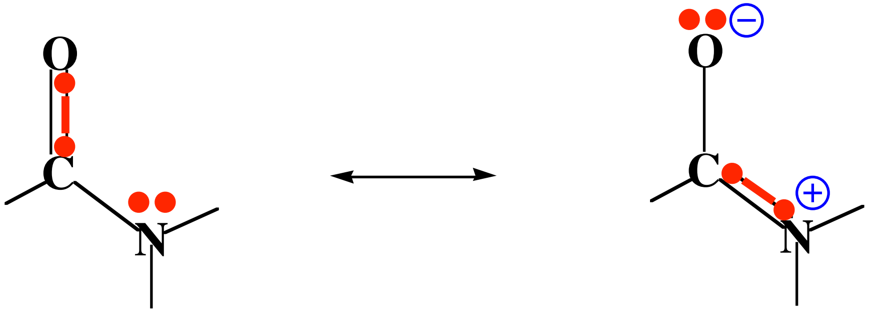
...but also insight !

VB computations in practice

- **Resonance energy / «diabatic states» :**

It is possible to compute a VB w.f. which does not correspond to a real quantum state : a single structure of a subset of structures

➡ computation of **Resonance Energies** (R.E.) :



1 **2**

$$\Psi_{(\mathbf{1}\leftrightarrow\mathbf{2})} = C_1(\Psi_{\mathbf{1}}) + C_2(\Psi_{\mathbf{2}})$$

1) Optimize $\Psi_{(\mathbf{1}\leftrightarrow\mathbf{2})}$

2) Optimize $\Psi_{\mathbf{1}}$ separately

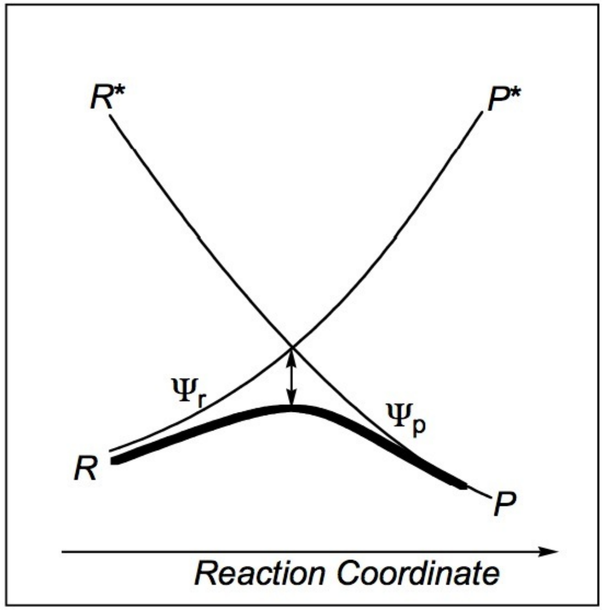
3) $\boxed{R.E. = E(\Psi_1) - E(\Psi_{(1\leftrightarrow 2)})}$

VB computations in practice

- **Chemical insight / «diabatic states» :**

It is possible to compute a VB w.f. which does not correspond to a real quantum state : a single structure of a subset of structures

➡ **Valence Bond diagrams** (Shaik and Pross) for reactivity :



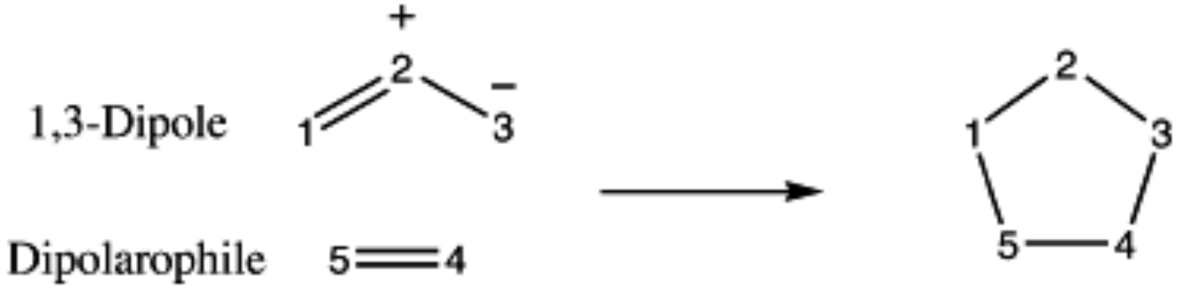
Part 4. lecture

Application

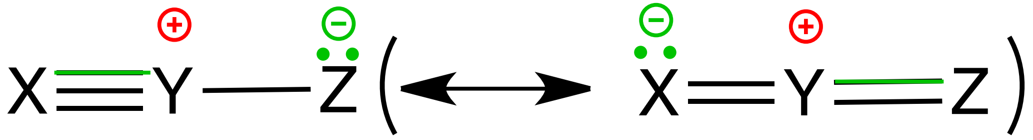
1,3-dipolar cycloadditions

1-3 dipolar cycloadditions

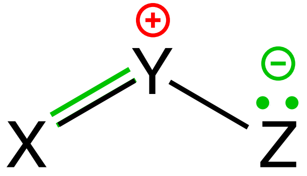
- Method for heterocyclic compounds synthesis :



- 1-3 dipole :
  - 1 or 2 π systems, **4 π electrons** on **3 centers** ;
  - Globally neutrals but **polarized** ;
  - Two families :



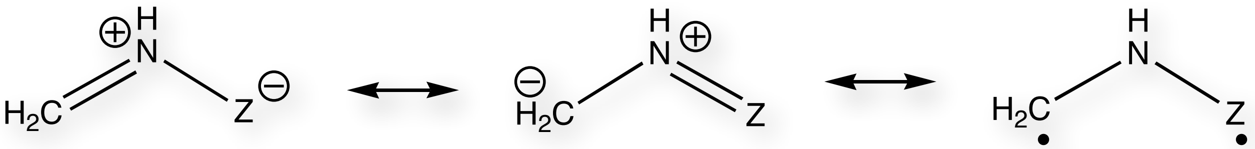
Propargylic (N_2O,...)



Allylic (O_3,...)

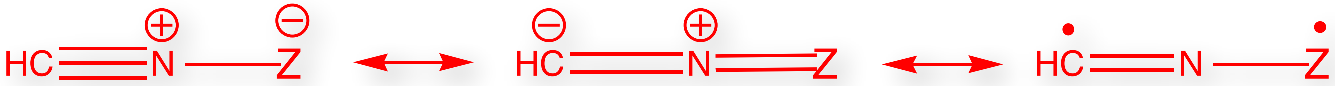
Some families of dipoles

Azomethine betaines :



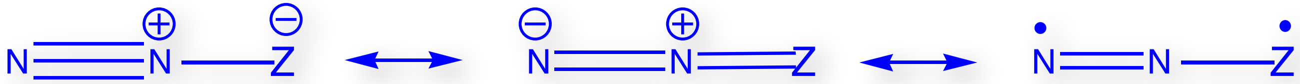
$Z = O, NH, CH_2$

Nitrilium betaines :



$Z = O, NH, CH_2$

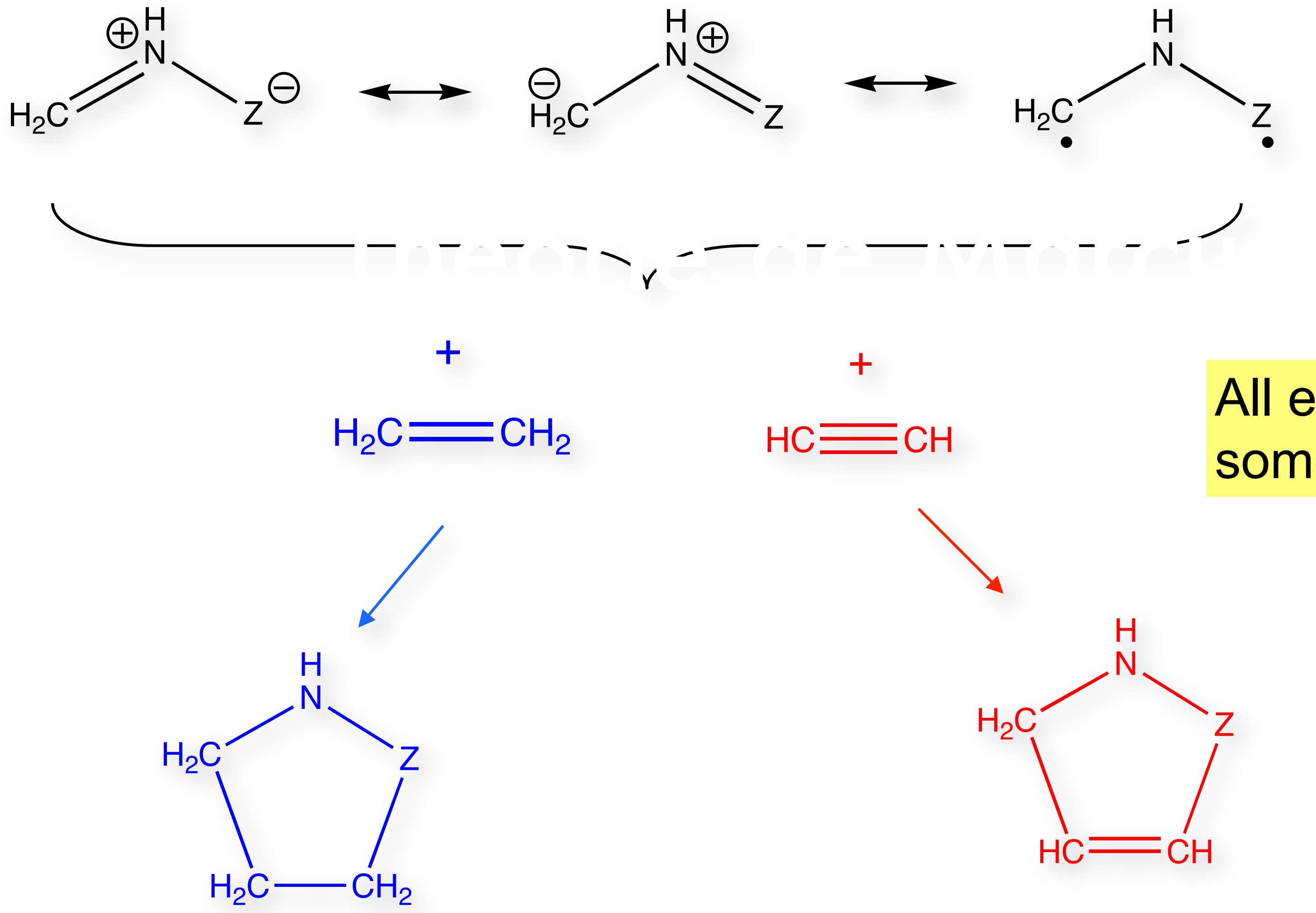
Diazonium betaines :



$Z = O, NH, CH_2$

Reactions studied

- Dipolarophiles : ethylene et acetylene :

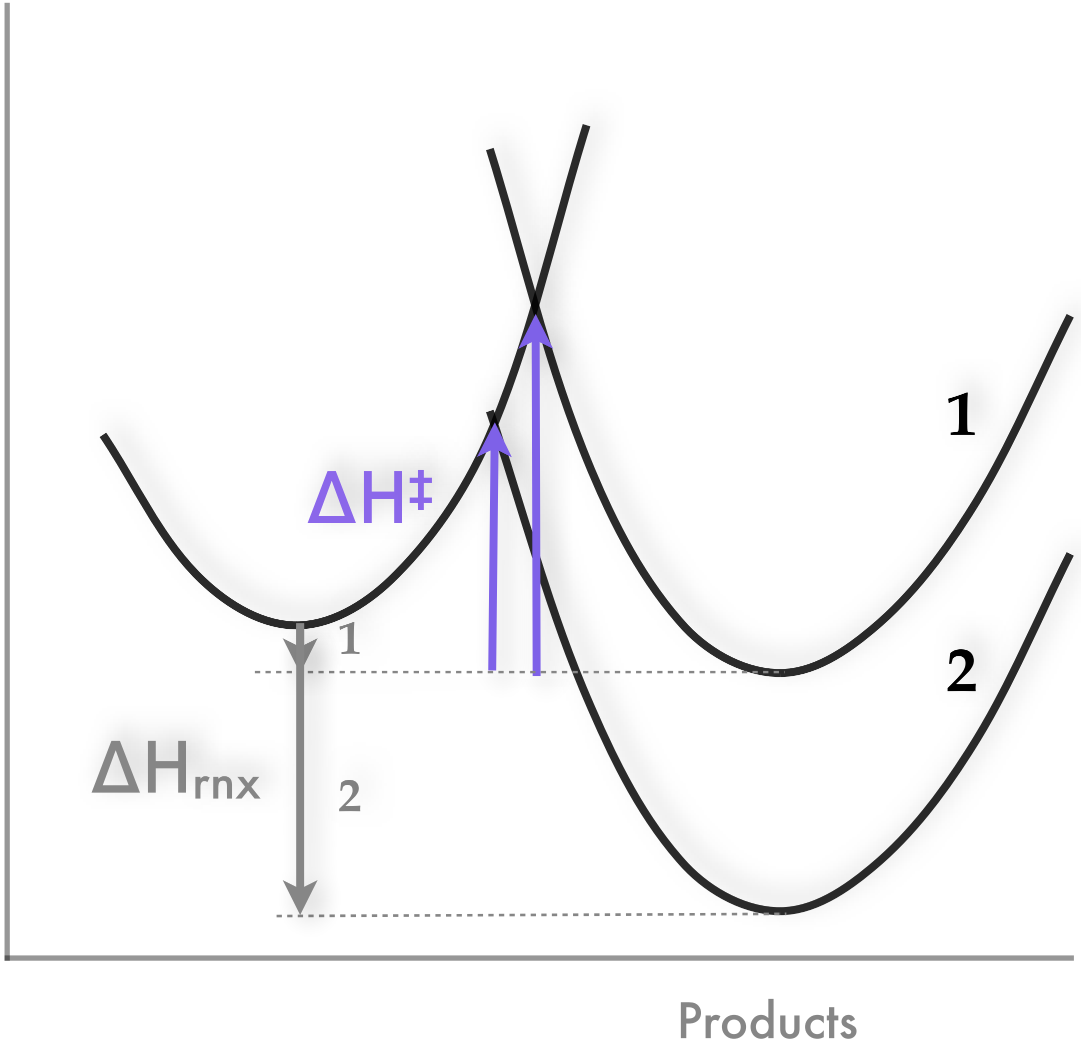


Z = O, NH, CH_2

All exothermic, but something funny…

Marcus theory ?

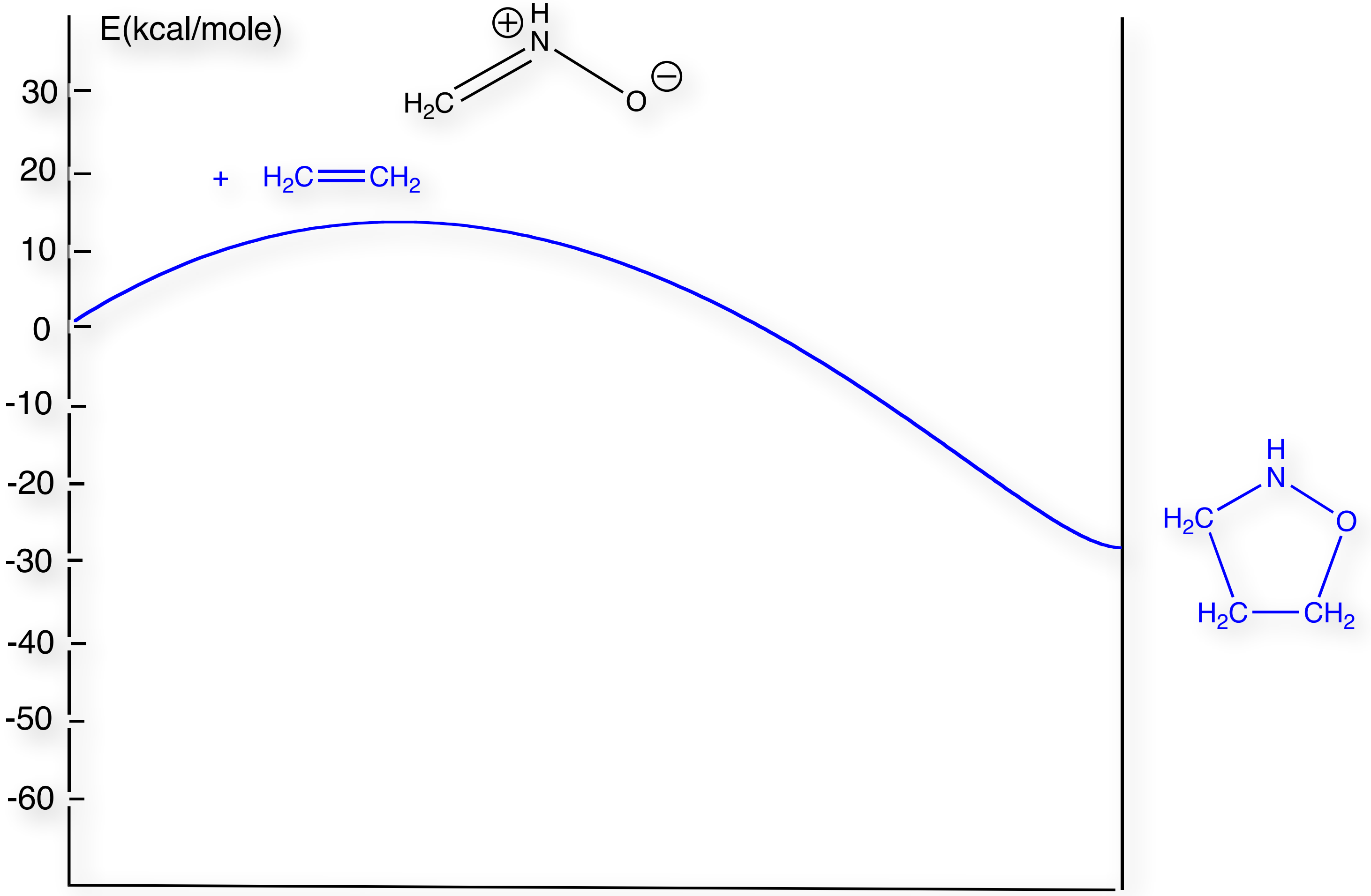
- Marcus : correlation between **barriers** and **enthalpies** :



the **more exothermic** the reaction, the **lower** the **barrier**

Marcus theory ?

- **Allylic** dipole ; addition on ethylene :



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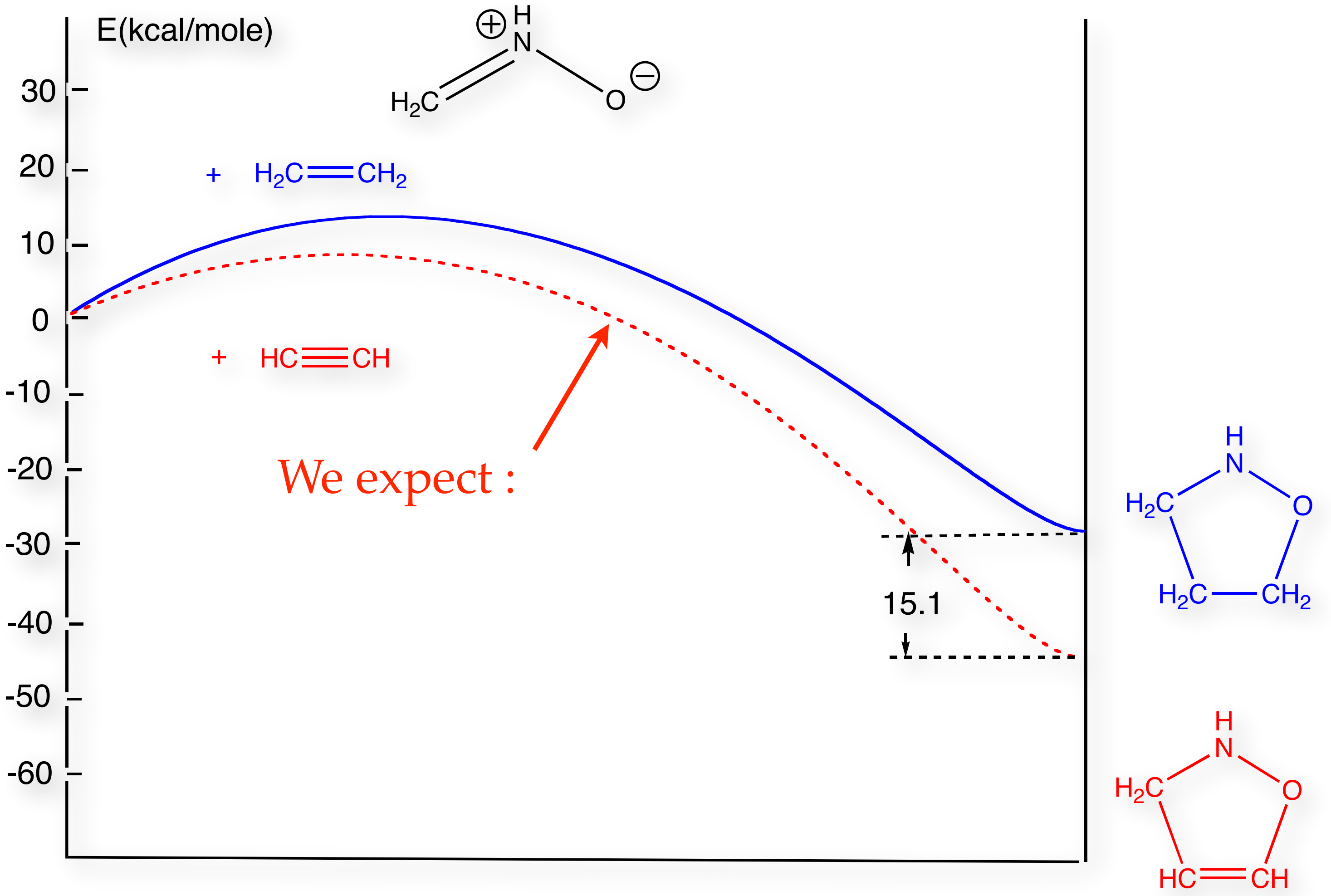

Marcus theory ?

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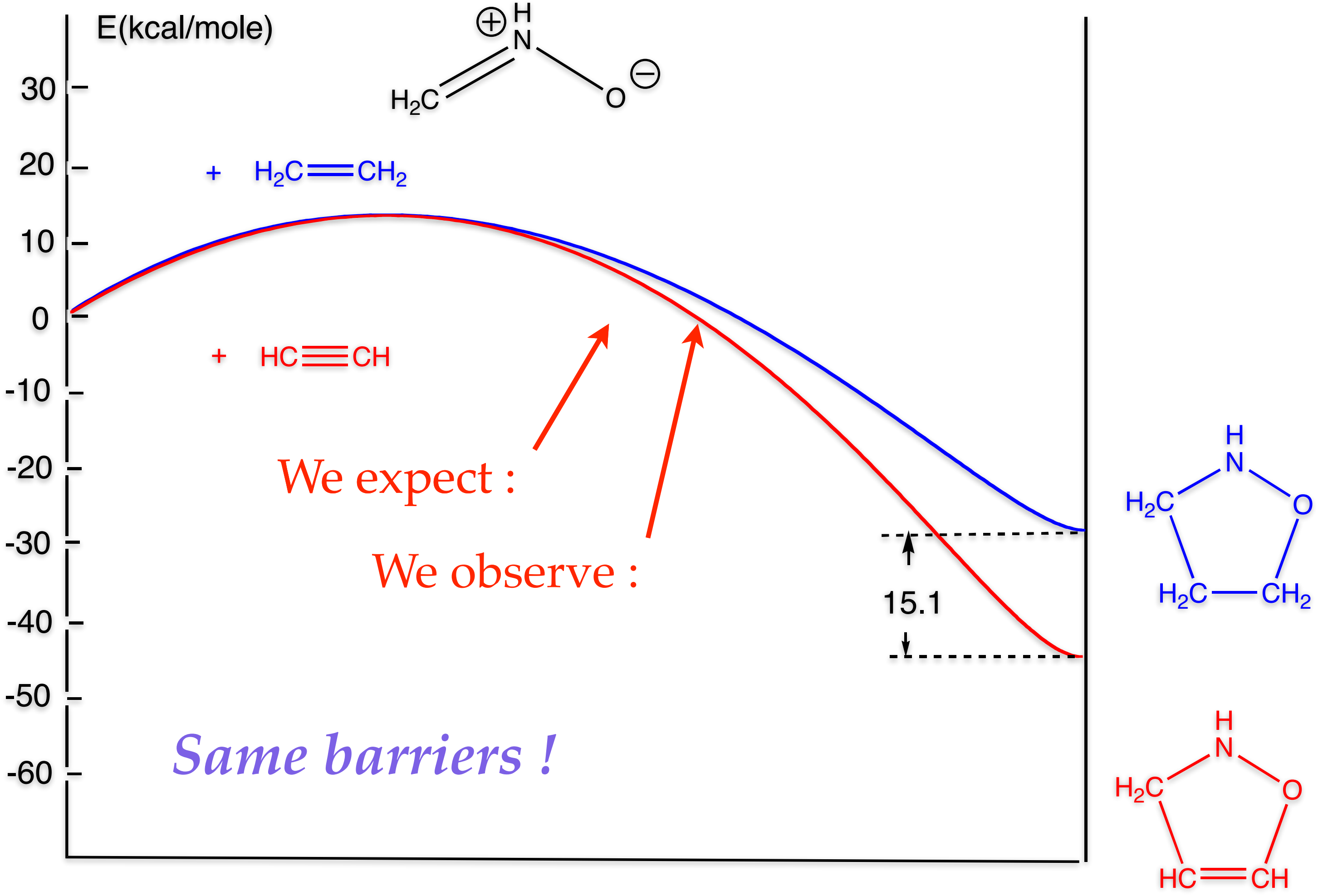


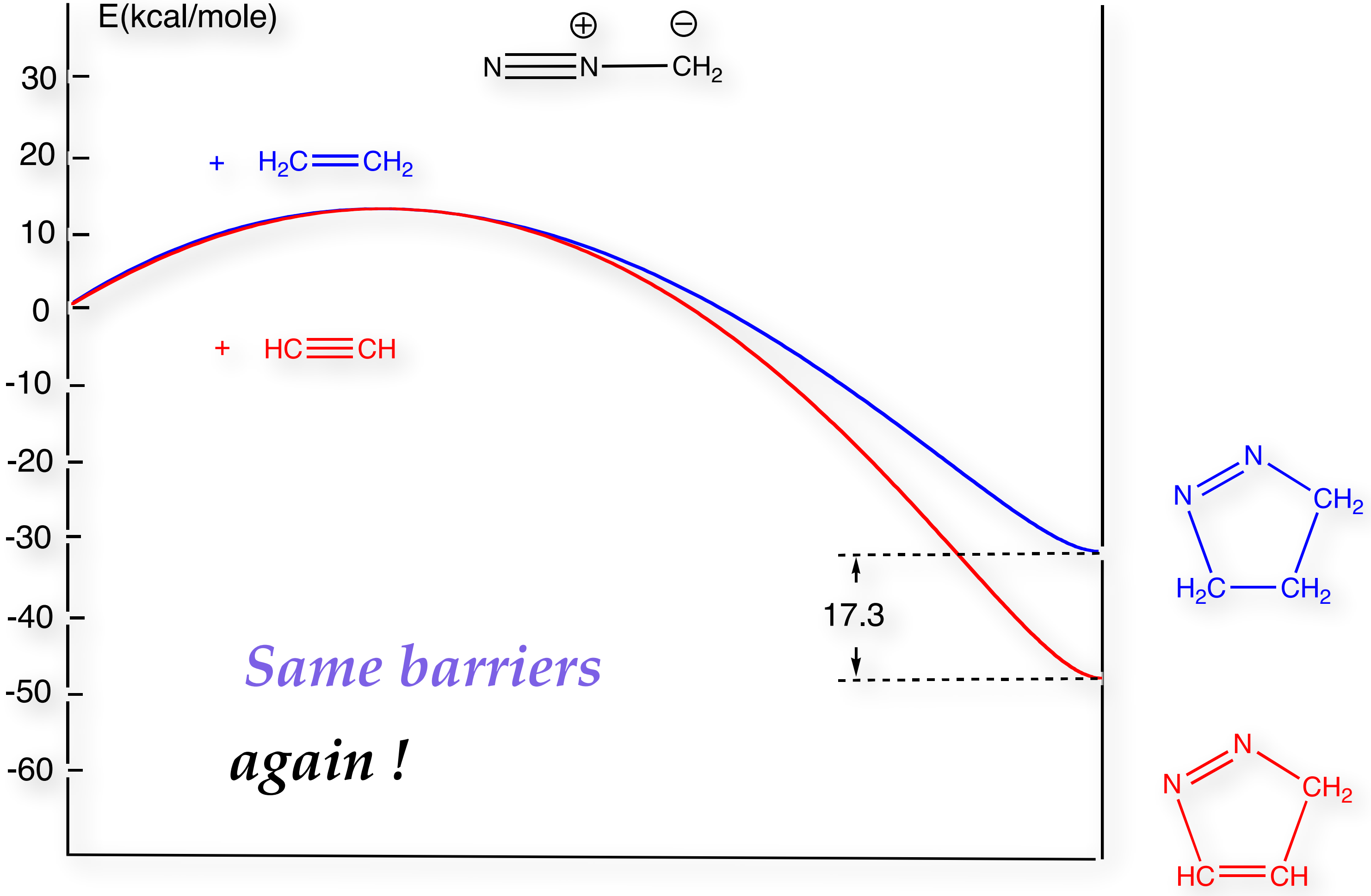
We expect :

We observe :

Same barriers !

Marcus theory ?

- **Propargylic** dipole

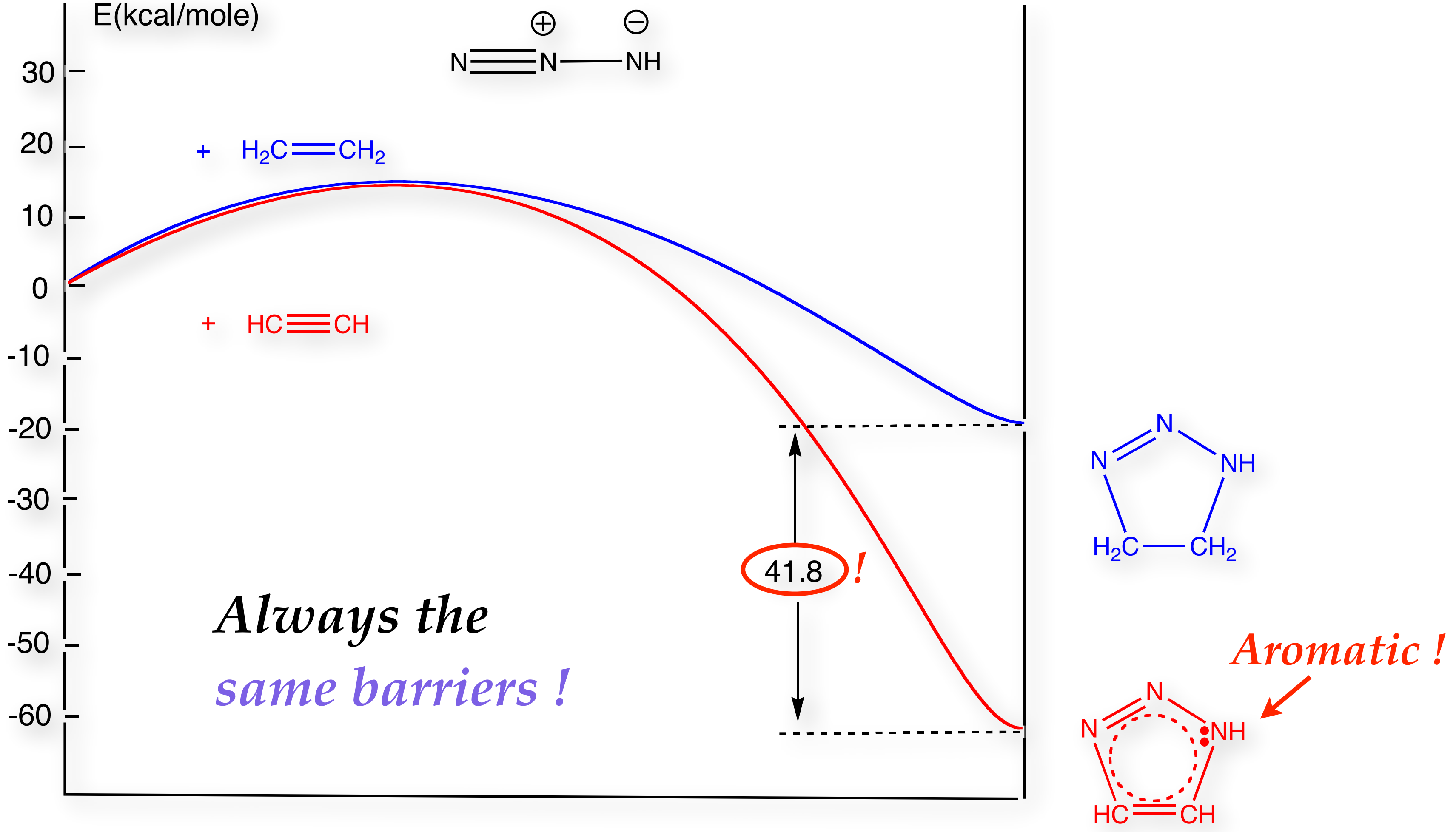


Same barriers

again !

Marcus theory ?

- **Propargylic** dipole



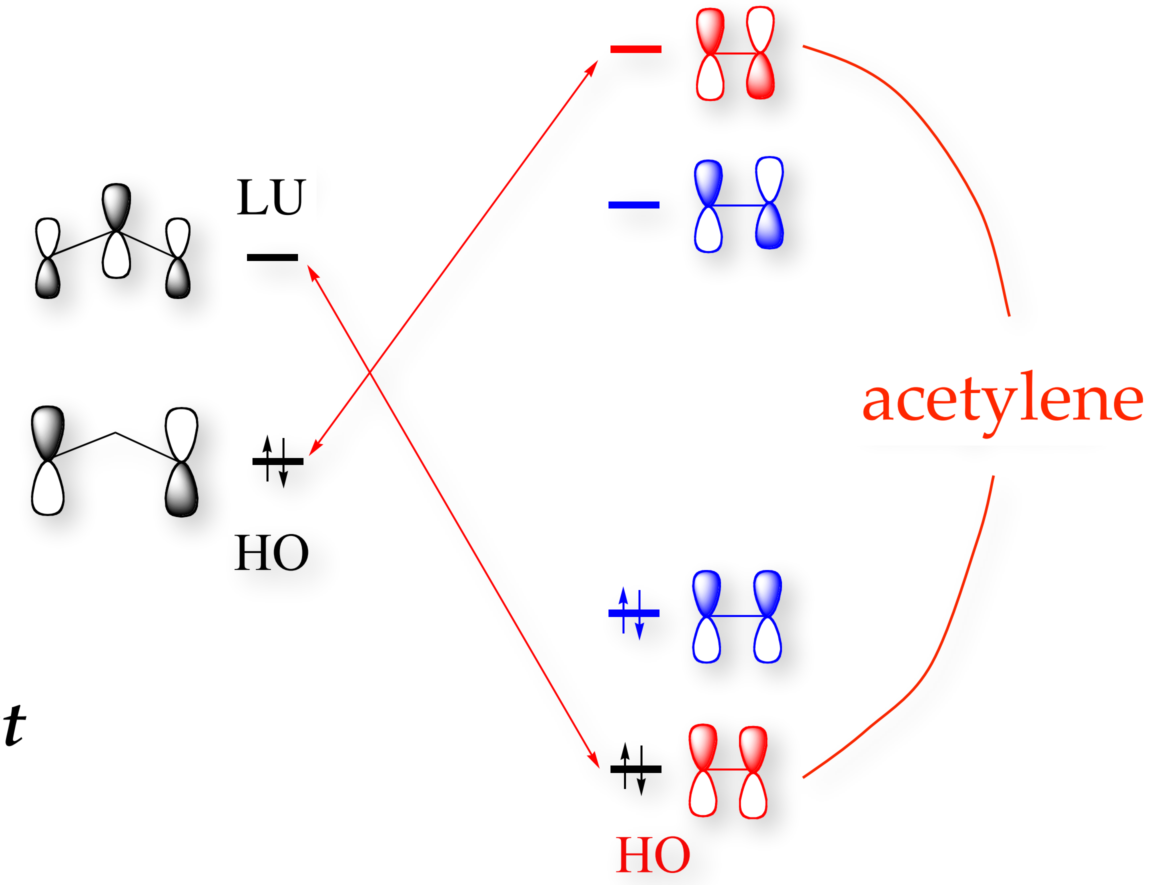
Always the

same barriers !

FMO theory ?

Small HOMO-LUMO energy difference between reactants

=> small barriers

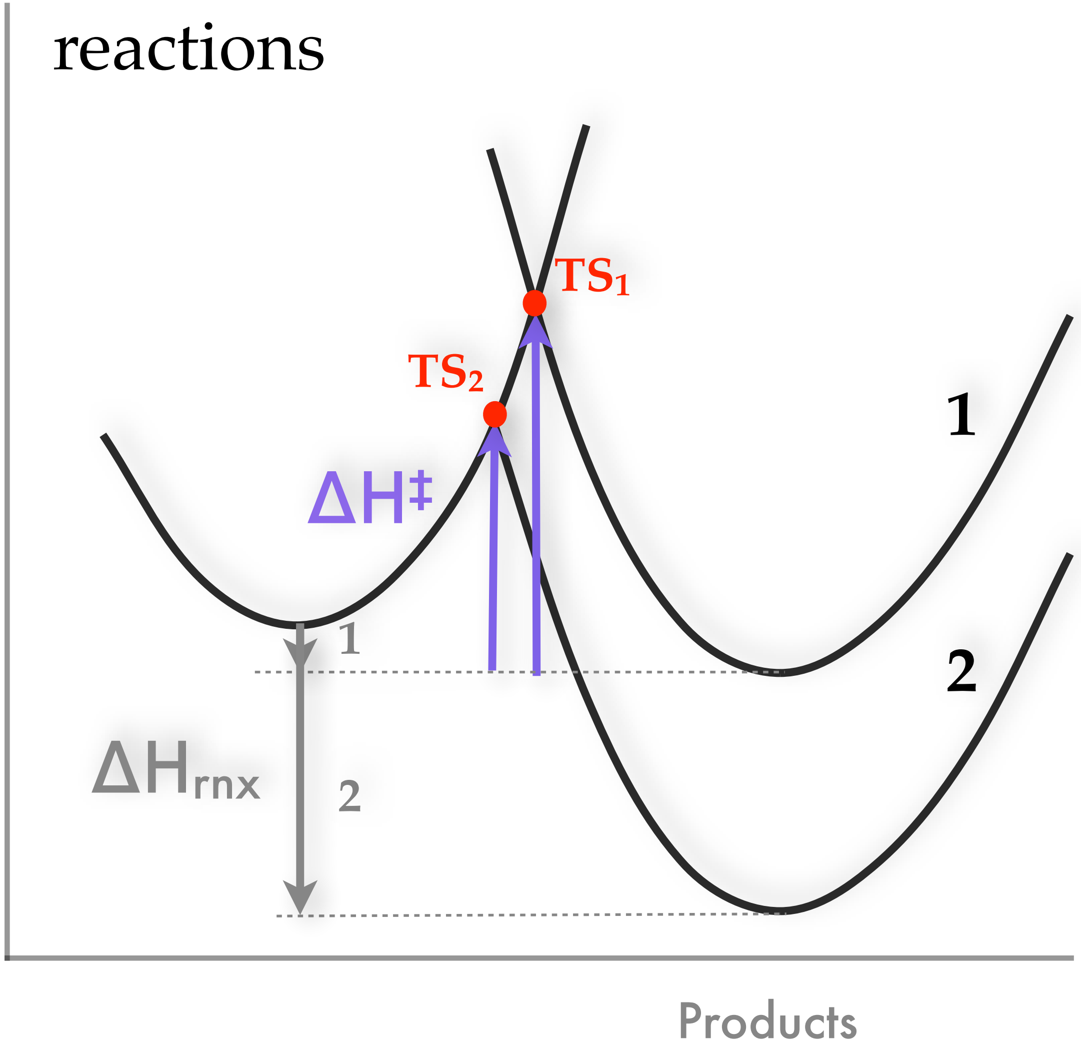


FMO ***would predict***

different barriers !

Hammond postulate ?

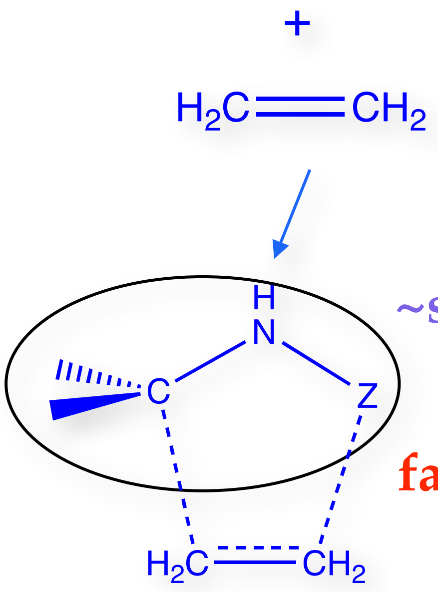
- Hammond : TS is more reactant-like for more exothermic reactions



Different enthalpies, different **TS geometries**

Hammond principle ?

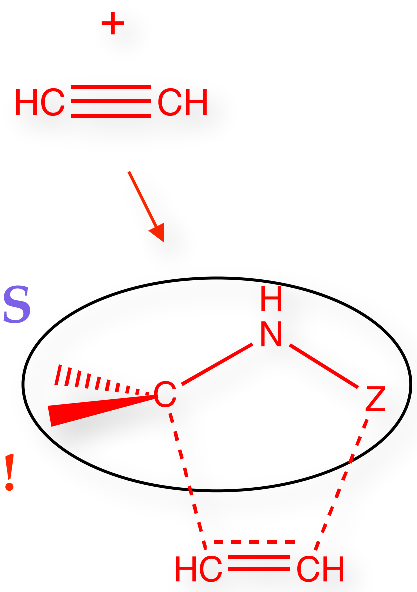
- All dipoles **distort** when going to TS :



~same dipole geometries at TS

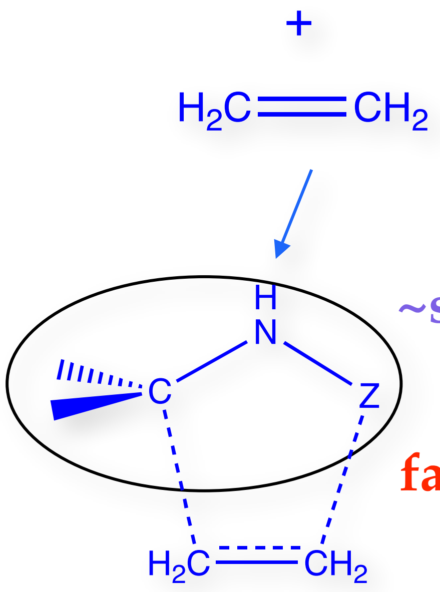
(systematic)

falsifies Hammond principle !



Hammond principle ?

- All dipoles **distort** when going to TS :



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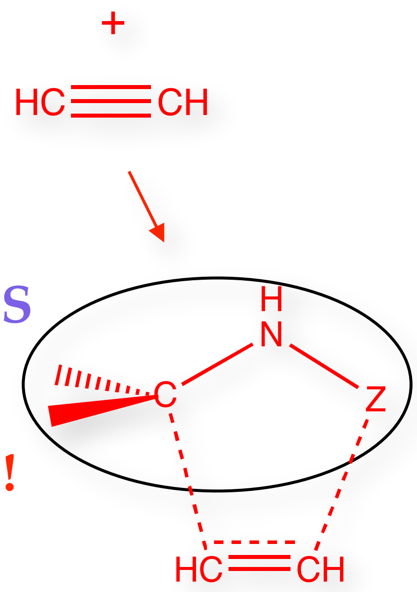


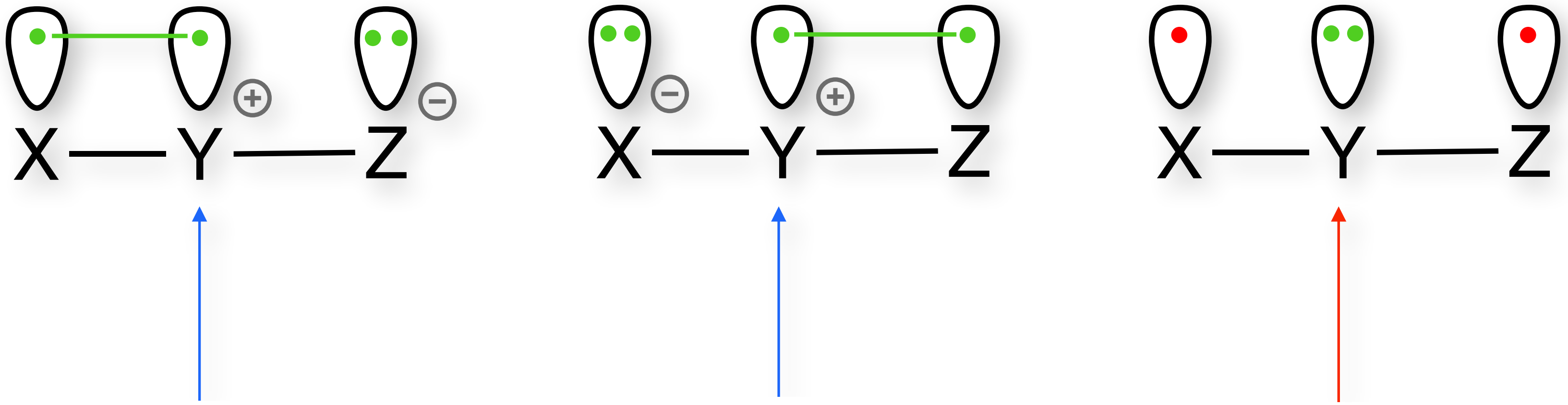
Ess & Houk**[*] **: barriers only depend on dipole distortion energies

... but why ?...

[*] Ess, D. H.; Houk, K. N. *J. Am. Chem. Soc.* **2008**, *130*, 10187

Ab initio VB calculations

- VB description :



Non reactive

Non reactive

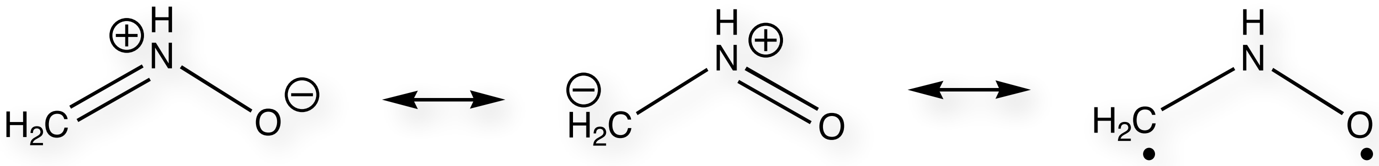
Reactive

- Combination of 3 resonant **structures**

- Diradical structure (neutral) may have a significant weight, and is reactive...

Ab initio VB calculations

- Importance of the diradical structure (BOVB calculations) :



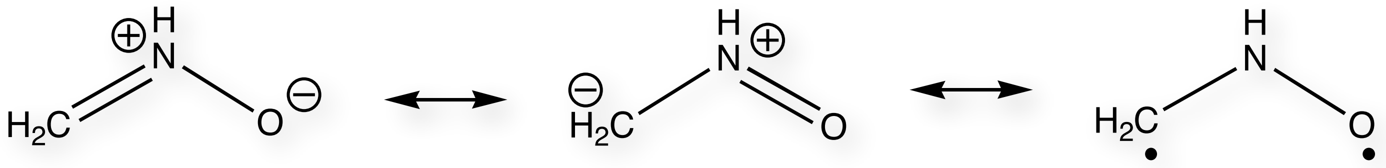
Reactants :	48,4%	18,0%	33,7%

- Diradical character is important !

B. Braida, C. Walter, B. Engels, P. C. Hiberty, *J. Am. Chem. Soc.* **2010**, 132, 7631

Ab initio VB calculations

- Importance of the diradical structure (BOVB calculations) :



Reactants :	48,4%	18,0%	33,7%
TS geometry :	41,7%	19,7%	38,6%

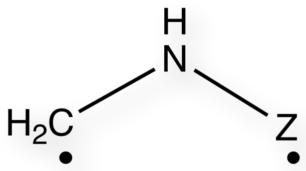
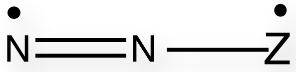
- Diradical character is important !

- Diradical character increases from reactants → TS !

B. Braida, C. Walter, B. Engels, P. C. Hiberty, *J. Am. Chem. Soc.* **2010**, 132, 7631

Ab initio VB calculations

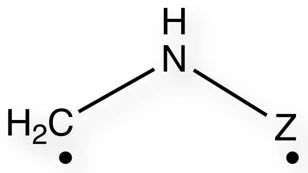
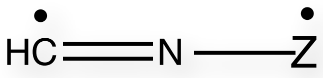
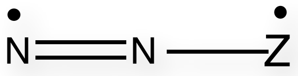
- Importance of the diradical structure (BOVB calculations) :

		Reactants :	TS :
	Z = O Z = NH Z = CH_2	33.7 38.0 41.3	38.6 43.2 46.6
	Z = O Z= NH Z = CH_2	21.3 26.5 26.3	32.1 35.7 35.4
	Z = O Z = NH Z= CH_2	21.6 25.1 27.7	31.6 34.4 36.4

B. Braida, C. Walter, B. Engels, P. C. Hiberty, *J. Am. Chem. Soc.* **2010**, 132, 7631

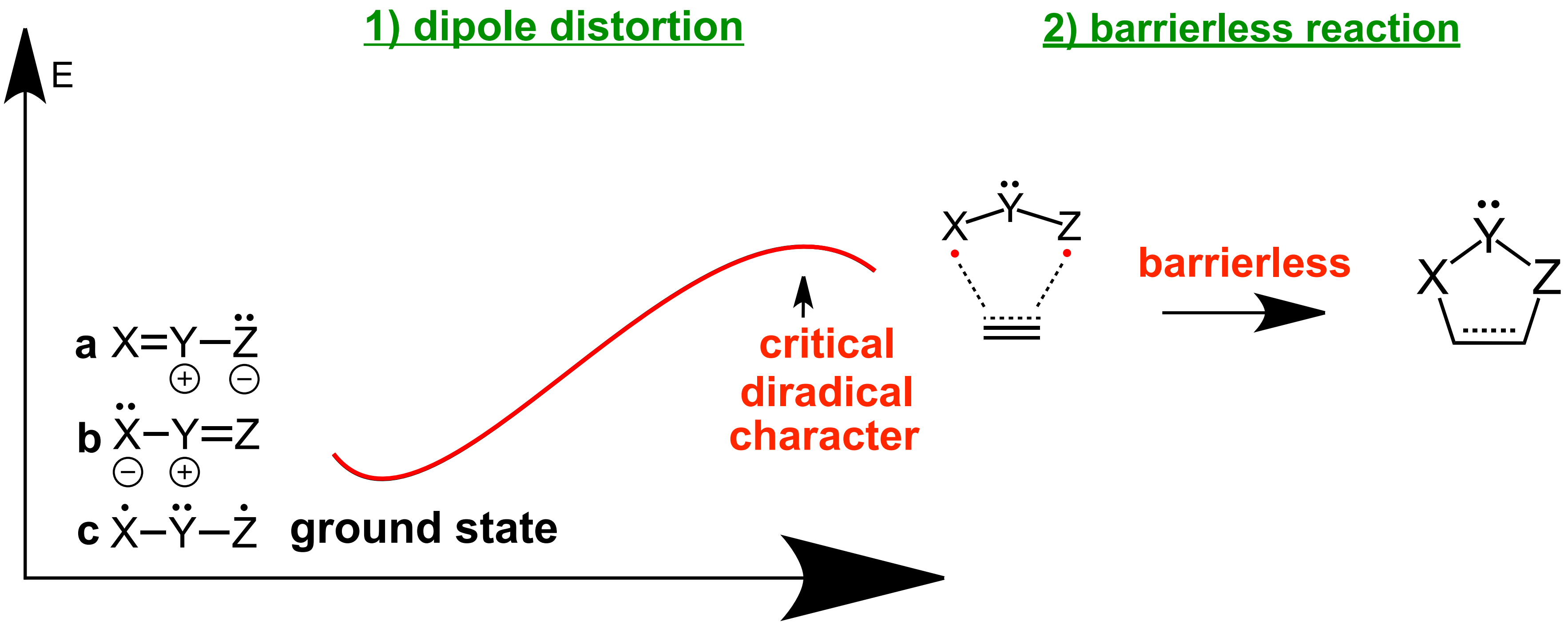
Ab initio VB calculations

- Importance of the diradical structure (BOVB calculations) :

		Reactants :	TS :
	Z = O	33.7	38.6
	Z = NH	38.0	43.2
	Z = CH_2	41.3	46.6
	Z = O	21.3	32.1
	Z= NH	26.5	35.7
	Z = CH_2	26.3	35.4
	Z = O	21.6	31.6
	Z = NH	25.1	34.4
	Z= CH_2	27.7	36.4

What if... dipole distortion would serve to **increase the diradical character** ?...

Ab initio VB calculations

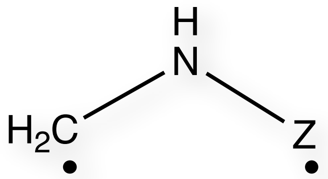


1) Dipole distortion ⟶ reach a **«critical» diradical character**

2) Dienophile attack (almost barrierless) !

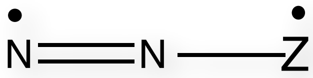
Ab initio VB calculations

1) If our postulated mechanism is correct :



Z = O	33.7
Z = NH	38.0
Z = CH_2	41.3

Z = O	21.3
Z= NH	26.5
Z = CH_2	26.3



Z = O	21.6
Z = NH	25.1
Z= CH_2	27.7

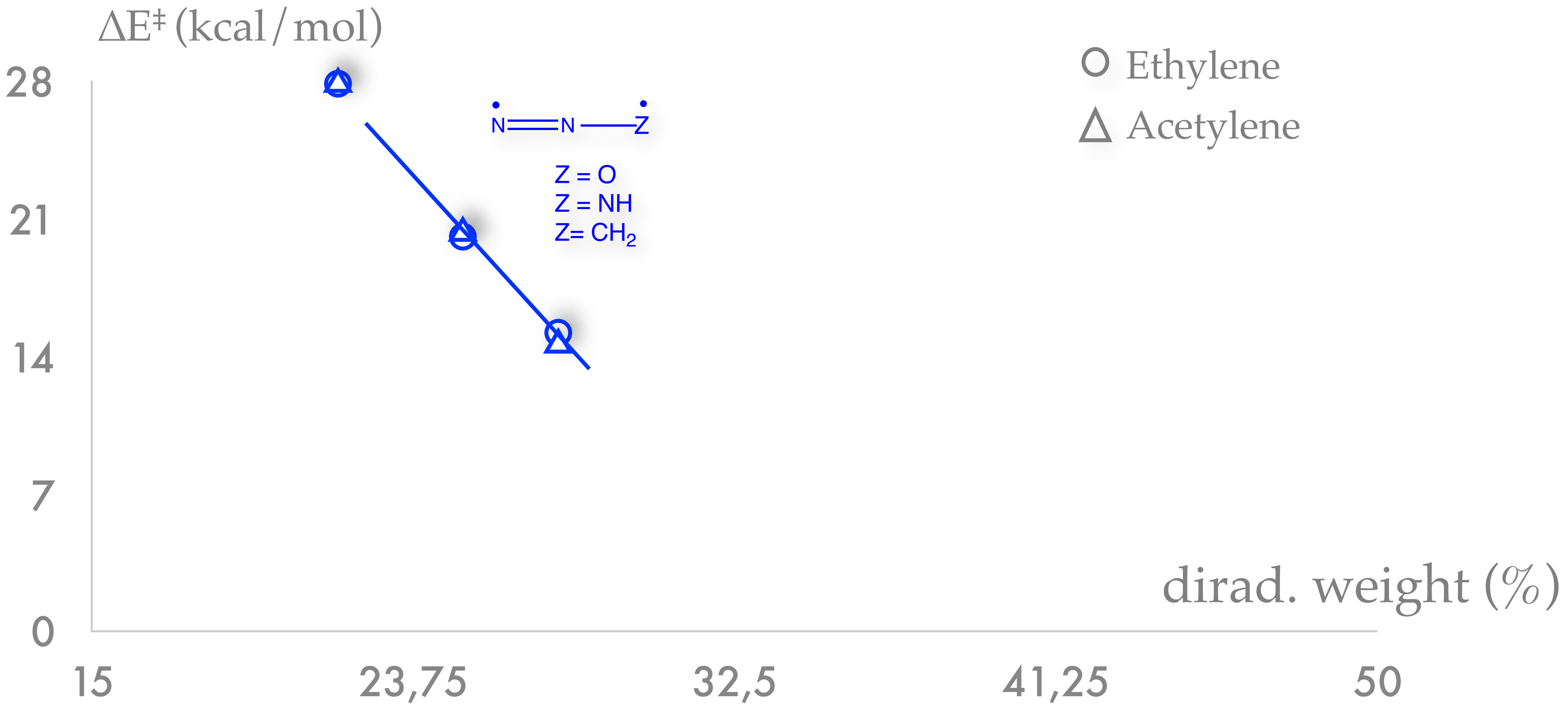
If a **«critical» diradical character** has to be reached for the reaction to proceed :

the **larger** the diradical weight in reactant, the **easier** the reaction

=> ***Inverse correlation***
*between diradical **weights***
*and reaction **barriers***

Ab initio VB calculations

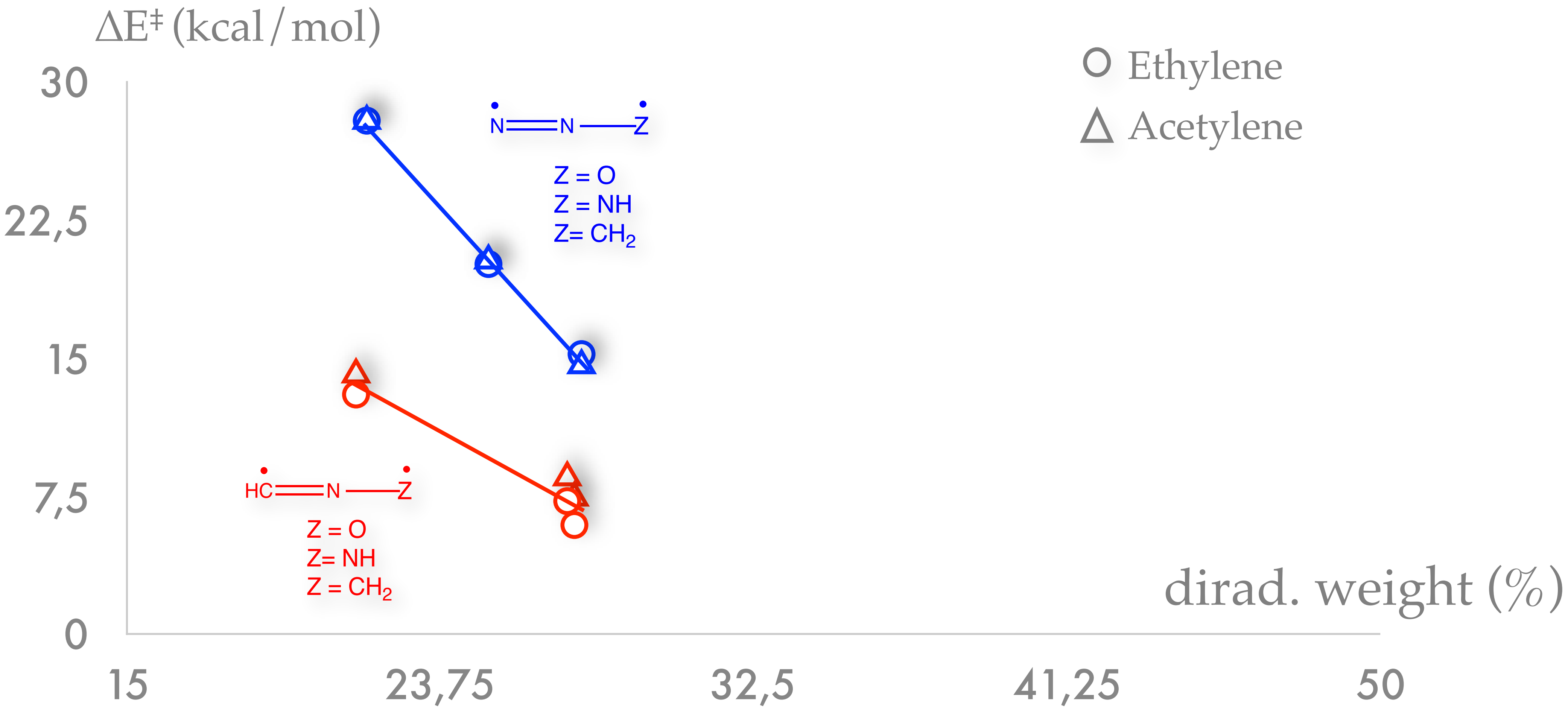
1) Correlation diradical **weights** / **barriers**



B. Braida, C. Walter, B. Engels, P. C. Hiberty, *J. Am. Chem. Soc.* **2010**, 132, 7631

Ab initio VB calculations

1) Correlation diradical **weights** / **barriers**



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Ab initio VB calculations

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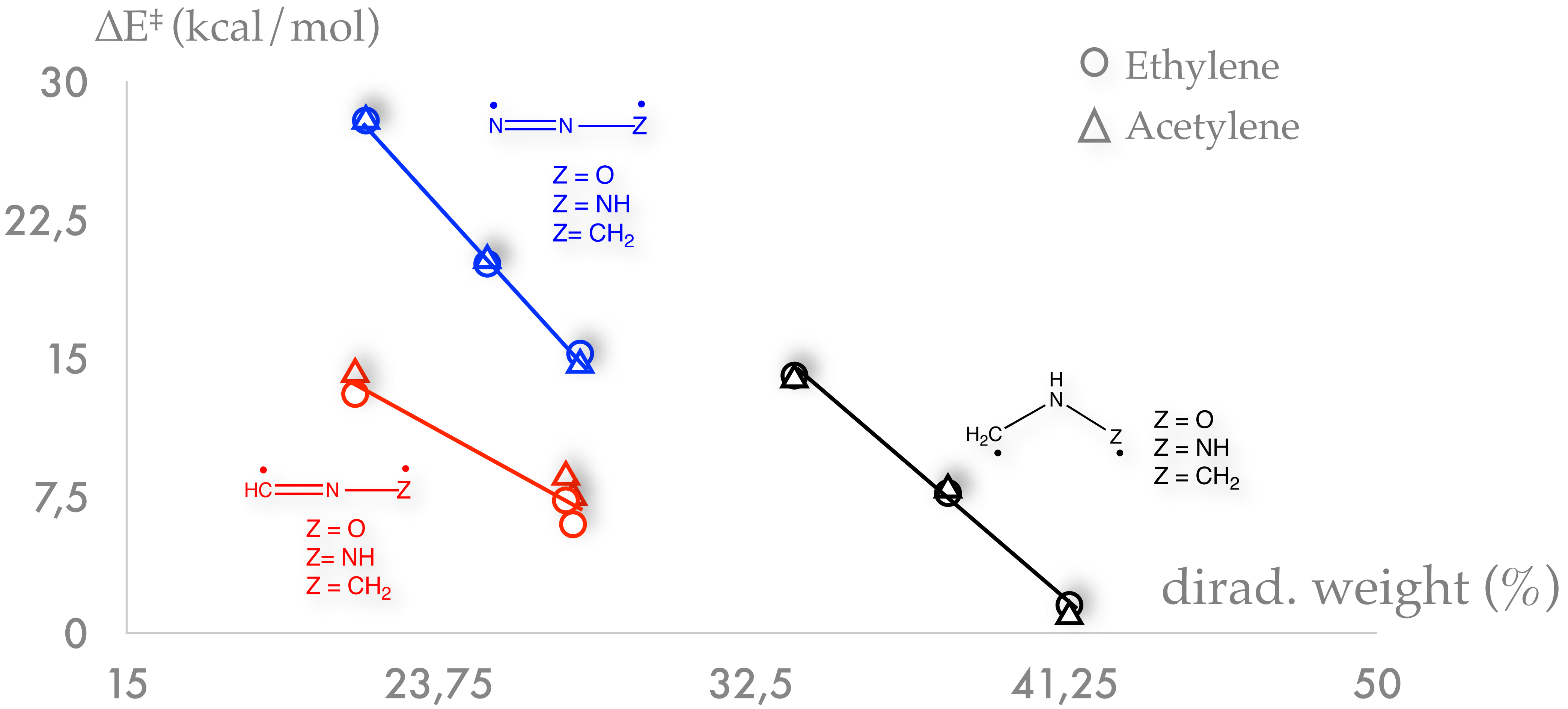

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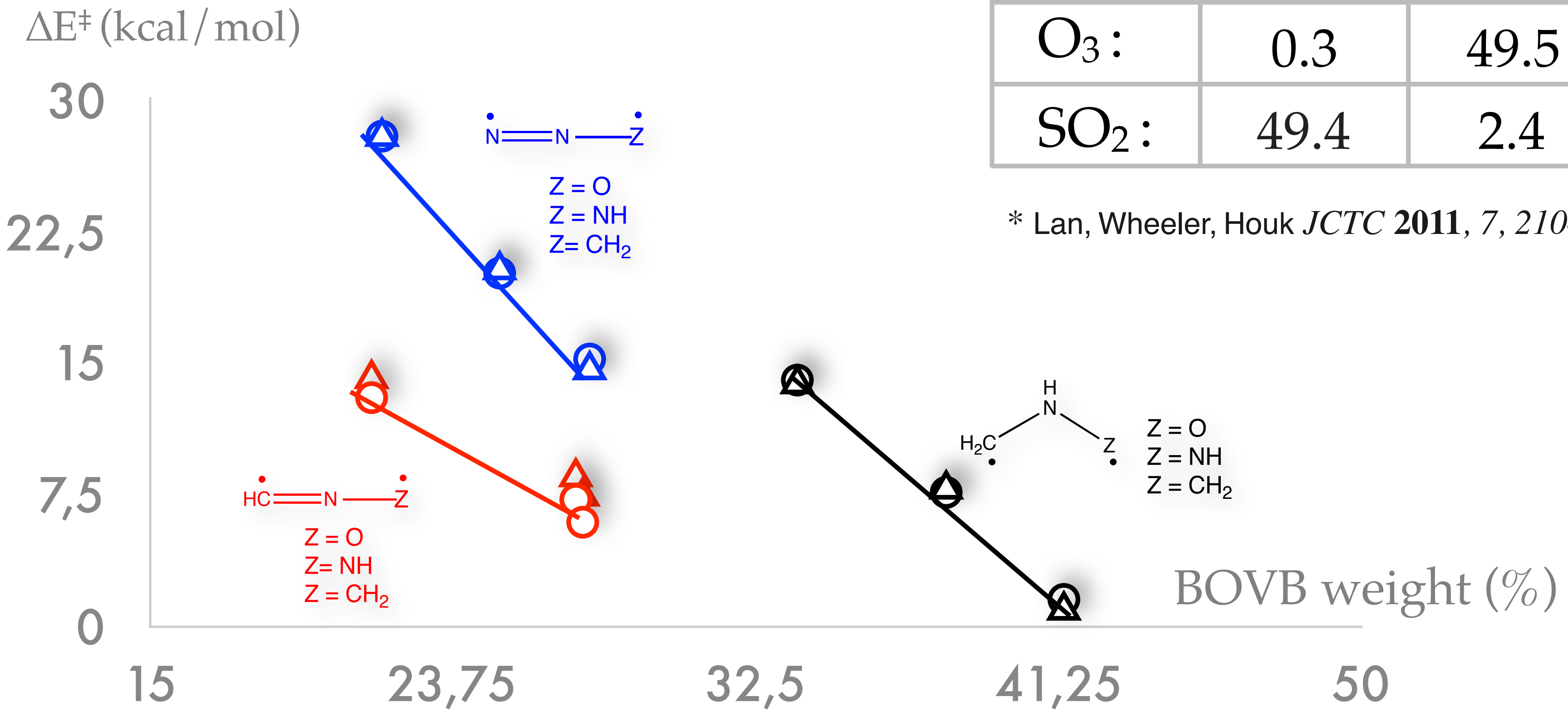
Ab initio VB calculations

1) Correlation diradical **weights** / **barriers**

Two extreme cases :*

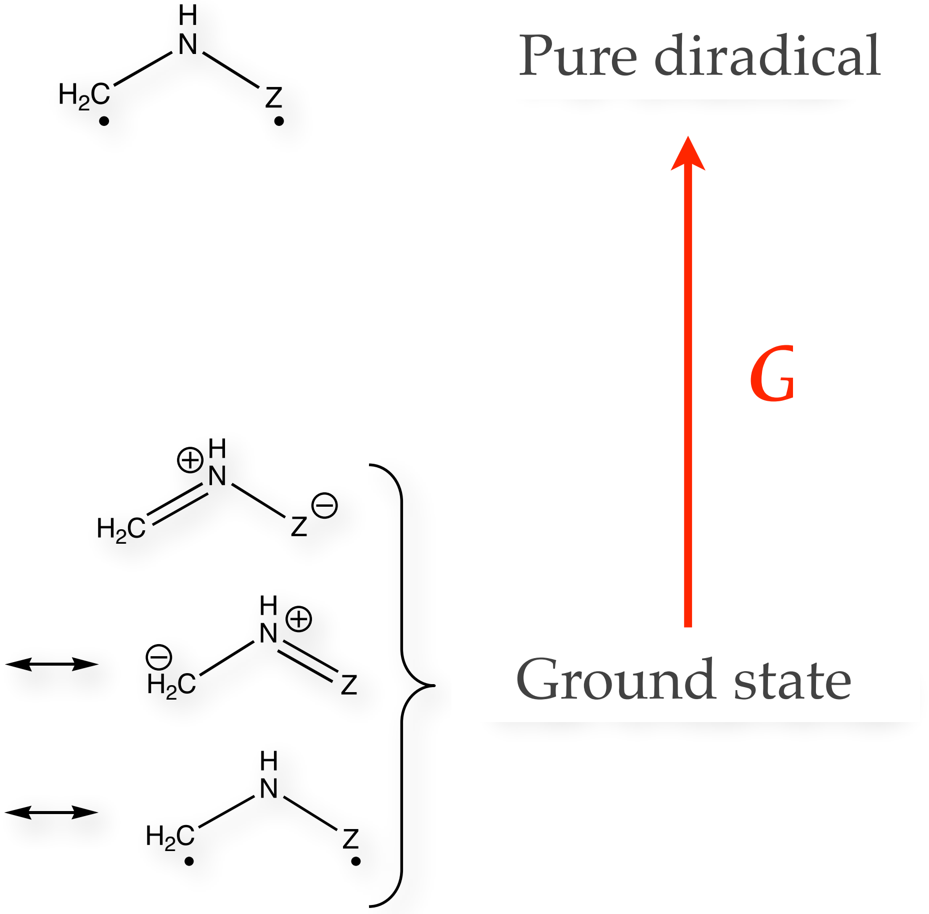
	ΔE‡	w (%)
O_3 :	0.3	49.5
SO_2 :	49.4	2.4

* Lan, Wheeler, Houk *JCTC* **2011**, *7*, *2104*



Ab initio VB calculations

2) If our postulated mechanism is correct :



Pure diradical

G

Ground state

Large diradical character in the reactant :

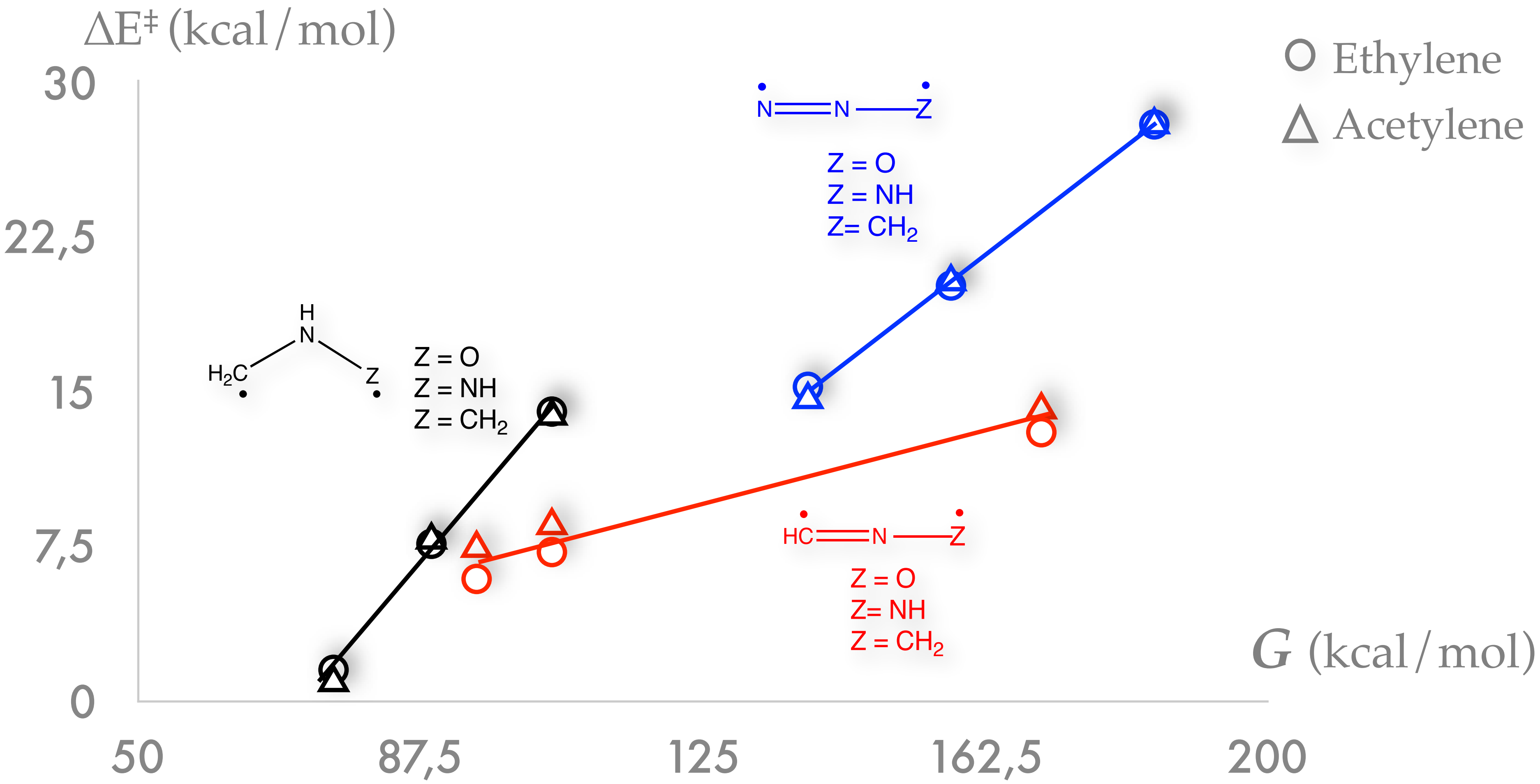
→ small *G*

→ small ΔH‡

$$\Delta H^{\ddagger} \propto G$$

Ab initio VB calculations

2) Correlation *G* / $\Delta H^{\ddagger}$:



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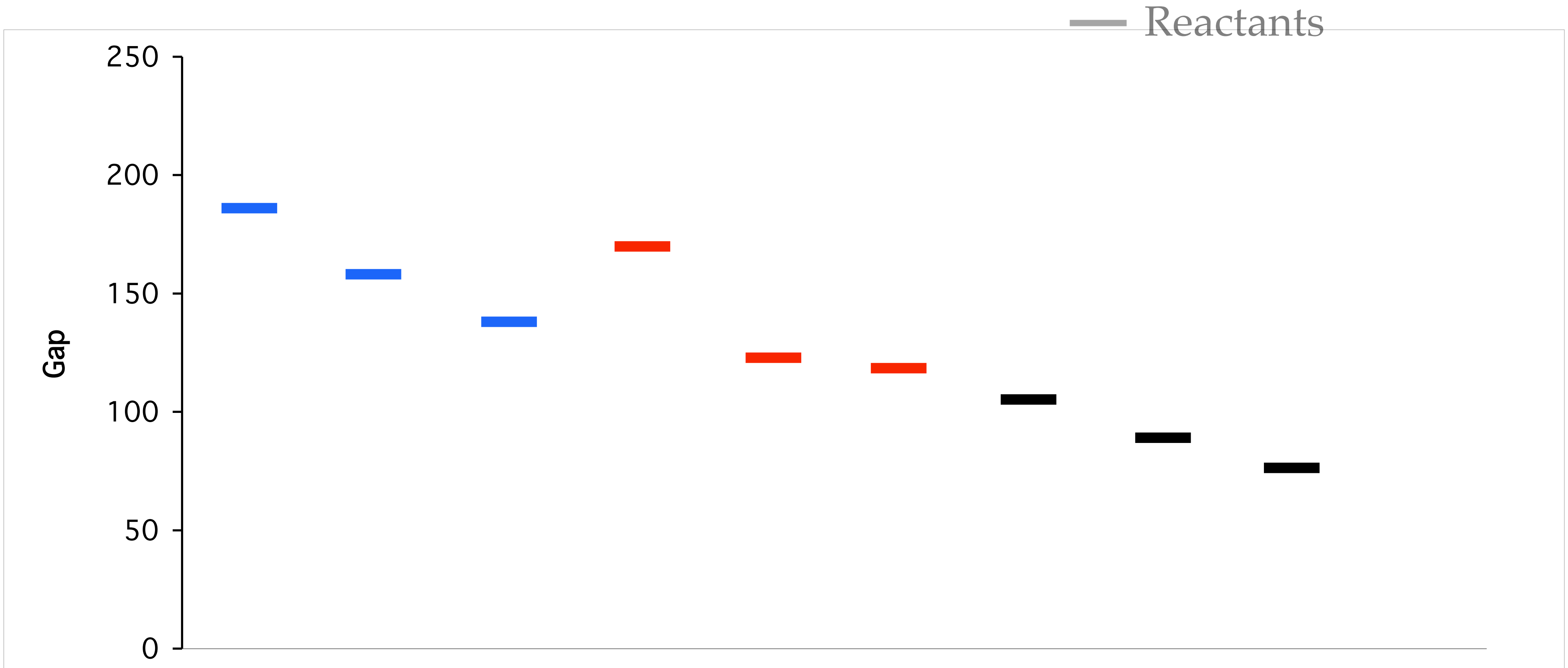
Ab initio VB calculations

- *G* : reactants :

Ab initio VB calculations

- *G* : reactants vs. TS :

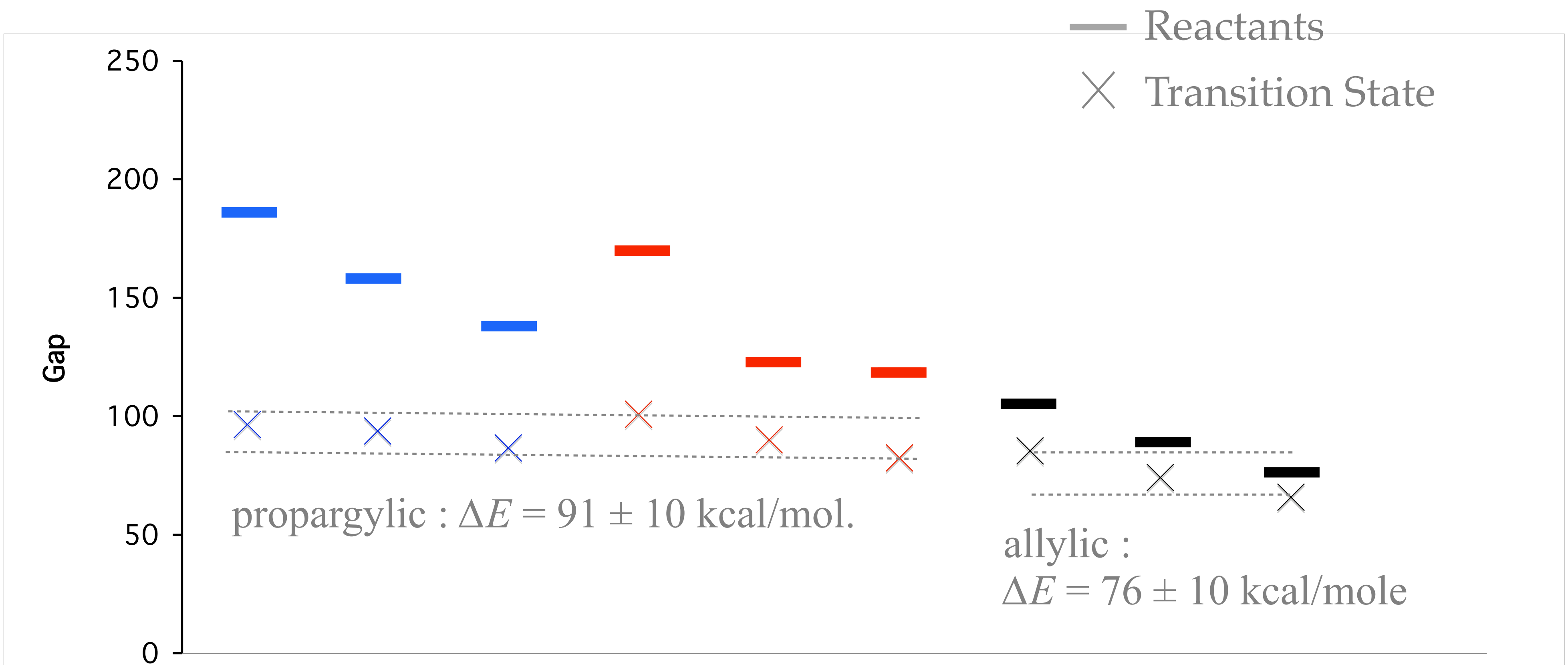


If dipoles bend to reach some particular «critical» diradical character

→ similar G for all dipoles in TS geometry !

Ab initio VB calculations

- *G* : reactants vs. TS :



propargylic : $\Delta E = 91 \pm 10$ kcal/mol.

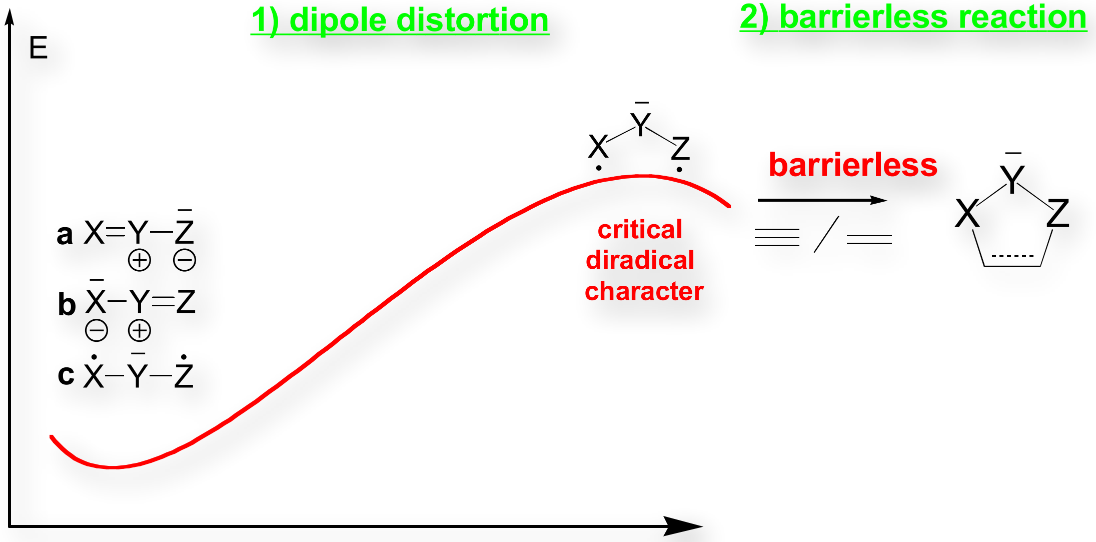
allylic :
$\Delta E = 76 \pm 10$ kcal/mole

If dipoles bend to reach some particular «critical» diradical character

→ similar G for all dipoles in TS geometry !

Conclusions

- 1,3-dipoles are special reactants (violate ordinary laws)
- A mechanism is proposed, consistent with accurate ab initio data
- The **diradical character** is a key factor and the correlating quantity
- Reaction barriers can be predicted from reactants' properties



Bernd Engels & Christof Walter   Philippe Hiberty

Würzburg University   **Univ. Paris Sud**

B. Braida, C. Walter, B. Engels, P. C. Hiberty, J. Am. Chem. Soc. 2010, 132, 7631*

Conclusions

VB theory allowed us to consider the 1,3 dipolar cycloaddition reaction from a different perspective :

(Prof. Keating, Dead Poets Society)

Part 3. Qualitative Valence Bond

Stop me at any time !

Qualitative VB

What we wan’t to calculate simple expressions for:

H expectation value

$$E_{VB} = \frac{\langle \Psi_{VB} | \hat{H} | \Psi_{VB} \rangle}{\langle \Psi_{VB} | \Psi_{VB} \rangle}$$

Overlap S

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

n electrons in N orbitals and a given spin state

Qualitative VB

⇒ **This is a « Hückel-type » version of VB theory**

- **Basic ingredients :**

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

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

Qualitative VB

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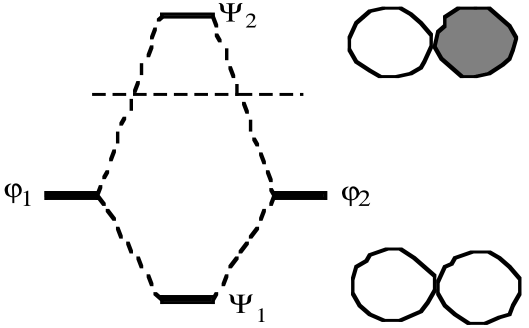
$$with : h^{eff}(i) = -\frac{1}{2}\nabla_{r_i}^2 - \frac{Z}{r_i} + \underbrace{\mathrm{Rep}(i)}_{\substack{averaged\\ repulsion}}$$

2) Parametrization : **ε, β, S**

Same as in Hückel theory :

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



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

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

Qualitative VB

- **Basic ingredients :**

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

  2) Parametrization : **ε, β, S**

Qualitative VB

- **Basic ingredients :**

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

2) Parametrization : **ε, β, S**

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

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

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

Qualitative VB

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

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

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

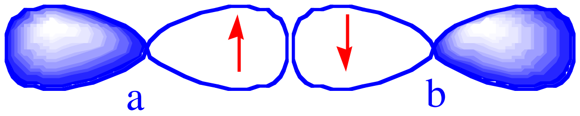
Neglect S_{ac} and h_{ac} if **a** and **c** are not nearest neighbors

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

Qualitative VB

- **Elementary interactions energies :**

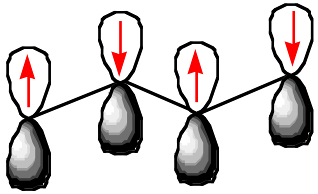
1) The QC state :



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

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

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

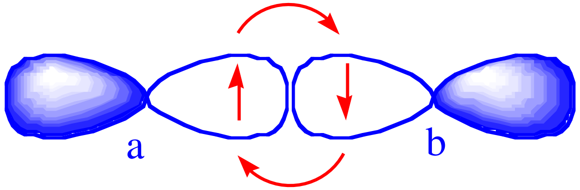


E=0

Qualitative VB

- **Elementary interactions energies :**

  2) The two electron bond :

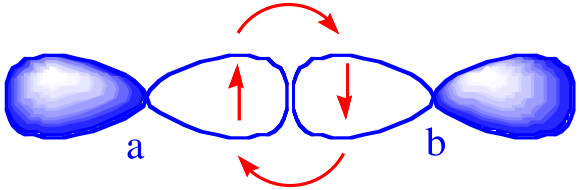


$$\Psi_{2e} \propto \left|a\bar{b}\right| + \left|b\bar{a}\right|$$

Qualitative VB

- **Elementary interactions energies :**

2) The two electron bond :



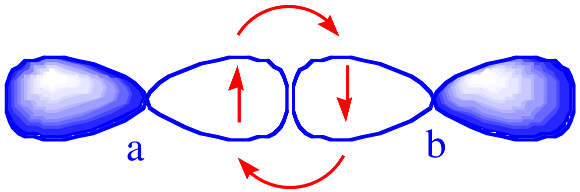
$$\Psi_{2e} \propto \left|a\bar{b}\right| + \left|b\bar{a}\right|$$

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

Qualitative VB

- **Elementary interactions energies :**

2) The two electron bond :



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

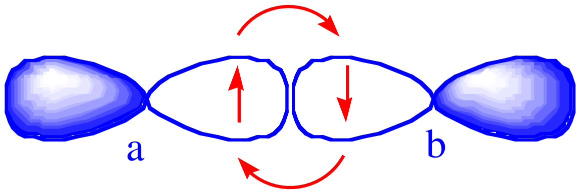
$$\overset{\langle\Psi|\widehat{H}^{eff}|\Psi\rangle}{\Rightarrow} \begin{cases} \text{Symmetric terms (two) :} \left\langle \left(\left|a\bar{b}\right|\right) \middle| \hat{h}_1 + \hat{h}_2 \middle| \left(\left|a\bar{b}\right|\right) \right\rangle = \varepsilon_1 + \varepsilon_2 = 0 \\ \text{Dissymmetric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

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

Qualitative VB

- **Elementary interactions energies :**

2) The two electron bond :



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

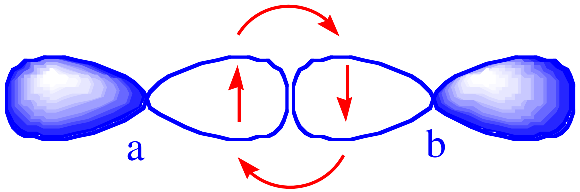
$$\overset{\langle\Psi|\widehat{H}^{eff}|\Psi\rangle}{\Rightarrow} \begin{cases} \text{Symmetric terms (two) :} \left\langle \left(\left|a\bar{b}\right|\right) \middle| \hat{h}_1 + \hat{h}_2 \middle| \left(\left|a\bar{b}\right|\right) \right\rangle = \varepsilon_1 + \varepsilon_2 = 0 \\ \text{Dissymmetric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

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

Qualitative VB

- **Elementary interactions energies :**

2) The two electron bond :



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

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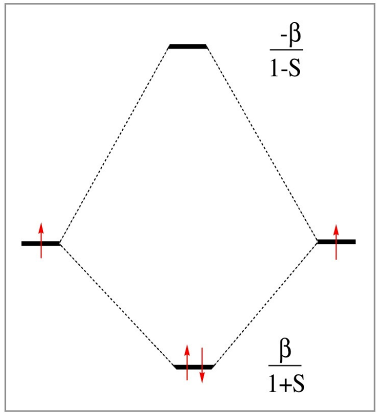
$$\Rightarrow E(2e) = \frac{+2\beta S}{1+S^2} = D_e(2e) \quad \approx +2\beta S$$

Different in MO-Hückel theory :

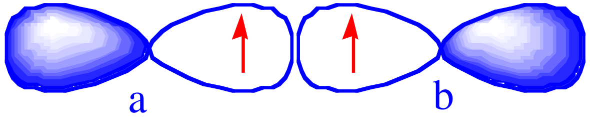


$D_e = 2\beta/(1+S)$

Qualitative VB

- **Elementary interactions energies :**

3) The triplet repulsion :

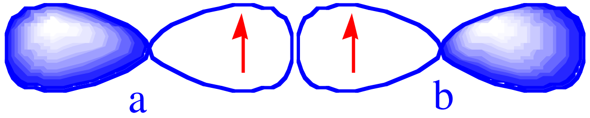


$$\Psi_T \propto |a\bar{b}| - |b\bar{a}|$$

Qualitative VB

- **Elementary interactions energies :**

3) The triplet repulsion :



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

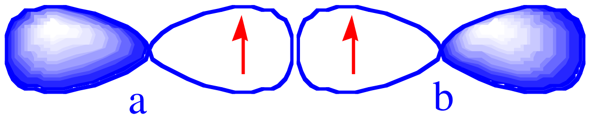
$$\overset{\langle\Psi|\hat{H}^{eff}|\Psi\rangle}{\Rightarrow} \begin{cases} \text{Symmetric terms (two) :} \left\langle (|a\bar{b}|) \middle| \hat{h}_1 + \hat{h}_2 \middle| (|a\bar{b}|) \right\rangle = \varepsilon_1 + \varepsilon_2 = 0 \\ \text{Disymmetric terms (two) :} - \left\langle (|a\bar{b}|)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

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

Qualitative VB

- **Elementary interactions energies :**

3) The triplet repulsion :



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

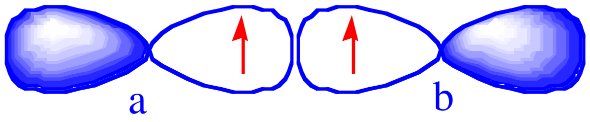
$$\overset{\langle\Psi|\widehat{H}^{eff}|\Psi\rangle}{\Rightarrow} \begin{cases} \text{Symmetric terms (two) :} \left\langle \left(\left|a\bar{b}\right|\right) \middle| \hat{h}_1 + \hat{h}_2 \middle| \left(\left|a\bar{b}\right|\right) \right\rangle = \varepsilon_1 + \varepsilon_2 = 0 \\ \text{Disymmetric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

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

Qualitative VB

- **Elementary interactions energies :**

3) The triplet repulsion :

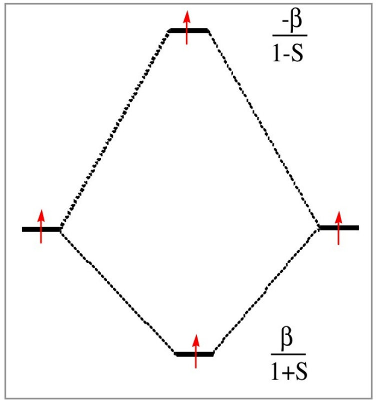


$$\Psi_T \propto |a\bar{b}| - |b\bar{a}|$$

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

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

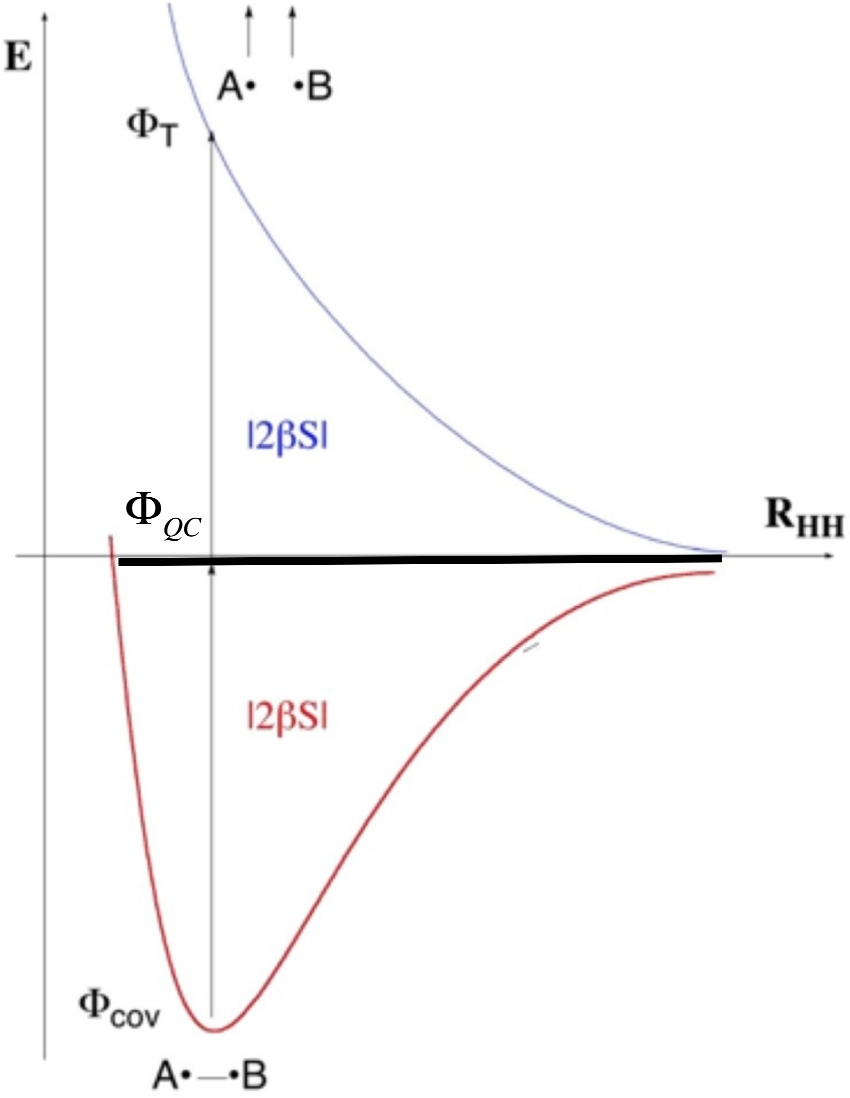
Same in MO-Hückel theory :



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

Qualitative VB

- **Elementary interactions energies :**



☞

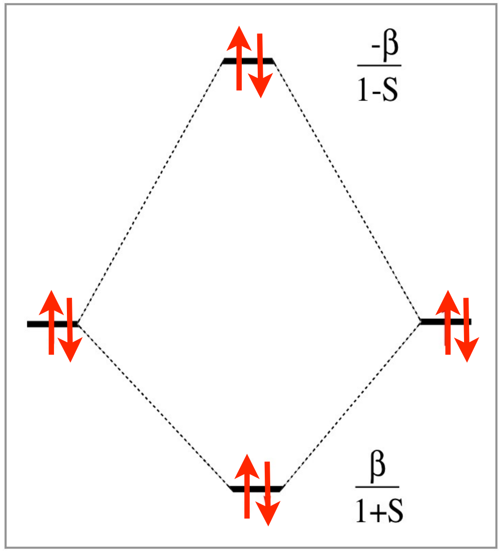
- Lecture 1 :

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

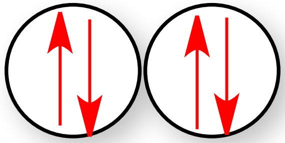
Qualitative VB

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

MO



VB



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

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

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

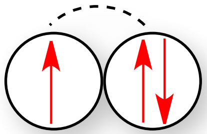
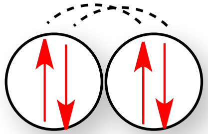
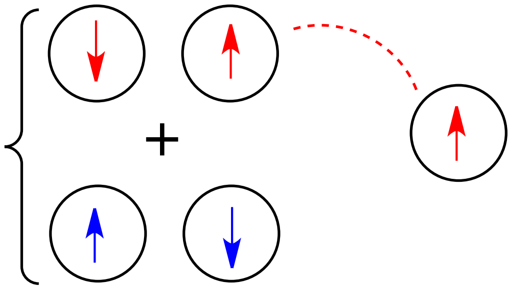
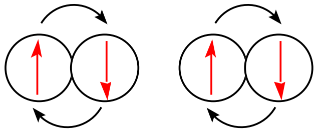
☜

⇒ **Twice the triplet repulsion**

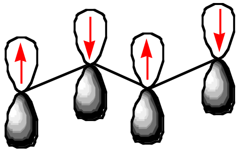
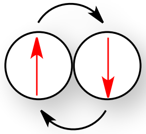
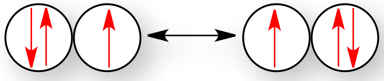
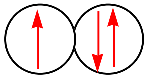
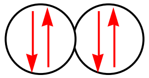
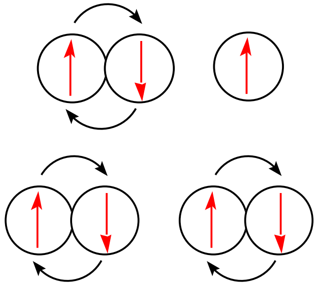
Qualitative VB

- **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

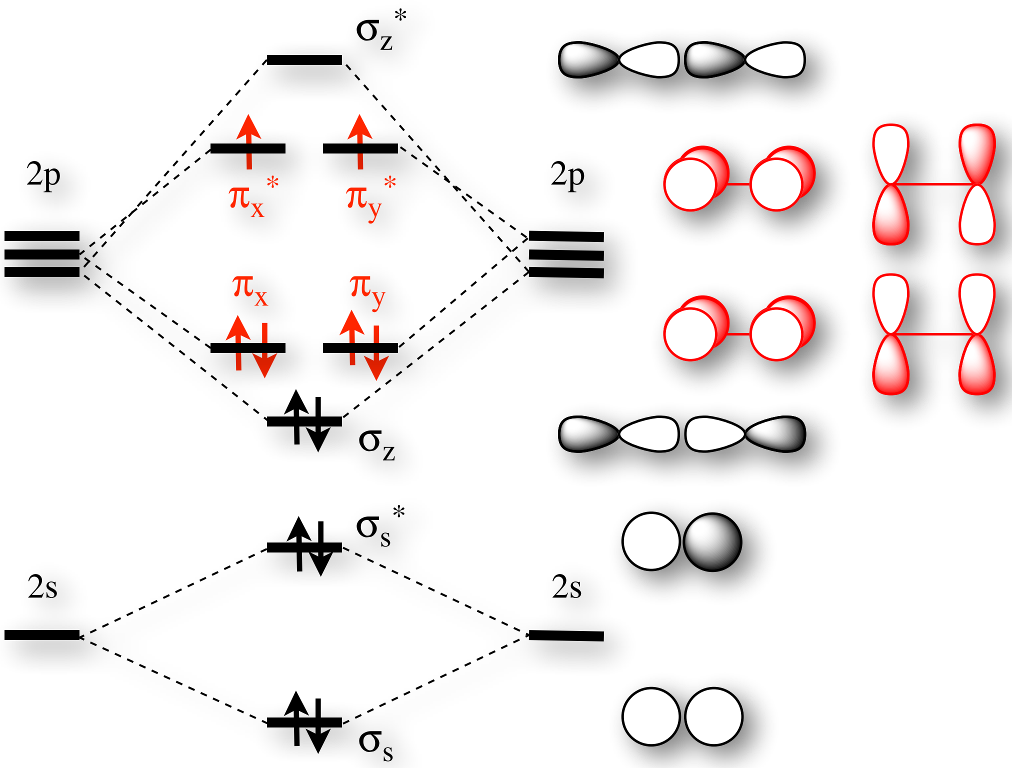
		VB	**MO**
spin-alternated det.		**0**	(VB only)
2-e bond (A–B) =		**$2\beta S/(1+ S^2)$**	**$2\beta/(1+S)$**
3-e bond(A∴B) =		**$\beta(1-3S)/(1-S^2)$**	Same as VB
triplet=3-e repulsion		$-2\beta S/(1-S^2)$	Same as VB
4-e repulsion		$-4\beta S/(1-S^2)$	Same as VB
bond…single e⁻ and bond...bond		$-\beta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

Qualitative VB

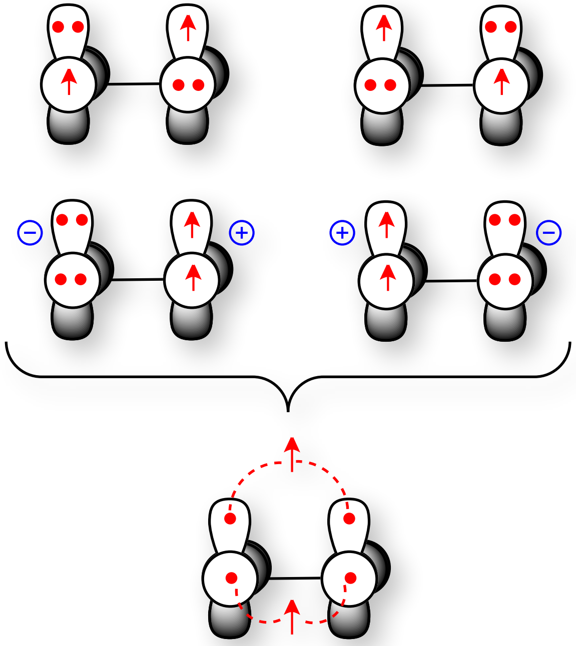
➡ **Exercise 4 : ground state of O_2 :**

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

MO



VB



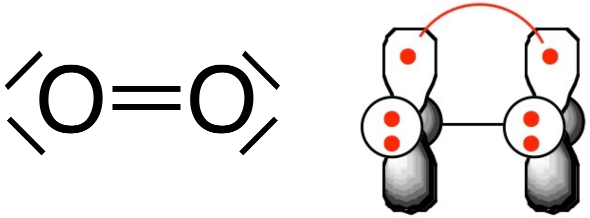
Qualitative VB

➡ Exercise 3 : ground state of O_2 :

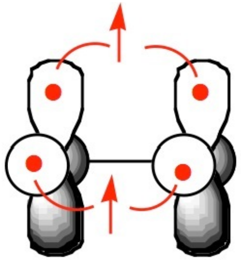
1) Calculate the energy expression for the π system of the lowest triplet state of the dioxygen molecule, at the qualitative VB level (using the complete expressions with denominators)

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.



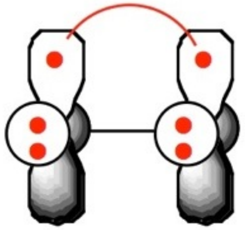
Singlet



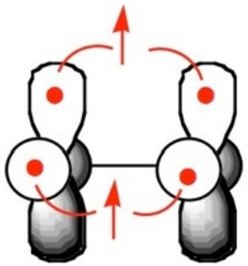
Triplet

Qualitative VB

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



$$\mathbf{E(S)} = 2\beta S\,/(1+S^2)\ -4\beta S\,/(1-S^2)$$



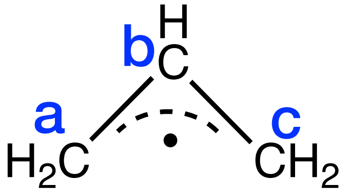
$$\mathbf{E(T)} = 2\beta\,(1 - 3S)/(1-S^2)$$

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

➡ *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.

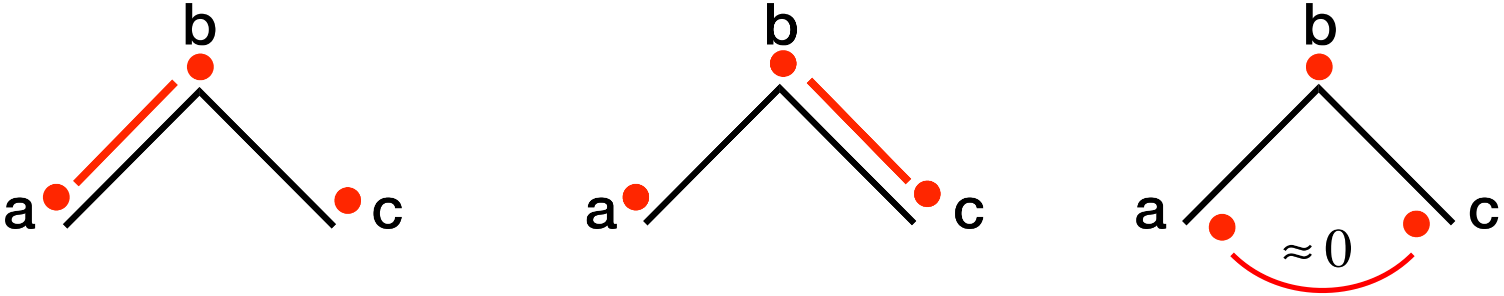
2) Show that the third structure can be expressed as a linear combination of the first two structures, and thus that only two of the three covalent structures form a complete basis of non-redundant structures (Rumer basis).

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 :**



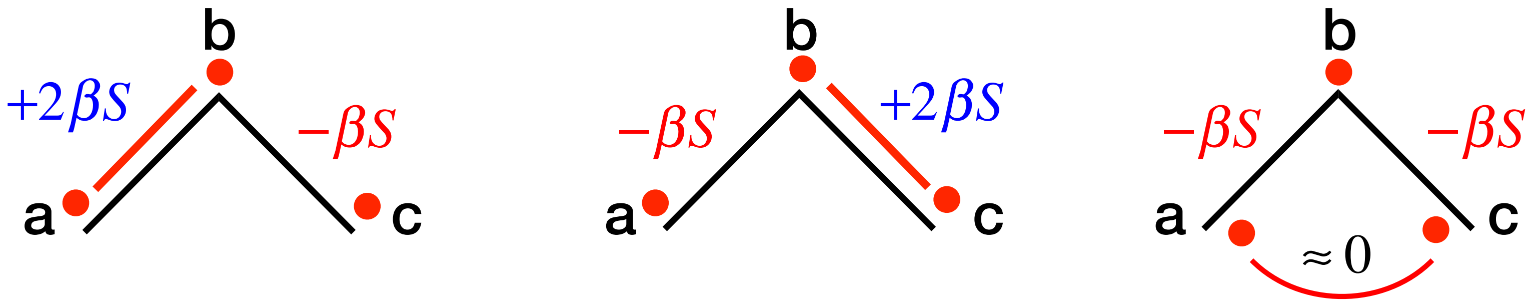
$$\psi(I) = \frac{1}{\sqrt{2}}\left(\left|a\bar{b}c\right| + \left|b\bar{a}c\right|\right)$$

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

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

Qualitative VB

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



$\Rightarrow E(I) = +\beta S < 0$ $\Rightarrow E(II) = +\beta S < 0$ $\Rightarrow E(III) = -2\beta S$

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

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

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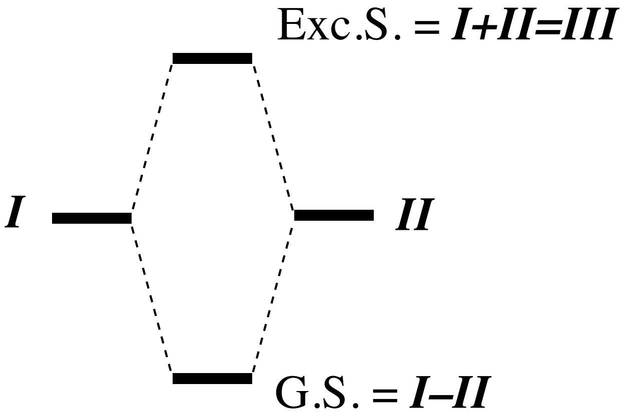
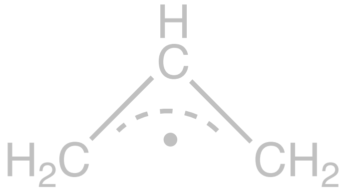


Qualitative VB

➡ Exercise 4 : spin polarization in allyl radical :



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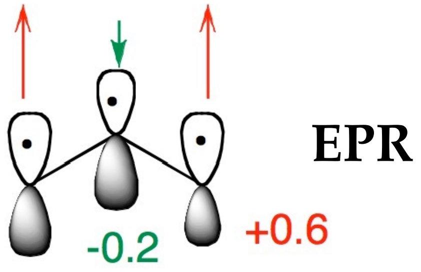
Continuation of the exercise : https://wiki.lct.jussieu.fr/workshop/index.php/VBTutorial2

Qualitative VB

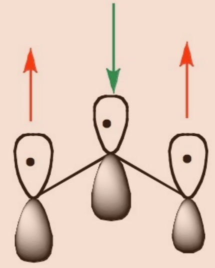
➡ Exercise 4 : spin polarization in allyl radical :

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



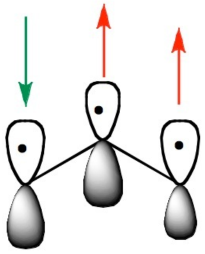
Spin density on center b : $\rho_b = \frac{1}{6}\left(\underbrace{c_2^2 + c_3^2}_{\text{alpha spin on b}} - \underbrace{c_1^2}_{\text{beta spin on b}}\right) = -0.33$

⇒ much closer to experiment than UHF



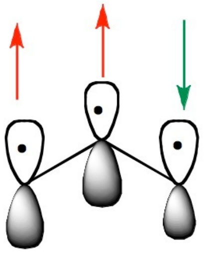
$|a\bar{b}c|$

$D_b = D_{QC}$



$|\bar{a}bc|$

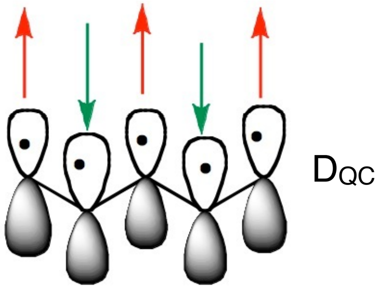
D_a



$|ab\bar{c}|$

D_c

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

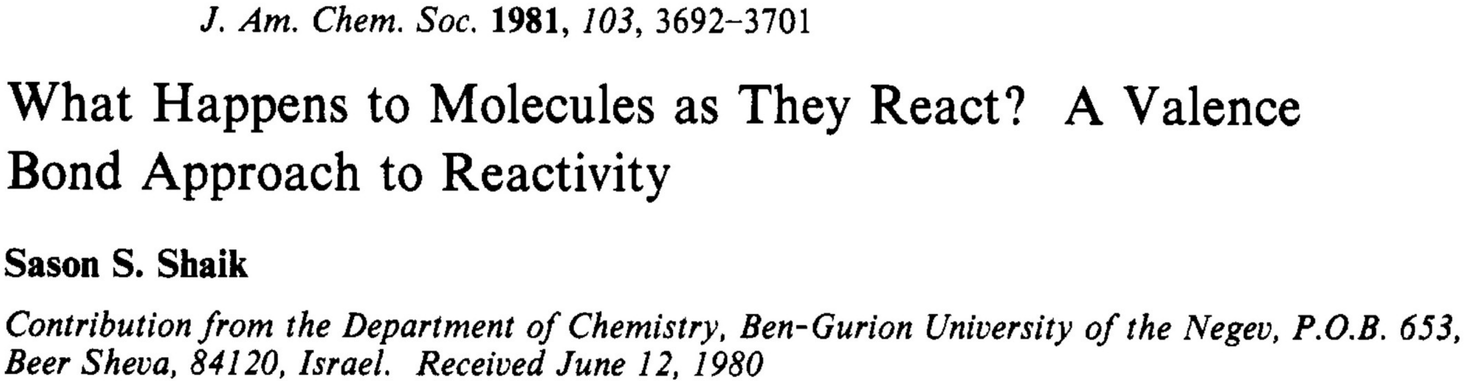


☜ General rule, works for all polyenes

Part 4. 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

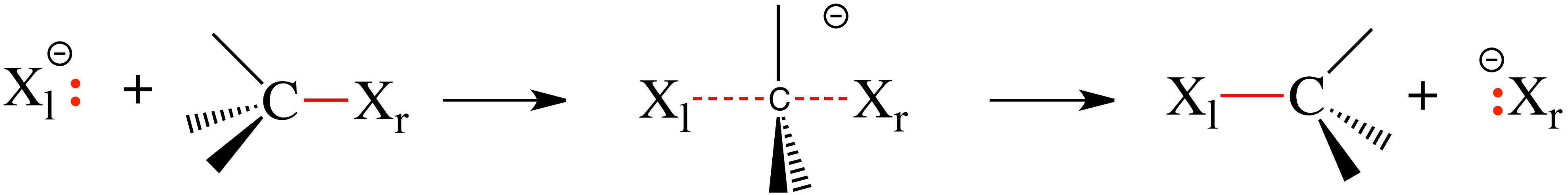
Contribution from the Department of Chemistry, Ben-Gurion University of the Negev, P.O.B. 653, Beer Sheva, 84120, Israel. Received June 12, 1980

- 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

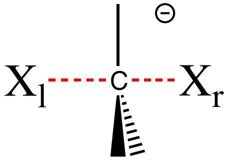
Principles

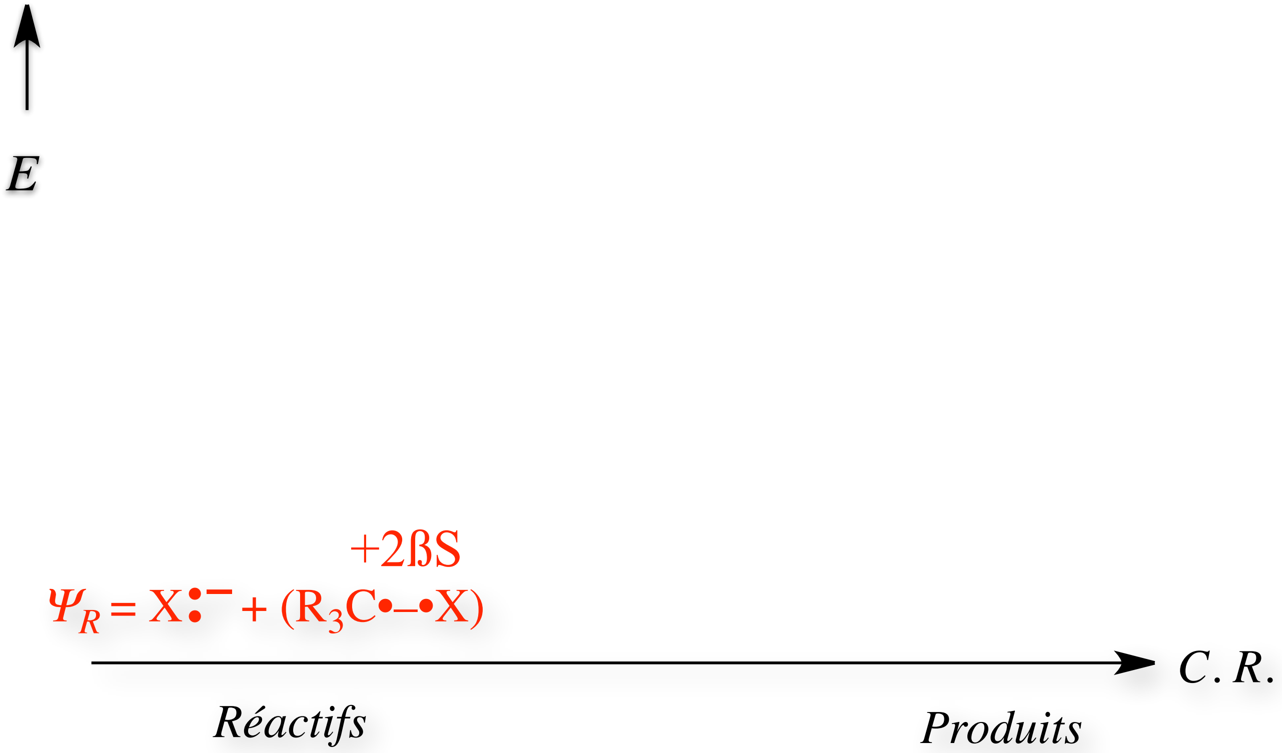
- VB diagram for the S_N2 reaction :



Principles

- VB diagram for the S_N2 reaction :





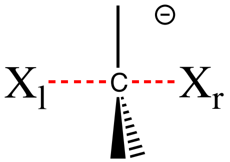
$$\Psi_R \propto \left| x_l \overline{x_l} (c \overline{x_r} + x_r \overline{c}) \right|$$

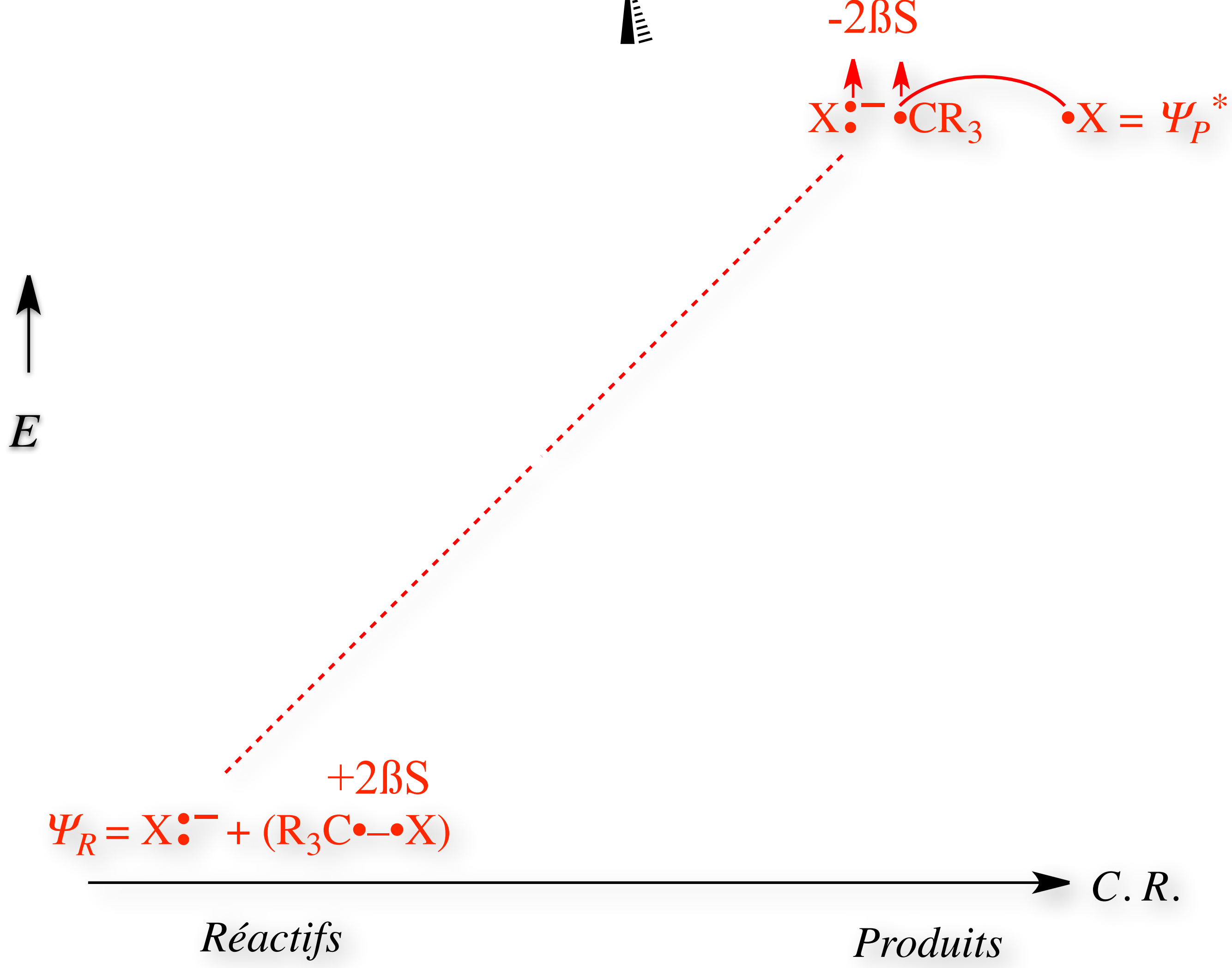
$+2\beta S$

$\Psi_R = X\colon^{-} + (R_3C\bullet\!-\!\bullet X)$

Principles

- VB diagram for the S_N2 reaction :

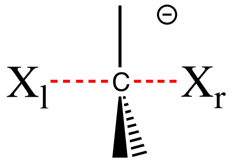


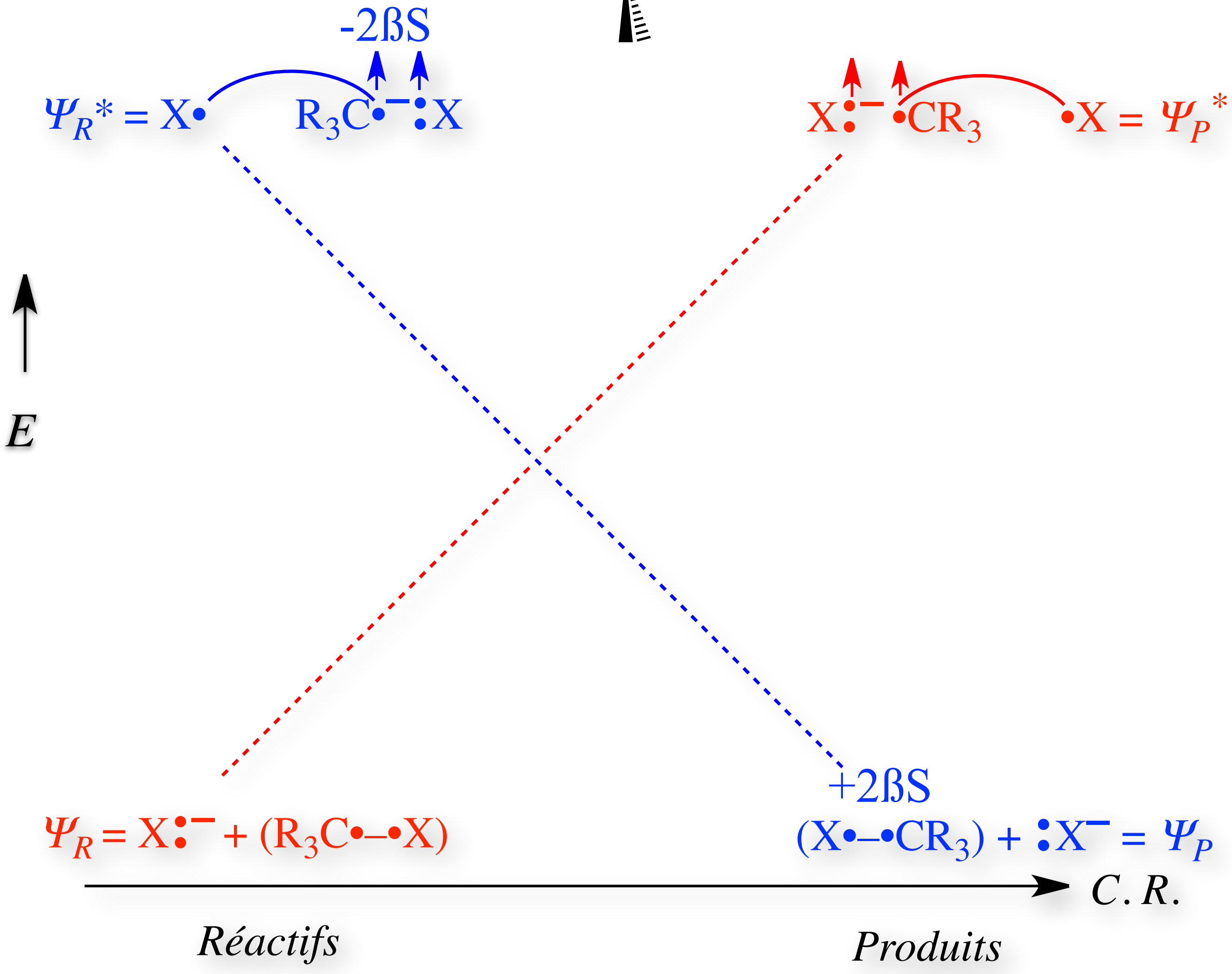


$$\Psi_R \propto \left| x_l \overline{x_l} \left(c \overline{x_r} + x_r \overline{c} \right) \right|$$

Principles

- VB diagram for the S_N2 reaction :





-2ßS

$\Psi_R^* = X\bullet \quad R_3C\bullet^{-}{:}X$

$X{:}^{-}\ \bullet CR_3 \quad \bullet X = \Psi_P^*$

E

+2ßS

$\Psi_R = X{:}^{-} + (R_3C\bullet\!-\!\bullet X)$

$(X\bullet\!-\!\bullet CR_3) + {:}X^{-} = \Psi_P$

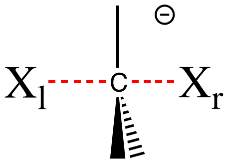
$C.R.$

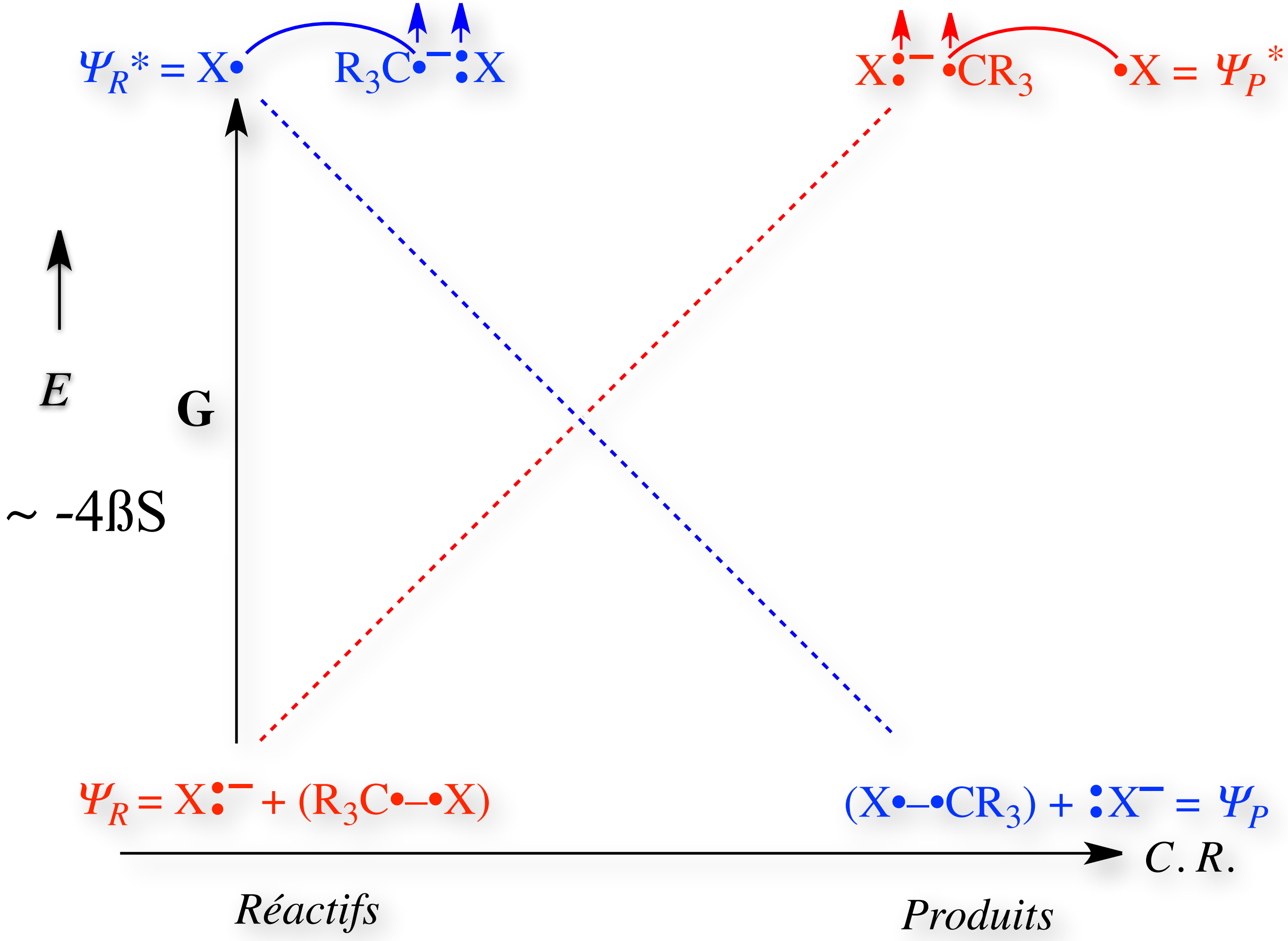
Réactifs

Produits

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

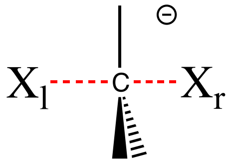
Principles

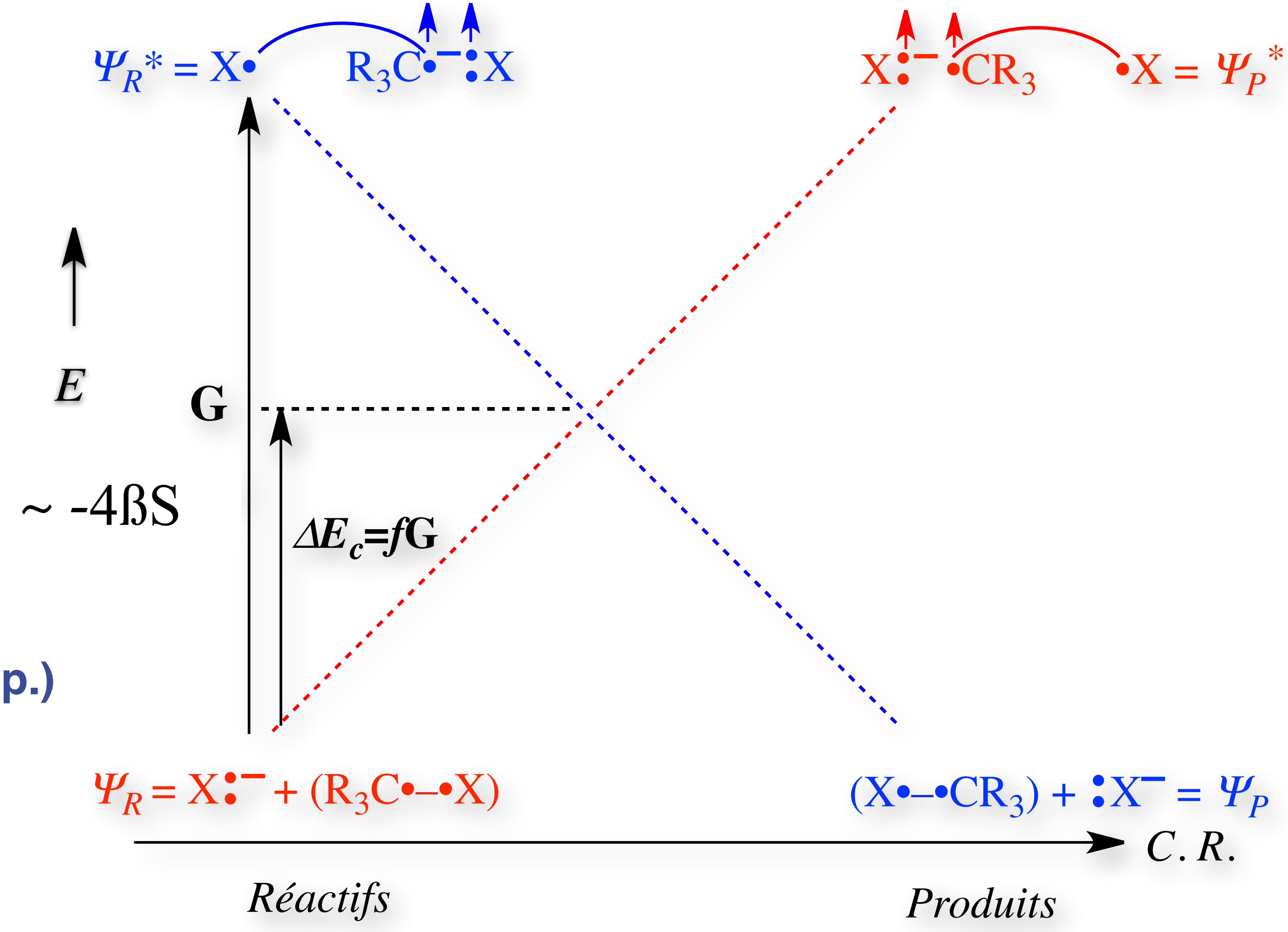
- VB diagram for the S_N2 reaction : 



Principles

- VB diagram for the S_N2 reaction :



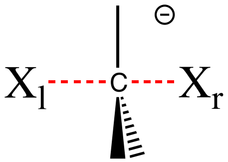


G : reactants' property (exp.)

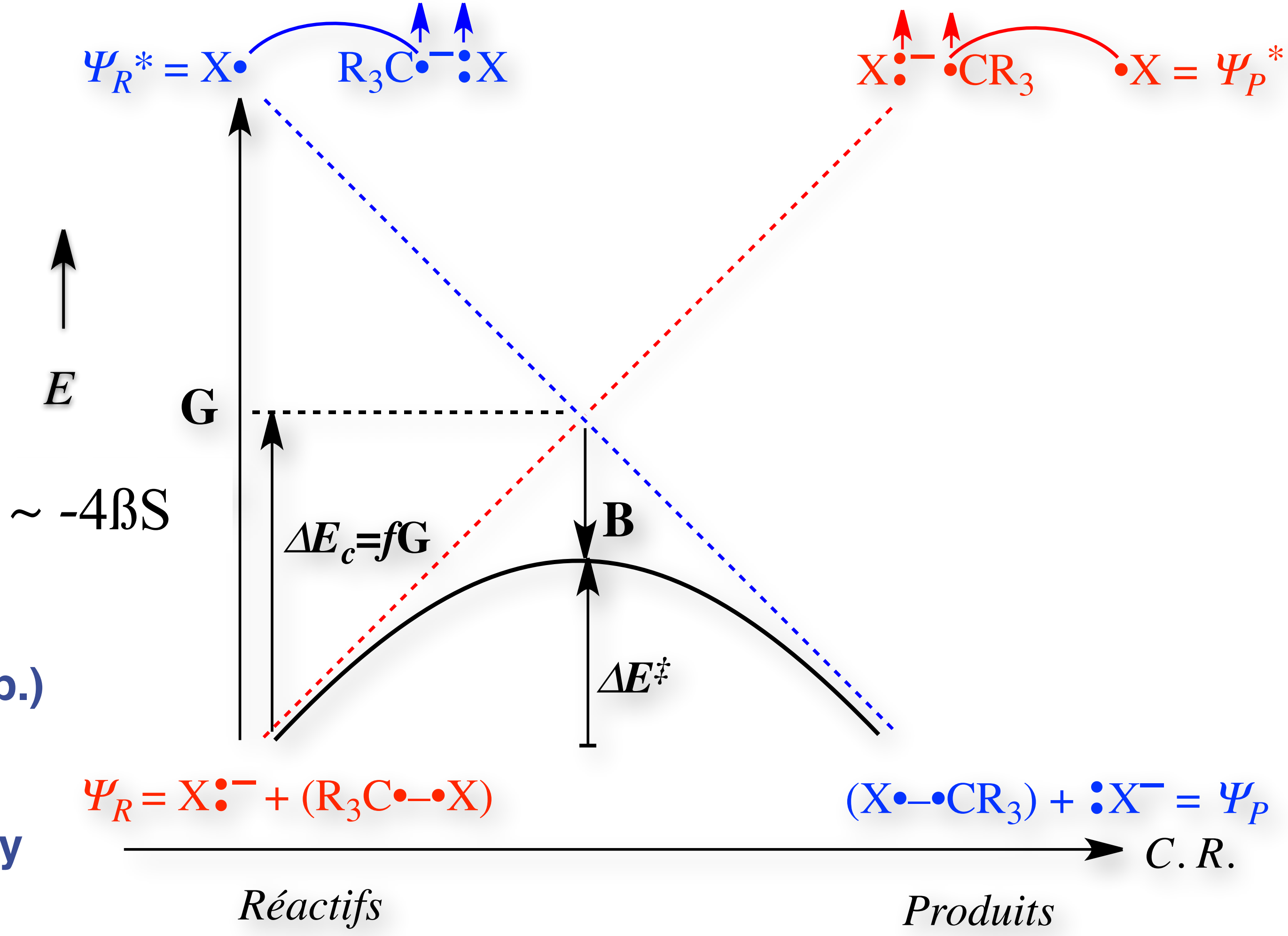
f : curvature factor

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

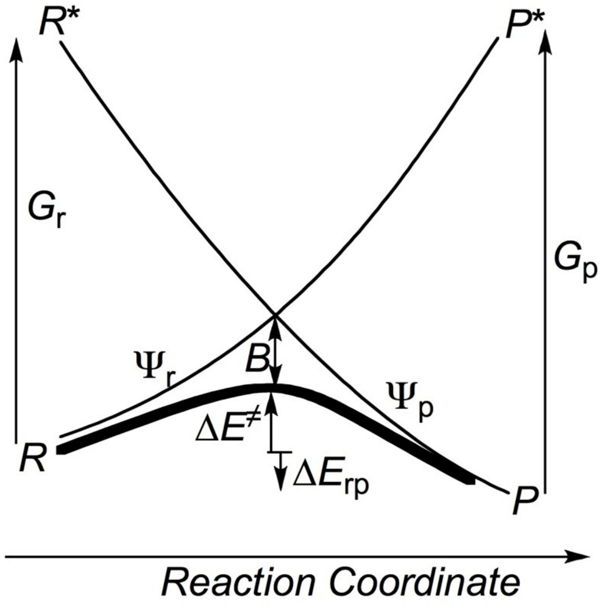
- Basic ingredients of the VB diagrams :

  - **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

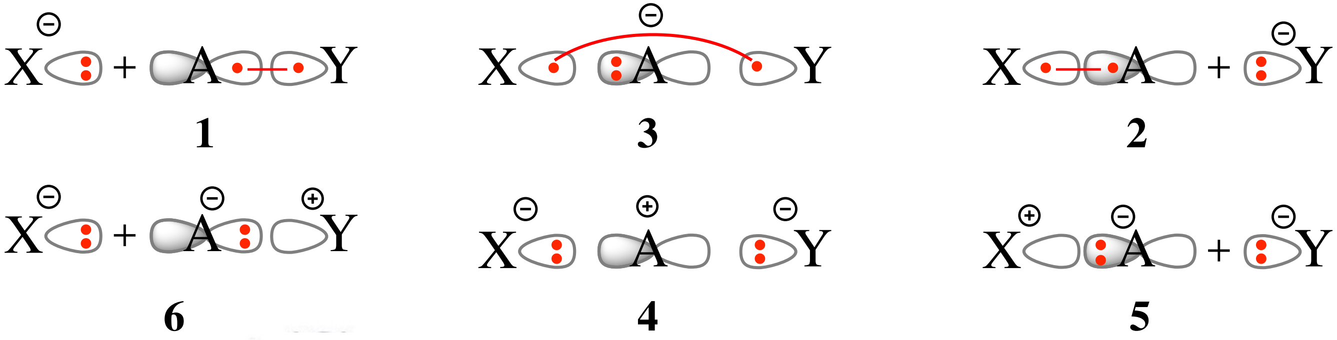
  ⇒ *f*G : gauges the total deformation and repulsive interactions R have to experience to achieve resonance with P

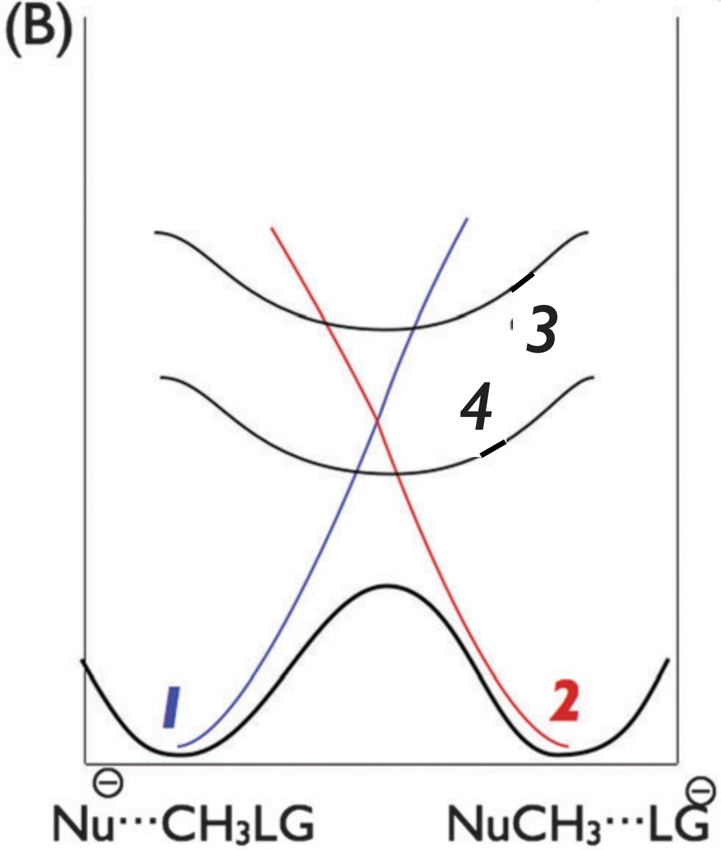
  - **B : resonance energy** of the TS due to VB mixing at the crossing point



Principles

- Exercice 2 (SN2):





Principles

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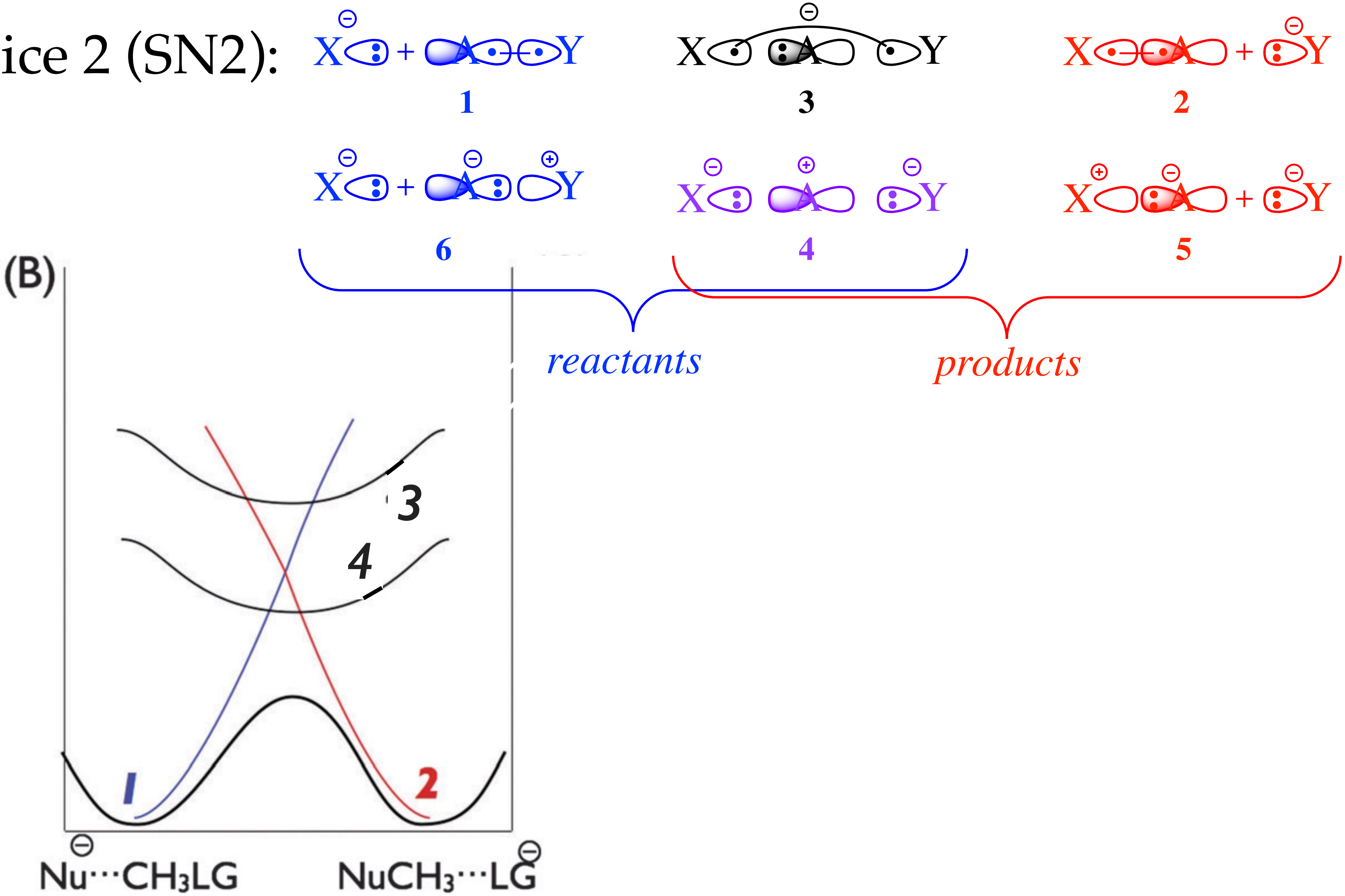
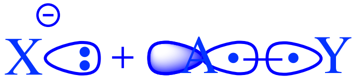
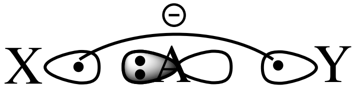


Principles

- Exercice 2 (SN2):



1



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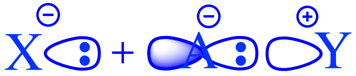
2



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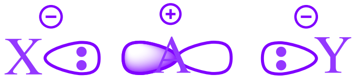

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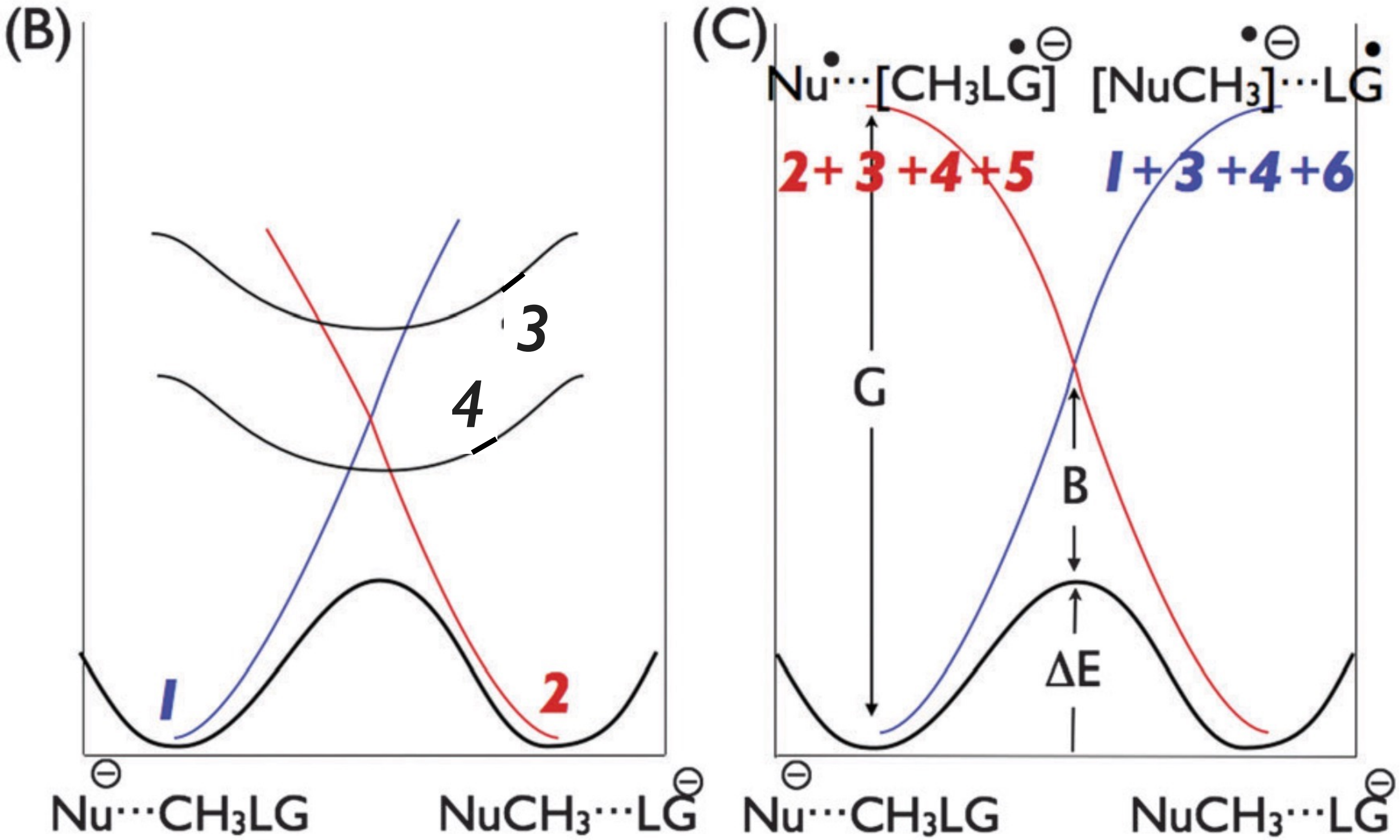
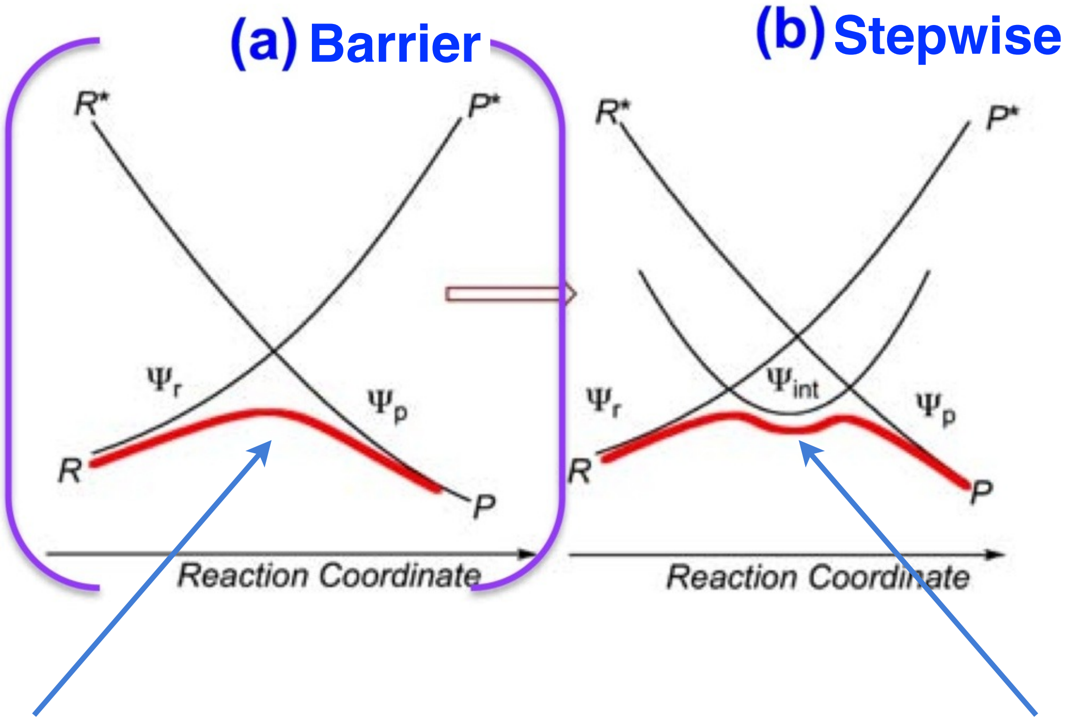


Principles

- 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»)

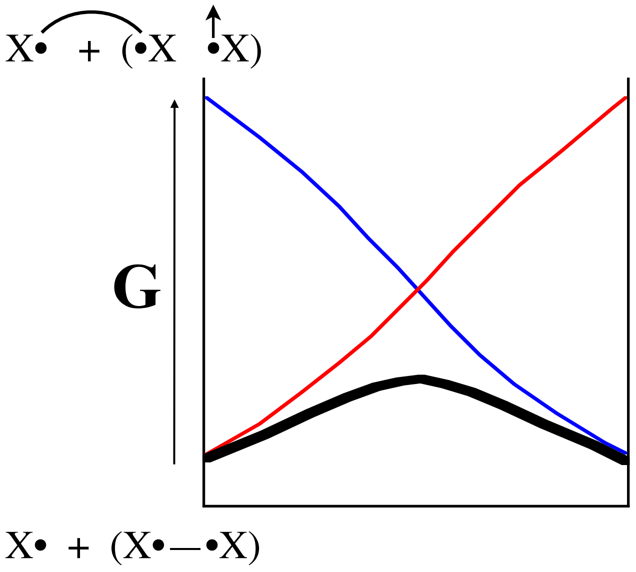
Illustrations

- **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

Illustrations

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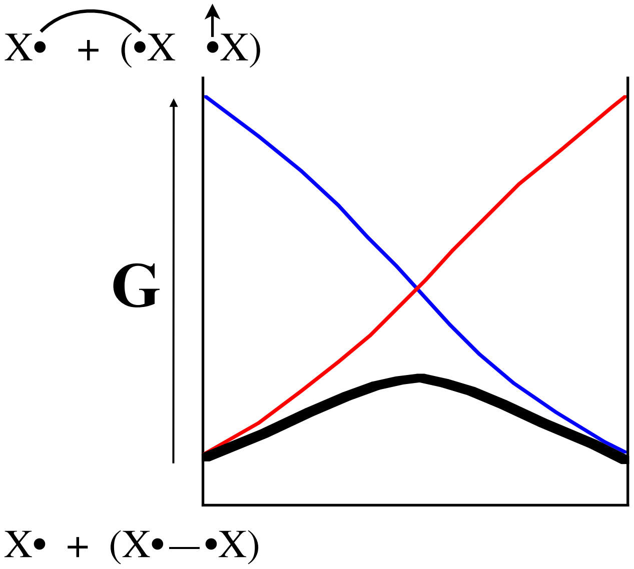

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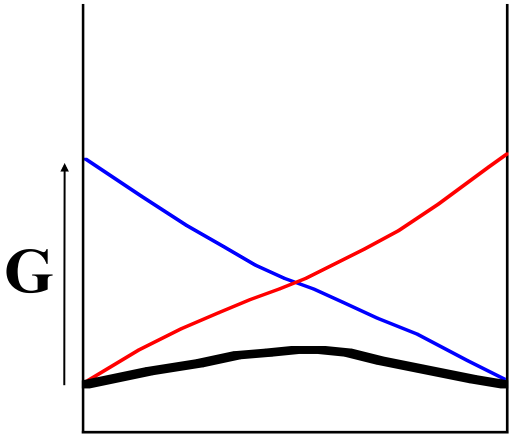

Weaker bonds (Cl_3):
Smaller barrier

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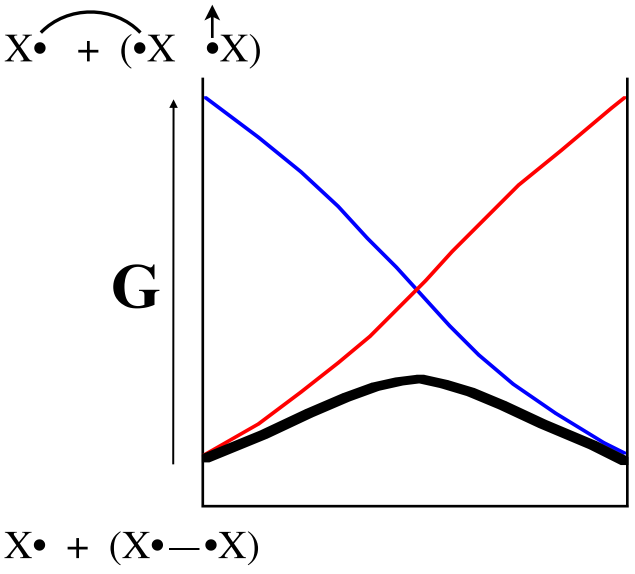

Strong bonds (H_3):
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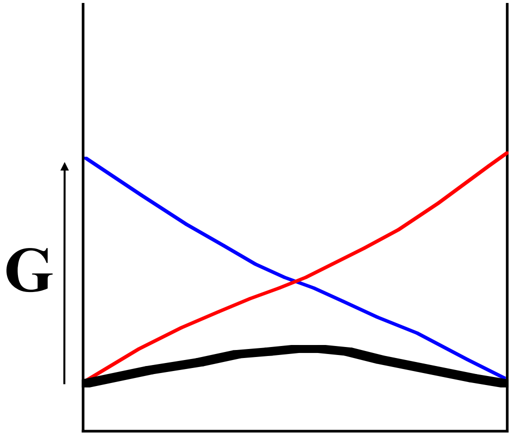

Weaker bonds (Cl_3):
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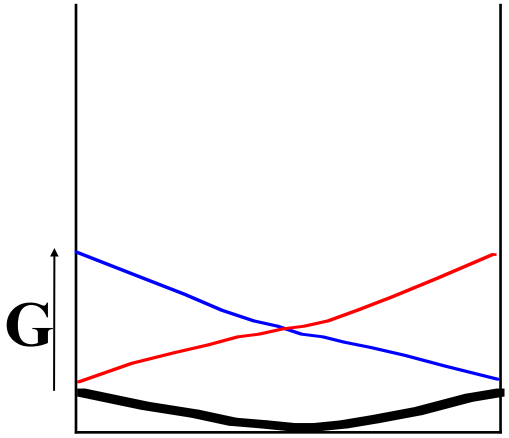
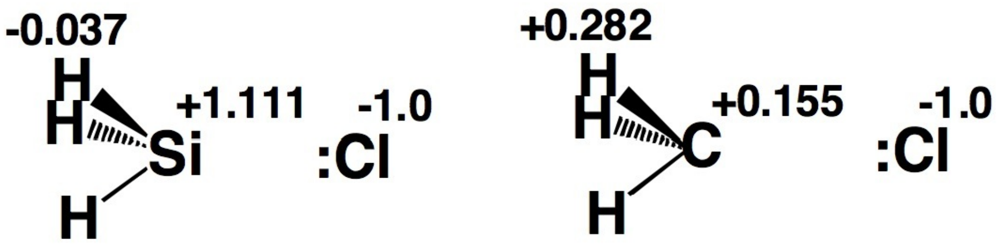


Weak bonds (Li_3):
Stable cluster

Illustrations

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

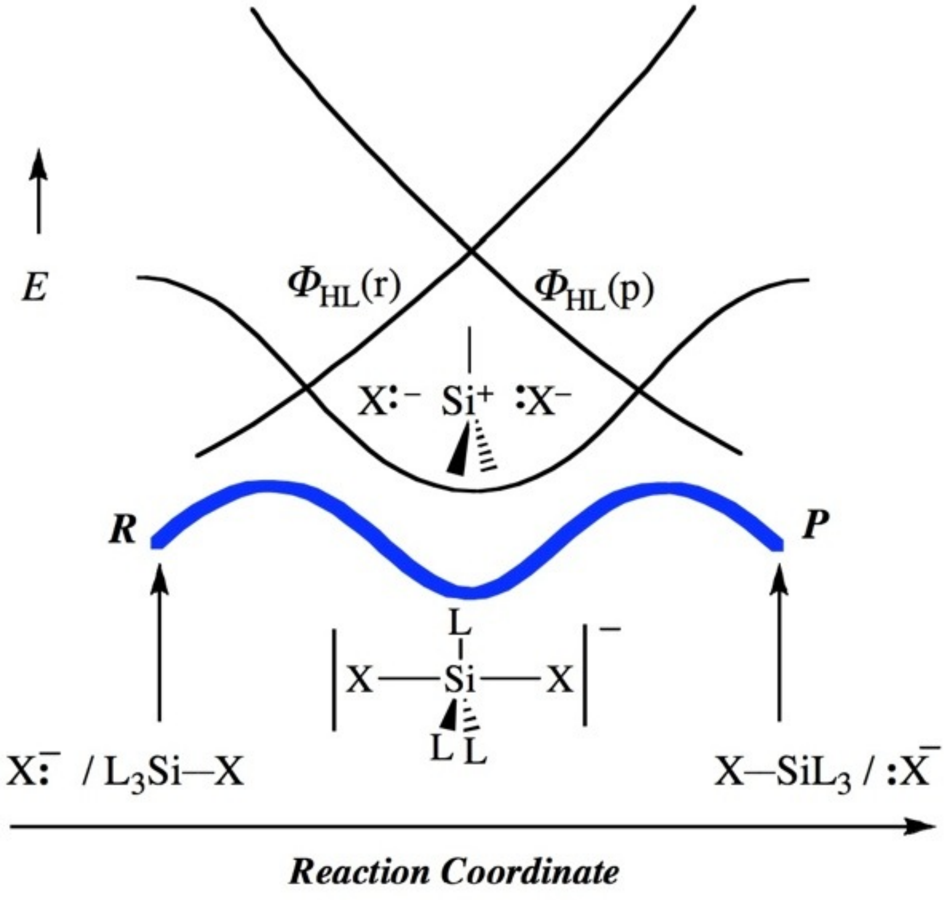


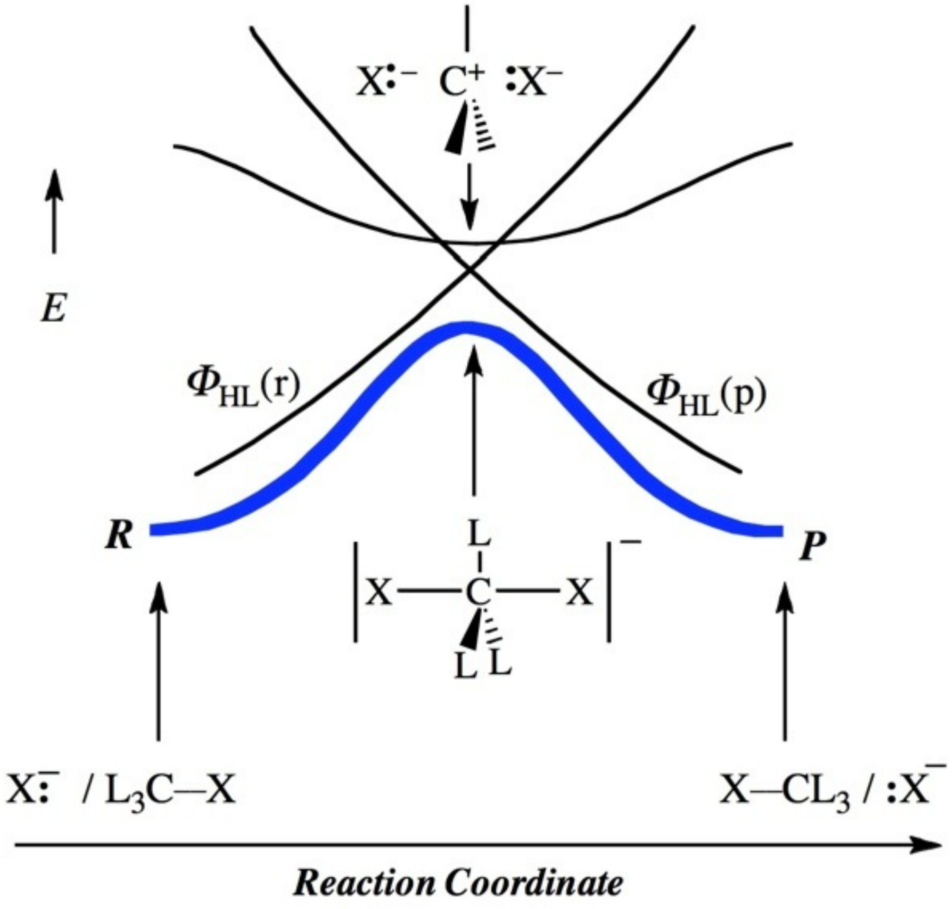
Positive charge localization on Si vs. delocalization on C

⇒ 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• + HF: impact of a single electron:

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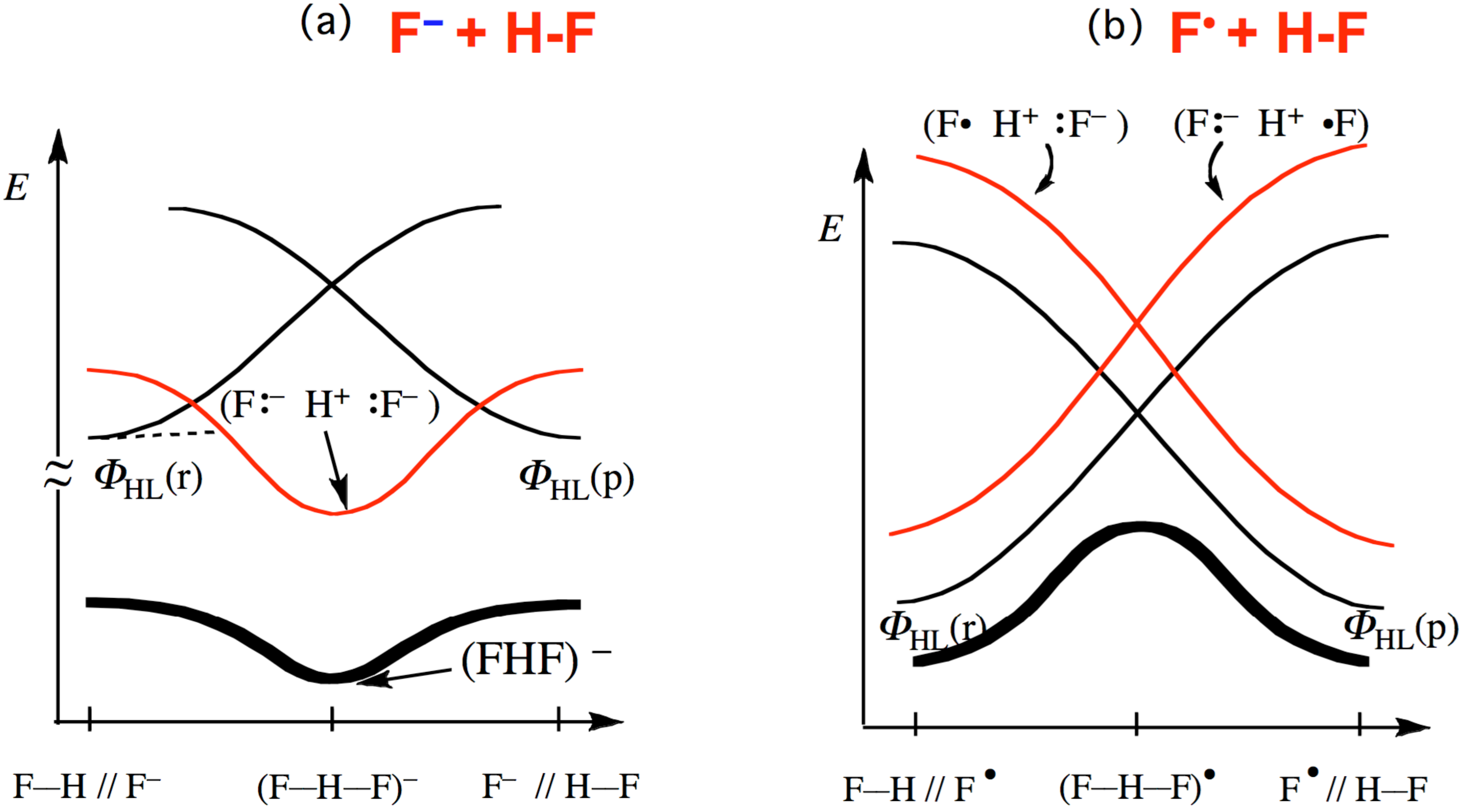


Conclusion

- 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

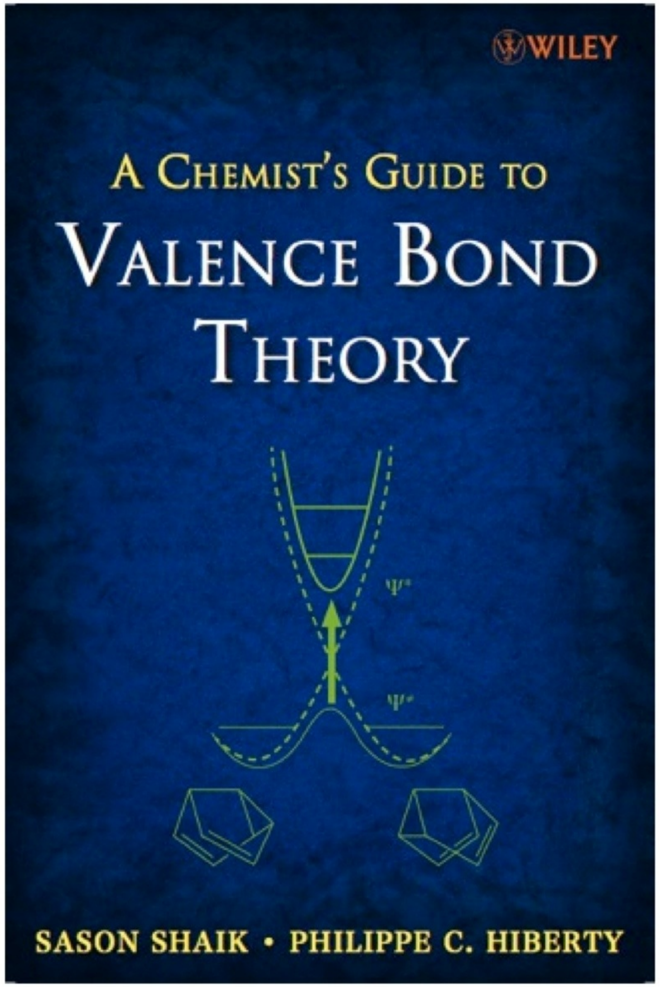
  - **quantitive proof** : by high level VB calculations

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...



WILEY

A CHEMIST'S GUIDE TO

VALENCE BOND

THEORY

SASON SHAIK • PHILIPPE C. HIBERTY

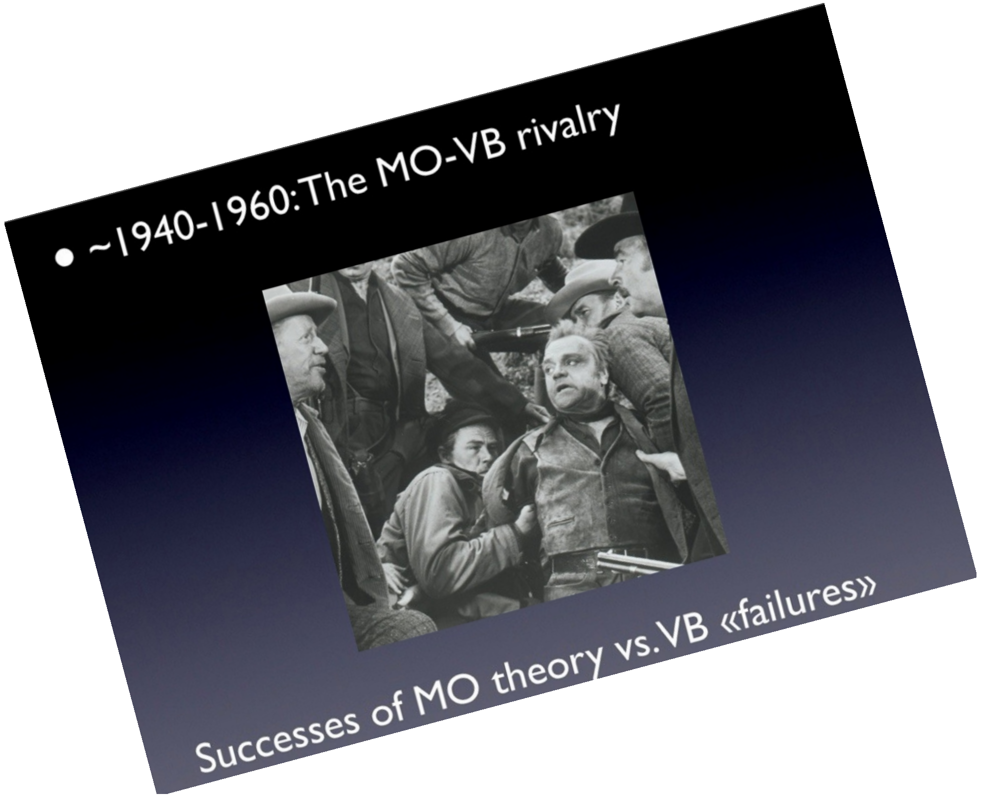
https://wiki.lct.jussieu.fr/workshop/index.php/VB_tutorial

Limits of VB theory

So, why everybody has not been doing VB ?

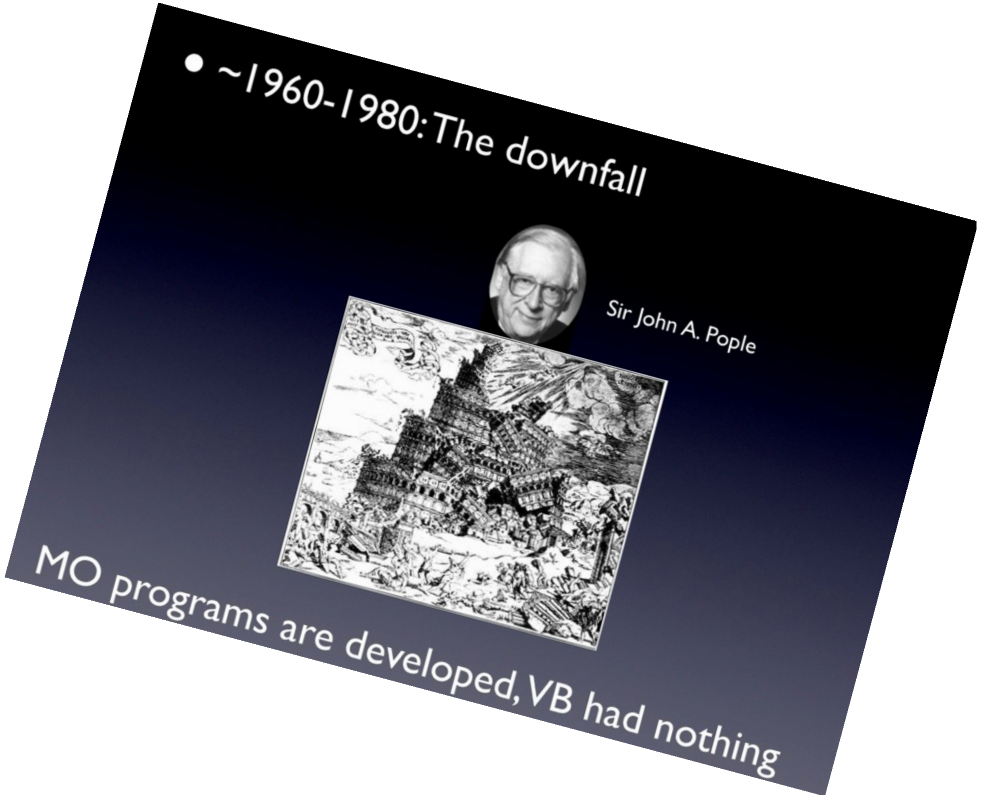
Limits of VB theory

- **Historical reasons :**



- ~1940-1960: The MO-VB rivalry

Successes of MO theory vs. VB «failures»



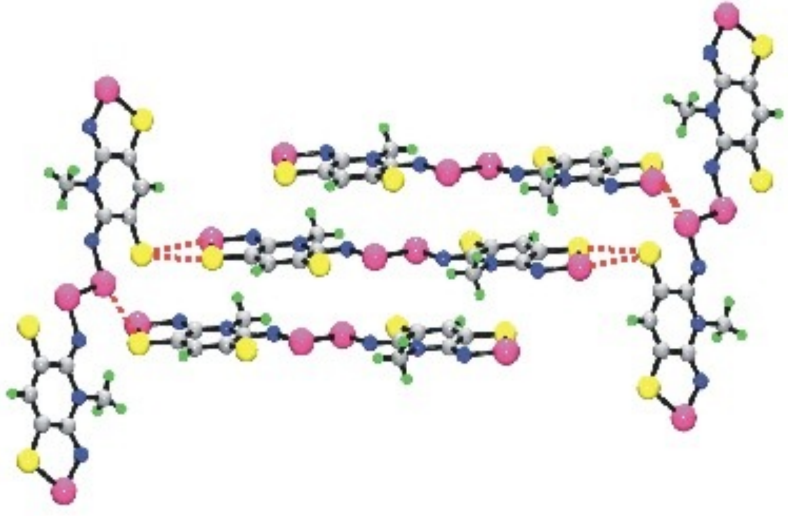
- ~1960-1980: The downfall

MO programs are developed, VB had nothing

Limits of VB theory

- **Moderate number of structures :**

• Given an active space, the selection of meaningful structures should be moderate (VBSCF : ~100s' ; BOVB : up to ~20)



No way !

• Large number of structure : computational issue, but also interpretative issue : VB theory may not be **relevant** in such cases

➡ VB is not a «universal theory» of electronic structure

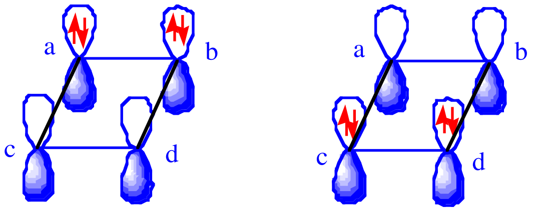
Limits of VB theory

- **Nonorthogonality :**

  - Working with non-orthogonal orbitals complicates a **LOT** all formulas :

$$\hat{H} = \sum_i \hat{h}_i + \sum_{i,j} \frac{1}{r_{ij}} \qquad\qquad \bar{\bar{H}}\bar{C} = E\bar{\bar{S}}\bar{C}$$

<u>Ex :</u> a 4e/4o pb :



..

$$|a\bar{a}b\bar{b}| \qquad |c\bar{c}d\bar{d}|$$

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$$\bar{\bar{H}}\bar{C} = E\bar{\bar{S}}\bar{C}$$

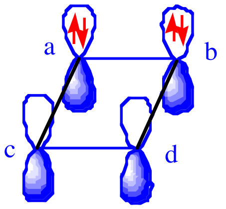
MO theory :

(orthogonal orbs.)

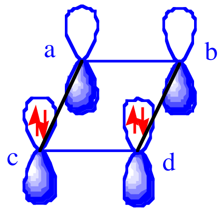
$$\bar{\bar{S}}$$

$$\begin{array}{c|cccccc}
|a\bar{a}b\bar{b}| & 1 & 0 & 0 & 0 & 0 & 0 \\
|a\bar{a}c\bar{c}| & 0 & 1 & 0 & 0 & 0 & 0 \\
 & 0 & 0 & 1 & 0 & 0 & 0 \\
\vdots & 0 & 0 & 0 & 1 & 0 & 0 \\
 & 0 & 0 & 0 & 0 & 1 & 0 \\
|c\bar{c}d\bar{d}| & 0 & 0 & 0 & 0 & 0 & 1
\end{array}$$

Ex : a 4e/4o pb :



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



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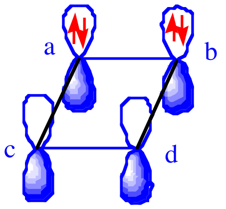
$$\bar{\bar{H}}$$

$$\begin{array}{c|c} |a\bar{a}b\bar{b}| & \times \quad \times \quad \times \quad \times \quad \times \quad 0 \\ |a\bar{a}c\bar{c}| & \times \quad \times \quad \times \quad \times \quad 0 \quad \times \\ & \times \quad \times \quad \times \quad 0 \quad \times \quad \times \\ \vdots & \times \quad \times \quad 0 \quad \times \quad \times \quad \times \\ & \times \quad 0 \quad \times \quad \times \quad \times \quad \times \\ |c\bar{c}d\bar{d}| & 0 \quad \times \quad \times \quad \times \quad \times \quad \times \end{array}$$

$$\langle D|\hat{H}|D'\rangle = \langle bb\frac{1}{r_{12}}cc\rangle$$

Ex : a 4e/4o pb :



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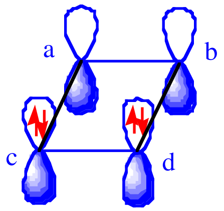

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VB theory :

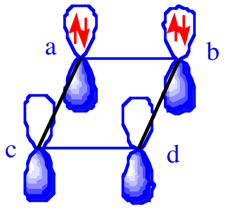
(nonorthogonal orbs.)

$$\bar{\bar{S}}$$

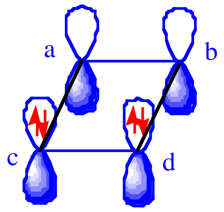
$$\begin{array}{c} |a\bar{a}b\bar{b}| \\ |a\bar{a}c\bar{c}| \\ \\ \vdots \\ \\ |c\bar{c}d\bar{d}| \end{array} \begin{pmatrix} 1 & \times & \times & \times & \times & \times \\ \times & 1 & \times & \times & \times & \times \\ \times & \times & 1 & \times & \times & \times \\ \times & \times & \times & 1 & \times & \times \\ \times & \times & \times & \times & 1 & \times \\ \times & \times & \times & \times & \times & 1 \end{pmatrix}$$

$$\langle D | D' \rangle = S_{ac}^2 S_{bd}^2 - 2S_{ad}S_{ac}S_{bd}S_{bc} + S_{ad}^2 S_{bc}^2$$

Ex : a 4e/4o pb :



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



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

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VB theory :

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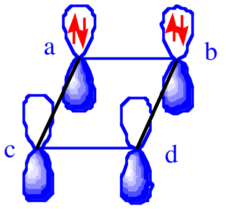
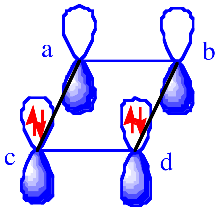
$$\bar{\bar{H}}$$

$$\begin{array}{c} \\ |a\bar{a}b\bar{b}| \\ |a\bar{a}c\bar{c}| \\ \vdots \\ \\ \\ |c\bar{c}d\bar{d}| \end{array} \begin{pmatrix} \times & \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times & \times \end{pmatrix}$$

<u>Ex :</u> a 4e/4o pb :



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



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

$$\langle D|\hat{H}|D'\rangle = 2(h_{ac}S_{ac}S_{bd}^2 - h_{ad}S_{ac}S_{bc}S_{bd} - h_{ac}S_{ad}S_{bd}S_{bc} + h_{ad}S_{ad}S_{bc}^2$$
$$+h_{bd}S_{bd}S_{ac}^2 - h_{bd}S_{ad}S_{ac}S_{bd} - h_{bd}S_{ac}S_{ad}S_{bc} + h_{bd}S_{bc}S_{ad}^2) + \langle aa\frac{1}{r_{12}}cc\rangle$$
$$+\langle aa\frac{1}{r_{12}}cc\rangle S_{bd}^2 + 4\langle ab\frac{1}{r_{12}}cd\rangle S_{ac}S_{bd} + \langle bb\frac{1}{r_{12}}dd\rangle S_{bd}^2 + \ldots$$

Limits of VB theory

- **Nonorthogonality :**

  - Working with non-orthogonal orbitals complicates a **<u>LOT</u>** all formulas :

  <u>Ex 2 :</u> (ic)VBPT2 formulas :

$$
\begin{aligned}
&\left\langle \Psi^{ij}_{x_1 y_1} \middle| \hat{H}_0 \middle| \Psi^{ij}_{x_2 y_2} \right\rangle = \left(E^{(0)}_{inact} - \varepsilon_i - \varepsilon_j \right) \left\langle \Psi^{ij}_{x_1 y_1} \middle| \Psi^{ij}_{x_2 y_2} \right\rangle \\
&+ \{ (4 s_{x_2 x_1} s_{y_2 y_1} - 2 s_{y_2 x_1} s_{x_2 y_1}) E^{(0)}_{act} \\
&+ 4 f_{x_2 x_1} s_{y_2 y_1} + 4 f_{y_2 y_1} s_{x_2 x_1} - 2 f_{x_2 y_1} s_{y_2 x_1} - 2 f_{y_2 x_1} s_{x_2 y_1} \\
&+ [(f_{tx_1} s_{x_2 y_1} s_{y_2 u} + f_{ty_1} s_{y_2 x_1} s_{x_2 u} - 2 f_{tx_1} s_{y_2 y_1} s_{x_2 u} - 2 f_{ty_1} s_{x_2 x_1} s_{y_2 u}) \\
&+ (f_{tx_2} s_{y_2 x_1} s_{y_1 u} + f_{ty_2} s_{x_2 y_1} s_{x_1 u} - 2 f_{tx_2} s_{y_2 y_1} s_{x_1 u} - 2 f_{ty_2} s_{x_2 x_1} s_{y_1 u}) \\
&+ (f_{y_2 x_1} s_{y_1 u} s_{x_2 t} + f_{x_2 y_1} s_{x_1 u} s_{y_2 t} - 2 f_{x_2 x_1} s_{y_1 u} s_{y_2 t} - 2 f_{y_2 y_1} s_{x_1 u} s_{x_2 t})] D^{tu} \\
&+ [f_{tu} (s_{y_2 x_1} s_{x_2 v} s_{y_1 w} + s_{x_2 y_1} s_{y_2 v} s_{x_1 w} - 2 s_{y_2 y_1} s_{x_2 v} s_{x_1 w} - 2 s_{x_2 x_1} s_{y_2 v} s_{y_1 w}) \\
&+ (f_{tx_1} s_{x_2 u} s_{y_1 v} s_{y_2 w} + f_{ty_1} s_{y_2 u} s_{x_1 v} s_{x_2 w} + f_{tx_2} s_{y_2 v} s_{x_1 u} s_{y_1 w} + f_{ty_2} s_{x_2 v} s_{y_1 u} s_{x_1 w})] \Pi^{tv,uw} \\
&+ f_{tu} s_{y_2 v_1} s_{x_2 w_1} s_{y_1 v_2} s_{x_1 w_2} \Gamma^{t v_1 w_1, u v_2 w_2} \} \\
&+ \delta^{ij} \{ (4 s_{x_2 y_1} s_{y_2 x_1} - 2 s_{x_2 x_1} s_{y_2 y_1}) E^{(0)}_{act} \\
&+ 4 f_{x_2 y_1} s_{y_2 x_1} + 4 f_{y_2 x_1} s_{x_2 y_1} - 2 s_{x_2 x_1} f_{y_2 y_1} - 2 f_{x_2 x_1} s_{y_2 y_1} \\
&+ [(f_{tx_2} s_{y_2 y_1} s_{x_1 u} + f_{ty_2} s_{x_2 x_1} s_{y_1 u} - 2 f_{ty_2} s_{x_2 y_1} s_{x_1 u} - 2 f_{tx_2} s_{y_2 x_1} s_{y_1 u}) \\
&+ (f_{ty_1} s_{x_2 x_1} s_{y_2 u} + f_{tx_1} s_{y_2 y_1} s_{x_2 u} - 2 f_{ty_1} s_{y_2 x_1} s_{x_2 u} - 2 f_{tx_1} s_{x_2 y_1} s_{y_2 u}) \\
&+ (f_{y_2 y_1} s_{x_1 u} s_{x_2 t} + f_{x_2 x_1} s_{y_1 u} s_{y_2 t} - 2 f_{x_2 y_1} s_{x_1 u} s_{y_2 t} - 2 f_{y_2 x_1} s_{y_1 u} s_{x_2 t})] D^{tu} \\
&[+ f_{tu} (s_{y_2 y_1} s_{x_2 v} s_{x_1 w} + s_{x_2 x_1} s_{y_2 v} s_{y_1 w} - 2 s_{x_2 y_1} s_{y_2 v} s_{x_1 w} - 2 s_{y_2 x_1} s_{x_2 v} s_{y_1 w}) \\
&+ (f_{ty_1} s_{x_2 u} s_{x_1 v} s_{y_2 w} + f_{tx_1} s_{y_2 u} s_{y_1 v} s_{x_2 w} + f_{tx_2} s_{y_1 u} s_{y_2 v} s_{x_1 w} + f_{ty_2} s_{x_1 u} s_{x_2 v} s_{y_1 w})] \Pi^{tv,uw} \\
&+ f_{tu} s_{y_2 v_1} s_{x_2 w_1} s_{x_1 v_2} s_{y_1 w_2} \Gamma^{t v_1 w_1, u v_2 w_2} \}
\end{aligned}
$$

Limits of VB theory

- **Nonorthogonality :**
  - Working with non-orthogonal orbitals complicates a **LOT**
  - Slowed dramatically the extension of VB community

But :

  - Now extremely efficient algorithms, based on advanced algebra:*
    1) Second Quantization Technique for non-orthogonal orbitals ;
    2) Tensor Analysis ;
    3) Automatic Formula/Code Generator

* *Chen Z., Chen X, and Wu W. J. Chem. Phys. 138, 164119 (2013)*

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