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ICS Summer school 2013

Valence Bond theory

Laboratoire de Chimie Théorique

Université Pierre et Marie Curie - Paris6

VB lectures

- Part. 1 - Basics of VB theory
- Part. 2 - *Ab initio* VB methods
- Part. 3 - Qualitative VB
- Part. 4 - VB diagrams for reactivity

(including paper exercices)

VB lectures

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VB lectures

Download the lecture slides :

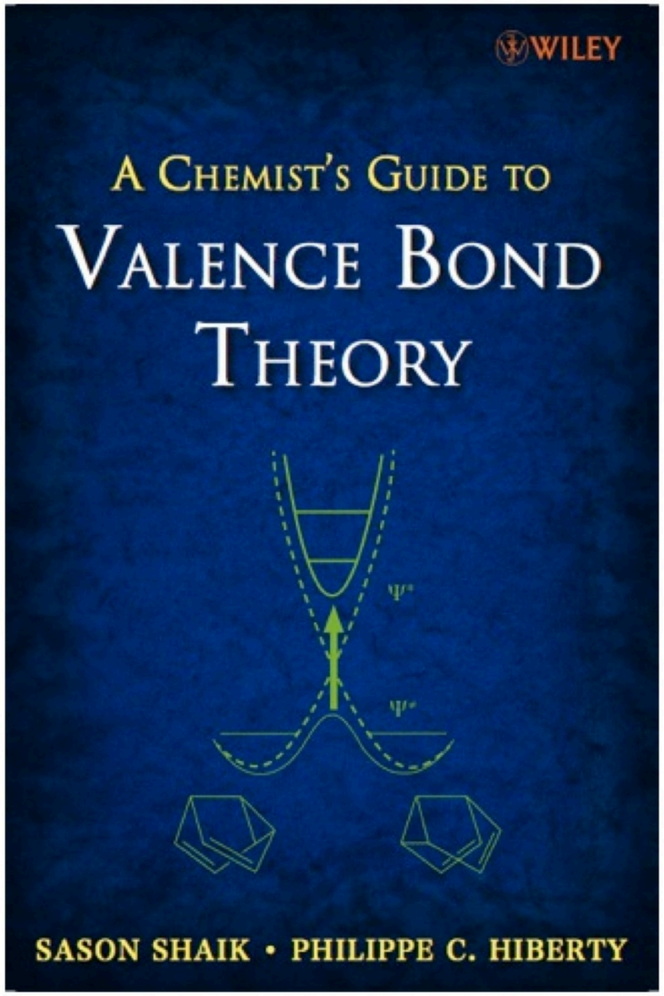
VB tutorials

- Tutoriel 1 : Basics of VB theory and XMVB program
- Tutoriel 2 : VB applications on PI systems

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

VB references

- Book :



- Reviews articles :

Motivation and purpose

Chemistry

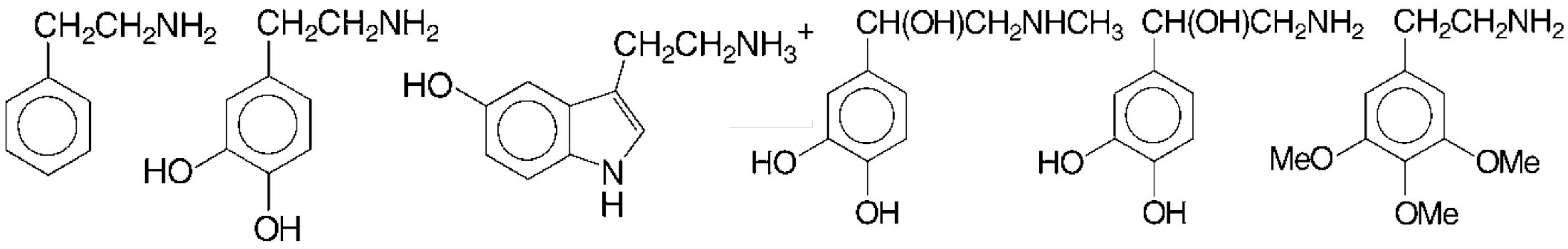
Why are we doing chemistry ? What is chemistry all about ?

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

* *S. Shaik, Angew. Chem. Int. Ed. 2003, 42, 3208–3215*

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

➡ There exists atoms which can bond together

➡ Bonds determines the molecular architecture, interactions, and reactivity of molecules

➡ This in turn determines properties of matter

Chemistry

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

Heuristic models

- Lewis' model :

THE ATOM AND THE MOLECULE.

By Gilbert N. Lewis.

JACS 1916, 762

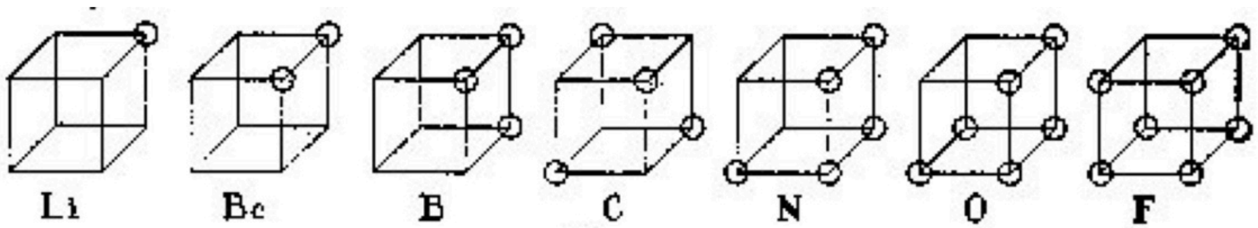
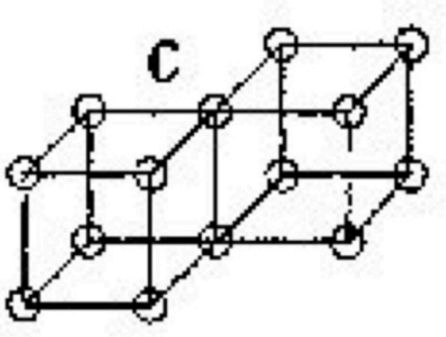


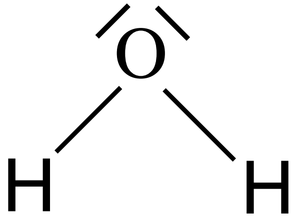
Fig. 2.



Heuristic models

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

Lewis' time

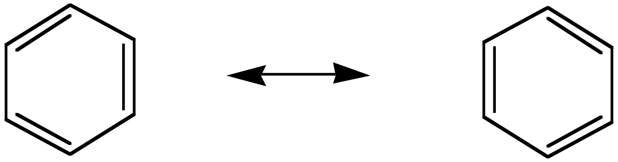


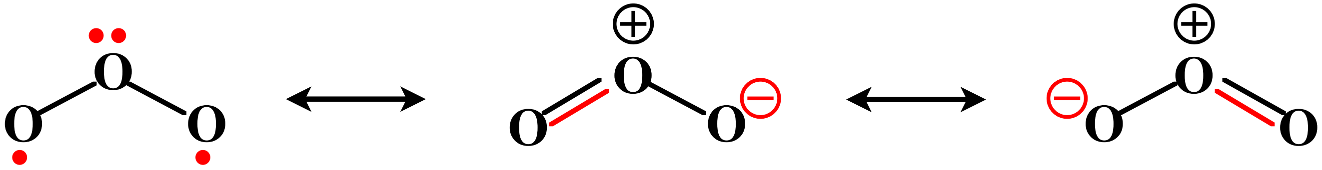
Today

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

Heuristic models

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

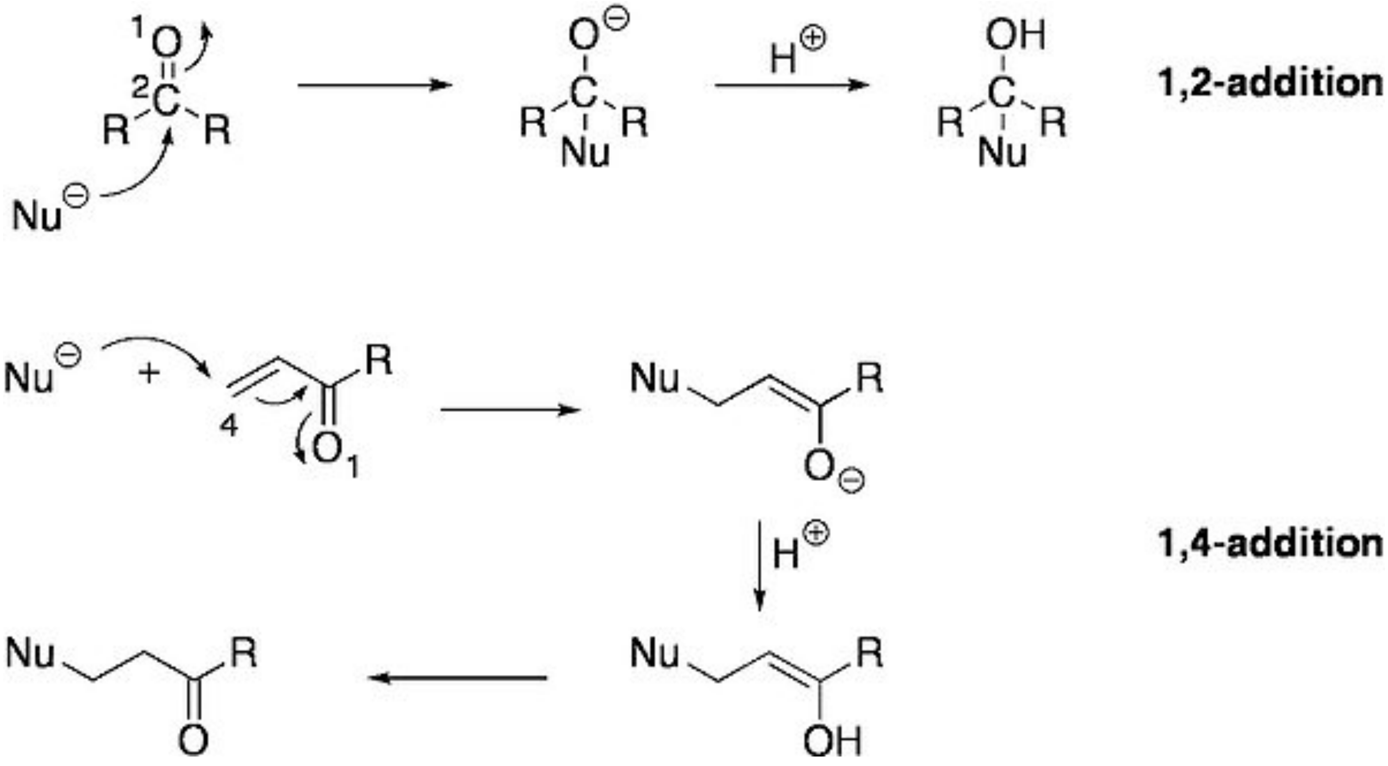




➡ when more than one Lewis structure is needed

Heuristic models

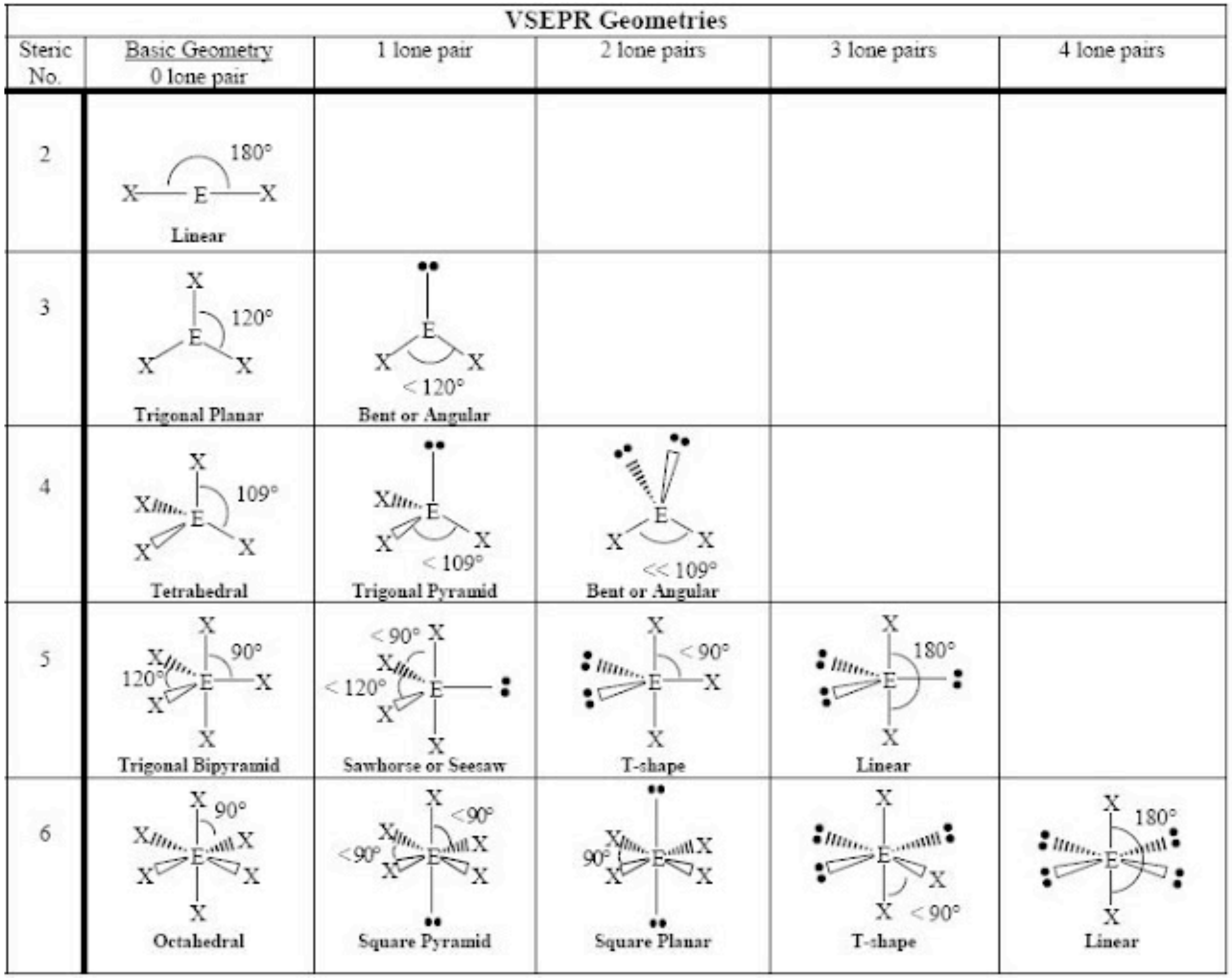
- Arrow-pushing language :



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

Heuristic models

- VSEPR model :



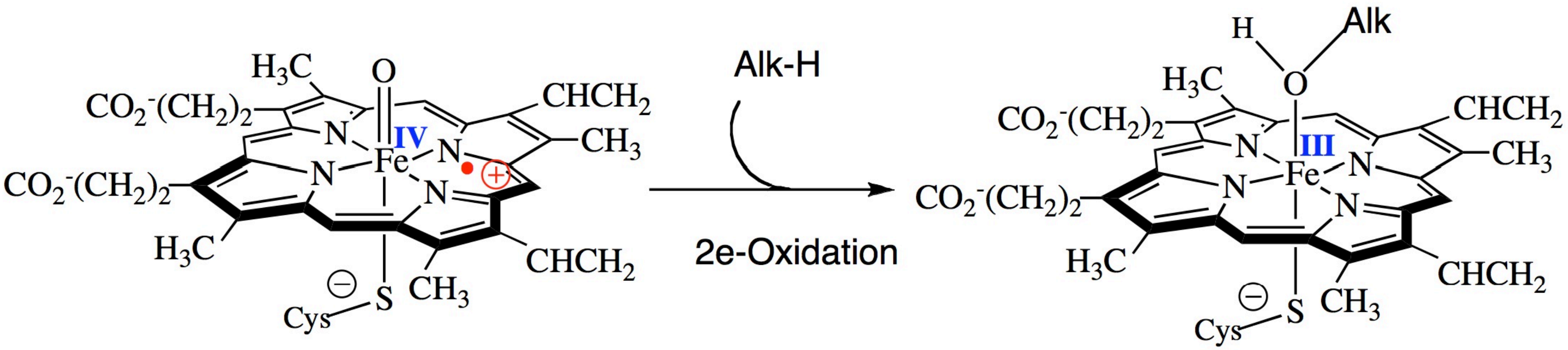
VSEPR Geometries

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal Planar	< 120° Bent or Angular			
4	109° Tetrahedral	< 109° Trigonal Pyramid	<< 109° Bent or Angular		
5	90° 120° Trigonal Bipyramid	< 90° < 120° Sawhorse or Seesaw	< 90° T-shape	180° Linear	
6	90° Octahedral	< 90° < 90° Square Pyramid	90° Square Planar	< 90° T-shape	180° Linear

➡ rationalization of molecular geometries

Quantum Chemistry

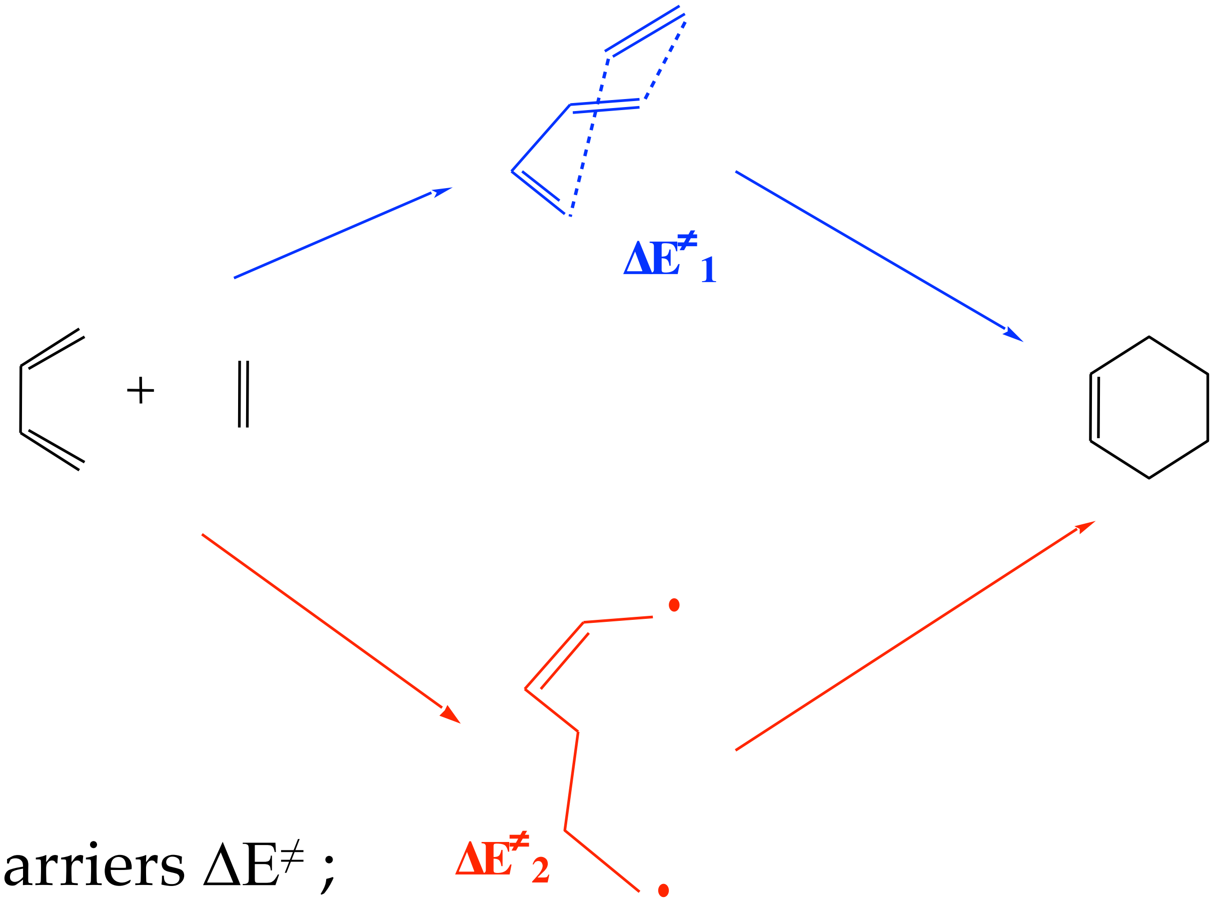
- Accurate quantum theory based calculations can provide :



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

Quantum Chemistry

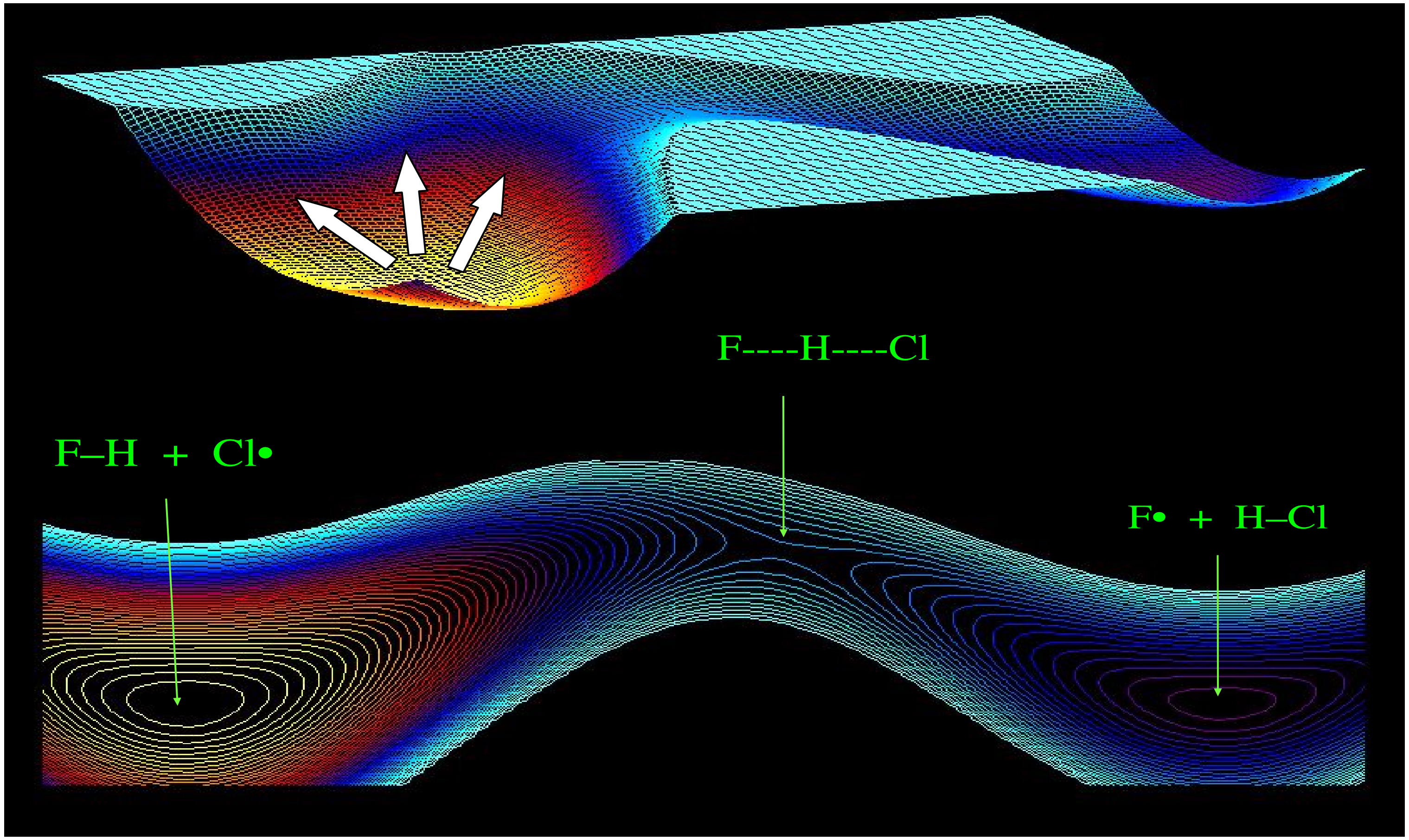
- Accurate quantum theory based calculations can provide :



  - accurate barriers ΔE≠ ;
  - details about reaction mechanisms

Quantum Chemistry

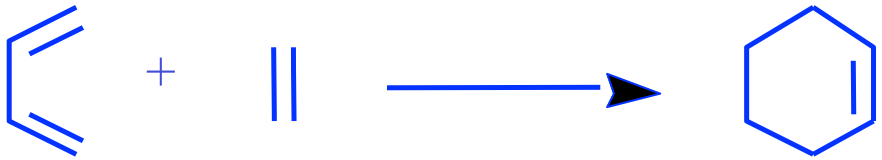
- Accurate quantum theory based calculations can provide :



  - detailed exploration of a potential energy surface

Quantum Chemistry

- ... but it does not (directly) provide :
  - human type of ***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}

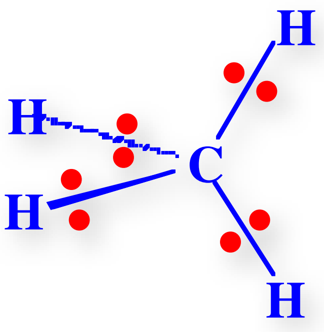
⇒ low barrier, easy

?

have to do the computation...

Chemists' «schizophrenia»

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



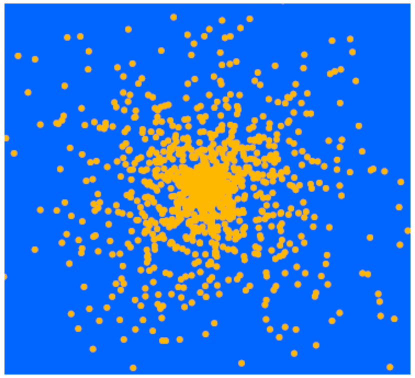
Lewis model, arrow-pushing language, VSEPR, hybridization,...

- Localized electron pairs

- Chemical bond concept

- **Quantitative theory** all-interacting delocalized particles vision :

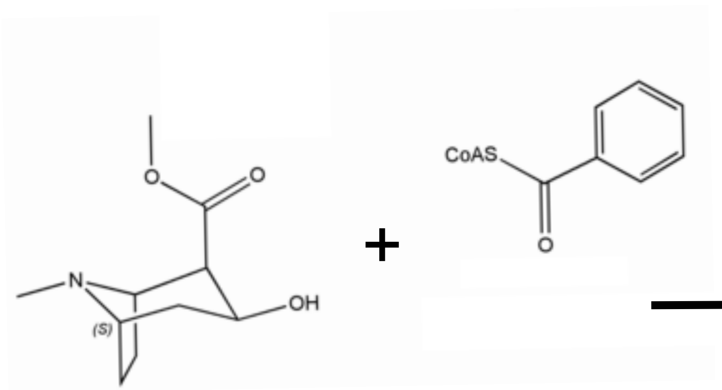
$$\hat{H}\Psi = E\Psi$$



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

- indistinguishable and all-interacting (no chemical bond)

Chemists' «schizophrenia»



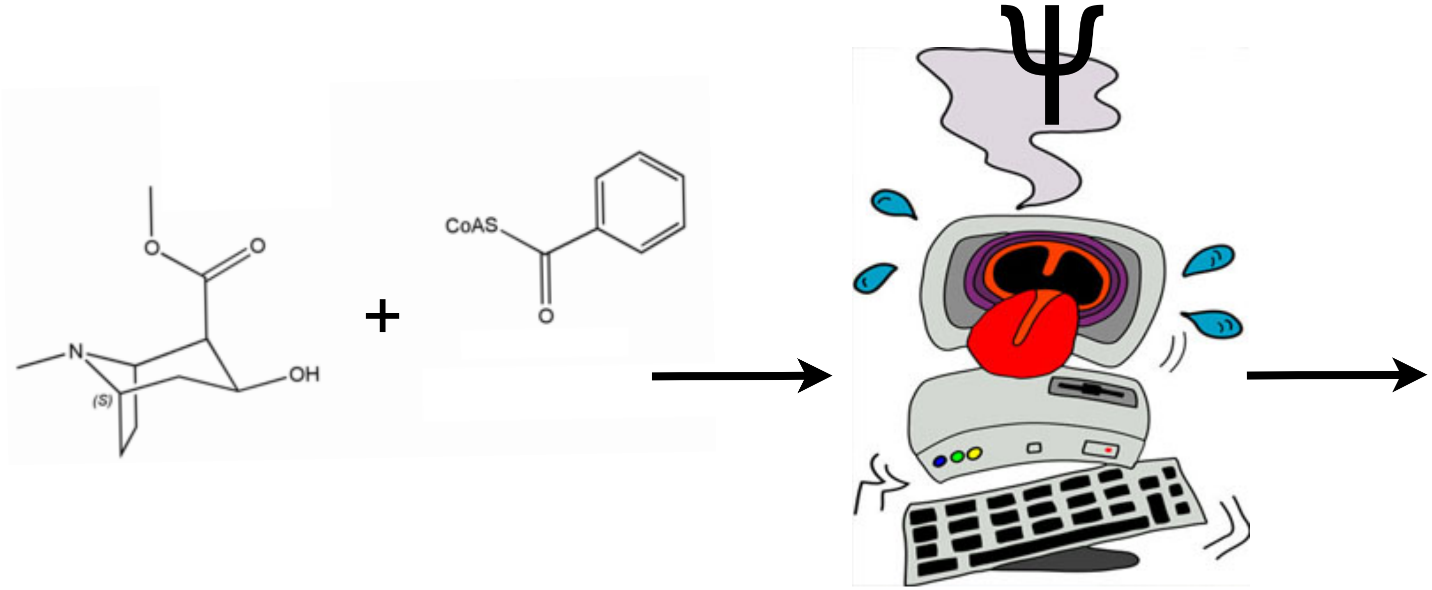
ΔH_{rnx}

$\Delta H^{\ddagger}$

Why ?...

etc.

Chemists' «schizophrenia»



ΔH_{rnx}

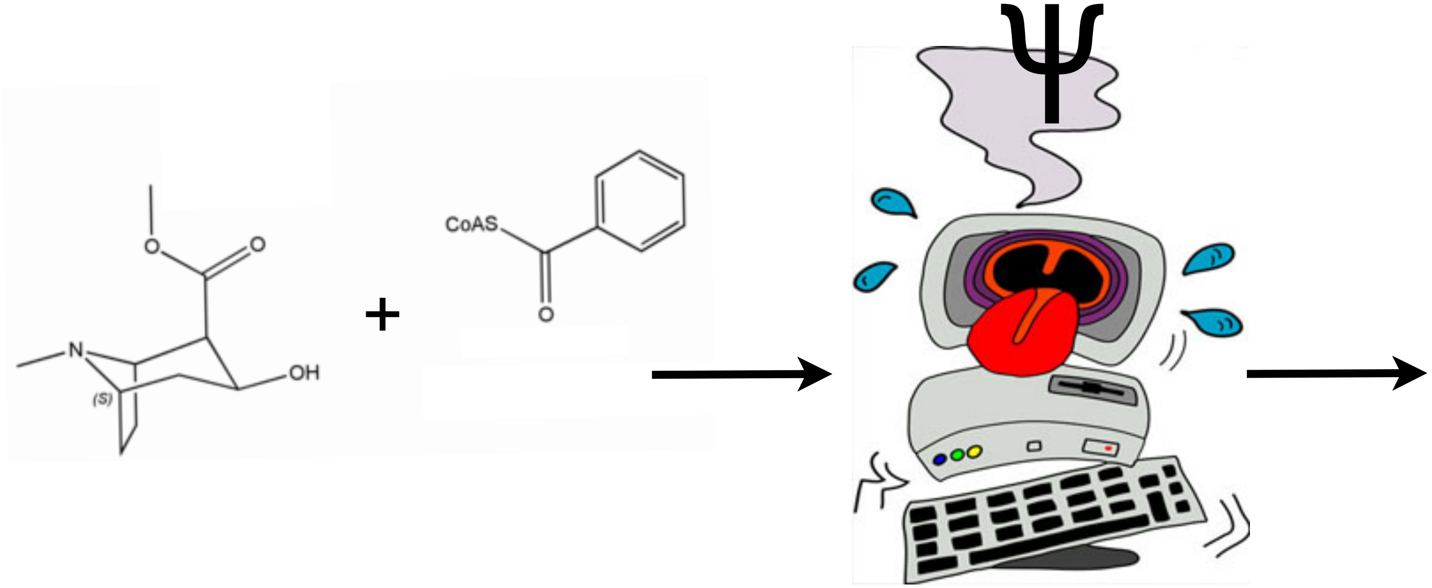
$\Delta H^{\ddagger}$

Why ?...

etc.

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

Chemists' «schizophrenia»



ΔH_{rnx}

$\Delta H^{\ddagger}$

etc.

Why ?...

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

Chemists' «schizophrenia»

The challenges :

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

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

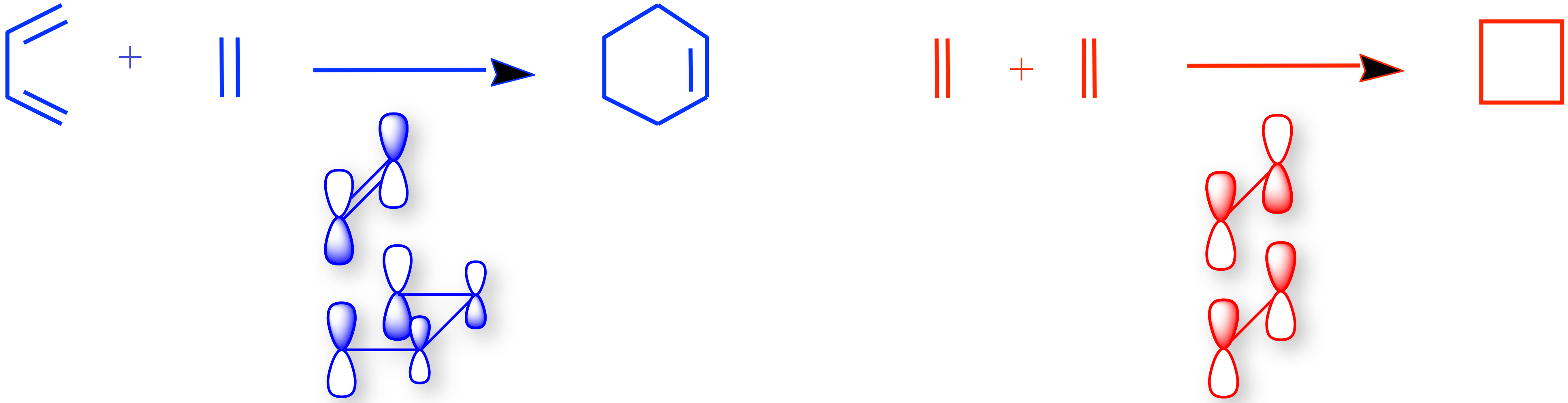
Interpretative methods

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

Interpretative methods

- Qualitative MO-based models :

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

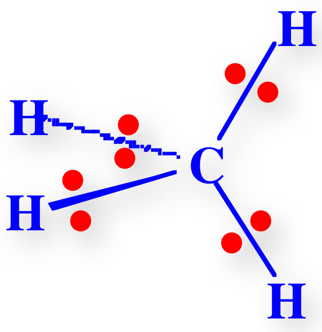


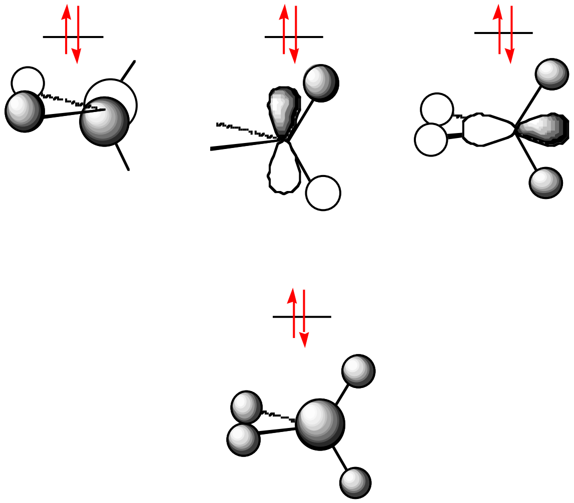
➡ Not quantitative (*a posteriori* rationalization)

Interpretative methods

- Qualitative MO-based models :

- **Localized** electron pairs	- **delocalized** picture
- **Chemical bond** concept	- **Indirect chemical bonding**

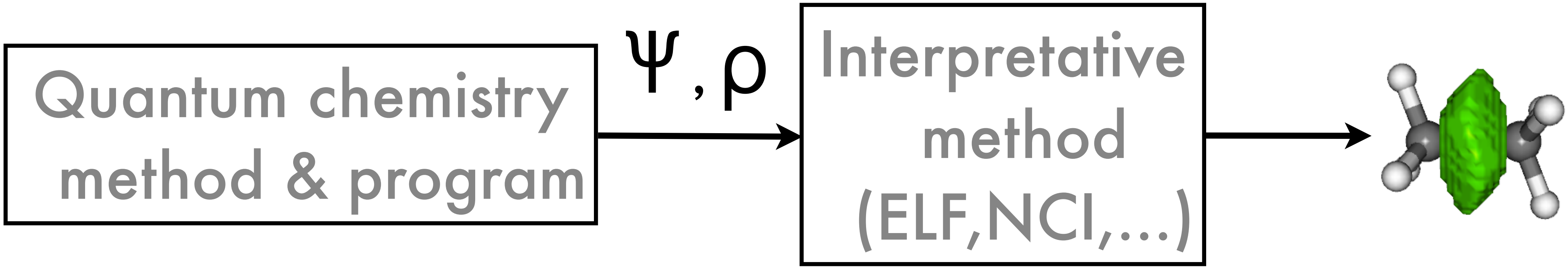




➡ No direct link with chemists' local vision

Interpretative methods

- Real space «topological» analysis :



Quantum chemistry method & program

Ψ, ρ

Interpretative method (ELF,NCI,...)

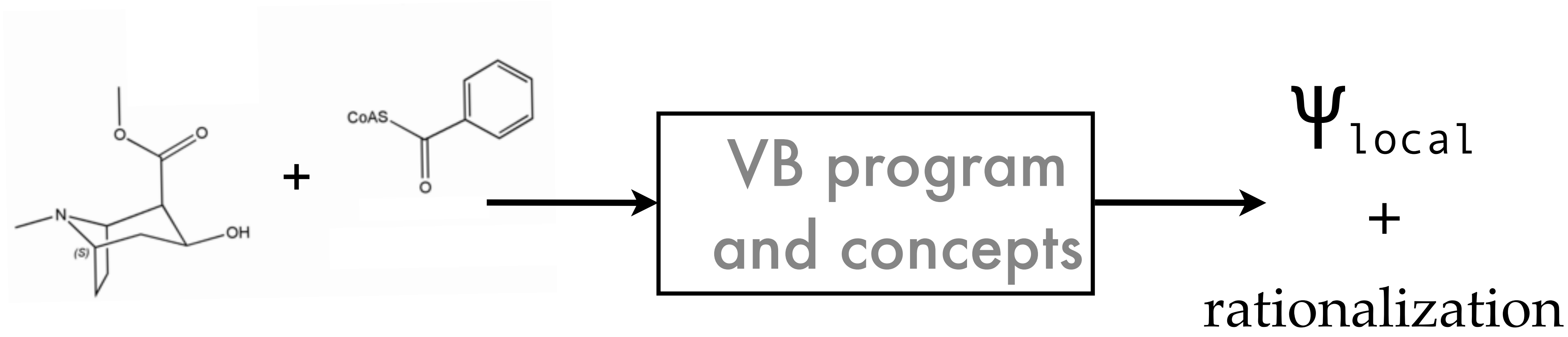
➡ Definition and **meaning** of localized regions not straightforward

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

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

Interpretative methods

- Valence bond theory :



VB program and concepts

$\Psi_{\mathtt{local}}$

+

rationalization

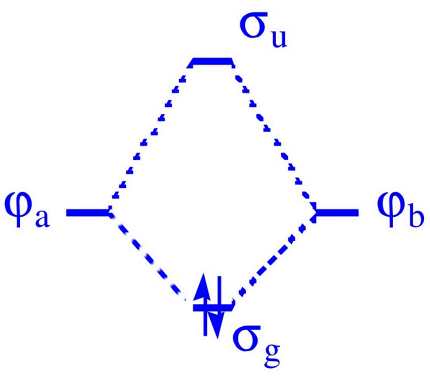
➡ A wavefunction (QC) method and «built-in» interpretative method at the same time

Part 1. Basics of VB theory

Heitler-London

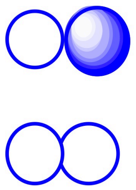
Dihydrogen molecule H_2 : H_a——H_b

- 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)

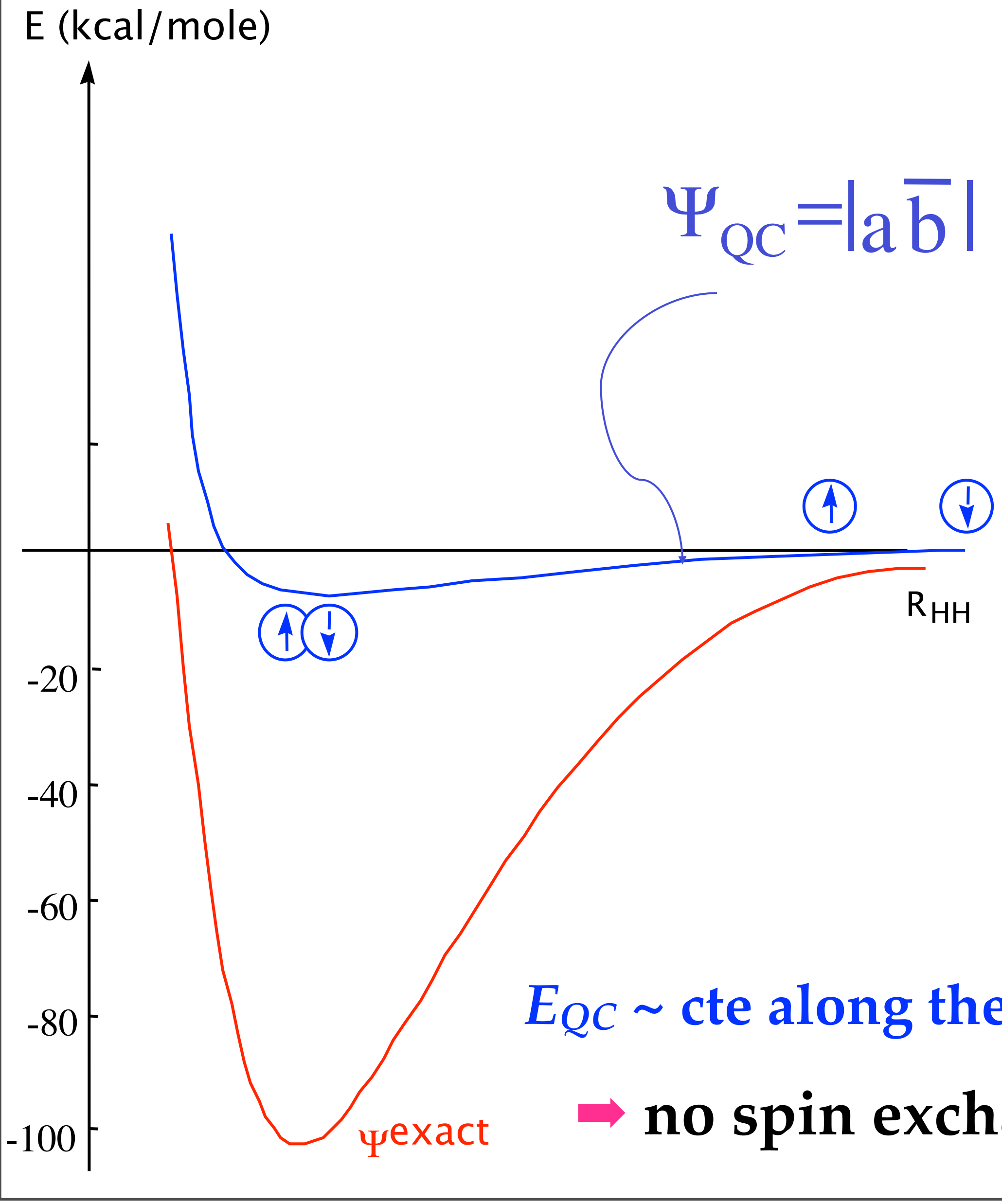
- Heitler-London (1927) :

$\Psi_{HL} = |\varphi_a \overline{\varphi_b}| - |\overline{\varphi_a} \varphi_b|$

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

➡ **basis of VB theory**

Heitler-London



- Quasi-Classical (QC) state :

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

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

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

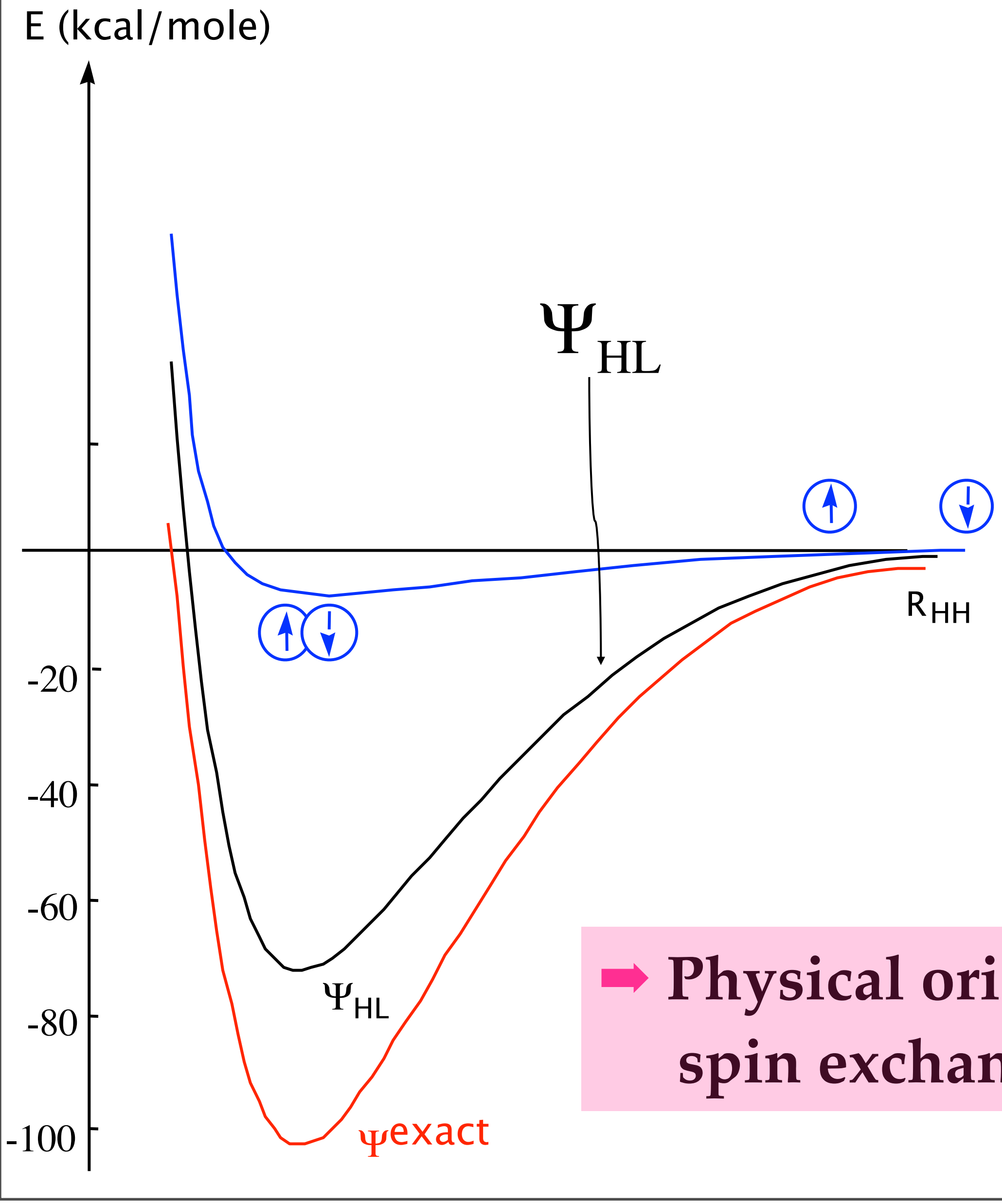
$$with : \begin{cases} h_{ii} = \iint i^*(1)i(1)h(1)d\tau_1 \\ J_{ab} = \iint a^*(1)a(1)\frac{1}{r_{12}}b^*(2)b(2)d\tau_1 d\tau_2 \end{cases}$$

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

E_{QC} ~ cte along the dissociation curve

➡ **no spin exchange ⇒ no bonding**

Heitler-London



- Heitler-London (HF) wf :

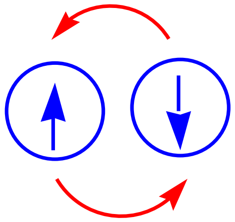
$$\boxed{\Psi_{HL} \propto |a\bar{b}| + |b\bar{a}|}$$

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

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

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

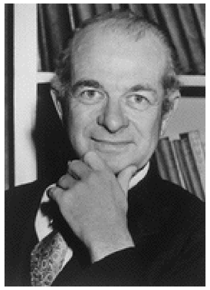
➡ **Physical origin of the chemical bond : spin exchange between AOs**

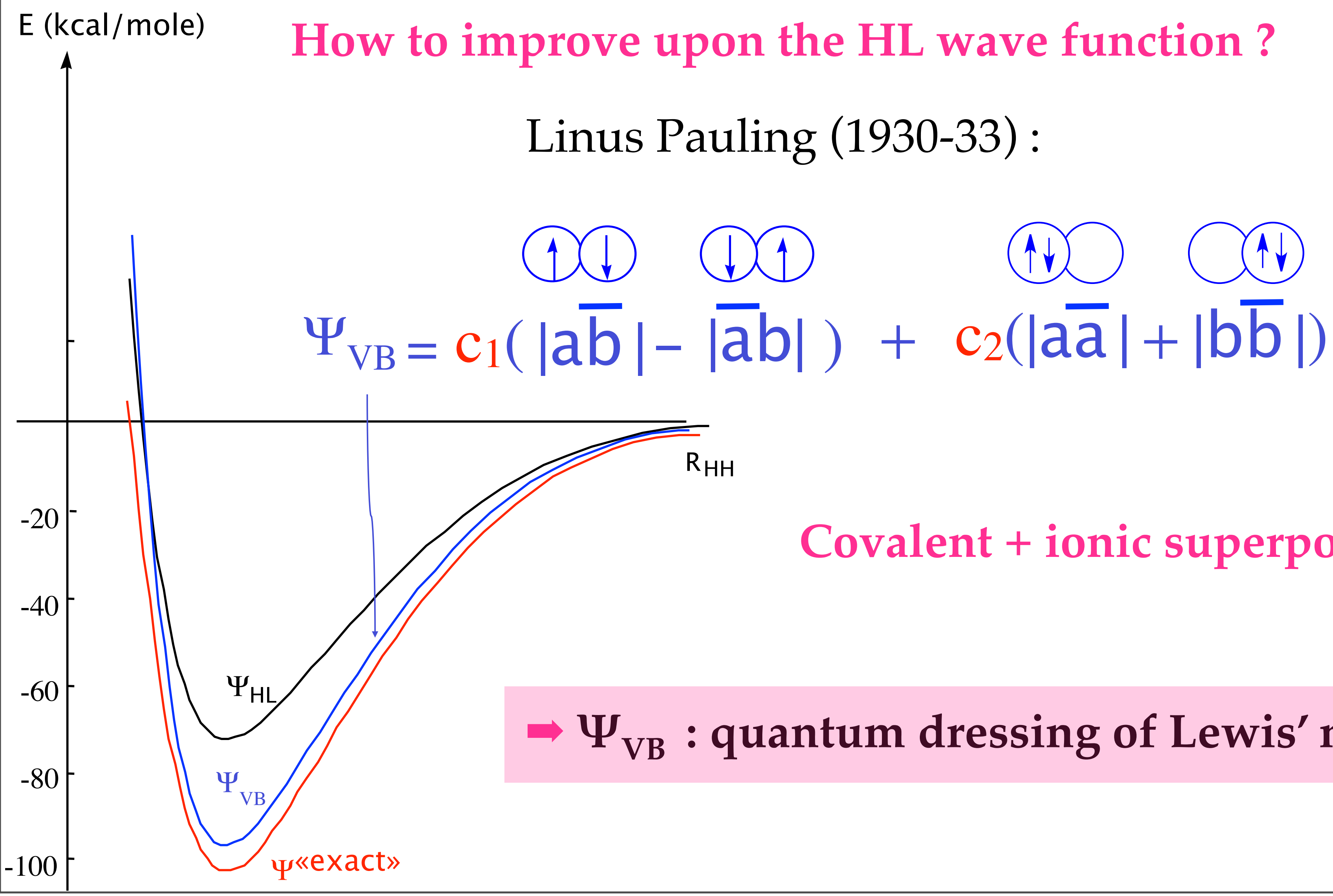


The VB wave function

How to improve upon the HL wave function ?

Linus Pauling (1930-33) :





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

Covalent + ionic superposition

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

Heitler-London

➡ Exercise 1 :

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

Heitler-London

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

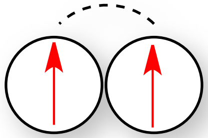
antisymetric ⇒ **Singlet**

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

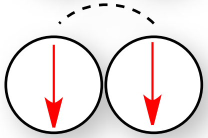
symetric ⇒ **Triplet (M_S=0)**

Note that :

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

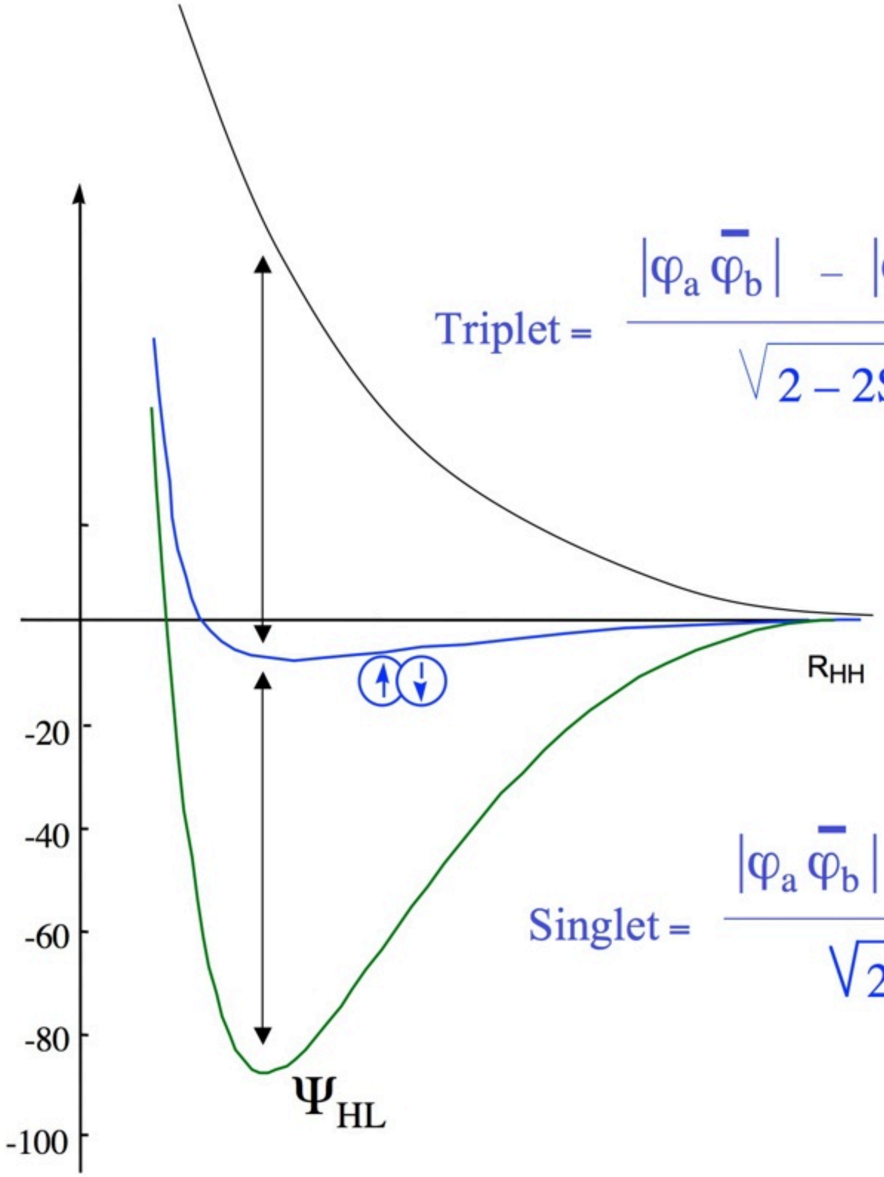


$$\Psi_T \propto |\bar{a}\bar{b}| = [a(1)b(2) - a(2)\,b(1)] \otimes [\beta(1)\,\beta(2)\,] \Rightarrow M_S = -1$$



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

Heitler-London



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

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

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

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

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

VB vs. MO

➡ Exercise 1 :

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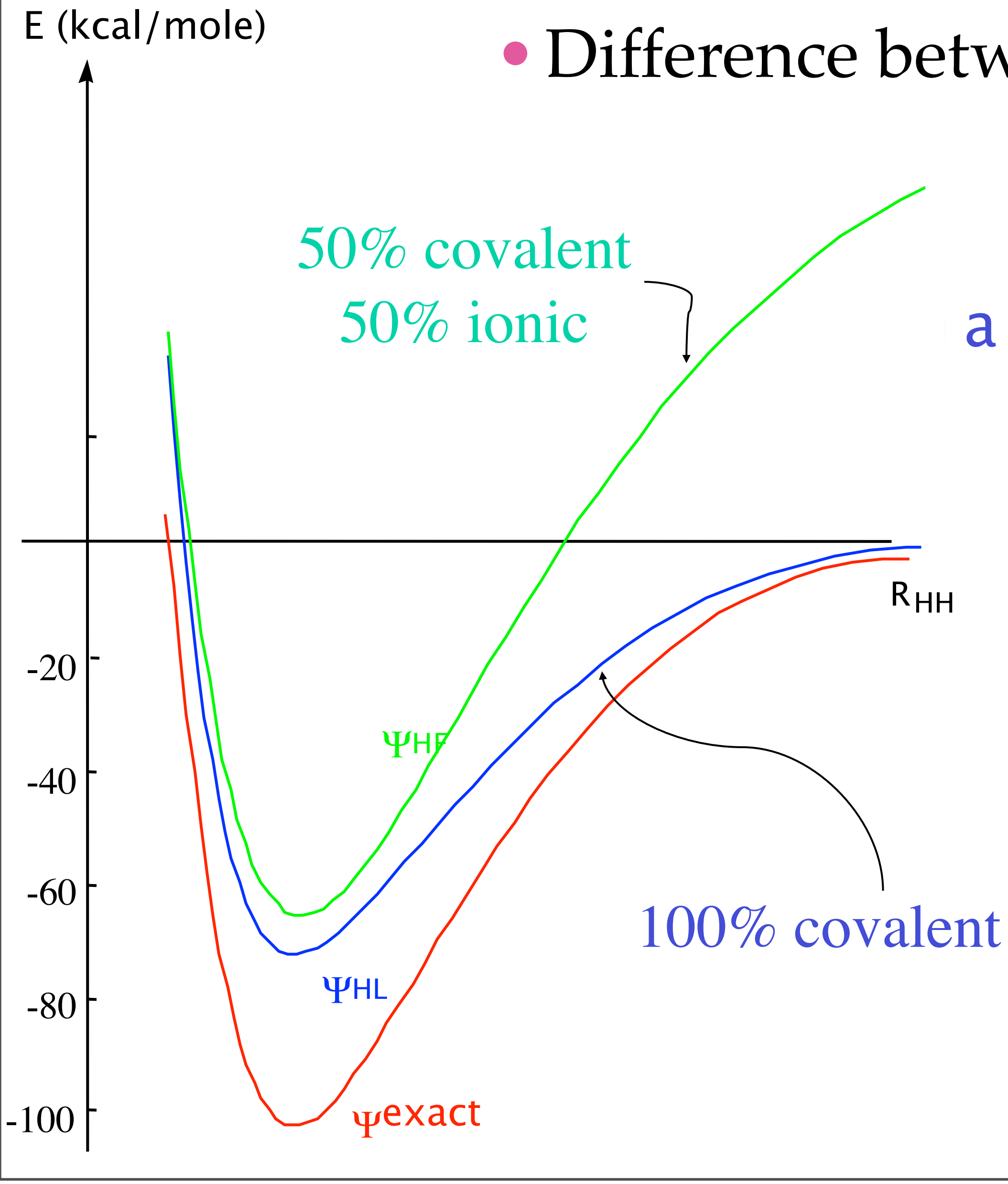
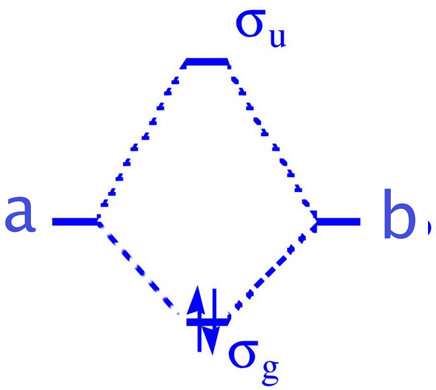
VB vs. MO

- Difference between HL and HF ?



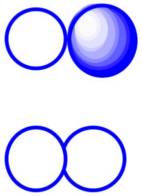
50% covalent
50% ionic

100% covalent



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

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



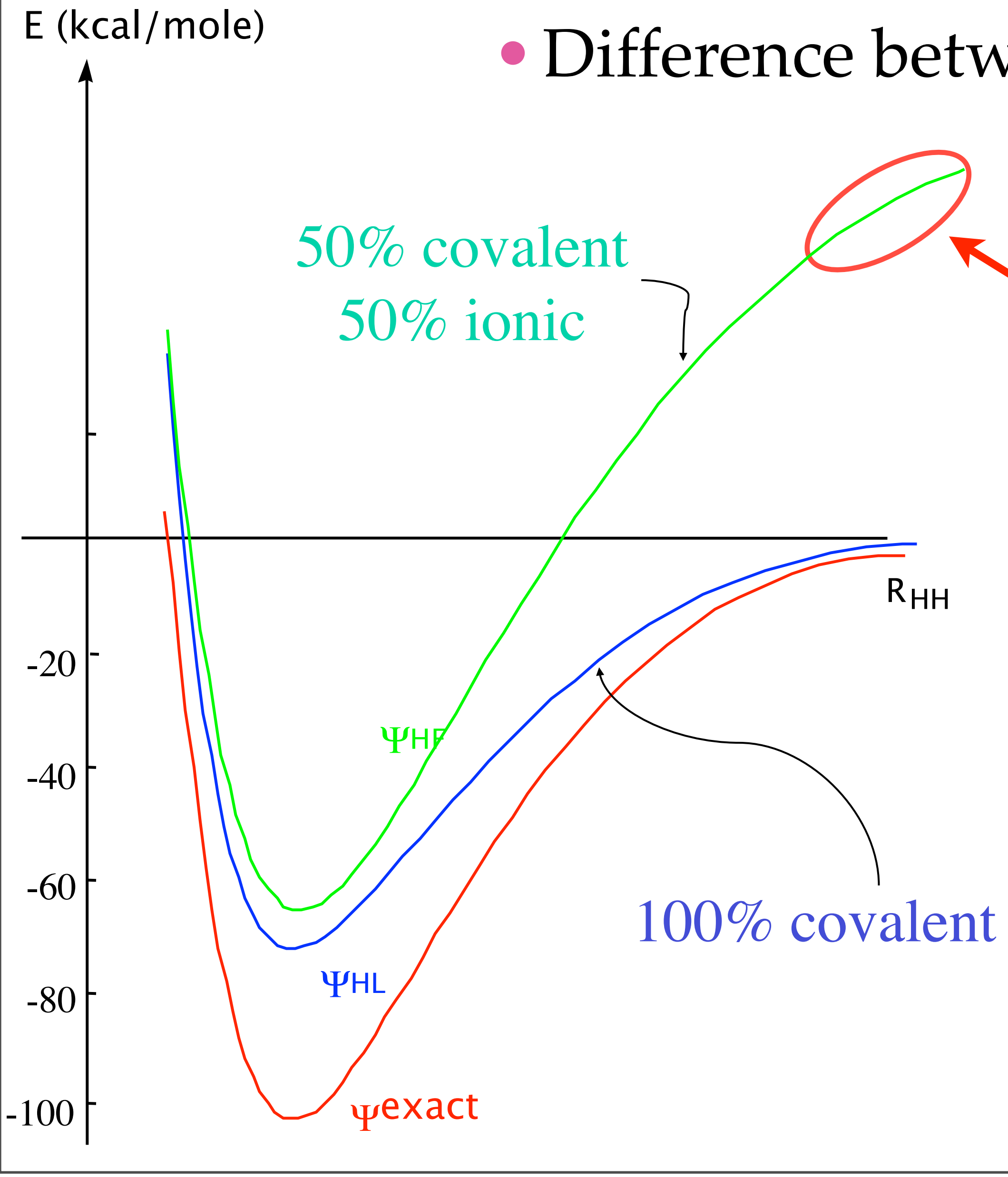
$$\Psi_{HF} = |\sigma_g \bar{\sigma}_g|$$

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

50% covalent 50% ionic

VB vs. MO

- Difference between HL and HF ?



50% covalent
50% ionic

100% covalent

wrong dissociation limit

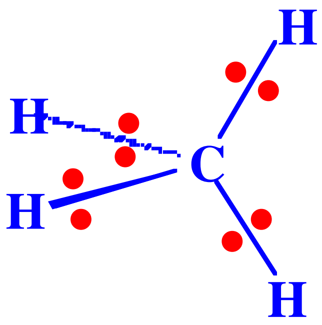
Optimal ≈ 70-80% covalent
30-20% ionic

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

The VB wave function

- Extension to the general case / 1) hybridization :

Lewis :

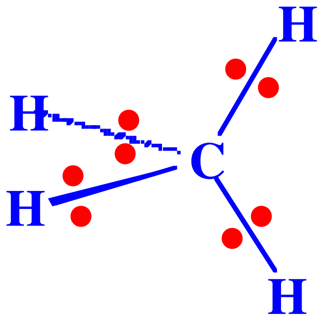


- We want to construct a VB w.f. which corresponds to Lewis' picture
- Which orbitals to use ?

The VB wave function

- Extension to the general case / 1) hybridization :

Lewis :



- We want to construct a VB w.f. which corresponds to Lewis' picture
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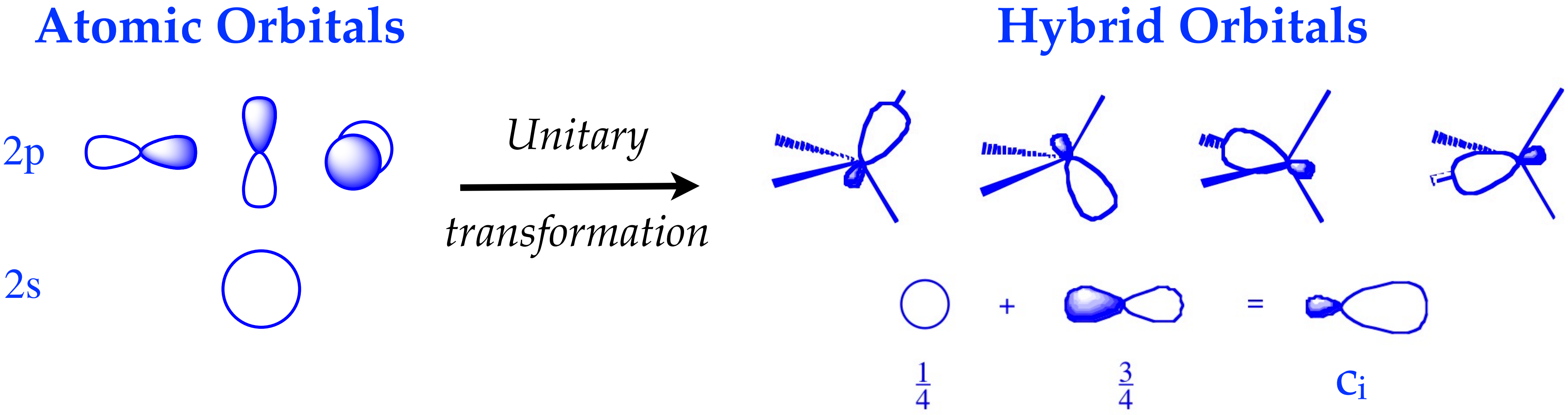


Atomic Orbitals

2p

2s

Unitary

transformation

Hybrid Orbitals

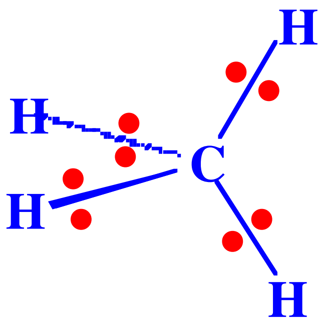
$$\frac{1}{4} + \frac{3}{4} = c_i$$

Four equivalent directional sp^3 orbitals

The VB wave function

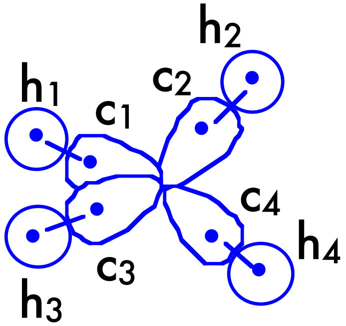
- Extension to the general case / 1) hybridization :

Lewis :



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

HL :



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

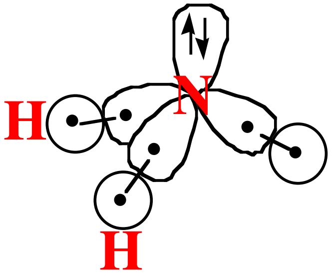
Electrons occupy **localized** orbitals (atomics, hybrids,...)

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

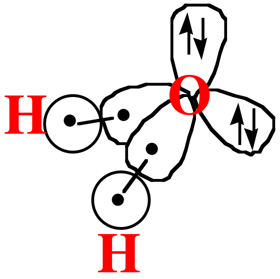
The VB wave function

- Extension to the general case / 1) hybridization :

« sp^3 »

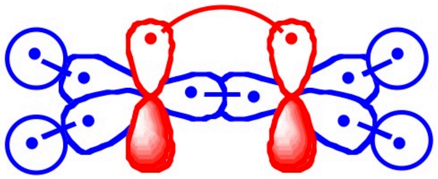


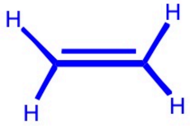
NH_3



H_2O

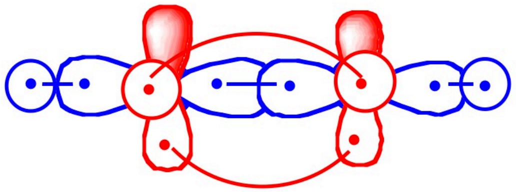
Three « sp^2 » hybrids
+ 2p$_z$ (unchanged)





Ethylen

Two « sp » hybrids
+ 2p$_x$ + 2p$_y$ (unchanged)



The VB wave function

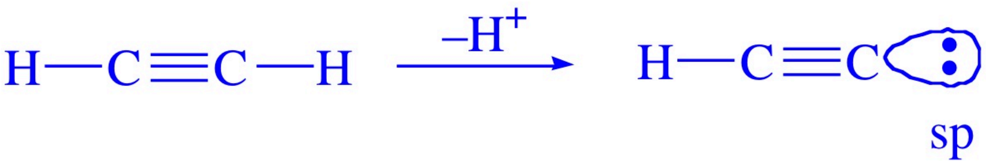
- Hybridization, a legitimate and useful concept :
  - Three categories of C–C bonds :

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

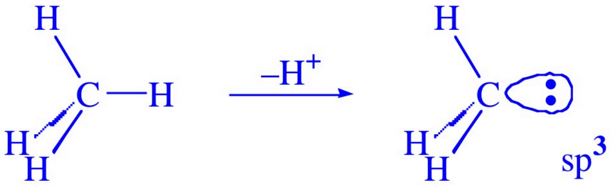
➡ Bond properties transferability

The VB wave function

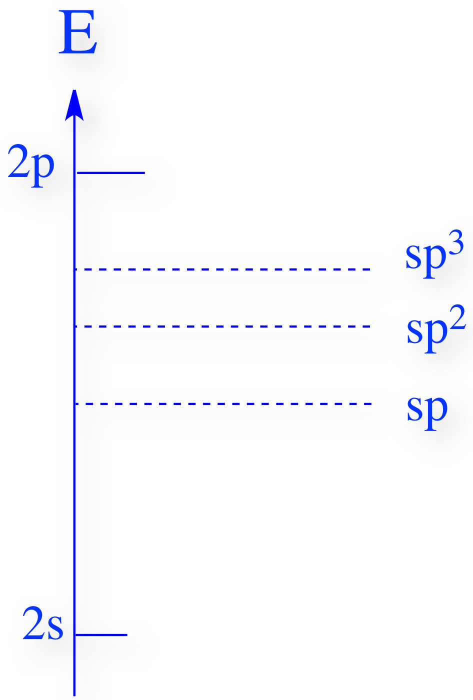
- Hybridization, a legitimate and useful concept :
  - Relative acidities of hydrocarbons :



pK(H–C≡C–H) ~ 25



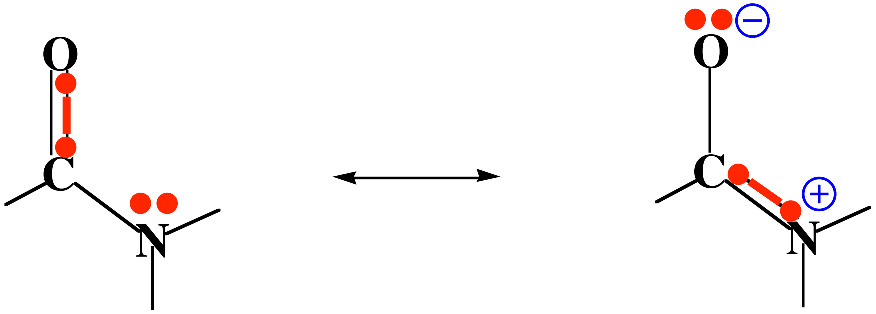
pK(CH_4) ~ 50



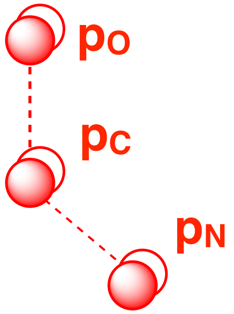
➡ $E(sp) < E(sp^3) \Rightarrow H\text{–}C{\equiv}C^- $ more stable than H_3C^-

The VB wave function

- Extension to the general case / 2) mesomery :



1 **2**



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

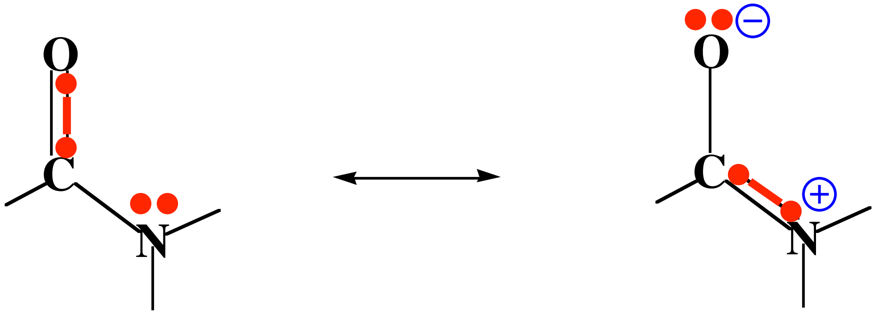
$$= C_1\left|p_N\overline{p_N}(p_O\overline{p_C} + p_C\overline{p_O})\right| + C_2\left|p_O\overline{p_O}(p_C\overline{p_N} + p_N\overline{p_C})\right|$$

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

The VB wave function

- Resonance concept :

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

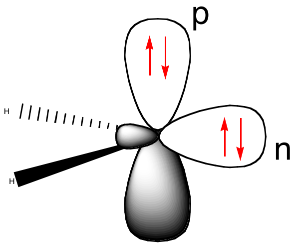


1 **2**

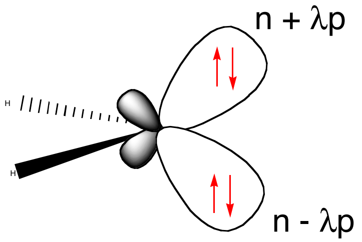
➡ The resonance concept is a central pillar of VB theory

VB vs. MO

➡ Exercise 2 :



Ψ_{MO}



Ψ_{VB}

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

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

VB vs. MO

➡ Exercise 2 (answer) :

1) $\Psi_{\mathrm{MO}} = |n\bar{n}p\bar{p}|$, $\Psi_{\mathrm{VB}} = |(n-\lambda p)(\bar{n}-\lambda\bar{p})(n+\lambda p)(\bar{n}+\lambda\bar{p})|$.

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

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

$$-\lambda|p\bar{n}n\bar{n}| - \lambda^2|p\bar{n}p\bar{n}| - \lambda^2|p\bar{n}n\bar{p}| - \lambda^3|p\bar{n}p\bar{p}|$$

$$-\lambda|n\bar{p}n\bar{n}| - \lambda^2|n\bar{p}p\bar{n}| - \lambda^2|n\bar{p}n\bar{p}| - \lambda^3|n\bar{p}p\bar{p}|$$

$$+\lambda^2|p\bar{p}n\bar{n}| + \lambda^3|p\bar{p}p\bar{n}| + \lambda^3|p\bar{p}n\bar{p}| + \lambda^4|p\bar{p}p\bar{p}|$$

After eliminating all determinants having two orbitals with the same spin, there remains : $\Psi_{\mathrm{VB}} = \lambda^2|n\bar{n}p\bar{p}| - \lambda^2|p\bar{n}n\bar{p}| - \lambda^2|n\bar{p}p\bar{n}| + \lambda^2|p\bar{p}n\bar{n}|$.

After permuting the columns and changing signs accordingly, there remains : $\Psi_{\mathrm{VB}} = 4\lambda^2|n\bar{n}p\bar{p}| = \Psi_{\mathrm{MO}}$ (if one includes normalization factors).

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

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)

In short

➡ VB theory :

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

Part 2. *Ab initio* Valence Bond

Overview

- Brief history
- Electron correlation
- VB methods including electron correlation
- VB computation in practice
- Limits of VB theory

- 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

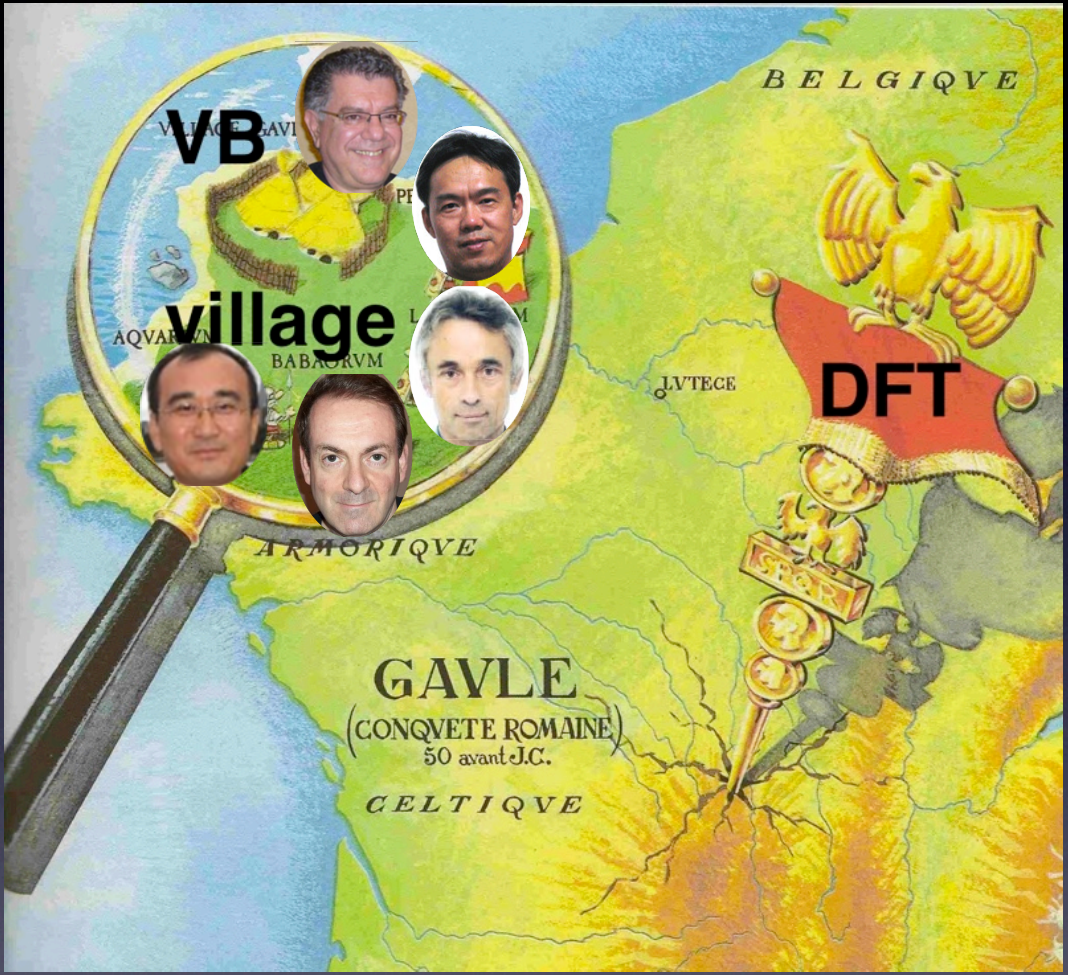
Successes of MO theory vs. VB «failures»

- ~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

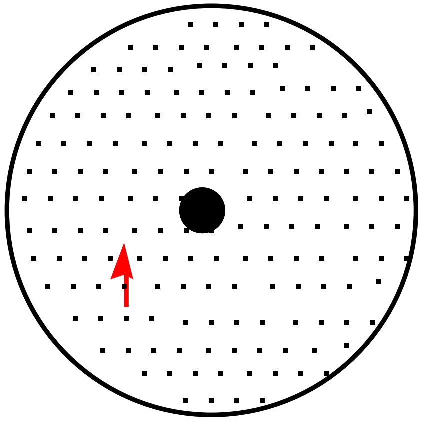
- 2012-...: awakening of the sleeping beauty?

All elements for a Valence Bond revival are ready

Electron correlation

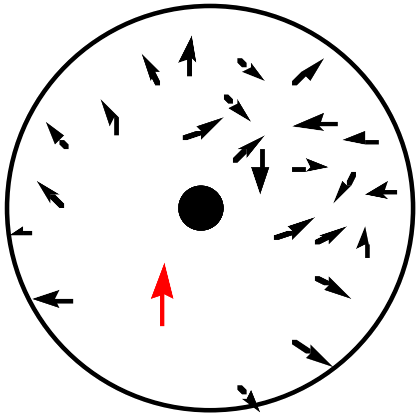
- Nature of electron correlation :
  - «Uncorrelated» (Ψ_{HF} or Ψ_{HL}) :

    Each electron feels the **mean field** created by all the other electrons



  - Correlated :

    Each electron **dynamically** affects the configuration of all the other electrons

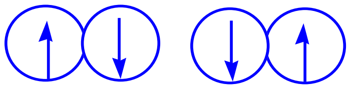


Electron correlation

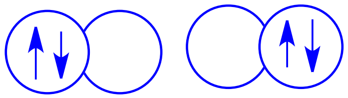
- «Uncorrelated» methods :

$$\hat{H} = \hat{T} + \hat{V}$$

Ψ_{HF} too much ionic :

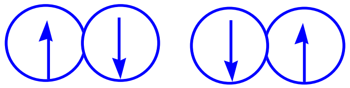


50% covalent



50% ionic

Ψ_{HL} no ionic :



100% covalent

$\hat{T}$ **is minimized** (e^- visit a larger box)

$\hat{V}_{ee}$ too large (high probability to find e^- in the same place)

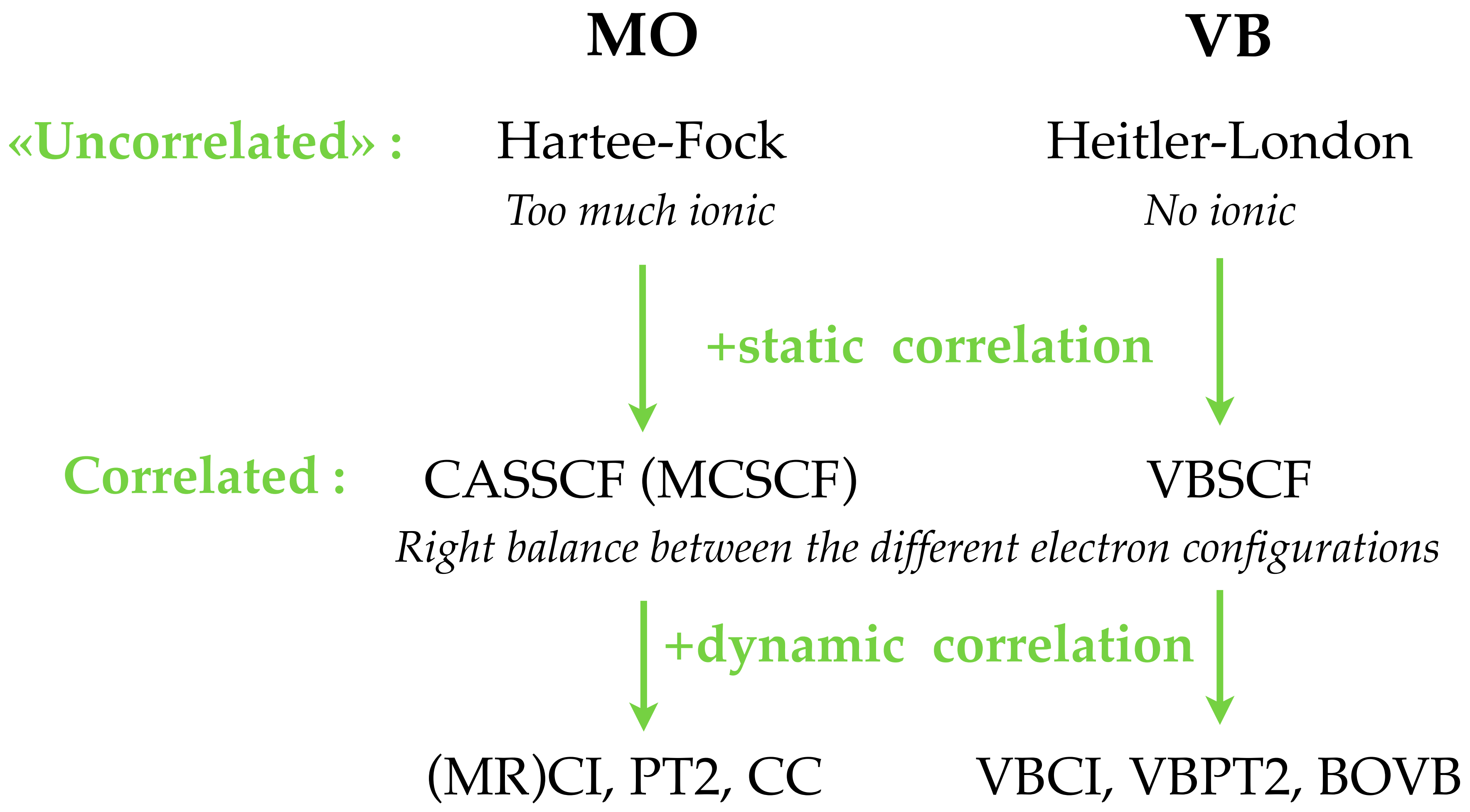
$\hat{T}$ too large (e^- visit a small box)

$\hat{V}_{ee}$ **is minimized** (low proba. to find e^- in the same place)

➡ The optimum is a balance between the two : role of electron correlation

Electron correlation

- Methods including electron correlation :



MO **VB**

«Uncorrelated» : Hartee-Fock Heitler-London

Too much ionic *No ionic*

+static correlation

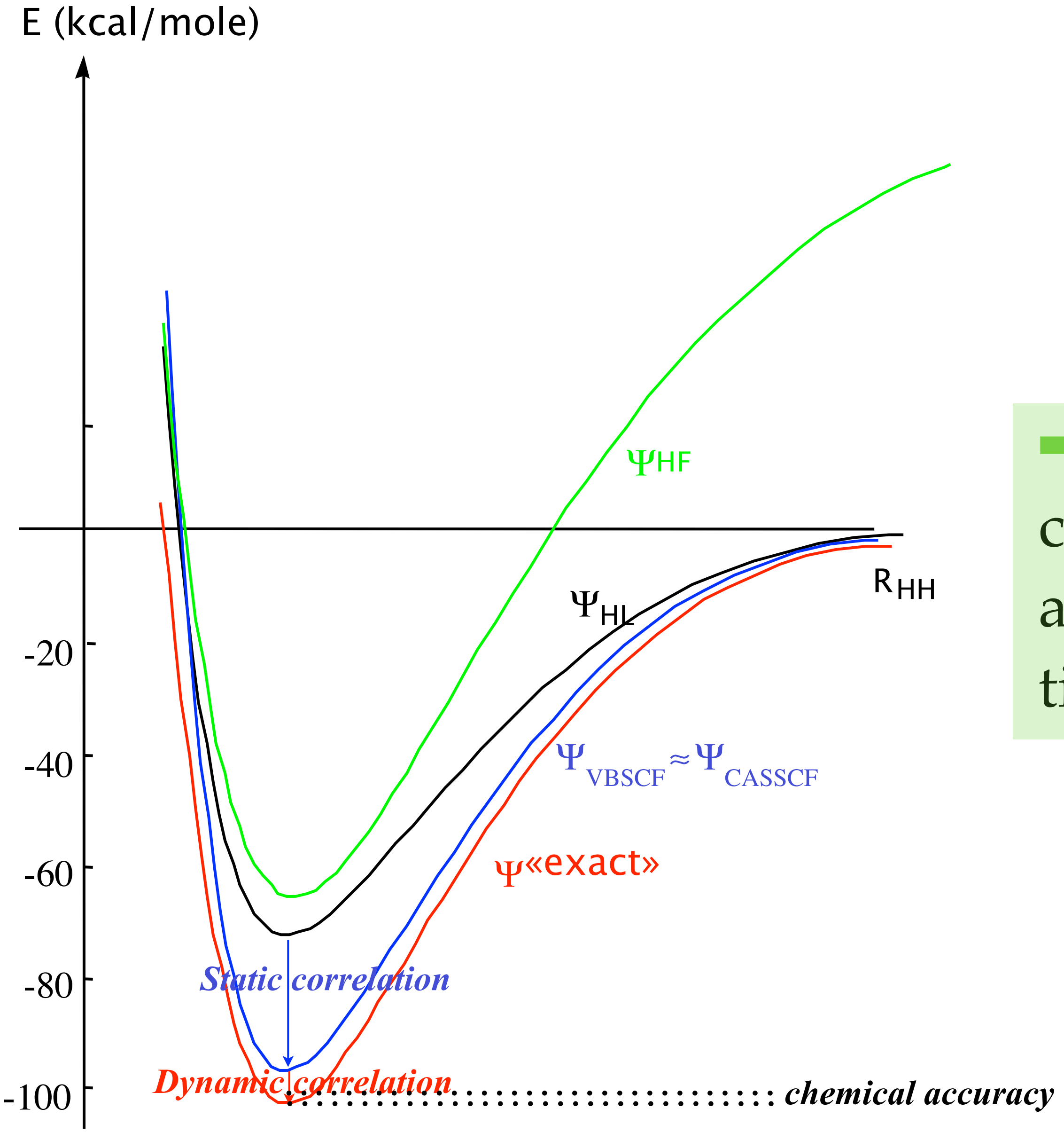
Correlated : CASSCF (MCSCF) VBSCF

Right balance between the different electron configurations

+dynamic correlation

(MR)CI, PT2, CC VBCI, VBPT2, BOVB

Electron correlation



➡ Including electron correlation is a tough problem, as we are dealing with very tiny energy differences

VB methods including correlation

- **The VBSCF method**
- **The BOVB method**
- **The VBCI method**

VB methods including correlation

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

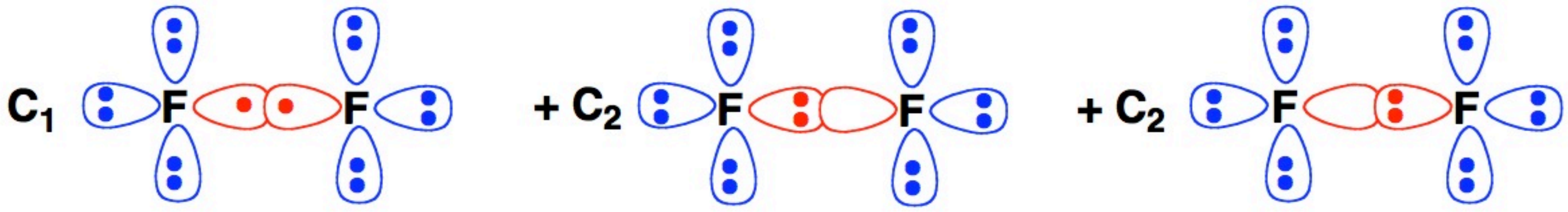
$$\boxed{\Psi_{VBSCF} = \sum_K C_K \Phi_K} \quad \text{with :} \begin{cases} \Phi_K(1,\ldots,N) = \hat{A}\{\prod_{i=1}^{N} \varphi_i(1)\Theta_K\} : \text{VB structures} \\ \{\varphi_i\} : \text{set of non-orthogonal (del)localized orbitals} \\ \qquad \text{expanded onto a set of basis functions } \{\chi_m\}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

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 :**

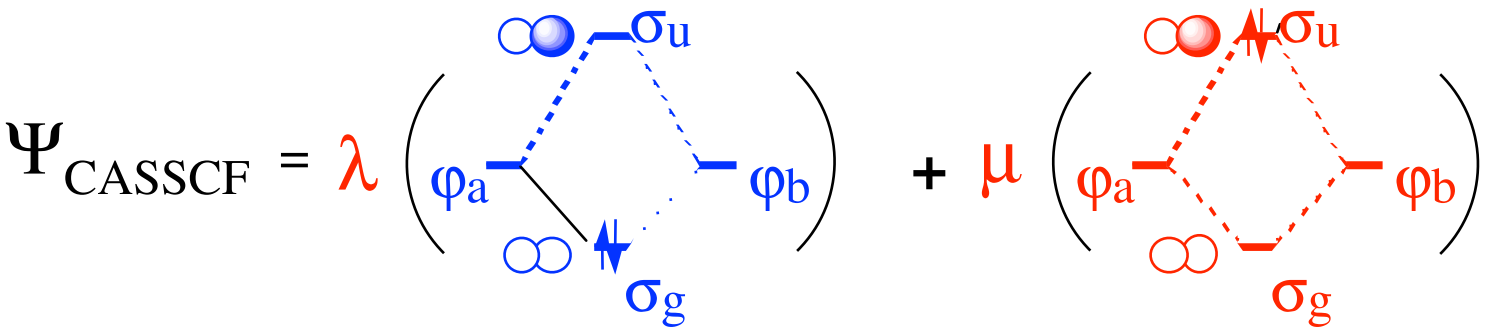


	F•—•F	F^-F^+	F^+F^-
HF :	50%	25%	25%
HL :	100%	0%	0%
VBSCF :	**80%**	**20%**	**20%**

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

VB methods including correlation

- **The VBSCF method :**
  - Comparison with CASSCF method :



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

$$|\sigma_u \bar{\sigma}_u| = |\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a| - |\varphi_a \bar{\varphi}_a| + |\varphi_b \bar{\varphi}_b|$$

➡ VBSCF and CASSCF identical (in minimal basis set)

$$\Psi_{CASSCF} = \mathbf{C_1} |\sigma_g \bar{\sigma}_g| + \mathbf{C_2} |\sigma_u \bar{\sigma}_u| = \boxed{\Psi_{VBSCF}}$$

VB methods including correlation

- **The VBSCF method :**
  - Accuracy :

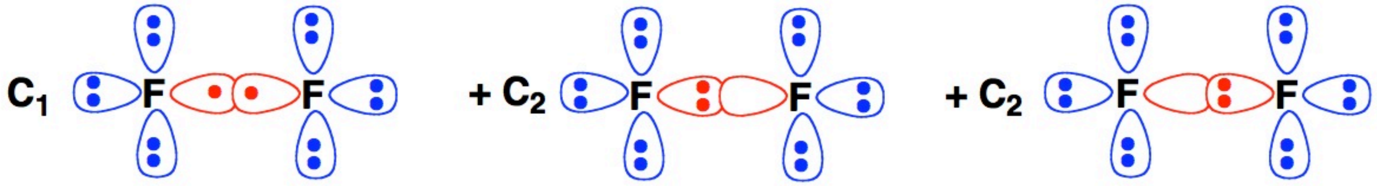
$$F{-}F \xrightarrow{\Delta E} F\bullet + F\bullet$$

	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 :



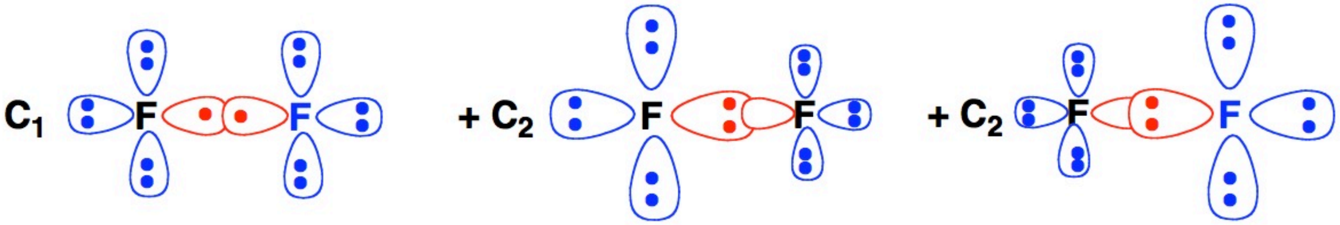
F•—•F

F^-F^+

F^+F^-

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

  - A better wave function would be :



Each structure has its own specific set of orbitals

VB methods including correlation

- **The BOVB* method :**

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

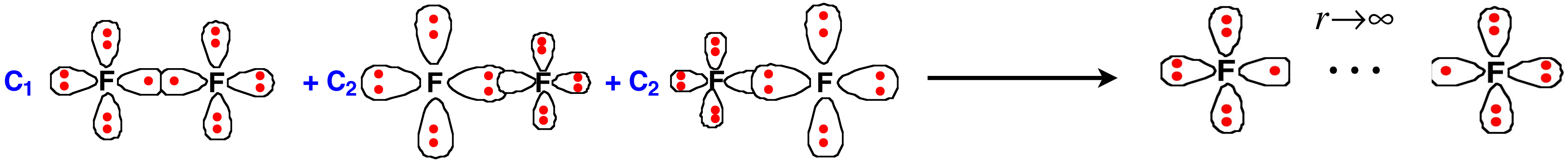
$$\boxed{\Psi_{BOVB} = \sum_K C_K \Phi_K^{BOVB}} \quad \text{with :} \begin{cases} \Phi_K^{BOVB}(1,\ldots,N) = \hat{A}\{\prod_{i=1}^{N} \varphi_i^K(1)\Theta_K\} \text{ : VB structures} \\ \{\varphi_i^K\} \text{ : set of non-orthogonal (del)localized orbitals for the structure K} \\ \quad \text{expanded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

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 :**
    - BOVB brings that part of dynamic correlation that varies during a reaction, i.e. the **differential electron correlation** :



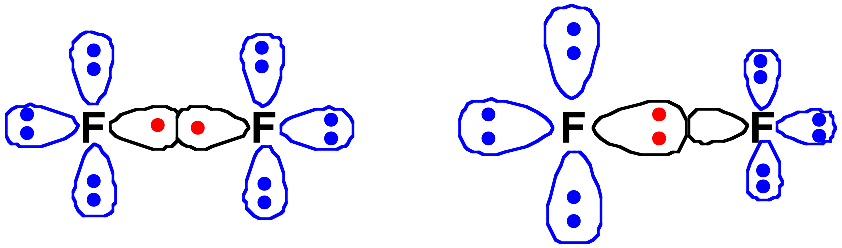
HF fragments

- BOVB keeps the same **compacity** as the VBSCF wave function
- BOVB provides a visual image of the role of electron correlation

VB methods including correlation

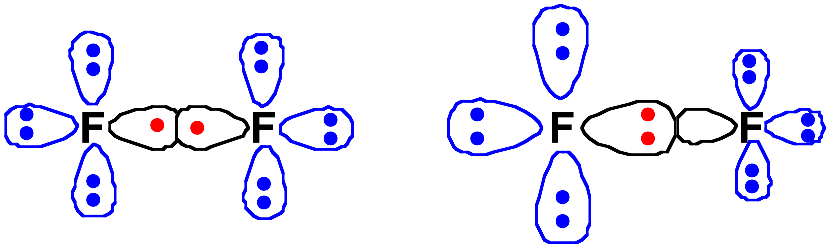
- **The BOVB method :**

- **L-BOVB :**



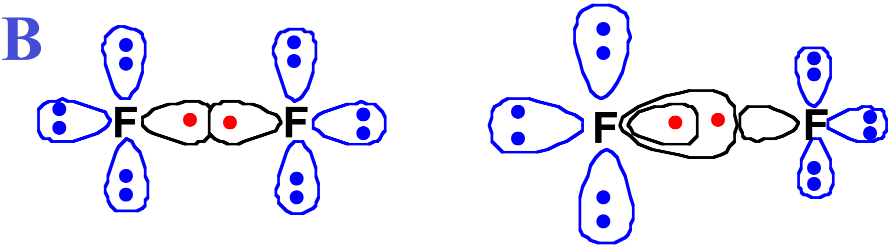
All orbitals are localized, ionics are closed-shell

- **D-BOVB :**



Spectator orbitals are delocalized in all structures

- **SD-BOVB**

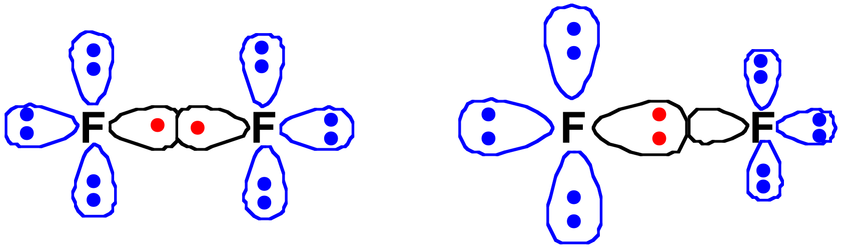


- Active orbitals are split in ionics
- Spectator orbitals are delocalized in all structures

VB methods including correlation

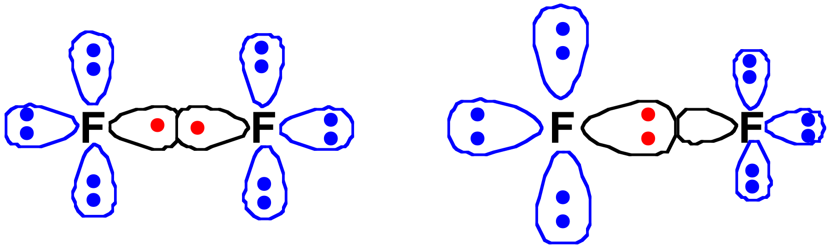
- **The BOVB method :**

- **L-BOVB :**



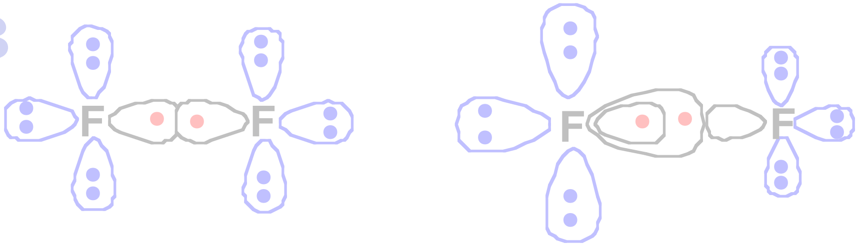
All orbitals are localized,
ionics are closed-shell

- **D-BOVB :**



Spectator orbitals are
delocalized in all structures

- **SD-BOVB**



- Active orbitals are split in ionics
- Spectator orbitals are
delocalized in all structures

VB methods including correlation

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

	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 VBCI* method :**

$$\Psi_{VBSCF} = \sum_K C_K \Phi_K^0 \qquad \Psi_{VBCI} = \sum_K C_K \Phi_K^0 + \sum_K \left(\sum_i C_K^i \Phi_K^i \right)$$

- Where Φ^0_K are the fundamental structures (obtained from VBSCF)

- and Φ^i_K are excited structures, built from Φ^0_K by replacing an occupied by a virtual orbital, but having the **same physical meaning** as Φ^0_K :

$$\Phi_K^{VBCI} = C_K \Phi_K^0 + \sum_i C_K^i \Phi_K^i$$

➡ The VBCI wave function is (much) larger than the VBSCF/BOVB one, but the interpretability is kept

* *Wu W., Song L., Cao Z., Zhang Q., and Shaik S. J. Phys. Chem. A, 2002, 106 (11), 2721-2726*

VB methods including correlation

- **The VBCI method :**

$$\Psi_{VBSCF} = \sum_K C_K \Phi_K^0 \qquad \Psi_{VBCI} = \sum_K C_K \Phi_K^0 + \sum_K \left(\sum_i C_K^i \Phi_K^i \right)$$

- Occupied orbitals are obtained from a VBSCF calculation :

$$\varphi_i^A(1) = \sum_m d_m^{i,A} \chi_m^A(1) \quad \text{where A is a molecular fragment}$$

- **Localized virtual orbitals** are generated from a Schmidt orthogonalization to occupied orbitals on their own fragments :

$$\chi'^A_m = \left(\chi_m - S_{mn} T_\nu^m S^{\mu\nu} \varphi_\mu \right)\Big|_{m,n\in A}$$

⇒ Φ^i_K keep the same physical meaning as Φ^0_K

VB methods including correlation

- **The VBCI method :**

- If a complete basis of structures is included, if all VBCI excitations (S,D,T,Q,...) are included, if basis set extended to infinity

⇒ converges to the «exact» (non-relativistic, 0K) solution of the Schrödinger equation

VB methods including correlation

- **The VBCI method :**

$$\Psi_{VBSCF} = \sum_K C_K \Phi_K^0 \qquad \Psi_{VBCI} = \sum_K C_K \Phi_K^0 + \sum_K \left(\sum_i C_K^i \Phi_K^i \right)$$

- The energy is obtained by :

$$E^{VBCI} = \frac{\left\langle \Psi^{VBCI} \middle| H \middle| \Psi^{VBCI} \right\rangle}{\left\langle \Psi^{VBCI} \middle| \Psi^{VBCI} \right\rangle} = \frac{\sum_{K,L} \sum_{i,j} C_K^i C_L^j \left\langle \Phi_K^i \middle| H \middle| \Phi_L^j \right\rangle}{\sum_{K,L} \sum_{i,j} C_K^i C_L^j \left\langle \Phi_K^i \middle| \Phi_L^j \right\rangle}$$

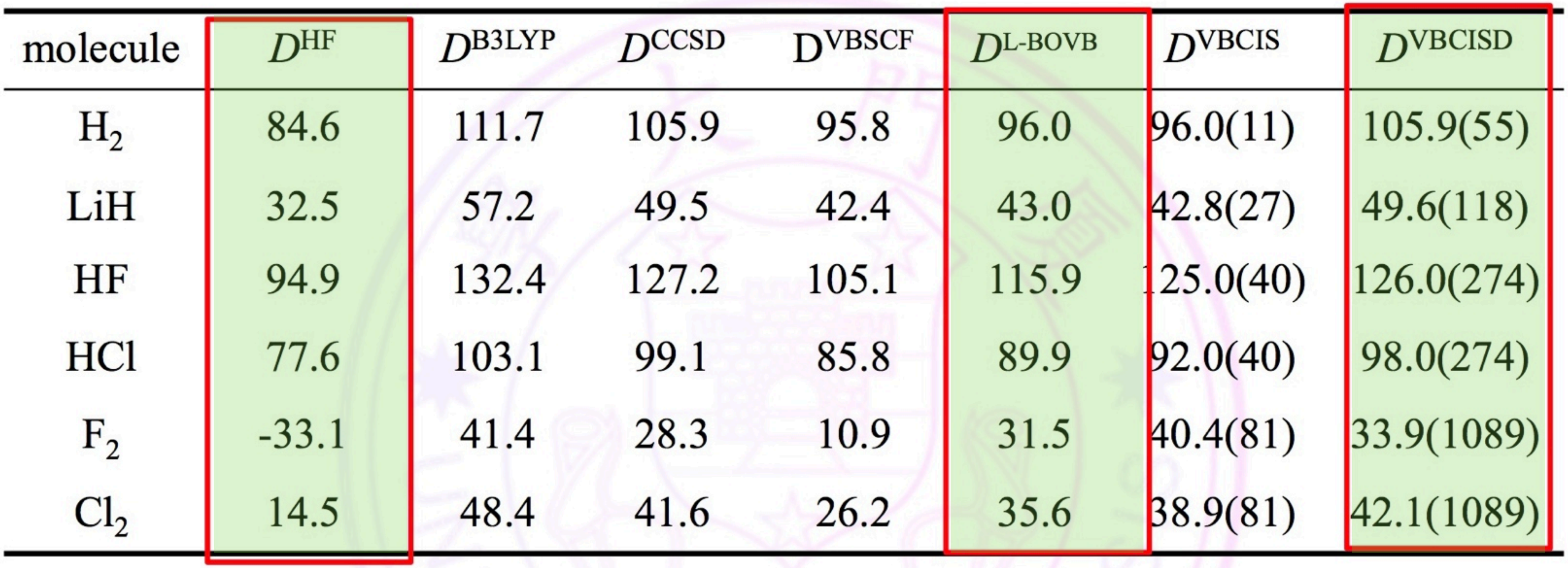
- A Davidson-type of correction to the energy also exists :

$$\Delta E_Q = (1 - \sum_K W_K) \Delta E_D \text{ with : } W_K = \sum_L \sum_{i,j} C_K^i C_L^j \left\langle \Phi_K^i \middle| \Phi_L^j \right\rangle$$

(estimate the contribution of quadruple excitations that are product of double excitations)

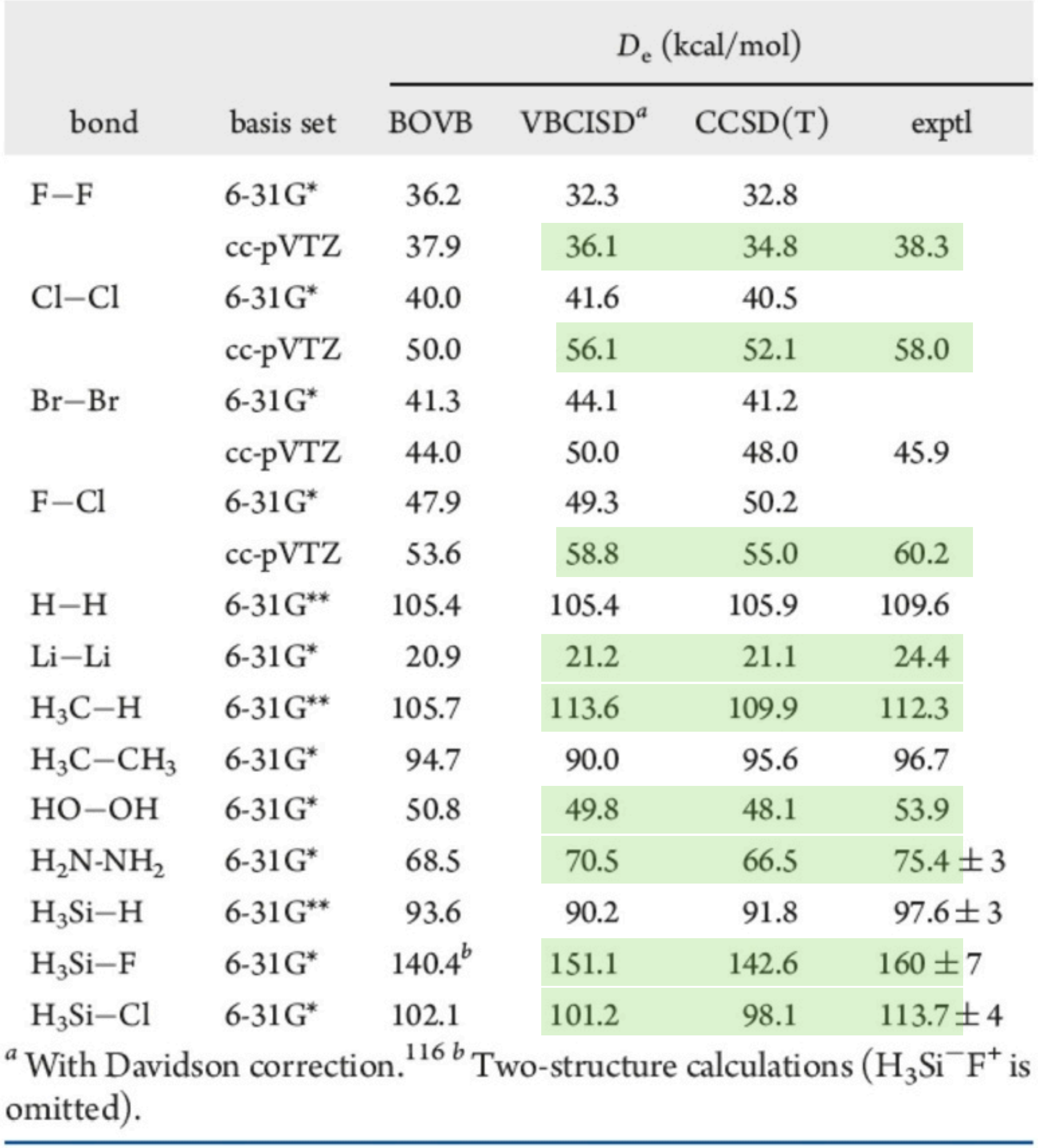
VB methods including correlation

- **Bond energies** (kcal.mol^{-1}) **with various methods :**



molecule	D^{HF}	D^{B3LYP}	D^{CCSD}	D^{VBSCF}	$D^{L\text{-}BOVB}$	D^{VBCIS}	D^{VBCISD}
H_2	84.6	111.7	105.9	95.8	96.0	96.0(11)	105.9(55)
LiH	32.5	57.2	49.5	42.4	43.0	42.8(27)	49.6(118)
HF	94.9	132.4	127.2	105.1	115.9	125.0(40)	126.0(274)
HCl	77.6	103.1	99.1	85.8	89.9	92.0(40)	98.0(274)
F_2	-33.1	41.4	28.3	10.9	31.5	40.4(81)	33.9(1089)
Cl_2	14.5	48.4	41.6	26.2	35.6	38.9(81)	42.1(1089)

VB methods including correlation



bond	basis set	D_e (kcal/mol)			
		BOVB	VBCISD[a]	CCSD(T)	exptl
F–F	6-31G*	36.2	32.3	32.8	
	cc-pVTZ	37.9	36.1	34.8	38.3
Cl–Cl	6-31G*	40.0	41.6	40.5	
	cc-pVTZ	50.0	56.1	52.1	58.0
Br–Br	6-31G*	41.3	44.1	41.2	
	cc-pVTZ	44.0	50.0	48.0	45.9
F–Cl	6-31G*	47.9	49.3	50.2	
	cc-pVTZ	53.6	58.8	55.0	60.2
H–H	6-31G**	105.4	105.4	105.9	109.6
Li–Li	6-31G*	20.9	21.2	21.1	24.4
H_3C–H	6-31G**	105.7	113.6	109.9	112.3
H_3C–CH_3	6-31G*	94.7	90.0	95.6	96.7
HO–OH	6-31G*	50.8	49.8	48.1	53.9
H_2N-NH_2	6-31G*	68.5	70.5	66.5	75.4 ± 3
H_3Si–H	6-31G**	93.6	90.2	91.8	97.6 ± 3
H_3Si–F	6-31G*	140.4[b]	151.1	142.6	160 ± 7
H_3Si–Cl	6-31G*	102.1	101.2	98.1	113.7 ± 4

[a] With Davidson correction.[116] [b] Two-structure calculations ($H_3Si^-F^+$ is omitted).

VB methods including correlation

- **The VBCI method :**

  - Very accurate (at the VBCISD+Davidson level)
  - Extremely simple to use
  - Full interpretability of the VB wave function is kept
  - but : it is very expensive...

➡ Benchmark VB method

VB methods including correlation

- **New *ab initio* VB methods in development :**

  - **(ic)VPBT2 :** very cheap, the interpretability of the VB w.f. is lost at the moment (delocalized virtual orbitals)...

  - **VBDFT :** cost «negligible» (VBSCF step), pb of double-counting of correlation effects, usual limitations of DFT

  - **VB-QMC :** very expensive but massively parallel algorithms (thousands of processors)

VB computations in practice

VB computations in practice

- **Basis of structures :**

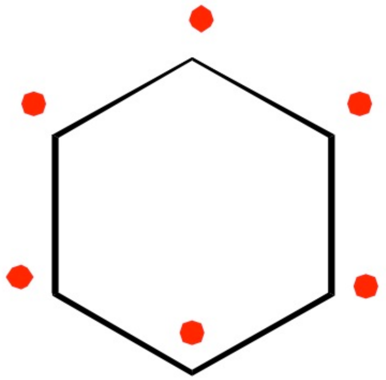
The VB w.f. is a superposition of structures (covalent, ionic,...) :

$$\Psi_{VB} = \sum_K C_K \Phi_K$$

C_K : coefficients

Φ_K : VB structures

➡ *Which structures to choose ?*



π system of benzene (**6e$^-$** in **6 orbitals**)

Three methods to generate a complete basis of structures :

- **Rumer's Rules**
- Weyl tableaux
- Young tableaux and operators

VB computations in practice

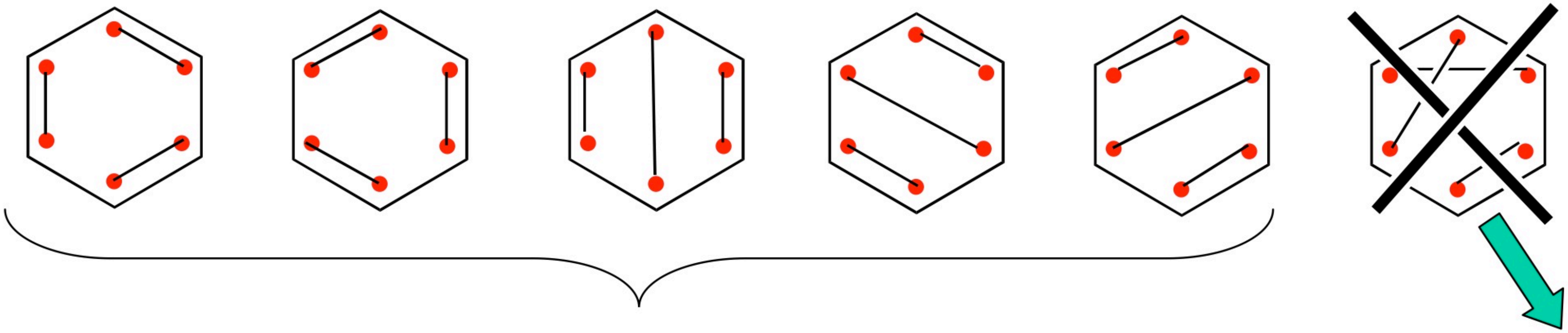
- **Basis of structures / graphical Rumer's method :**
  - Generation of a complete basis of covalent structures :

1) *Put the orbitals around an imaginary circle*
2) *Generate all possible couplings not displaying crossing bonds*

VB computations in practice

- **Basis of structures / graphical Rumer's method :**
  - Generation of a complete basis of covalent structures :

1) *Put the orbitals around an imaginary circle*
2) *Generate all possible couplings **not displaying crossing bonds***



- Complete and non-redundant set of VB structures
- VB structures are «chemically meaningful»

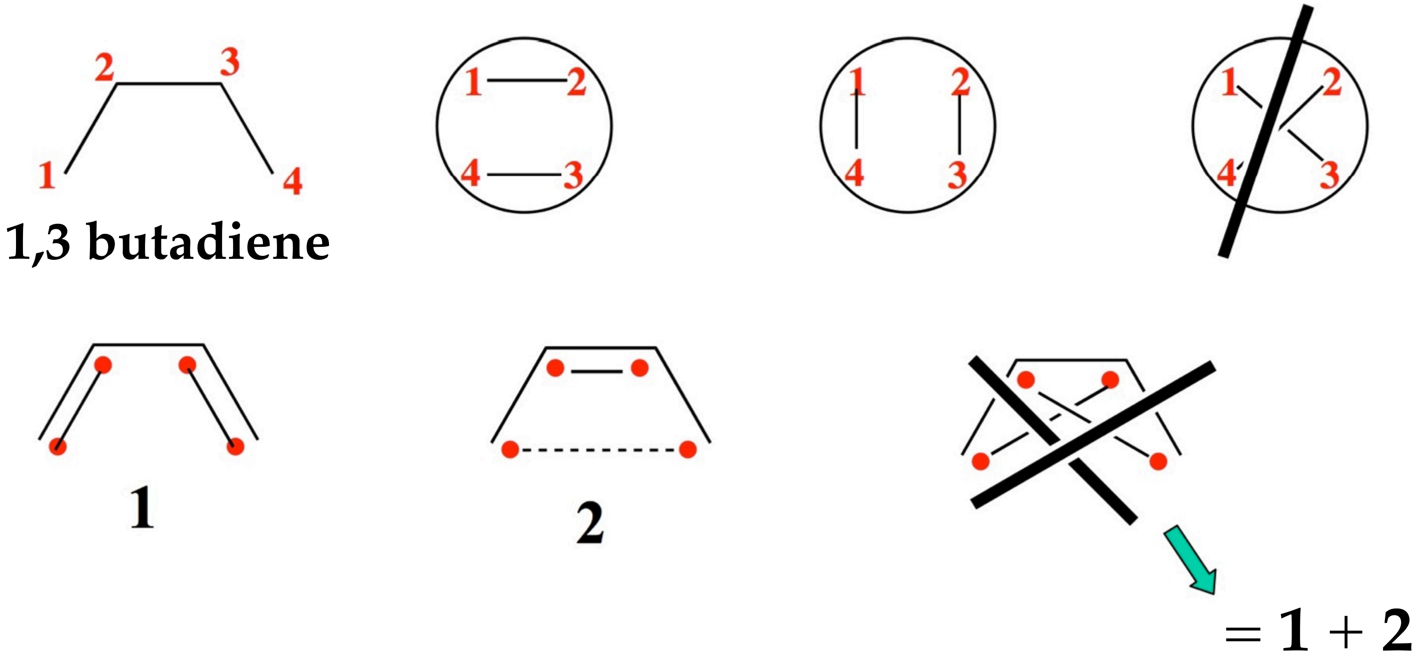
- Redundant
- «Chemically meaninless»

VB computations in practice

- **Basis of structures / graphical Rumer's method :**
  - Generation of a complete basis of covalent structures :

1) Put the orbitals around an imaginary circle

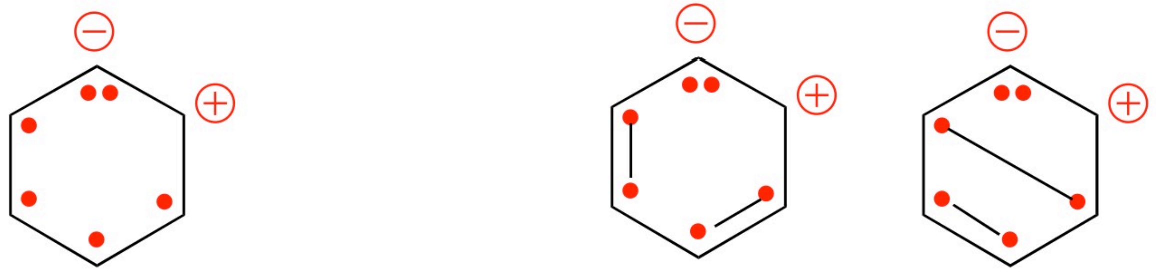
2) Generate all possible couplings not displaying crossing bonds



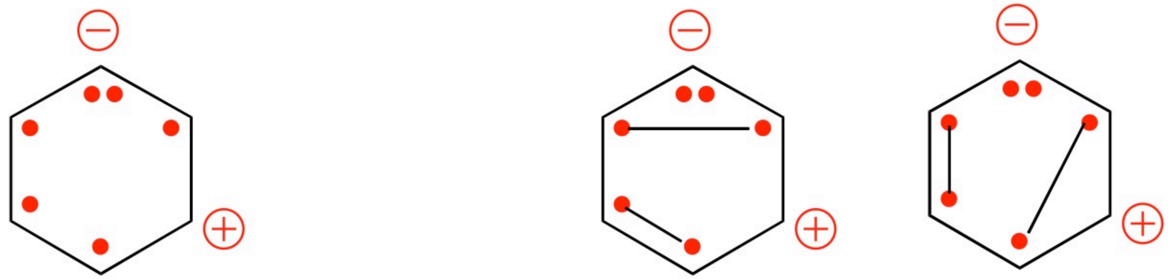
VB computations in practice

- **Basis of structures / graphical Rumer's method :**
  - Generation of a complete basis of ionic structures :

1) Choose a distribution of charges (configuration)
2) Apply Rumer's rules on the rest of the system



3) Repeat 1) and 2) for all other configurations :



and so on...

VB computations in practice

- **Basis of structures / size limit :**
  - Total number of covalent structures :

Weyl's formula: $$f_S^N = \frac{(2S+1)N!}{(\frac{1}{2}N+S+1)!(\frac{1}{2}N-S)!}.$$

N	4	6	8	10	12	…
f_S^N	2	5	14	42	132	…

Exponential wall !

  - Total number of covalent + ionic structures :

Weyl's formula : $$g_S^{N,m} = \frac{2S+1}{m+1}\begin{pmatrix} m+1 \\ \frac{N}{2}+S+1 \end{pmatrix}\begin{pmatrix} m+1 \\ \frac{N}{2}-S \end{pmatrix}$$

N=m	4	6	8	14	28
f_S^N	20	175	1764	2.76×10^6	2.07×10^{14}

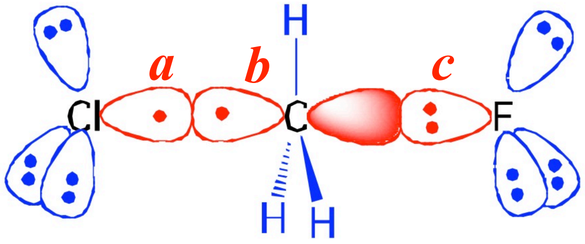
VB computations in practice

- **Choice of an active space :**
  - Not all electrons are treated at the VB level :
    - an **active space** of electrons/orbitals treated at the **VB level**
    - **the rest** (called inactive or «spectators») at the **MO level**

$$\Psi_{VB} = \sum_K C_K \Phi_K \text{ with: } \Phi_K = \left|\{inactives\}\{actives\}\right|$$

  - Active space chosen depending on the chemical problem :

Example : SN2 Transition state :
a **4-e/3-orbital** VB system



$$\Phi_1 = \left|\sigma_1\sigma_2...\sigma_9(a\bar{b} + b\bar{a})c\bar{c}\right|$$

VB computations in practice

- **Definition of the orbitals :**
  - **Active (VB)** orbitals **must always** be **strictly localized**
  - **Inactive (MO)** orbitals are preferably **delocalized**

➡ **Exercise 3 :**

1) We consider a Heitler-London wave-function for H_2 made of two orbitals φ_a and φ_b partly delocalized onto the other center : $\varphi_a = a + \varepsilon b$, $\varphi_b = b + \varepsilon a$, with a and b (strictly localized) atomic orbitals *a* and *b*.

2) Expand this wave-function in a basis of the atomic orbitals.

3) Is it legitimate to also incorporate ionic structures to this w.f. ?

VB computations in practice

- **Definition of the orbitals :**

➡ **Exercise 3 :**

$$\Psi = \left|\varphi_a \overline{\varphi_b}\right| + \left|\varphi_b \overline{\varphi_a}\right| = \left|(a+\varepsilon b)\overline{(b+\varepsilon a)}\right| + \left|(b+\varepsilon a)\overline{(a+\varepsilon b)}\right|$$

$$= \ldots = (1+\varepsilon^2)\underbrace{\left(\left|a\bar{b}\right| + \left|b\bar{a}\right|\right)}_{\text{covalent}} + 2\varepsilon\underbrace{\left(\left|a\bar{a}\right| + \left|b\bar{b}\right|\right)}_{\text{ionic}}$$

- Active orbitals delocalized ⇒ ionic structures ***implicitely*** included (GVB / Spin Coupled methods)

- Active orbitals delocalized + explicit ionic structures ⇒ **redundancies** in the wave functions (instabilities,...)

➡ **Active (VB)** orbitals **must always** be **strictly localized**

VB computations in practice

- **Chemical insight / structure weights :**

From computed {C$_K$} coefficients : $\Psi_{VB}(1,\ldots,N)=\sum_K C_K \Phi_K(1,\ldots,N)$

we can extract {W$_K$} structure weights which verify : $\boxed{\sum_K W_K = 1}$

➡ quantification of the statistical importance of the ≠ structures
usually expressed in % (100W$_K$)

- Most used : **Chirgwin-Coulson weights** :

$$\langle \Psi_{VB} | \Psi_{VB} \rangle = \sum_K \sum_I C_K C_I S_{KI} = 1 \Rightarrow \boxed{W_K = C_K^2 + \sum_{I \neq K} C_K C_I S_{KI}} \quad \text{with: } S_{KI} = \langle \Phi_K | \Phi_I \rangle$$

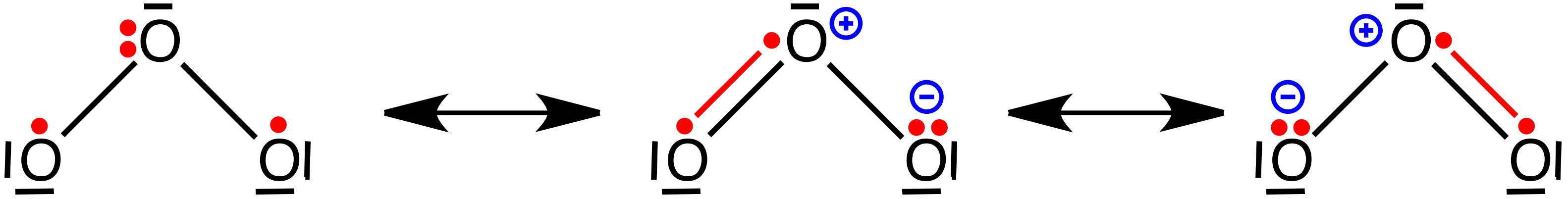
- Other options : Hiberty, Lowdin, Gallup (inverse) weights

VB computations in practice

- **Chemical insight / structure weights :**

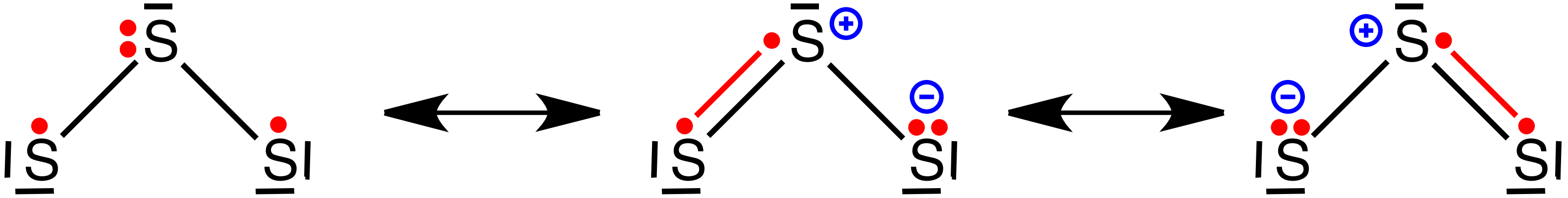
<u>Ex :</u> reactivity of ozone vs. trisulfur :

Very reactive



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

Not reactive



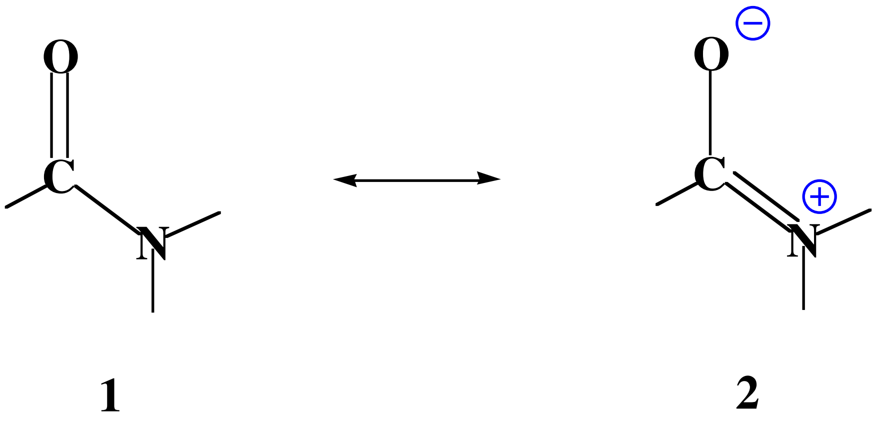
8% **24%** **24%**

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

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



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

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

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

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

R.E. = 37 kcal/mol

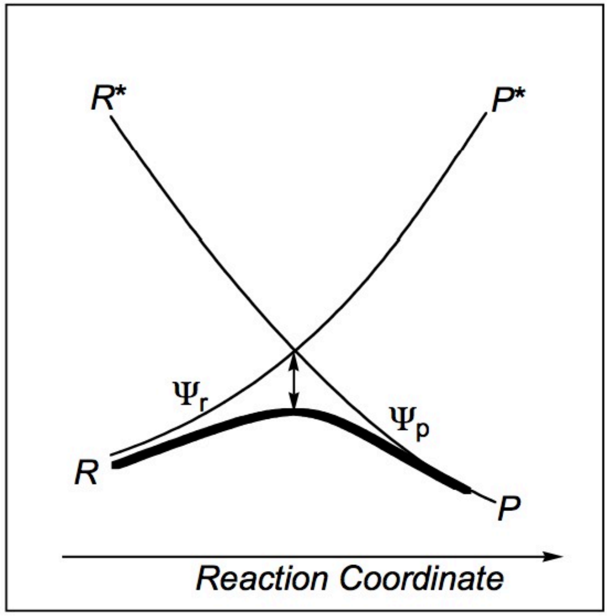
⇒ formamide rotation barrier is due to π resonance energy

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 :



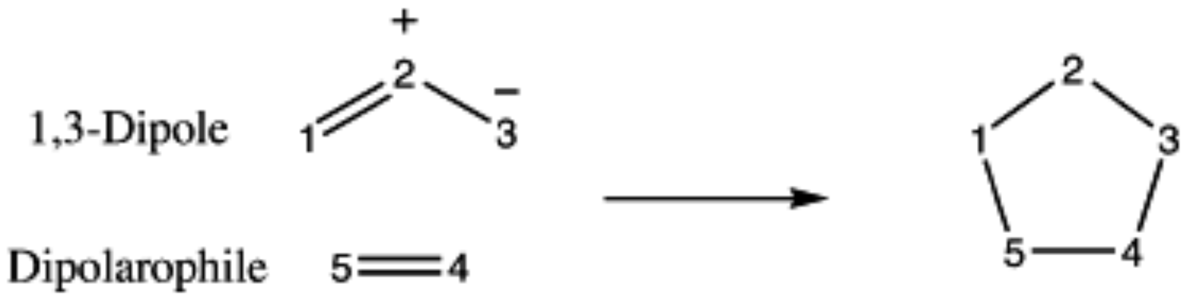
Part 4. lecture

Application

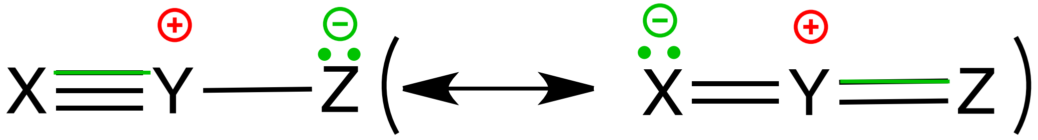
1,3-dipolar cycloadditions

1-3 dipolar cycloadditions

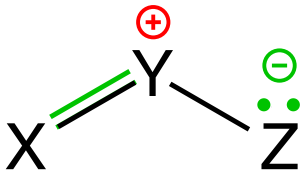
- Method for heterocyclic compounds synthesis :



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



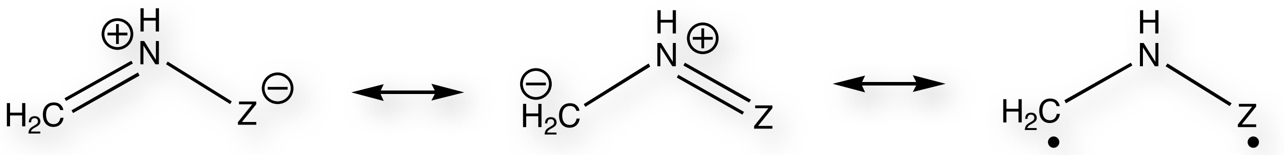
Propargylic (N_2O,...)



Allylic (O_3,...)

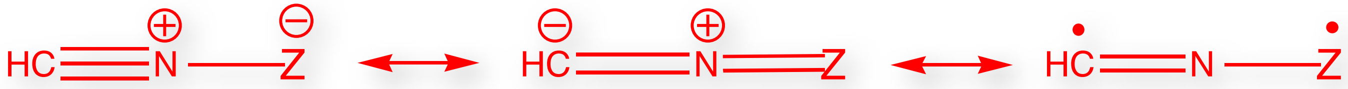
Some families of dipoles

Azomethine betaines :



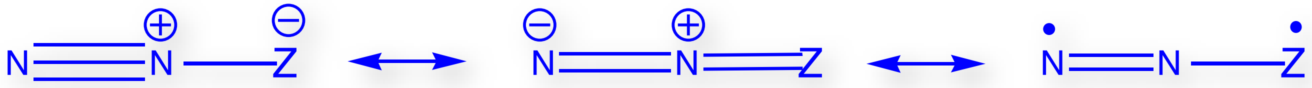
$Z = O, NH, CH_2$

Nitrilium betaines :



$Z = O, NH, CH_2$

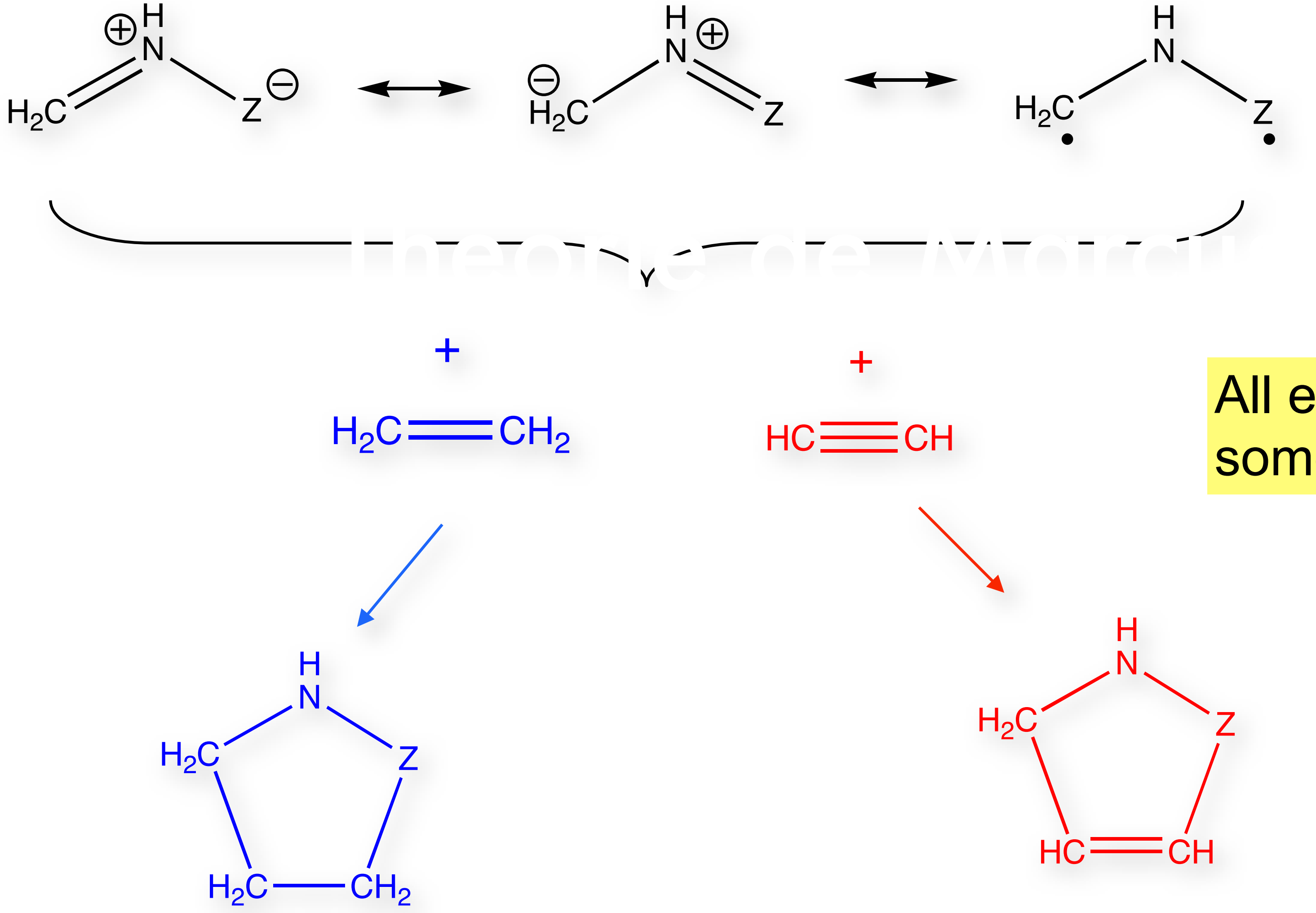
Diazonium betaines :



$Z = O, NH, CH_2$

Reactions studied

- Dipolarophiles : ethylene et acetylene :

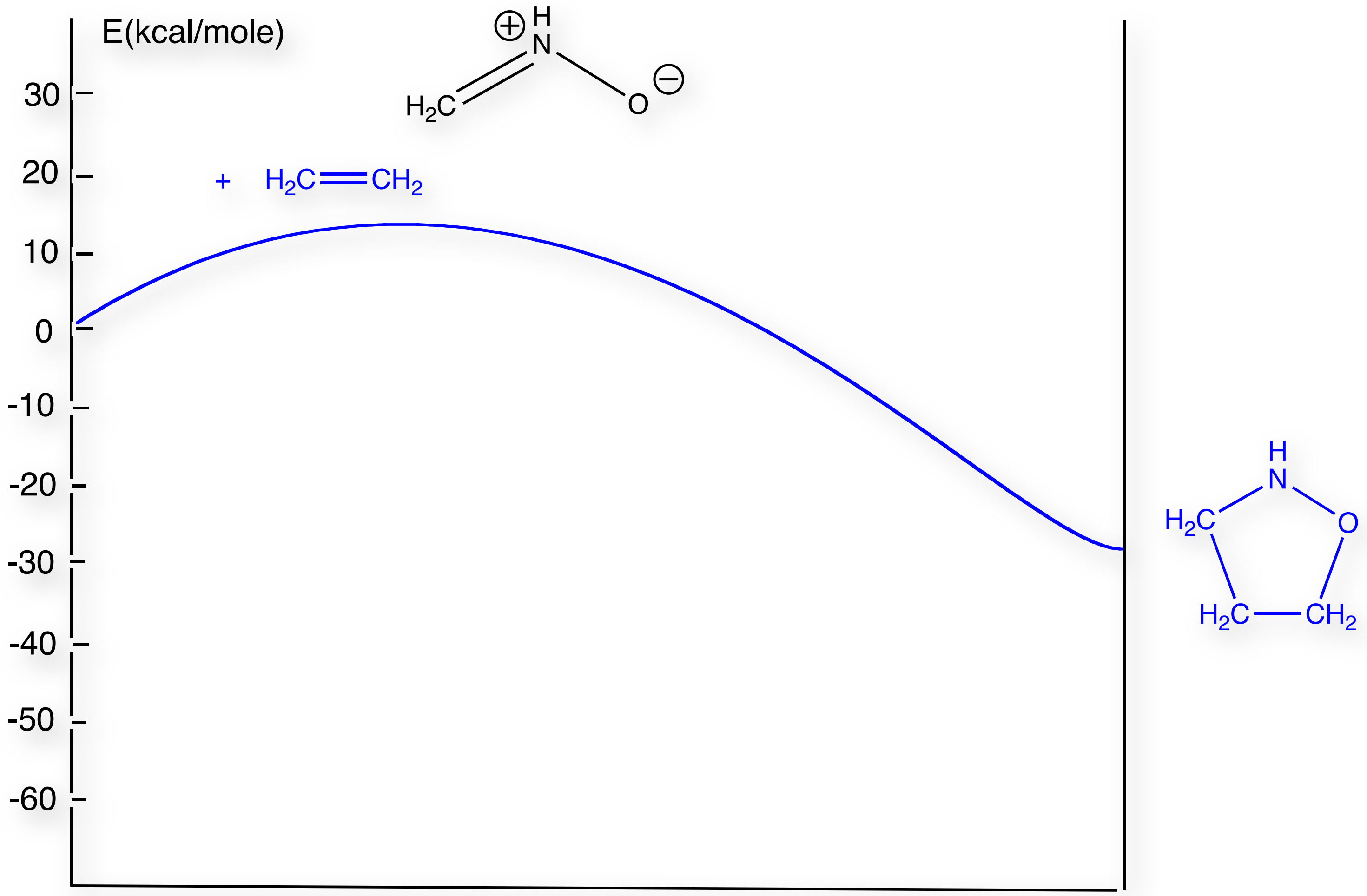


Z = O, NH, CH_2

All exothermic, but something funny…

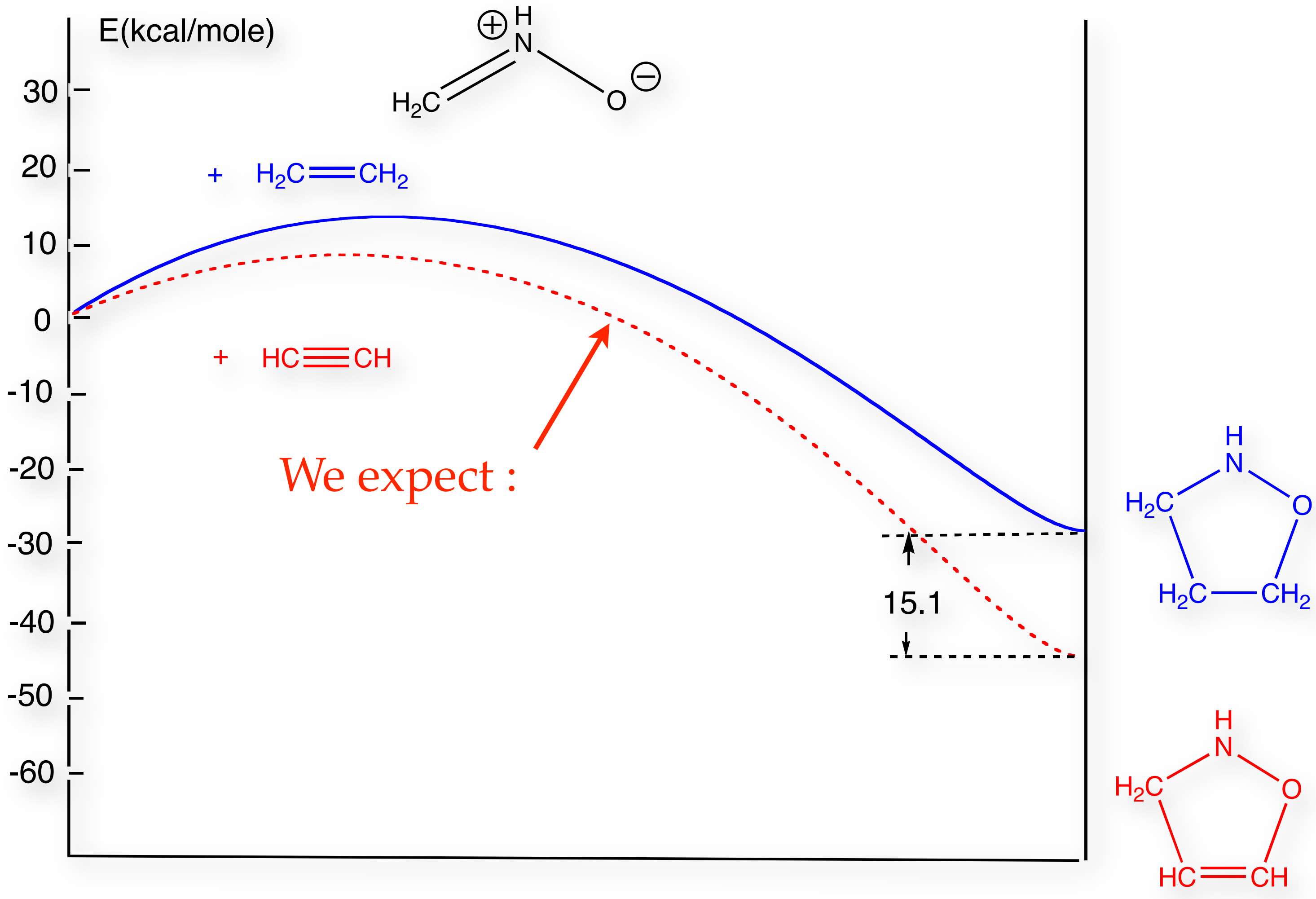
Marcus theory ?

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



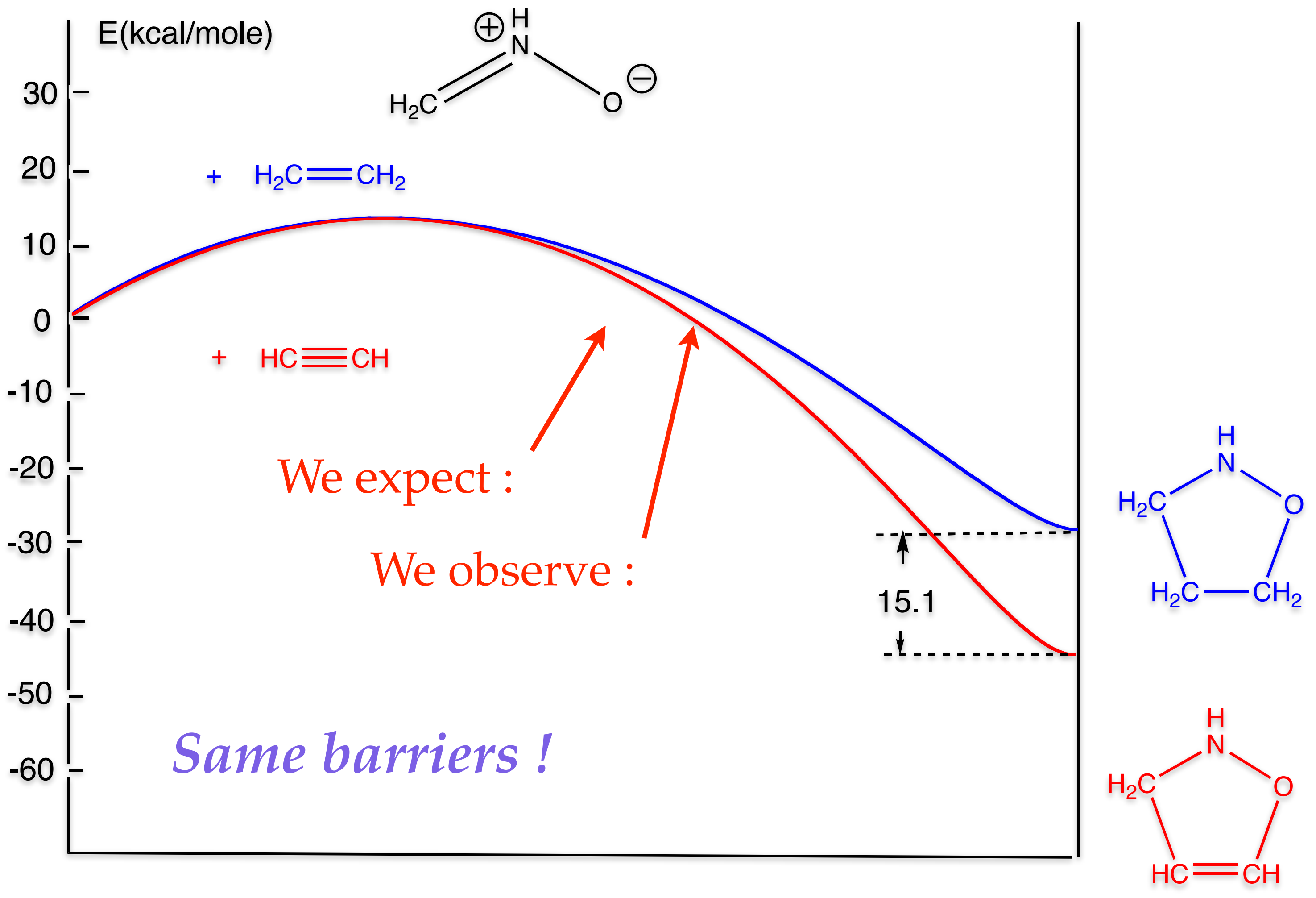
Marcus theory ?

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



Marcus theory ?

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



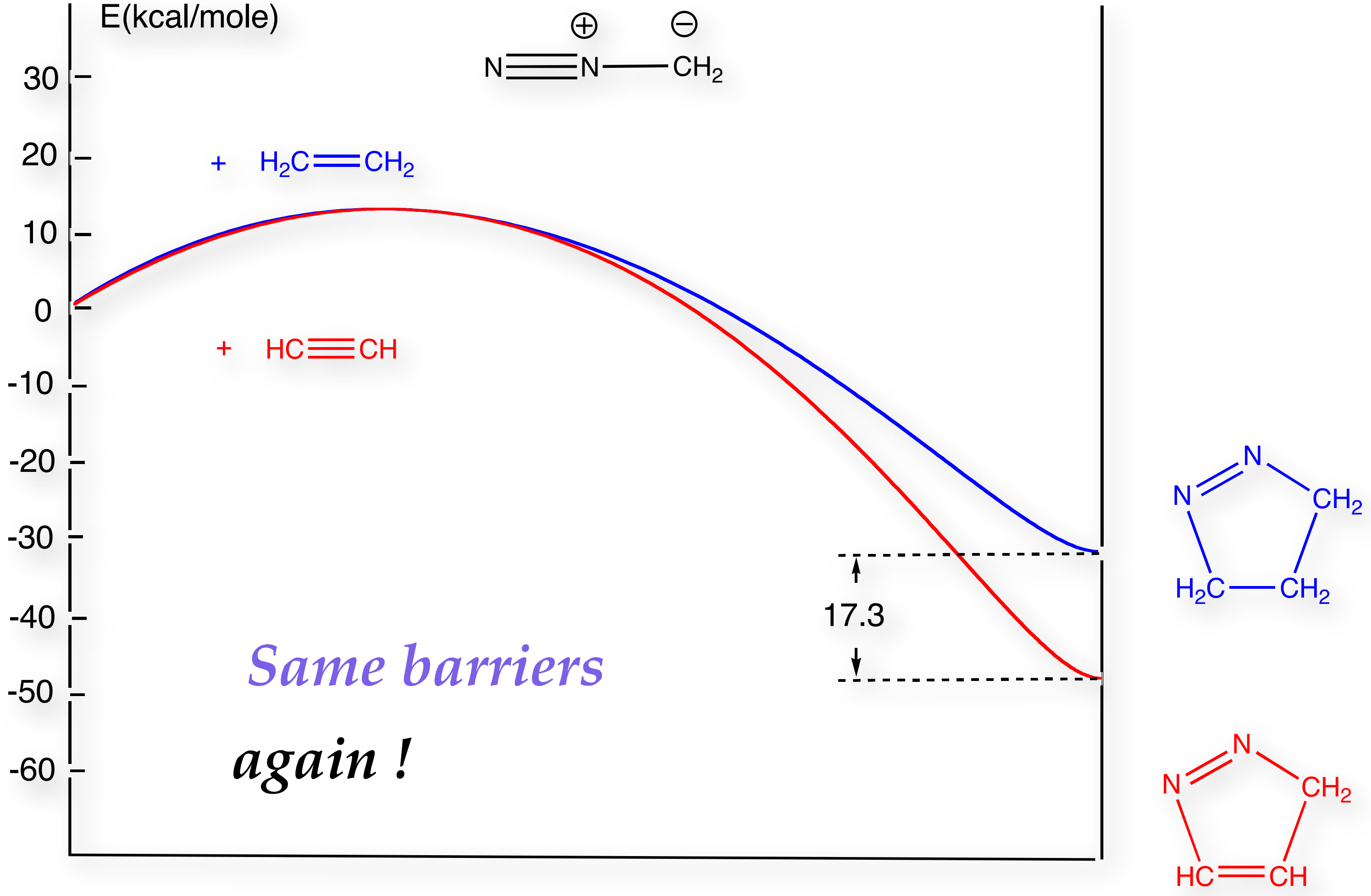
We expect :

We observe :

Same barriers !

Marcus theory ?

- **Propargylic** dipole

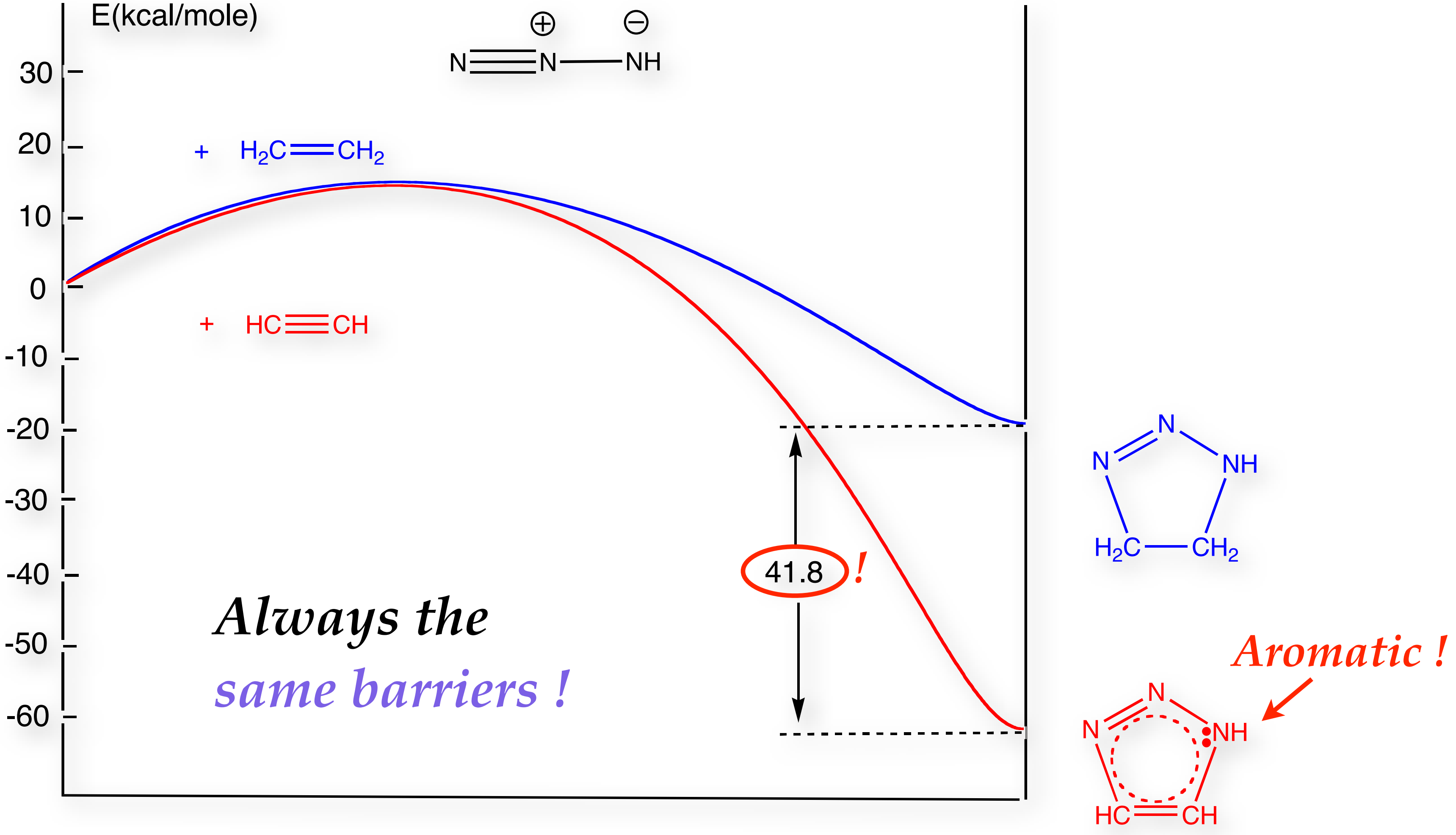


Same barriers

again !

Marcus theory ?

- **Propargylic** dipole

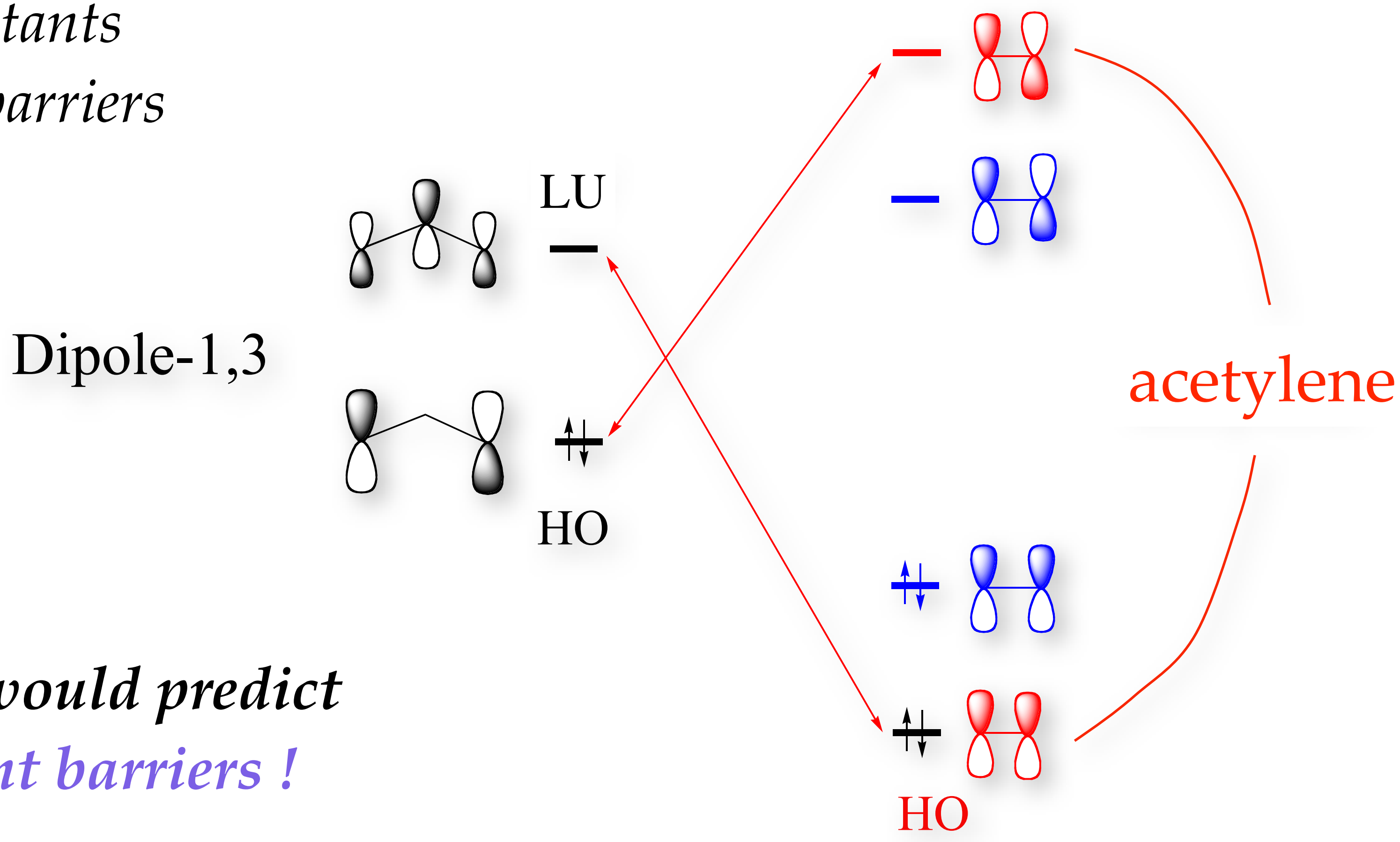


Always the
same barriers !

FMO theory ?

Small HOMO-LUMO energy difference between reactants

=> small barriers

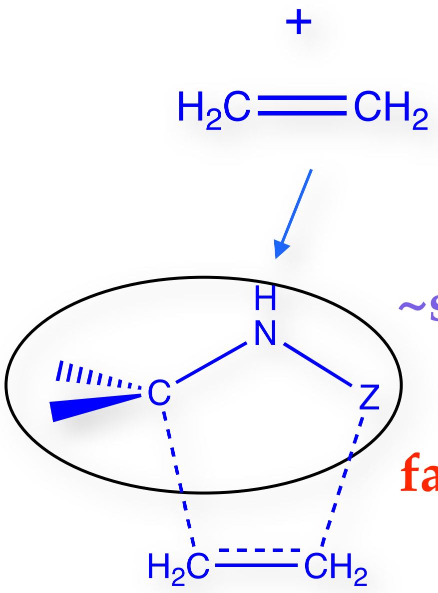


***FMO** would predict*

different barriers !

Hammond principle ?

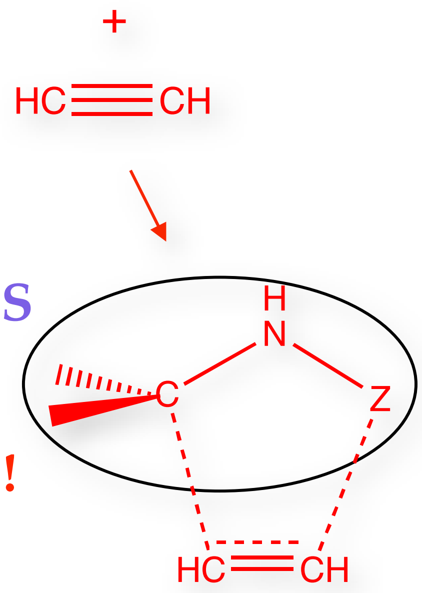
- All dipoles **distort** when going to TS :



~same dipole geometries at TS

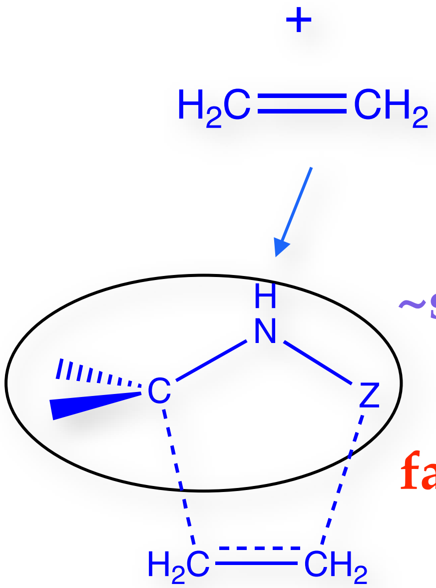
(systematic)

falsifies Hammond principle !



Hammond principle ?

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



~same dipole geometries at TS

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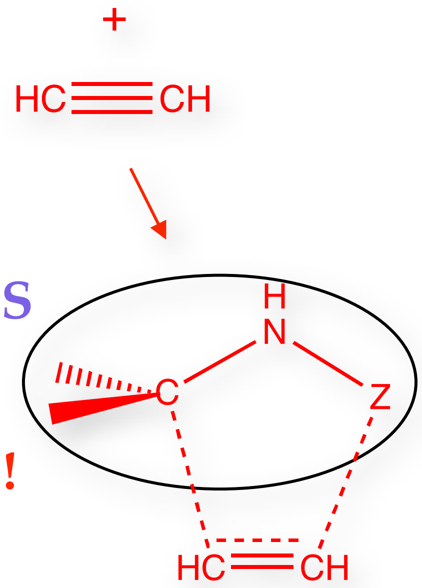


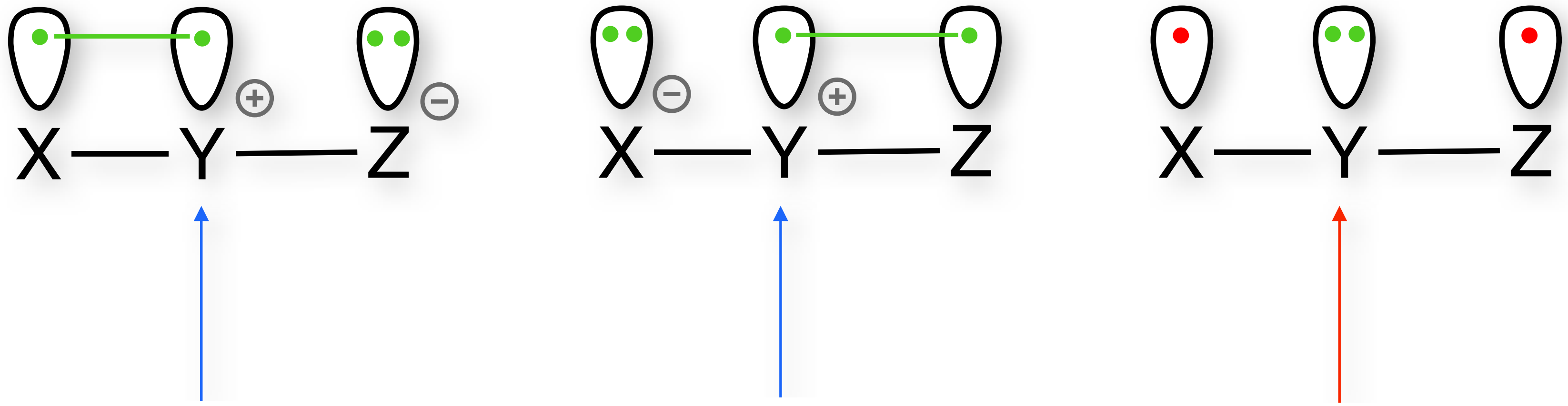
Ess & Houk* : barriers only depend on dipole distortion energies

… 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

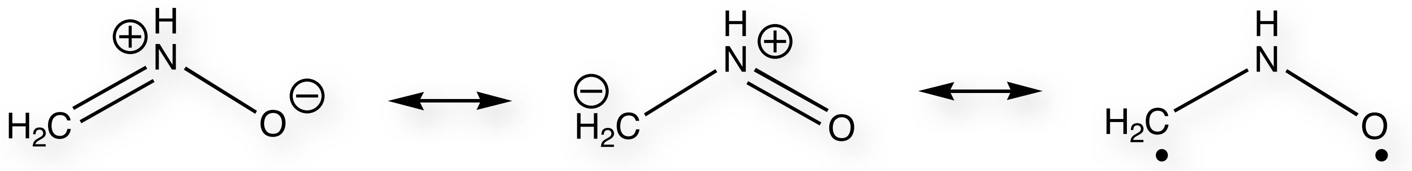
Reactive

- 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) :



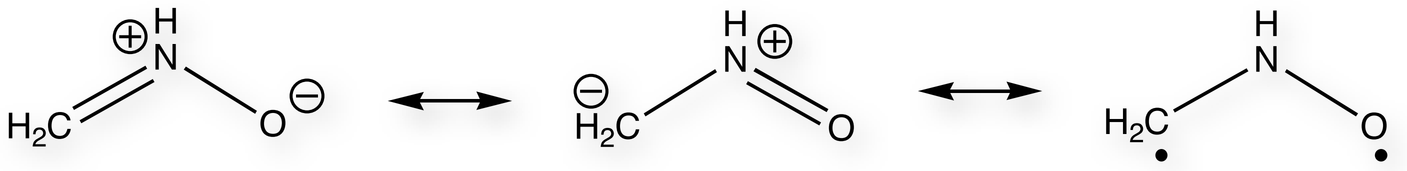
Reactants : 48,4% 18,0% 33,7%

- 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%

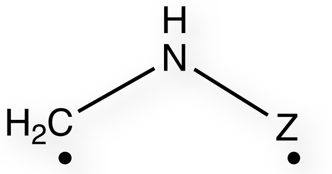
- Diradical character is important !

- Diradical character increases from reactants → TS !

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

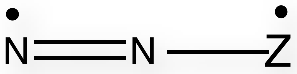
Ab initio VB calculations

- Importance of the diradical structure (BOVB calculations) :



	Reactants :	TS :
Z = O	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

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

Ab initio VB calculations

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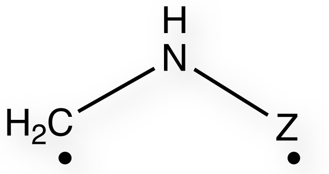	$Z = O$	33.7	38.6
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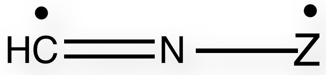	$Z = O$	21.3	32.1
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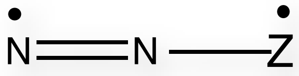	$Z = O$	21.6	31.6
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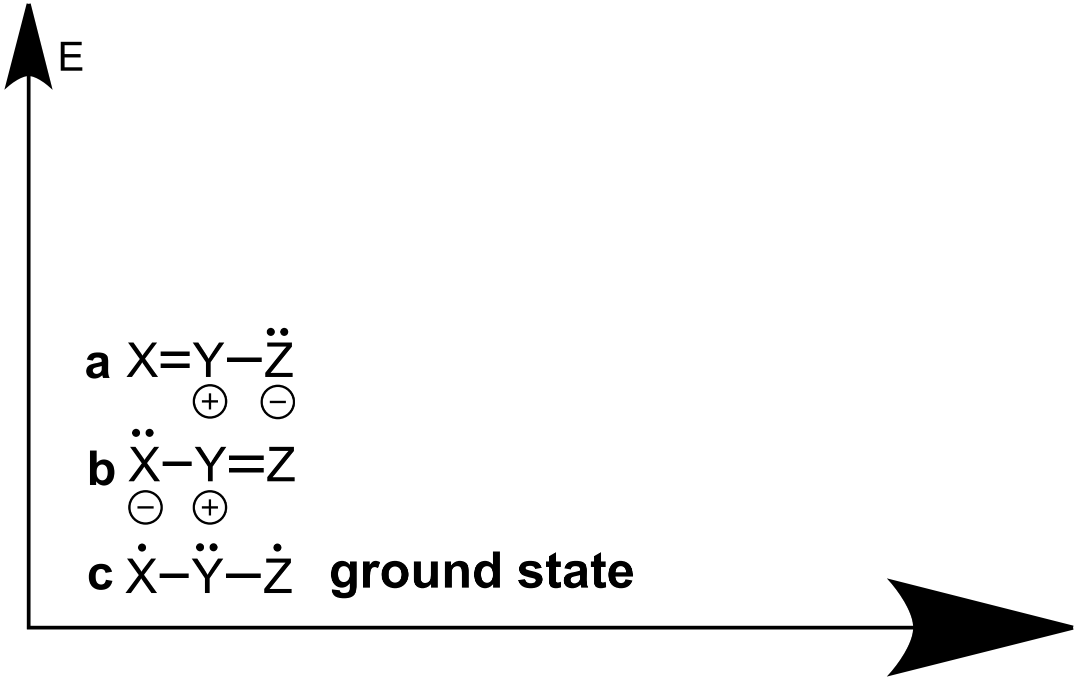
	$Z= CH_2$	27.7	36.4

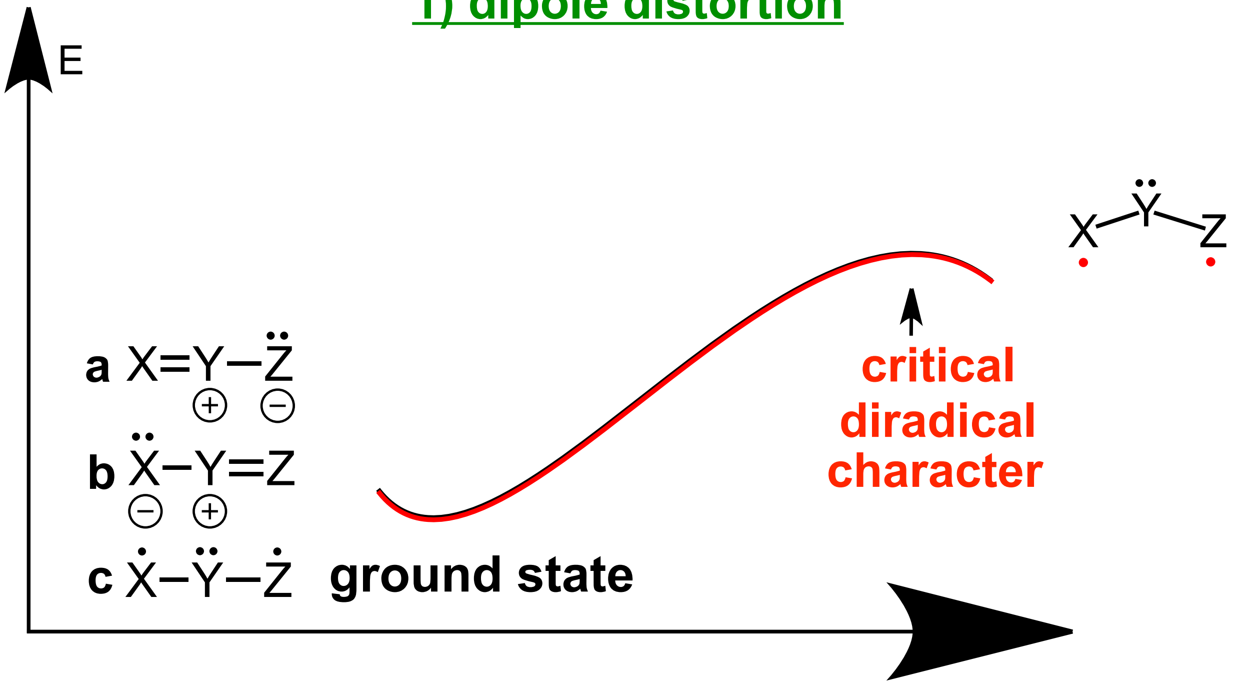
What if... dipole distortion would serve to
increase the diradical character ?...

Ab initio VB calculations



Ab initio VB calculations

1) dipole distortion

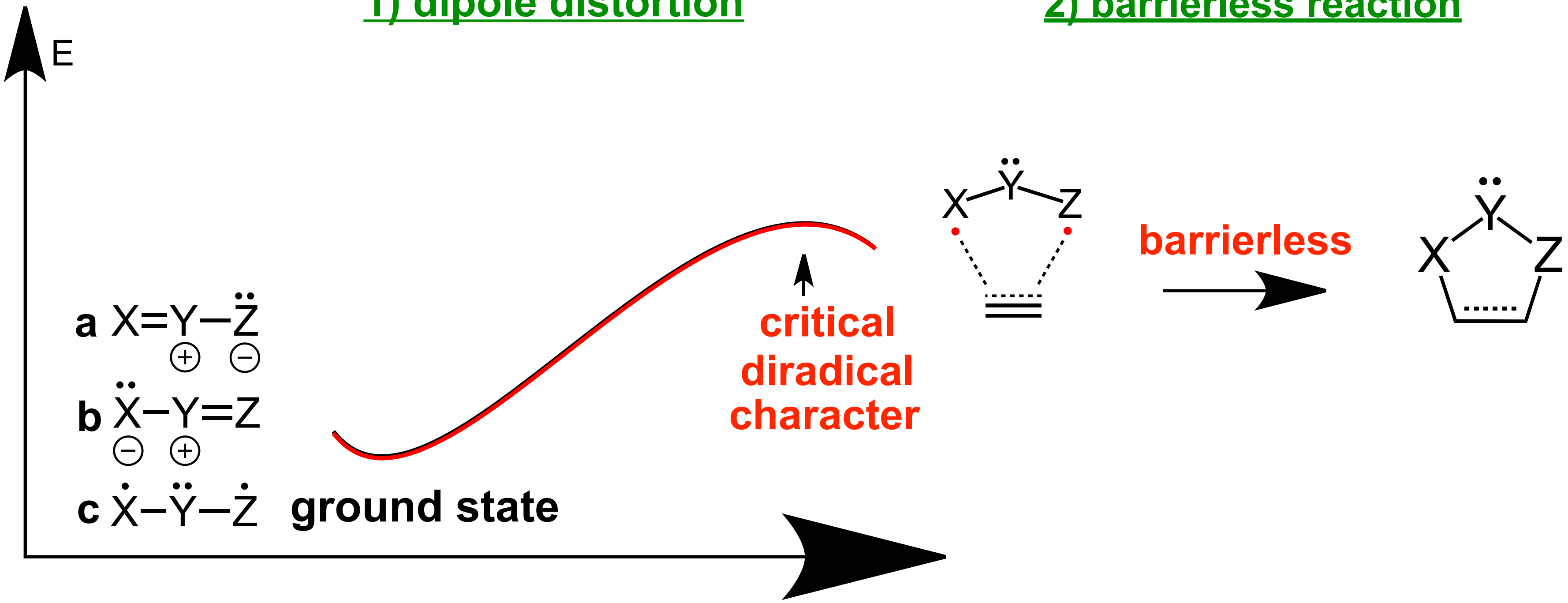


1) Dipole distortion ⟶ reach a **«critical» diradical character**

Ab initio VB calculations

1) dipole distortion

2) barrierless reaction



E

a X=Y−$\ddot{Z}$ ⊕ ⊖

b $\ddot{X}$−Y=Z ⊖ ⊕

c $\dot{X}$−$\ddot{Y}$−$\dot{Z}$ **ground state**

critical diradical character

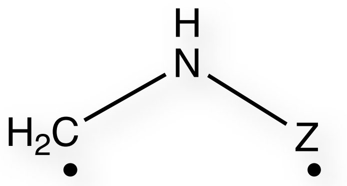
barrierless

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

2) Dienophile attack (almost barrierless) !

Ab initio VB calculations

1) If our postulated mechanism is correct :



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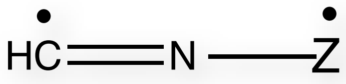

Z = O	21.3
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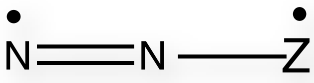


Z = O	21.6
Z = NH	25.1
Z= CH_2	27.7

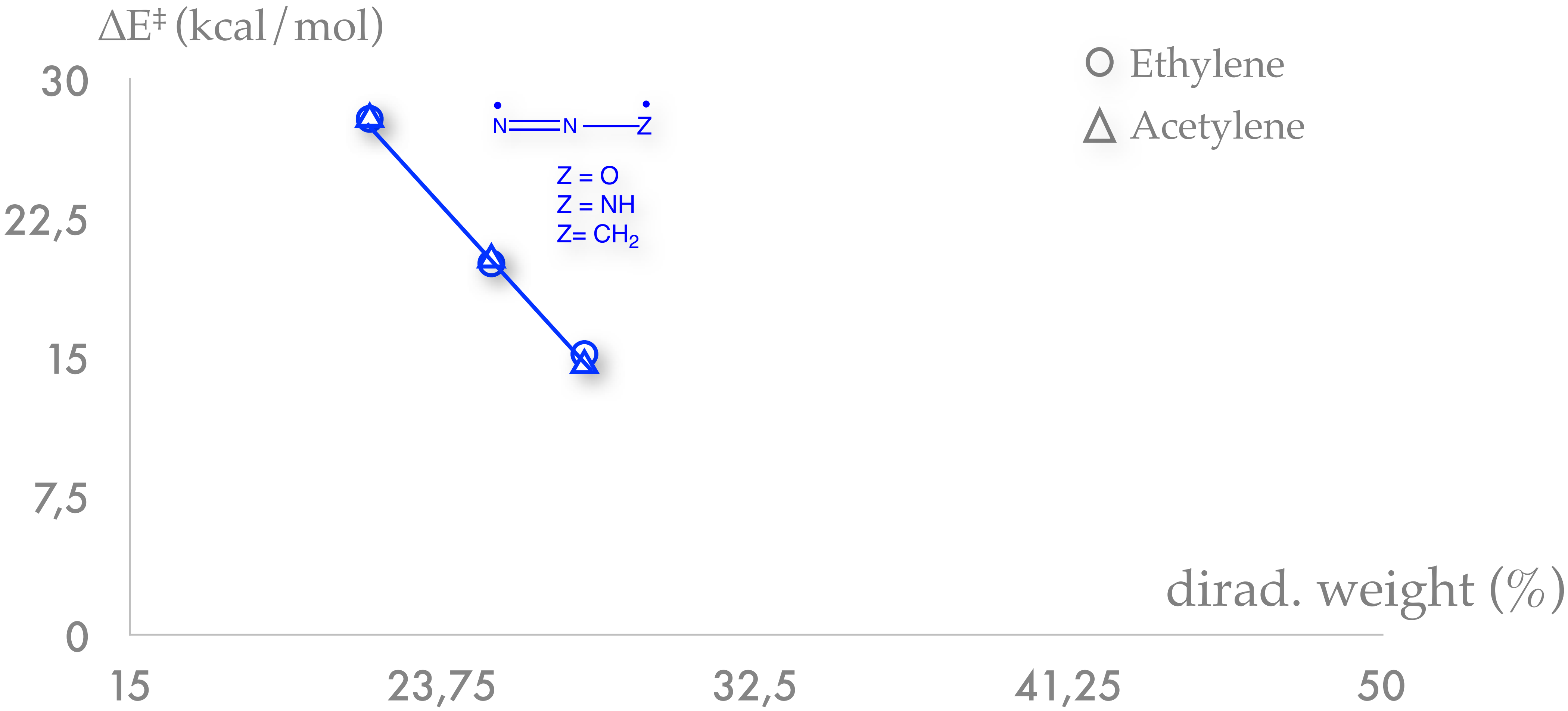
If a **«critical» diradical character** has to be reached for the reaction to proceed :

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**



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Ab initio VB calculations

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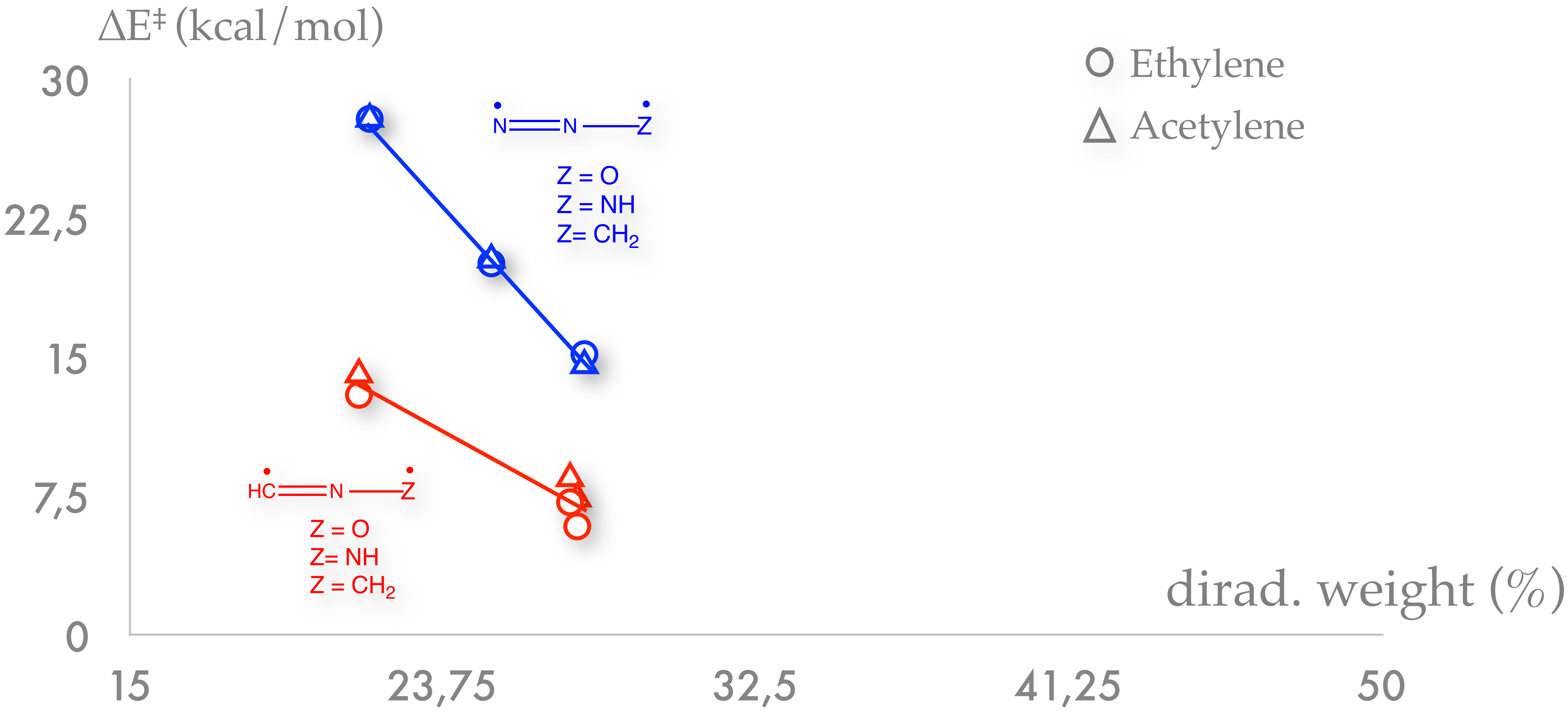

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Ab initio VB calculations

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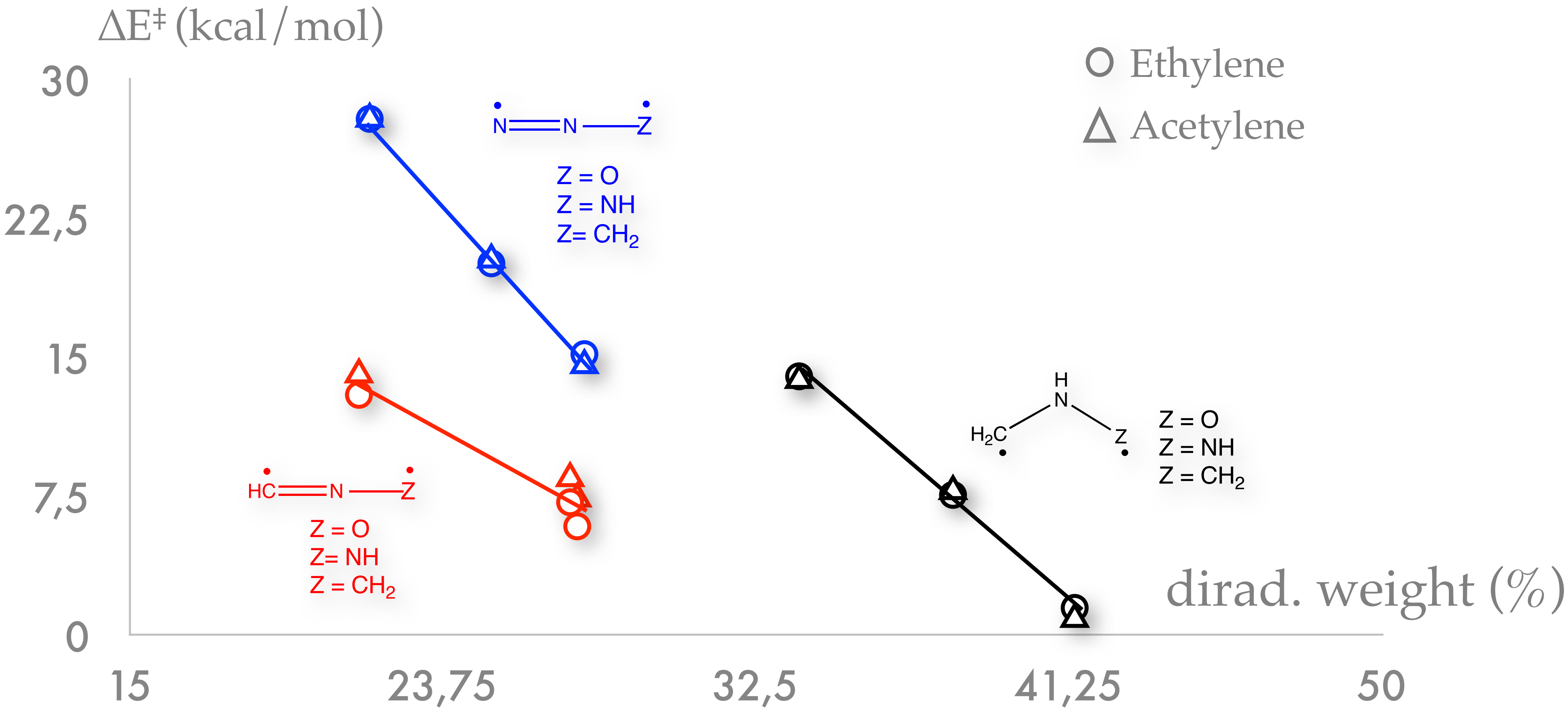

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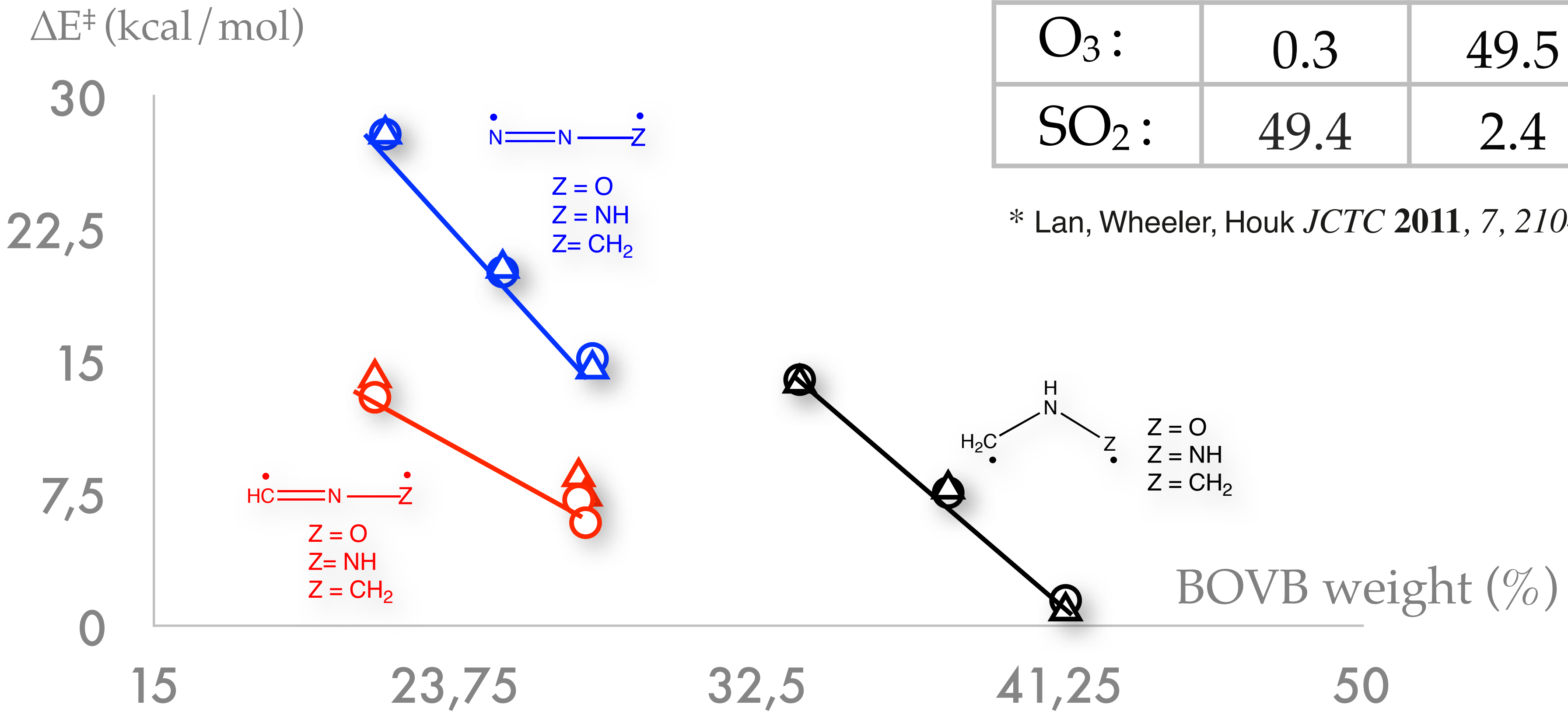
Ab initio VB calculations

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

Two extreme cases :*

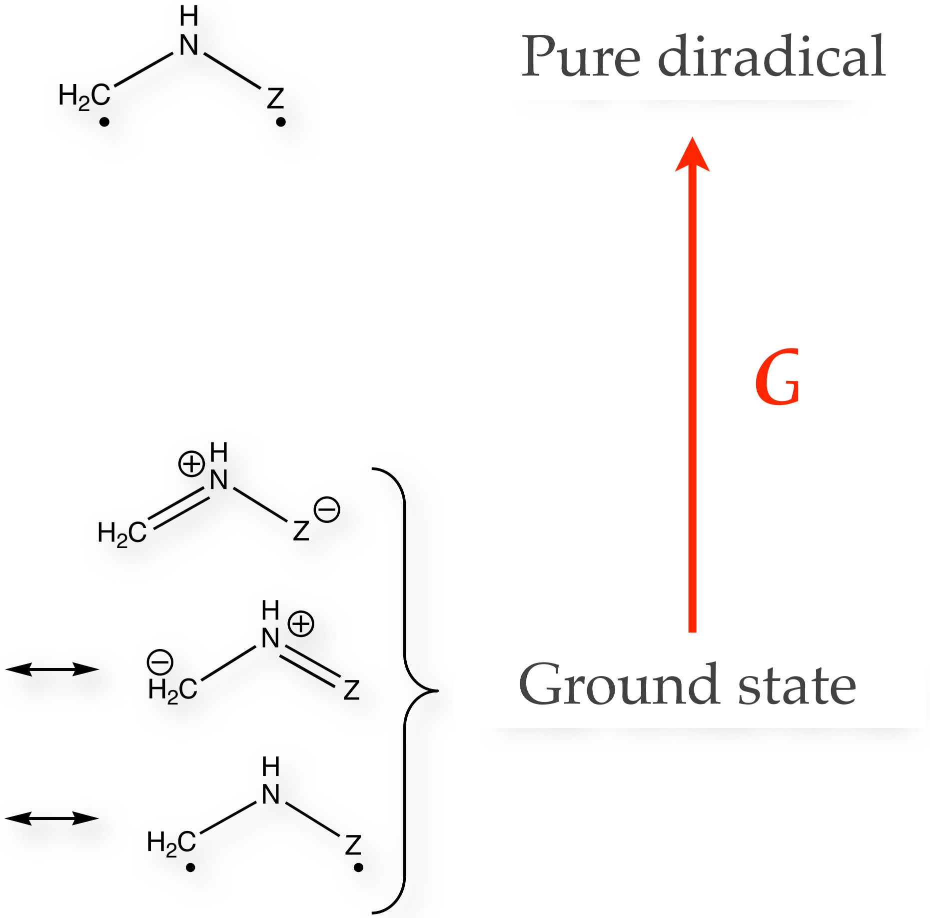
	ΔE‡	w (%)
O_3 :	0.3	49.5
SO_2 :	49.4	2.4

* 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*

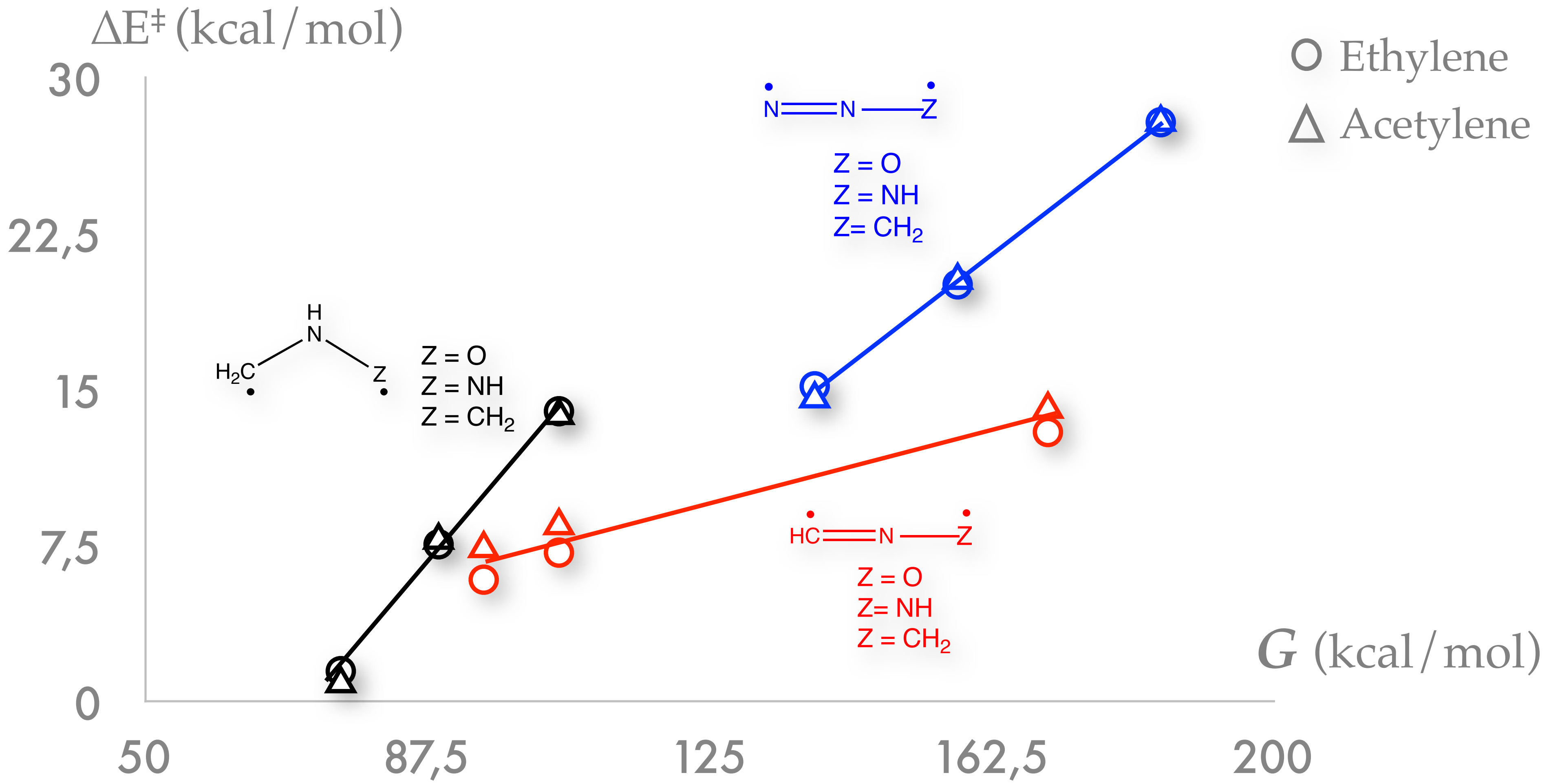
→ small $\Delta H^{‡}$

$\Delta H^{‡}=fG$

$(f>0)$

Ab initio VB calculations

2) Correlation *G* / ΔH‡ :



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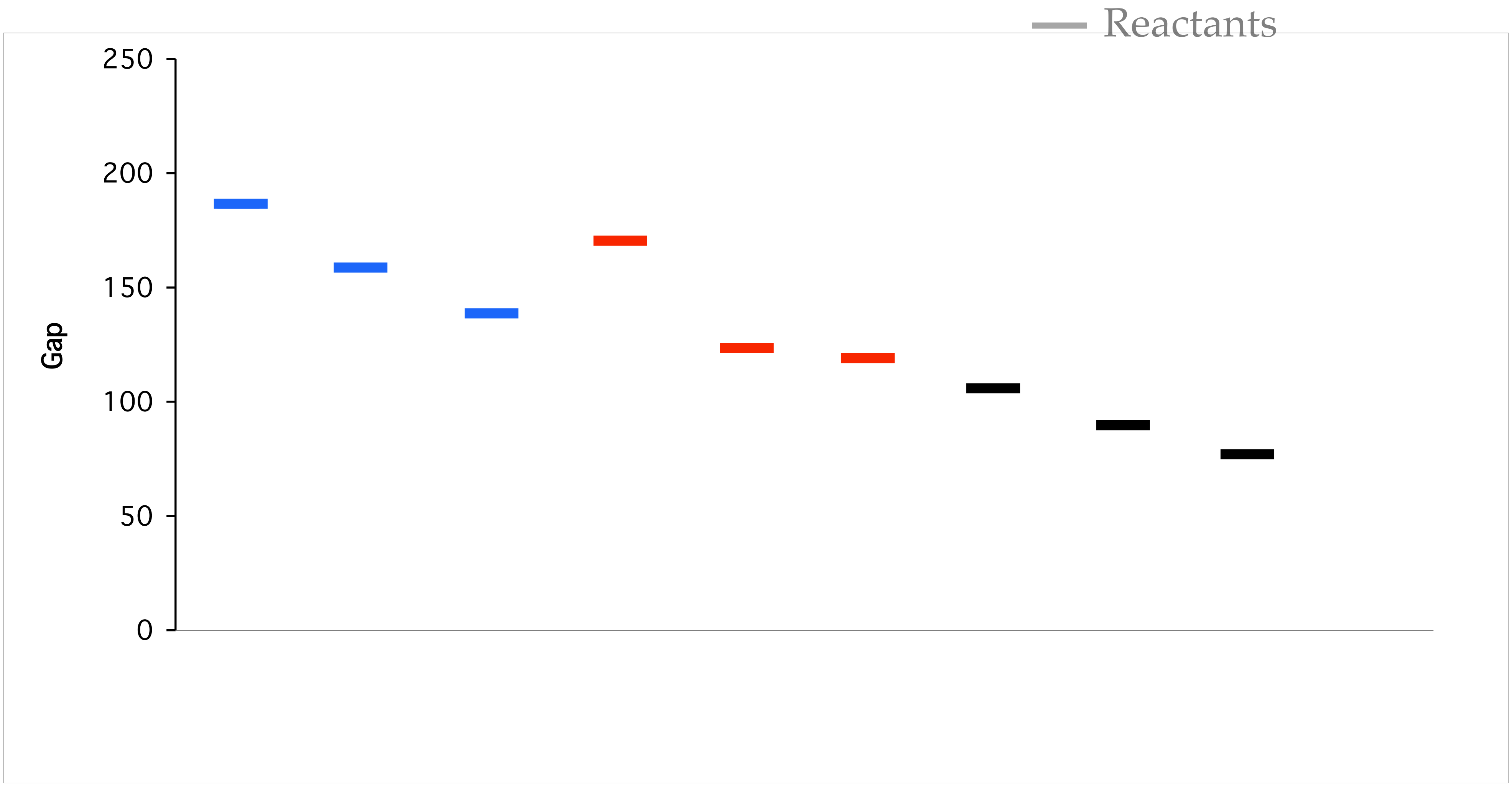
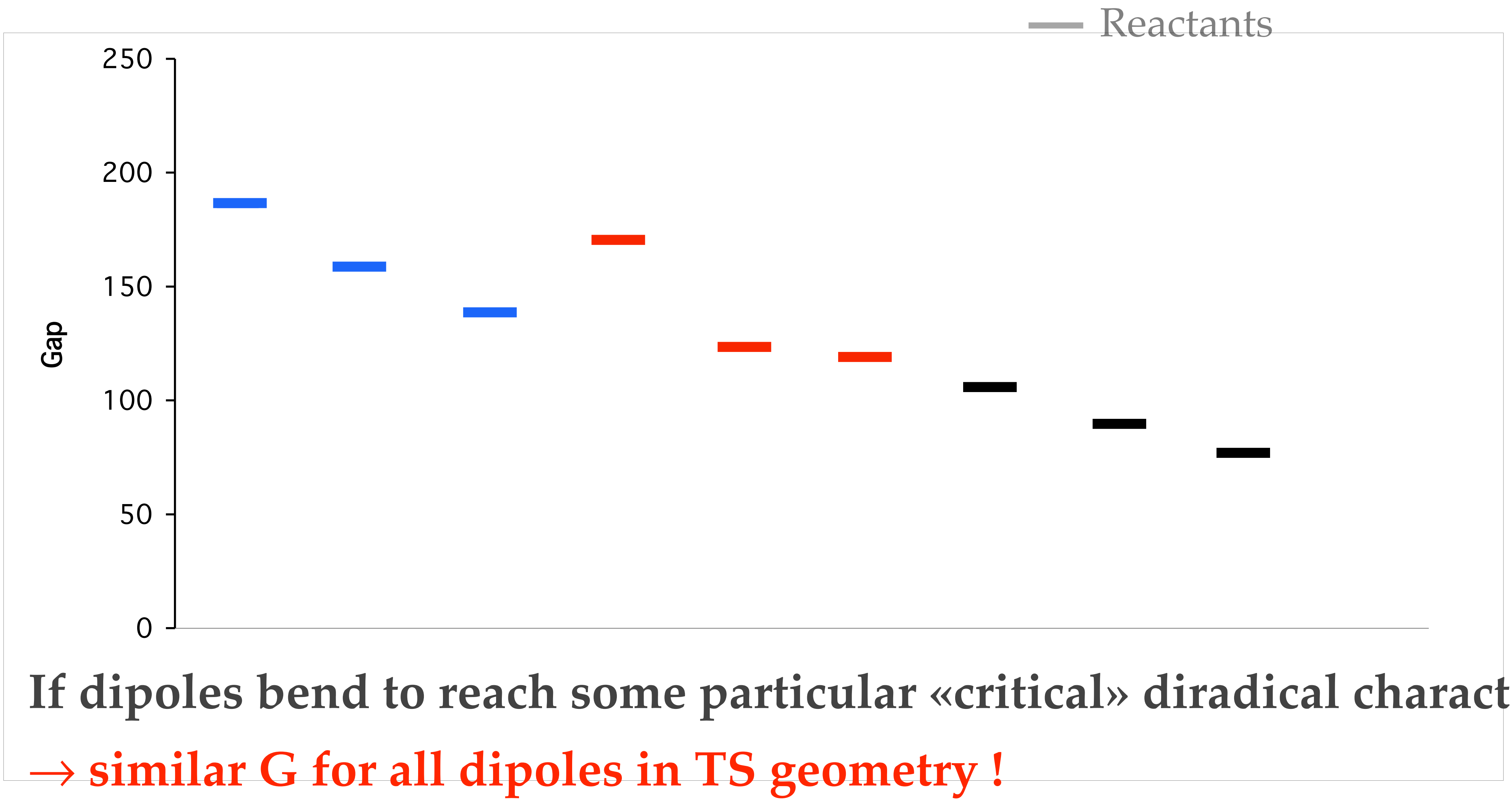
Ab initio VB calculations

- *G* : reactants :



Ab initio VB calculations

- *G* : reactants vs. TS :

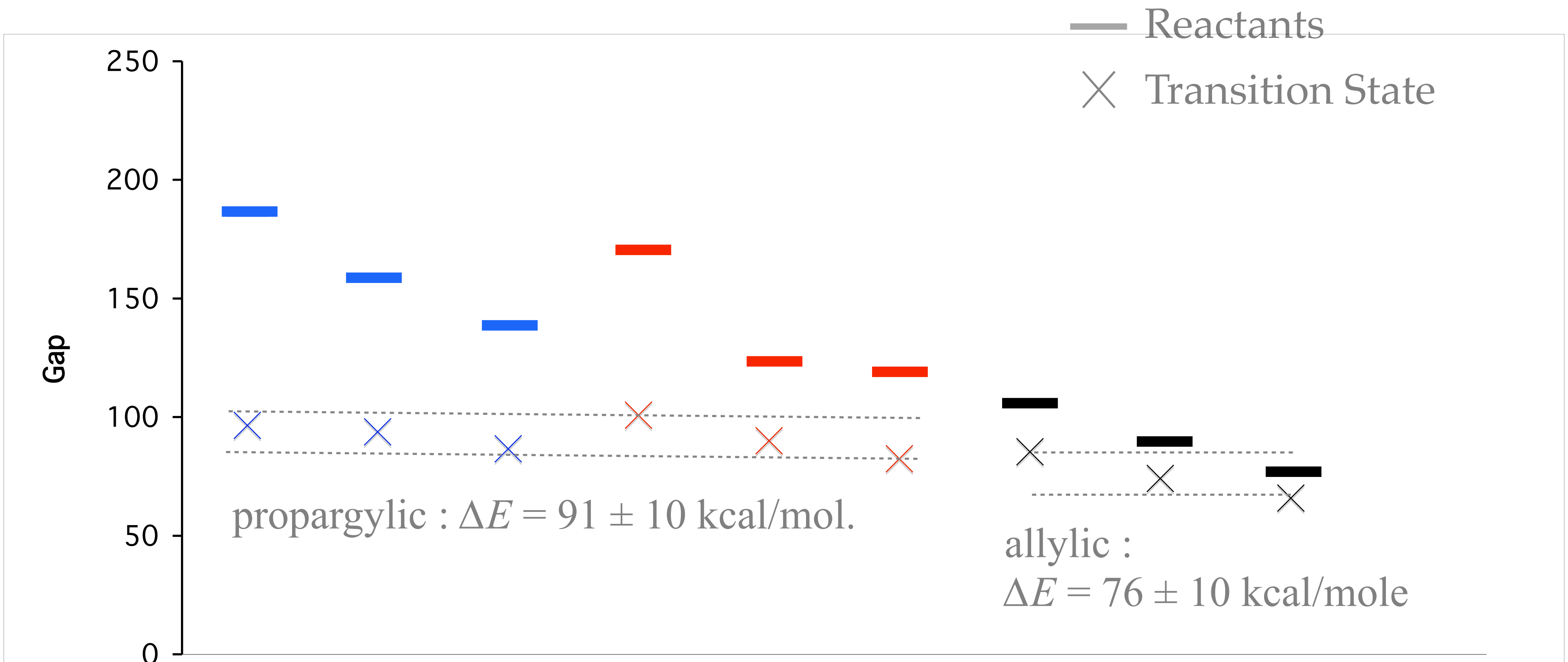


If dipoles bend to reach some particular «critical» diradical character

→ similar G for all dipoles in TS geometry !

Ab initio VB calculations

- *G* : reactants vs. TS :

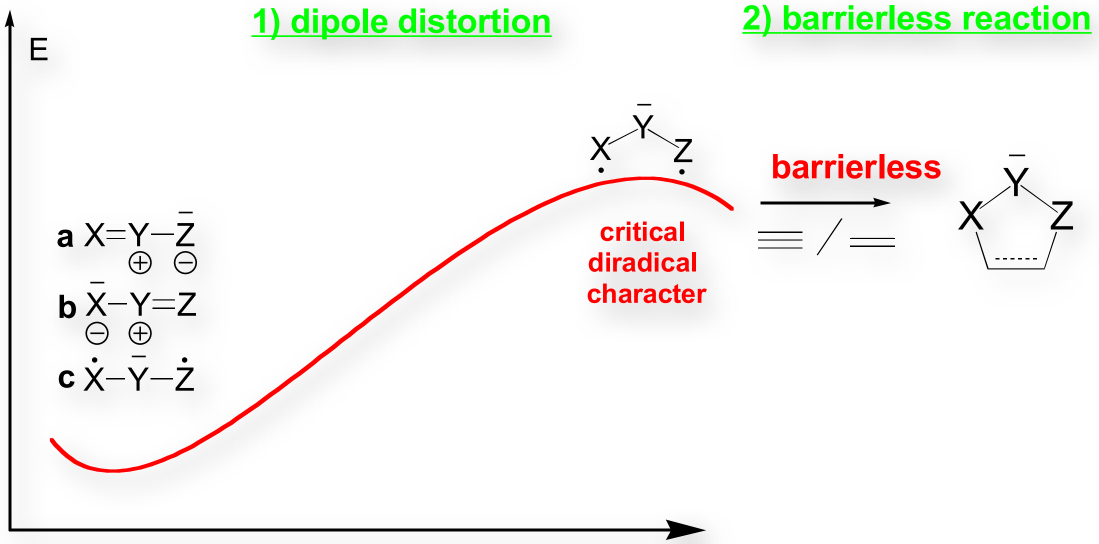


If dipoles bend to reach some particular «critical» diradical character

→ 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



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Conclusions

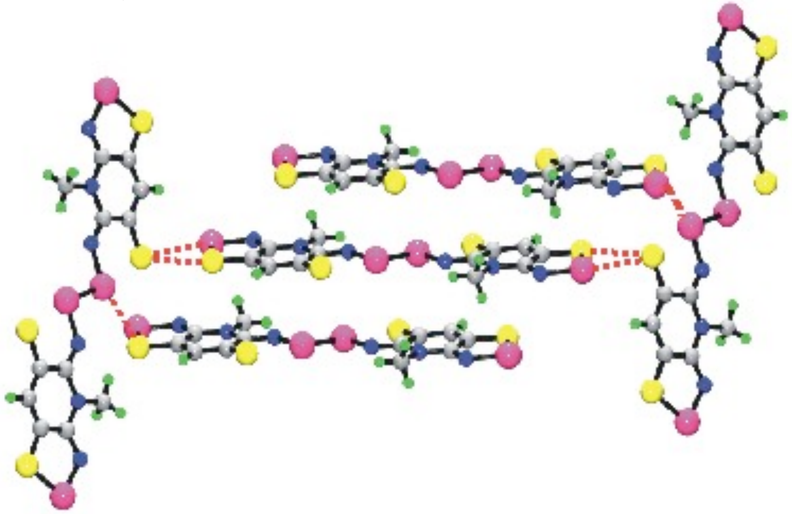
VB theory allowed us to consider the 1,3 dipolar cycloaddition reaction from a different perspective :

(Prof. Keating, Dead Poets Society)

Limits of VB theory

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 chemistry**

Limits of VB theory

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

$$\hat{H} = \sum_i \hat{h}_i + \sum_{i,j} \frac{1}{r_{ij}}$$

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

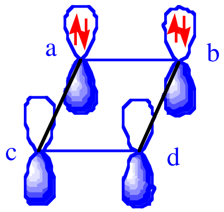
MO theory :

(orthogonal orbs.)

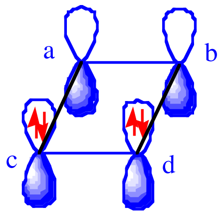
$$\bar{\bar{S}}$$

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

Ex : a 4e/4o pb :



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



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

...

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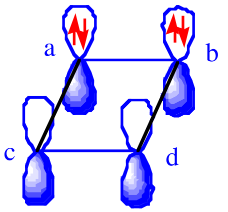
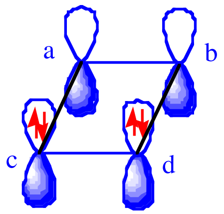
$$\begin{array}{c} \\ |a\bar{a}b\bar{b}| \\ |a\bar{a}c\bar{c}| \\ \vdots \\ \\ \\ |c\bar{c}d\bar{d}| \end{array} \quad \begin{array}{c} \bar{\bar{H}} \\ \begin{pmatrix} \times & \times & \times & \times & \times & 0 \\ \times & \times & \times & \times & 0 & \times \\ \times & \times & \times & 0 & \times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

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

Ex : a 4e/4o pb :



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



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

...

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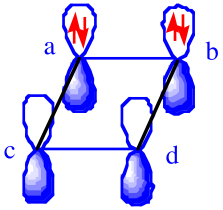
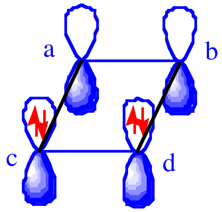
$$\bar{\bar{S}}$$

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

Ex : a 4e/4o pb :



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



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

...

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

Limits of VB theory

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$$\overline{\overline{H}}\,\overline{C} = E\,\overline{\overline{S}}\,\overline{C}$$

MO theory :

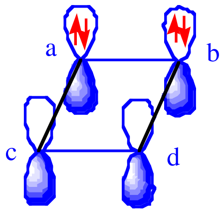
(orthogonal orbs.)

$$\overline{\overline{H}}$$

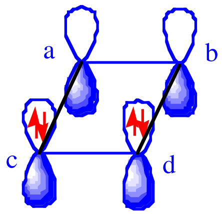
$$\begin{array}{c} |a\bar{a}b\bar{b}| \\ |a\bar{a}c\bar{c}| \\ \\ \vdots \\ \\ |c\bar{c}d\bar{d}| \end{array} \begin{pmatrix} \times & \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times & \times \\ \times & \times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

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

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



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



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

Limits of VB theory

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

    Ex 2 : (ic)VBPT2 formulas :

$$
\begin{aligned}
&\langle \Psi_{x_1 y_1}^{ij} | \hat{H}_0 | \Psi_{x_2 y_2}^{ij} \rangle = (E_{inact}^{(0)} - \varepsilon_i - \varepsilon_j) \langle \Psi_{x_1 y_1}^{ij} | \Psi_{x_2 y_2}^{ij} \rangle \\
&+ \{ (4 s_{x_2 x_1} s_{y_2 y_1} - 2 s_{y_2 x_1} s_{x_2 y_1}) E_{act}^{(0)} \\
&+ 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_{act}^{(0)} \\
&+ 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 :

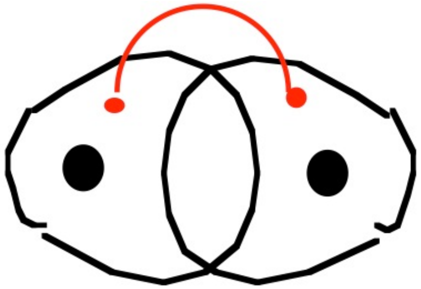
  - Now extremely efficient algorithms, based on advanced algebra:*

    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)*
* *Chen Z., Chen X, and Wu W. J. Chem. Phys. 138, 164120 (2013)*

Limits of VB theory

- **Moderate overlap between active orbitals :**
  - Large overlap between active orbitals : the meaning of the VB wave function (covalent vs. ionic) may be lost :



$S \approx 0.5$ or less : ok

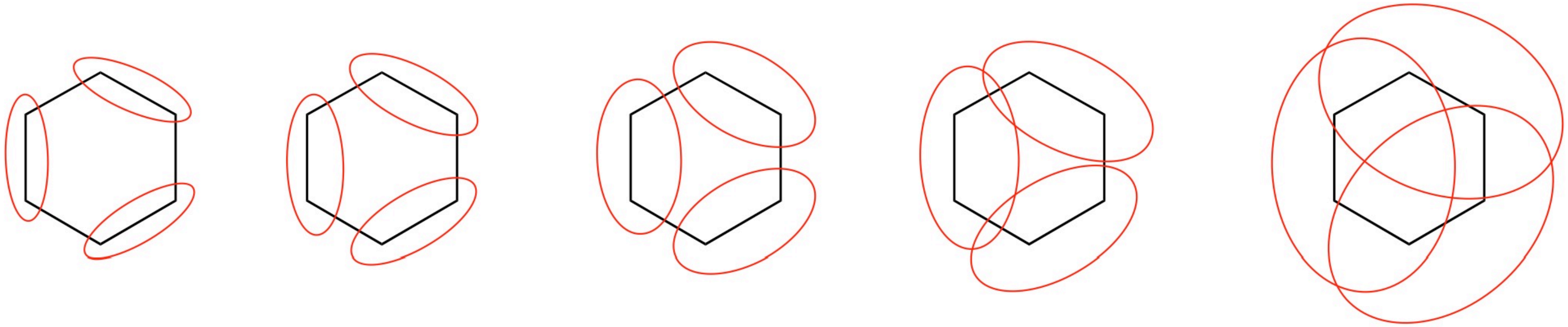
H_2/ LiH : $S \approx 0.8$!

☝

basically the only two
really pathologic cases

Limits of VB theory

- **Moderate overlap between active orbitals :**

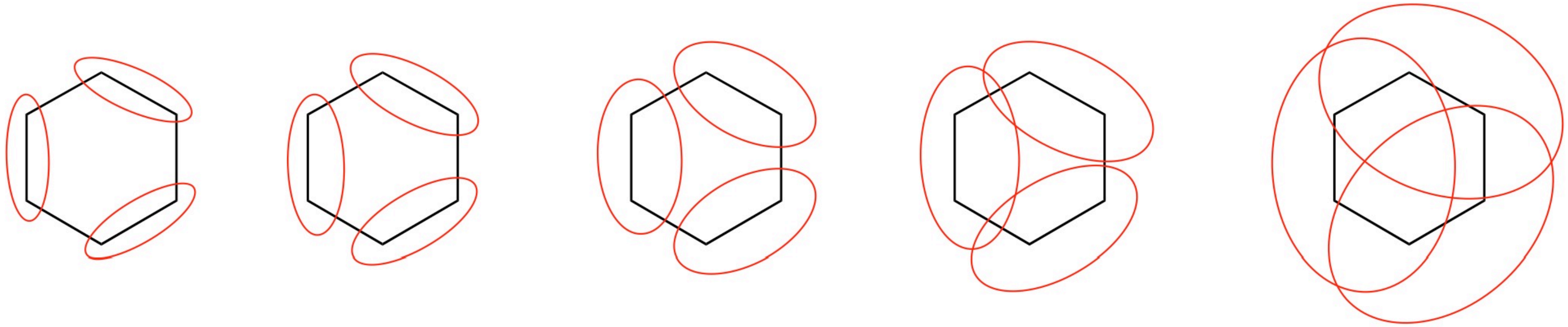


- If very large basis sets are used, any one-center AO can take the shape of a fully delocalized MO ⇒ R.E. abnormally small, technical issue (BOVB),...

«The more accurate the calculations become, the more the concepts tend to vanish into thin air.» (R. S. Mulliken)

Limits of VB theory

- **Moderate overlap between active orbitals :**



DZ+P TZ+P aug-TZ+P aug-QZ+P aug-5Z+P

The good news is :

• Up to **triple-zeta basis set without diffuse functions*** usually allows to get close enough to chemical accuracy while still avoiding this problem

* *Except if the system is anionic*

Limits of VB theory

- Moderate number of structures
- Nonorthogonality (not any more)
- Moderate basis set size
- **Kow-how and expertise**, whereas VB is hardly taught any more

It's up to you (tutorials) !

Part 3. Qualitative Valence Bond

Qualitative VB

- **Basic ingredients :**

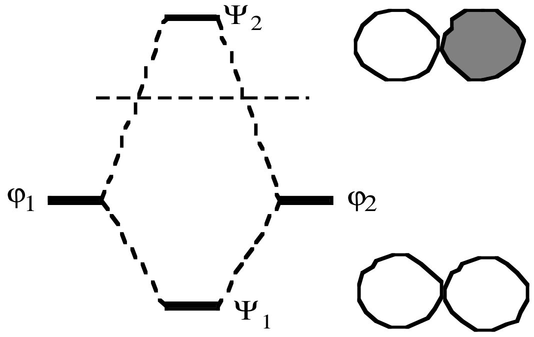
1) Effective Hamiltonian : $\mathbf{H}^{\mathbf{eff}} = \mathbf{h}^{\mathbf{eff}}(1) + \mathbf{h}^{\mathbf{eff}}(2) + \mathbf{h}^{\mathbf{eff}}(3) + \ldots.$

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

2) Parametrization : **ε, β, S**

Same as in Hückel theory :

$$\begin{cases} \varepsilon_i = h_{ii} : \text{orbital i self-energy} \\ \beta : \text{resonance integral} \\ S : \text{overlap integral} \end{cases}$$



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

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

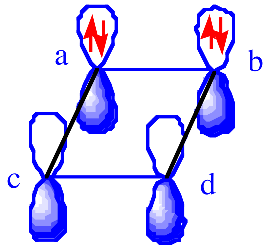
Qualitative VB

- **General calculus rules :**

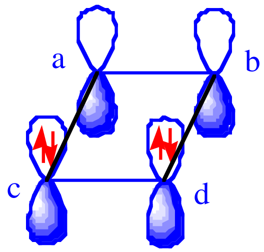
1) Rule for calculating determinant overlaps :

Generate permutations :

- between identical spins
- only one side



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



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

$$\left\langle \left(\left|a\bar{a}b\bar{b}\right|\right) \middle| \left(\left|c\bar{c}d\bar{d}\right|\right) \right\rangle = \left\langle a(1)\bar{a}(2)b(3)\bar{b}(4) \middle| c(1)\bar{c}(2)d(3)\bar{d}(4) \right\rangle$$

$$- \left\langle a(1)\bar{a}(2)b(3)\bar{b}(4) \middle| d(1)\bar{c}(2)c(3)\bar{d}(4) \right\rangle + \ldots$$

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

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

Qualitative VB

- **General calculus rules :**

2) Rule for calculating Hamiltonian matrix elements :

Generate permutations :

- between identical spins
- only one side

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

$$\left\langle \left(\left|a\bar{a}b\bar{b}\right|\right) \middle| \hat{h}_1 \middle| \left(\left|c\bar{c}d\bar{d}\right|\right) \right\rangle = \left\langle a(1)\bar{a}(2)b(3)\bar{b}(4) \middle| \hat{h}_1 \middle| c(1)\bar{c}(2)d(3)\bar{d}(4) \right\rangle$$

$$- \left\langle a(1)\bar{a}(2)b(3)\bar{b}(4) \middle| \hat{h}_1 \middle| d(1)\bar{c}(2)c(3)\bar{d}(4) \right\rangle$$

$$- \left\langle a(1)\bar{a}(2)b(3)\bar{b}(4) \middle| \hat{h}_1 \middle| c(1)\bar{d}(2)d(3)\bar{c}(4) \right\rangle$$

$$+ \left\langle a(1)\bar{a}(2)b(3)\bar{b}(4) \middle| \hat{h}_1 \middle| d(1)\bar{d}(2)c(3)\bar{c}(4) \right\rangle$$

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

Qualitative VB

- **General calculus rules :**

2) Rule for calculating Hamiltonian matrix elements :

Generate permutations :

- between identical spins
- only one side

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

$$\left\langle (|a\bar{a}b\bar{b}|) \middle| \hat{h}_1 \middle| (|c\bar{c}d\bar{d}|) \right\rangle = \ldots = h_{ac}S_{ac}S_{bd}^2 - h_{ad}S_{ac}S_{bc}S_{bd} - h_{ac}S_{ad}S_{bd}S_{bc} + h_{ad}S_{ad}S_{bc}^2$$

Then repeat :

$$\left\langle (|a\bar{a}b\bar{b}|) \middle| \hat{h}_2 \middle| (|c\bar{c}d\bar{d}|) \right\rangle = \ldots$$

$$\left\langle (|a\bar{a}b\bar{b}|) \middle| \hat{h}_3 \middle| (|c\bar{c}d\bar{d}|) \right\rangle = \ldots$$

Quite tedious !

$$\left\langle (|a\bar{a}b\bar{b}|) \middle| \hat{h}_4 \middle| (|c\bar{c}d\bar{d}|) \right\rangle = \ldots$$

Qualitative VB

- **Simplified expressions :**

1) Choice of an origin of energies (shift) : $\beta_{ab} = h_{ab} - \frac{1}{2}(\varepsilon_a + \varepsilon_b)$

$\Rightarrow$ new energy scale where : $\sum_i \varepsilon_i = 0$

<u>*Example :*</u>

$$E(|a\bar{a}b\bar{b}|) = N^2(\underbrace{2\varepsilon_a + 2\varepsilon_b}_{=0} \underbrace{-2\varepsilon_a S_{ab}^2 - 2\varepsilon_b S_{ab}^2}_{-2(\varepsilon_a+\varepsilon_b)S_{ab}^2=0} - 4h_{ab}S_{ab} + 4h_{ab}S_{ab}^3) = N^2(-4\beta_{ab}S_{ab})(1 - S_{ab}^2)$$

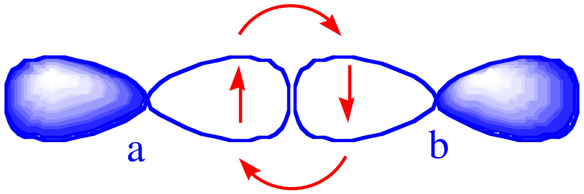
2) Approximations :

- Determinants which differ by + than 2 spinorbitals: $\langle \Omega | H^{eff} | \Omega' \rangle \approx 0$
- Neglect S_{ac} and h_{ac} if **a** and **c** are not nearest neighbourgs
- Neglect high overlaps power terms (S^2 or + b.r.t dominant terms)

Qualitative VB

- **Elementary interactions energies :**

1) The two electron bond :

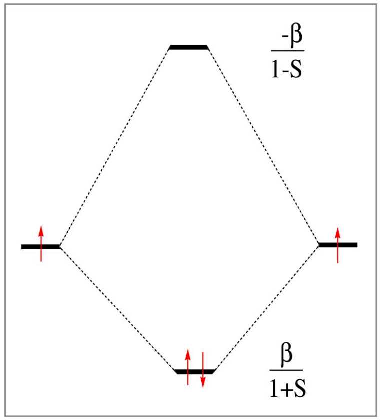


$$\Psi_{2e} = \frac{|a\bar{b}| + |b\bar{a}|}{\sqrt{2(1+S^2)}}$$

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

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

Different in MO-Hückel theory :

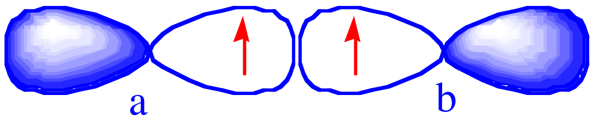


$D_e = 2\beta/(1+S)$

Qualitative VB

- **Elementary interactions energies :**

2) The triplet (2e) repulsion :

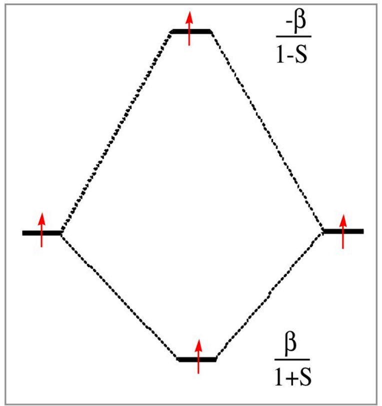


$$\Psi_T = \frac{|a\bar{b}| - |b\bar{a}|}{\sqrt{2(1-S^2)}}$$

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

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

Same in MO-Hückel theory :



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

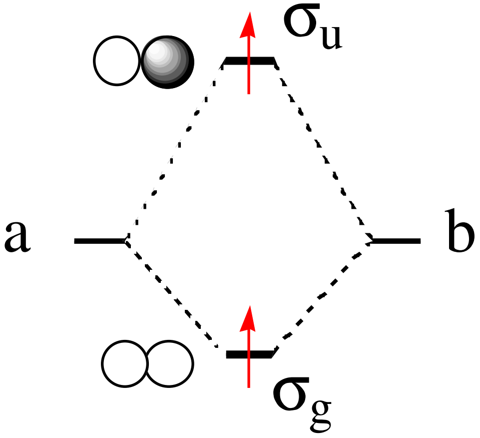
Qualitative VB

- **Elementary interactions energies :**

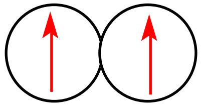
  2) The triplet (2e) repulsion :

Why is it the *same* in qualitative VB and in MO-Hückel theory ?

MO



VB



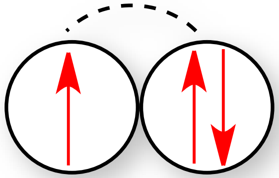
$$\psi_{VB} \propto |ab|$$

$$\psi_{MO} \propto |\sigma_g \sigma_u| = |(a+b)(a-b)| = |\cancel{a}a| + |\cancel{b}b| + |ba| - |ab| \propto \psi_{VB}$$

Qualitative VB

- **Elementary interactions energies :**

3) The 3e repulsion :



$$\Psi(3e_{rep}) = \frac{|ab\bar{b}|}{\sqrt{1-S^2}}$$

$$\overset{\langle\Psi|\hat{H}^{eff}|\Psi\rangle}{\Rightarrow} \left\langle (|ab\bar{b}|) \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 \middle| (|ab\bar{b}|) \right\rangle =$$

$$\underbrace{\left\langle a(1)b(2)\bar{b}(3) \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 \middle| a(1)b(2)\bar{b}(3) \right\rangle}_{\varepsilon_1+\varepsilon_2+\varepsilon_3} - \underbrace{\left\langle a(1)b(2)\bar{b}(3) \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 \middle| b(1)a(2)\bar{b}(3) \right\rangle}_{-\beta S-\beta S}$$

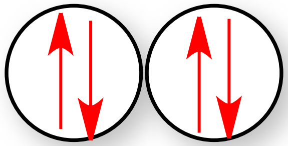
$$\Rightarrow \boxed{E(3e_{rep}) = \frac{-2\beta S}{1-S^2}}$$

Same as triplet

Qualitative VB

- **Elementary interactions energies :**

4) The 4e repulsion :



➡ **Exercise 3 :**

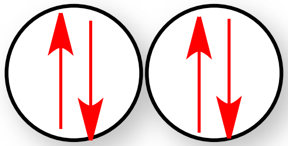
1) Calculate the energy expression of the 4e repulsion at the qualitative VB level.

2) Compare this results with the energy expression obtained from MO-Hückel level.

Qualitative VB

- **Elementary interactions energies :**

4) The 4e repulsion :



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

$$\overset{\langle\Psi|\hat{H}^{eff}|\Psi\rangle}{\Rightarrow} \Big\langle (|ab\bar{a}\bar{b}|) \Big| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{h}_4 \Big| (|ab\bar{a}\bar{b}|) \Big\rangle =$$

$$\underbrace{\Big\langle a(1)b(2)\bar{a}(3)\bar{b}(4) \Big| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{h}_4 \Big| a(1)b(2)\bar{a}(3)\bar{b}(4) \Big\rangle}_{\varepsilon_1+\varepsilon_2+\varepsilon_3+\varepsilon_4=0} - \underbrace{\Big\langle a(1)b(2)\bar{a}(3)\bar{b}(4) \Big| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{h}_4 \Big| b(1)a(2)\bar{a}(3)\bar{b}(4) \Big\rangle}_{\beta S+\beta S+0}$$

$$-\underbrace{\Big\langle a(1)b(2)\bar{a}(3)\bar{b}(4) \Big| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{h}_4 \Big| a(1)b(2)\bar{b}(3)\bar{a}(4) \Big\rangle}_{0+\beta S+\beta S} + \underbrace{\Big\langle a(1)b(2)\bar{a}(3)\bar{b}(4) \Big| \hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{h}_4 \Big| b(1)a(2)\bar{b}(3)\bar{a}(4) \Big\rangle}_{4\beta S^3}$$

$$\Rightarrow E(4e_{rep}) = \frac{-4\beta S + 4\beta S^3}{(1-S^2)^2} = \frac{-4\beta S}{1-S^2}$$

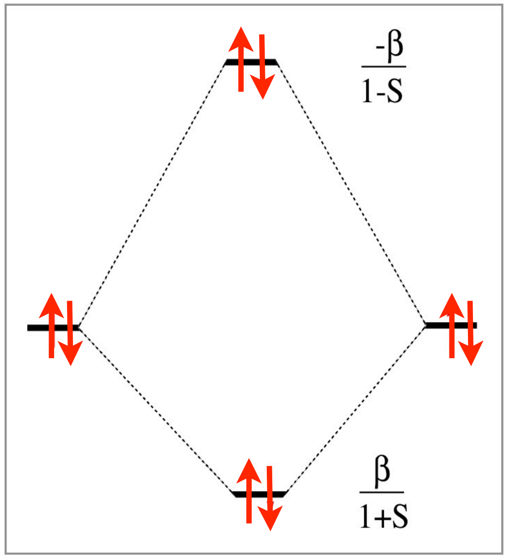
Double as triplet and 3e repulsion

Qualitative VB

- **Elementary interactions energies :**

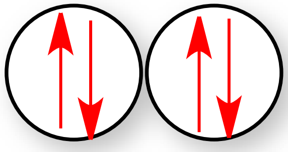
4) The 4e repulsion :

MO



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

VB



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

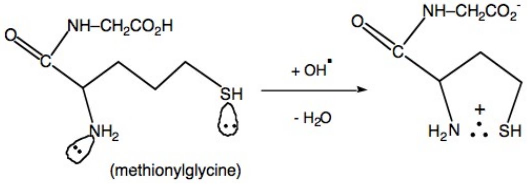
$$\boxed{E(4e_{rep}) = \frac{-4\beta S}{1-S^2}}$$

Qualitative VB

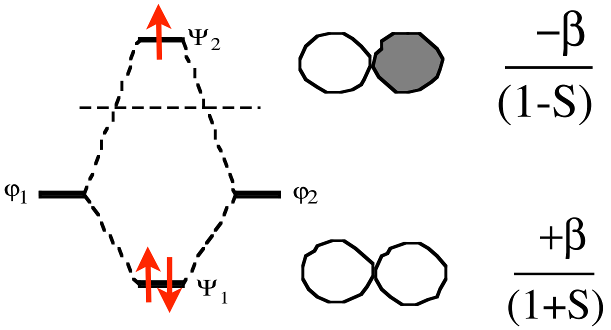
- **Elementary interactions energies :**

5) The 3e bond :

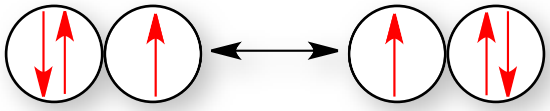
Examples : He_2^+, $RS\overset{\ominus}{\therefore}SR'$,
radical intermediates :



MO



VB



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

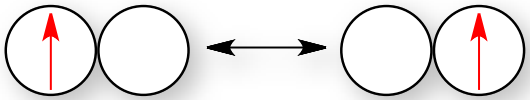
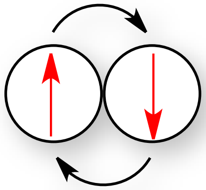
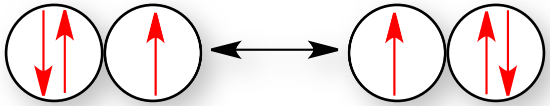
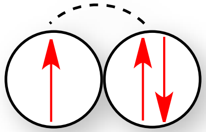
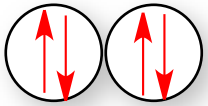
$$\Psi_{MO} \propto |\sigma\bar{\sigma}\sigma^*| = |(a+b)\overline{(a+b)}(a-b)^*| = \ldots = -|a\bar{a}b| - |b\bar{b}a| \propto \Psi_{VB}$$

$$\Rightarrow \quad D_e = \frac{\beta(1-3S)}{(1-S^2)} \quad \Rightarrow \quad \boxed{S_{opt} \approx 0.17}$$

Remind for later use !

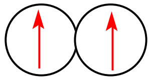
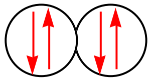
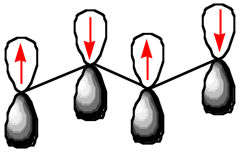
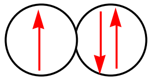
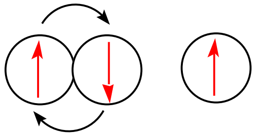
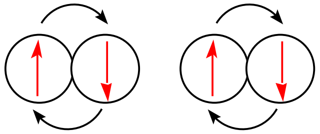
Qualitative VB

- **Elementary interactions energies :**

		VB	**MO**
1-e bond (A↑B) =		$\frac{ß}{1+S}$	$\frac{ß}{1+S}$
2-e bond (A–B) =		$\frac{2ßS}{1+S^2}$	$\frac{2ß}{1+S}$
3-e bond(A∴B) =		$\frac{ß(1-3S)}{1-S^2}$	$\frac{ß(1-3S)}{1-S^2}$
Triplet / 3-e repulsion (A↓↑ ↑B) =		$\frac{-2ßS}{1-S^2}$	$\frac{-2ßS}{1-S^2}$
4-e repulsion (A↑↓ ↓↑B) =		$\frac{-4ßS}{1-S^2}$	$\frac{-4ßS}{1-S^2}$

Qualitative VB

Energy of a determinant with *n* (neighboring↑↑): $\dfrac{-2n\beta S}{1-S^2}$

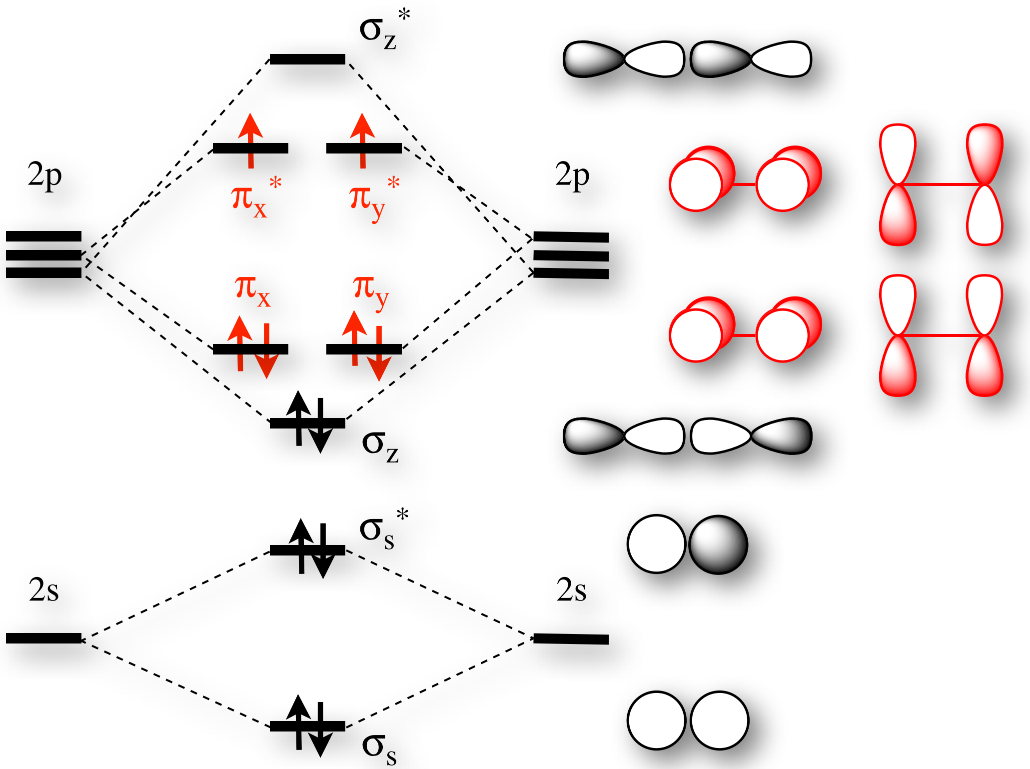
triplet repulsion		$-2\beta S/(1-S^2)$	(VB and MO)
4-e repulsion		$-4\beta S/(1-S^2)$	(VB and MO)
spin-alternated determinant		0	(VB only)
3-e repulsion		$-2\beta S/(1-S^2)$	(VB only)
bond… single electron		$-\beta S/(1-S^2)$	(VB only)
bond… bond		$-\beta S/(1-S^2)$	(VB only)

Qualitative VB

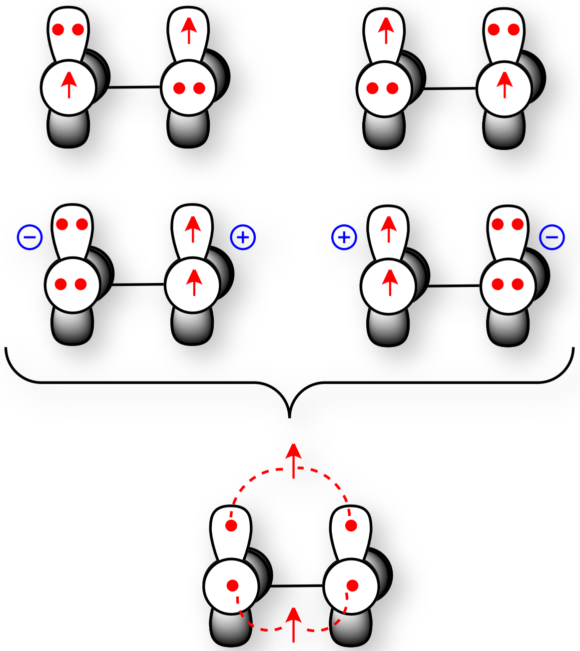
- **Application : ground state of O_2 :**

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

MO



VB



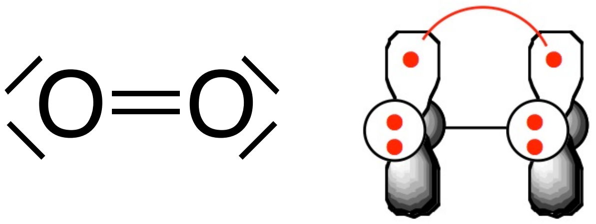
Qualitative VB

➡ Exercise 4 : ground state of O2 :

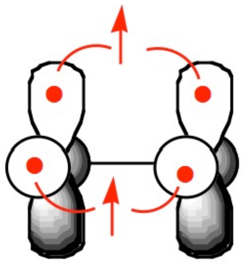
1) Calculate the energy expression for the π system of the lowest triplet state of the dioxygen molecule, at the qualitative VB level.

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.



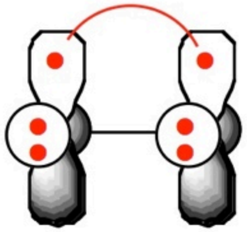
Singlet



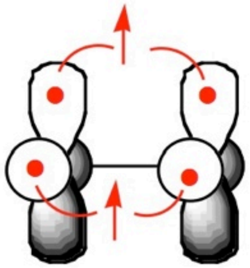
Triplet

Qualitative VB

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



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



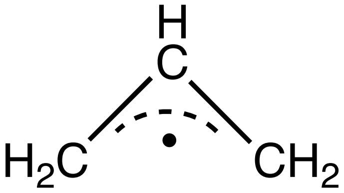
$$\mathbf{E(T)} = 2\beta\,(1\,-\,3S)/(1-S^2)$$

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

➡ *The triplet state is always the lower*

Qualitative VB

➡ Exercise 5 : 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.

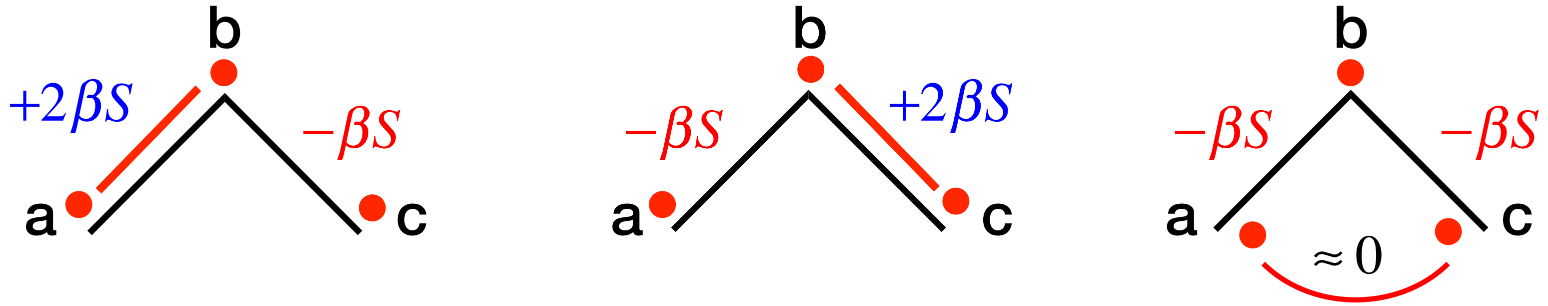
2) Show that the third structure can be expressed as a linear combination of the first two structures, and thus that only two of the three covalent structures form a complete basis of non-redundant structures (Rumer basis).

3) EPR measurements show that the spin density on the central atom is +0.2, whereas a value of -1. is predicted at the RHF 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 5 : spin polarization in allyl radical :**

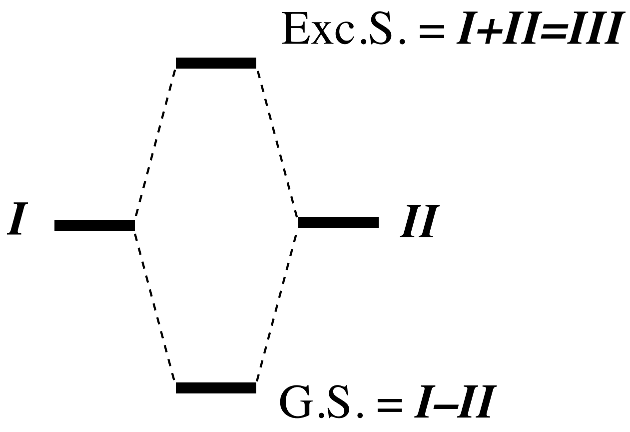


$$\Rightarrow E(I) = +\beta S < 0 \qquad \Rightarrow E(II) = +\beta S < 0 \qquad \Rightarrow E(III) = -2\beta S$$

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

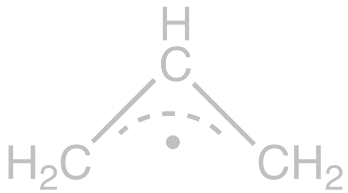
$$\psi(II) = \frac{1}{\sqrt{2}}\left(\left|ab\bar{c}\right| + \left|ac\bar{b}\right|\right)$$

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



Qualitative VB

➡ Exercise 5 : 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).

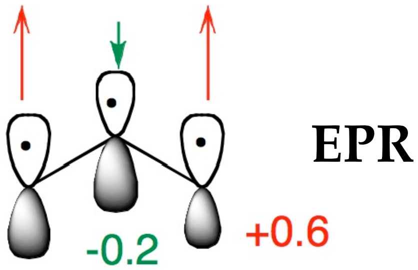
3) EPR measurements show that the spin density on the central atom is +0.2, whereas a value of -1. is predicted at the RHF level. Express the HL w.f. corresponding to the ground state, and calculate the predicted spin density.

Qualitative VB

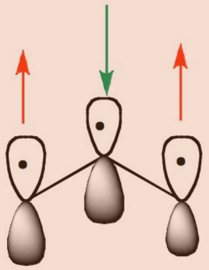
➡ Exercise 5 : spin polarization in allyl radical :

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

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

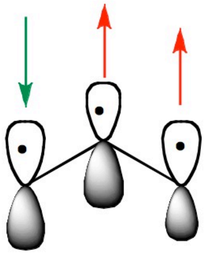


⇒ much closer to experiment than RHF (and also UHF)



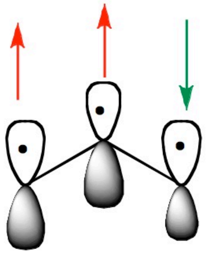
$|a\bar{b}c|$

$D_b = D_{QC}$



$|\bar{a}bc|$

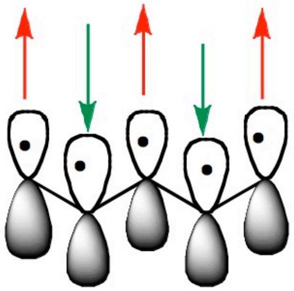
D_a



$|ab\bar{c}|$

D_c

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



D_{QC}

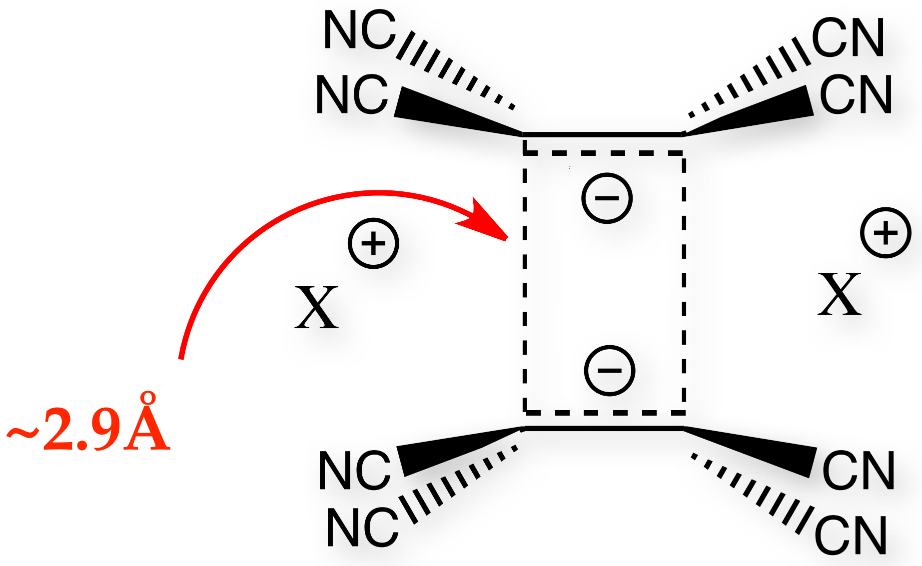
☜ General rule, works for all polyenes

Application

Electronic structure of the DTCNE dimer

«Pancake bonding»

- $DTCNE_2^{2-}$:



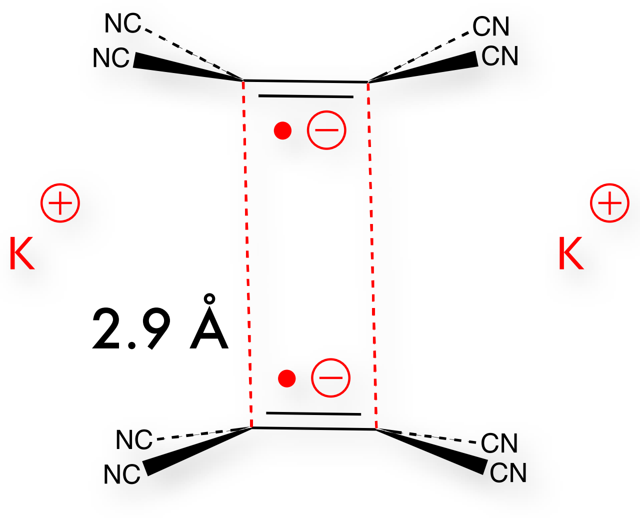
X^+ : Na^+, Cs^+, $[iPr_4N]^+$, $[Cr(C_6Me_3H_3)_2]^+$, ...

Electrostatic complex ?...

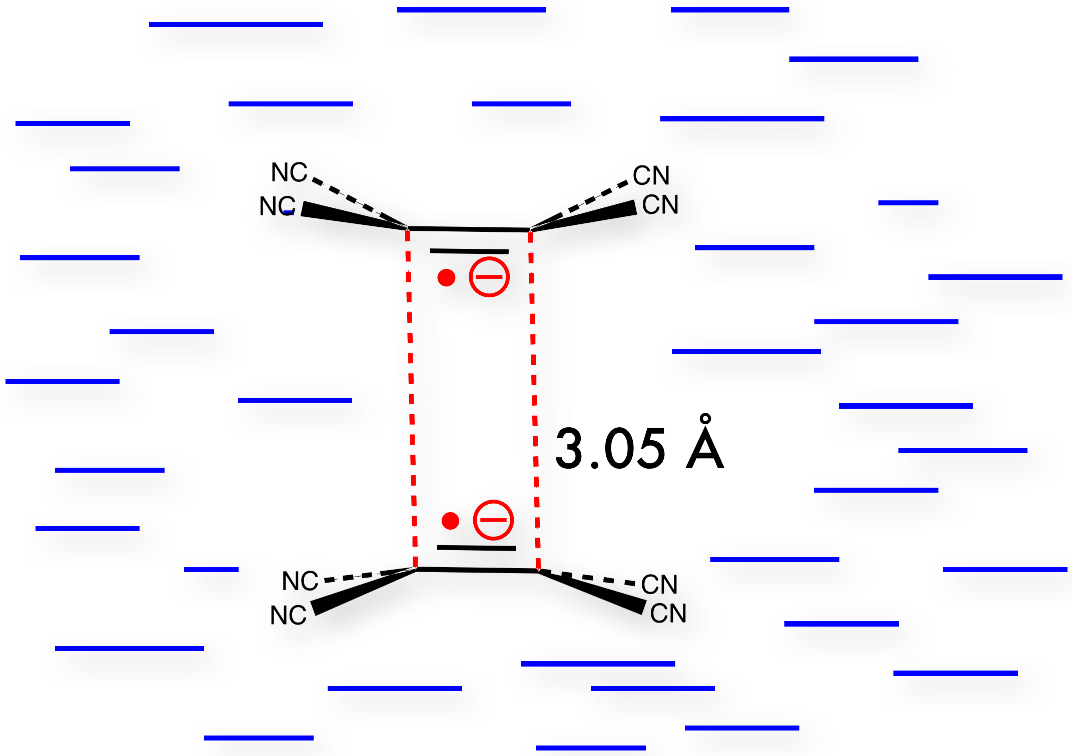
- Strong bonds
- Same bonding distance whatever the size of the cations !

«Pancake bonding»

- DTCNE$_2^{2-}$:



Stable in the crystal



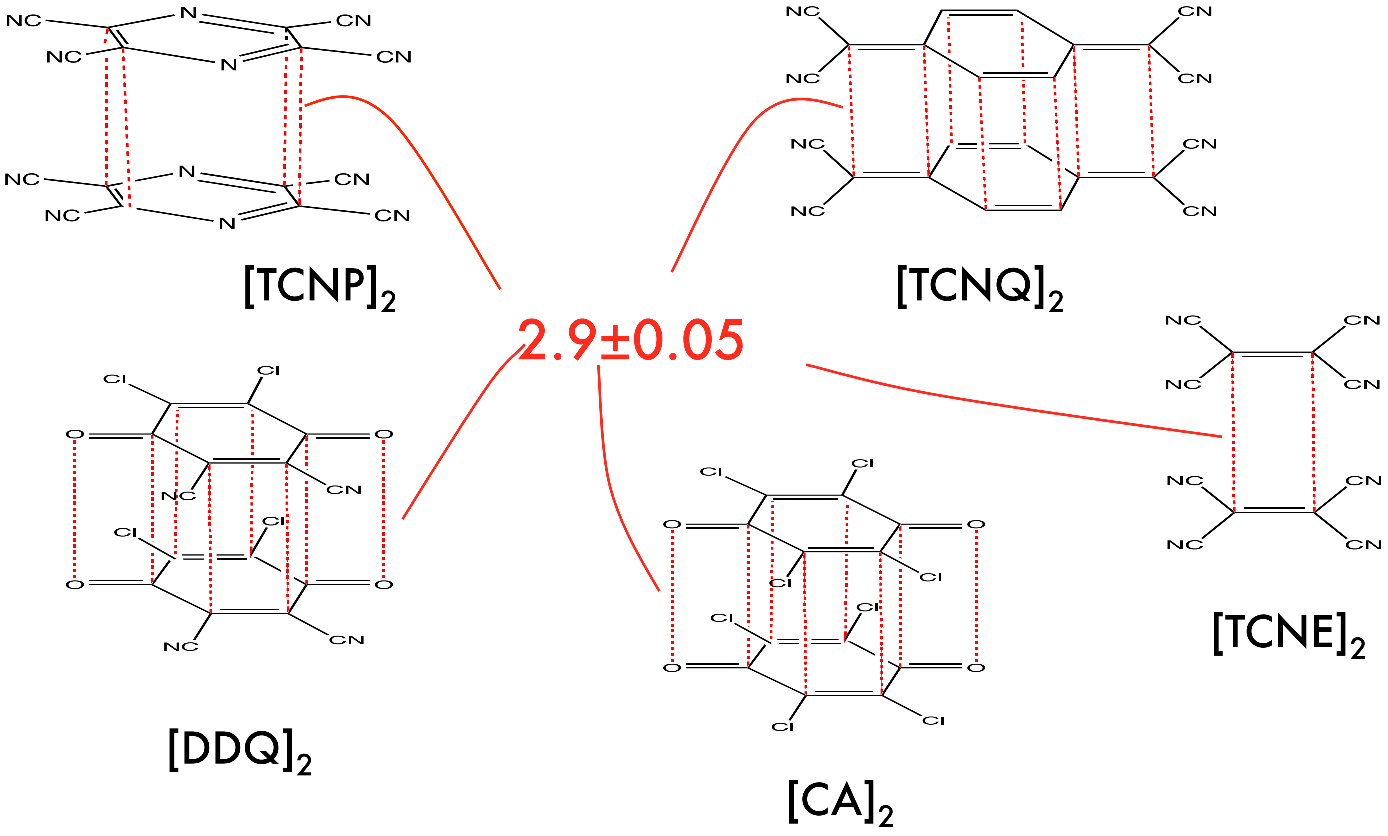
Stable in solution

- Same bonding distance whatever the environment !

⇒ not only electrostatic… also an interfragment bond

«Pancake bonding»

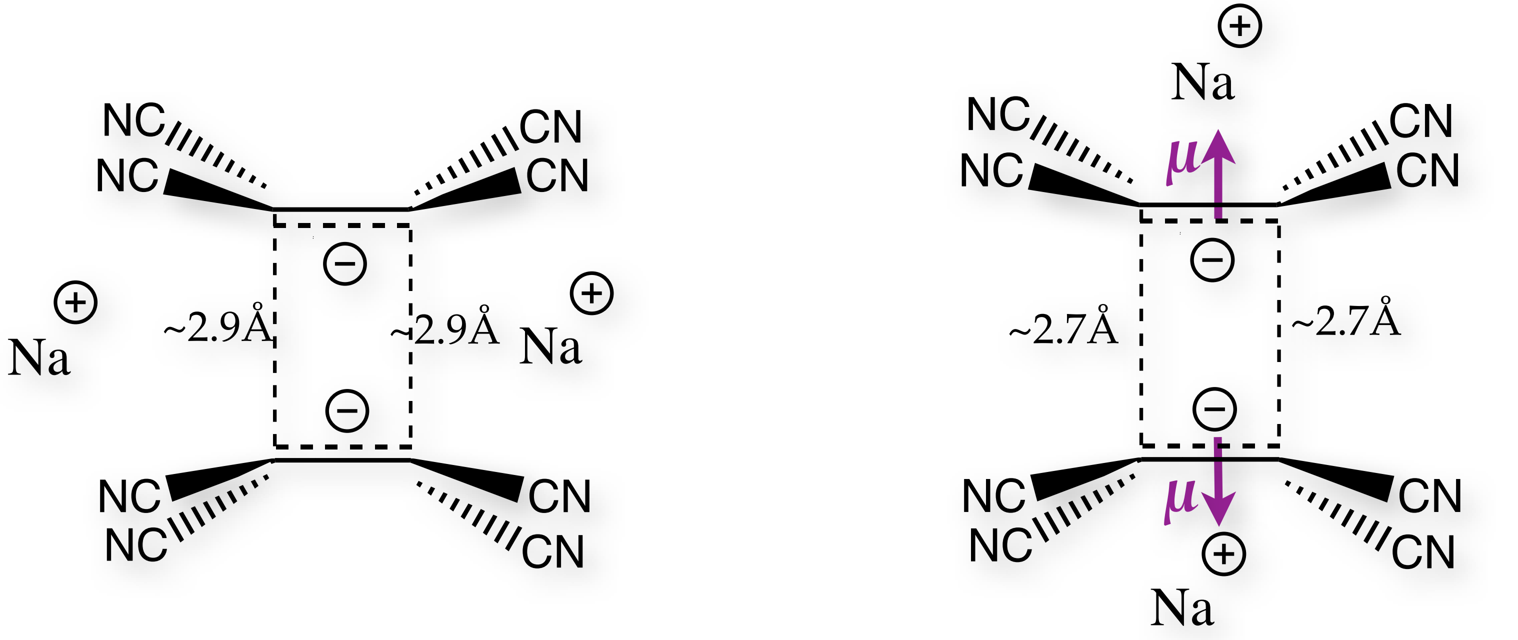
- Other «pancake bonding» systems :



- Same bonding distance whatever the system !
- $d_{C\text{---}C}$ < sum of vdW radii (3.45Å) , but much longer than C-C 2e bonds (1.54Å)

«Pancake bonding»

- What kind of bonding in $DTCNE_2^{2-}$?



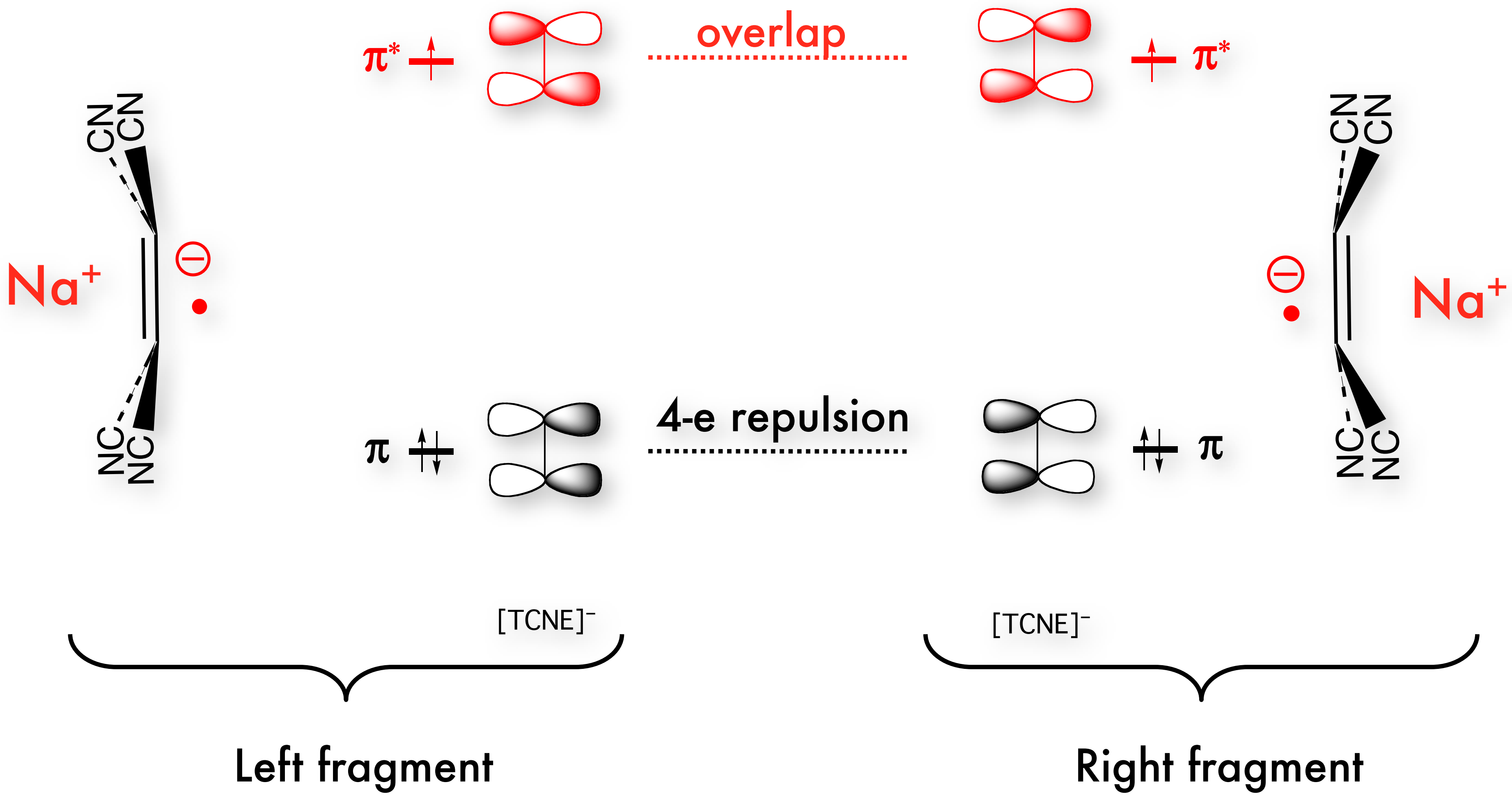
$D_e \approx 80.\ kcal/mol$

!

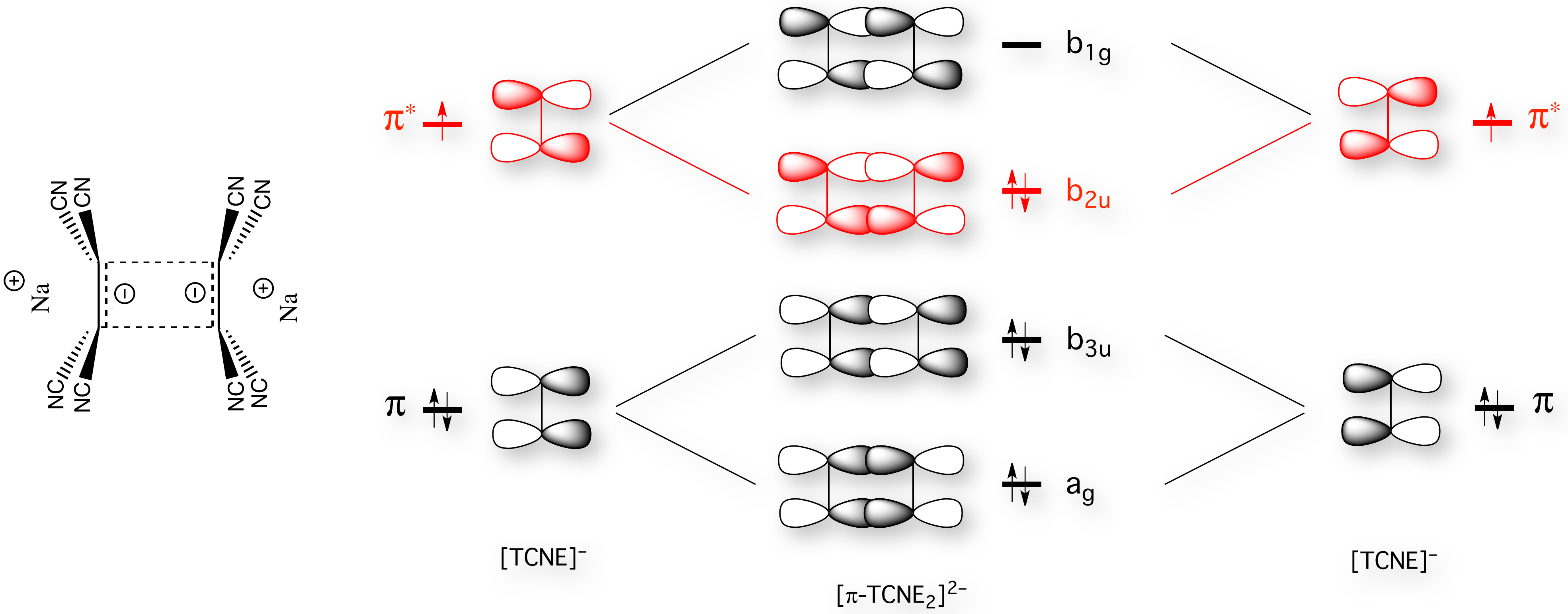
$D_e \approx 11.\ kcal/mol$

Right geom : significant bonding force overcome repulsive electrostatics !

Qualitative MO analysis

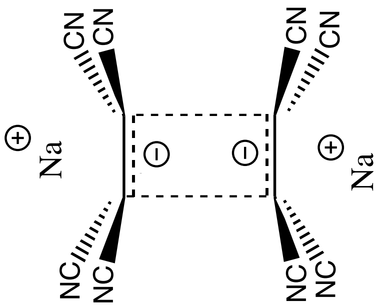


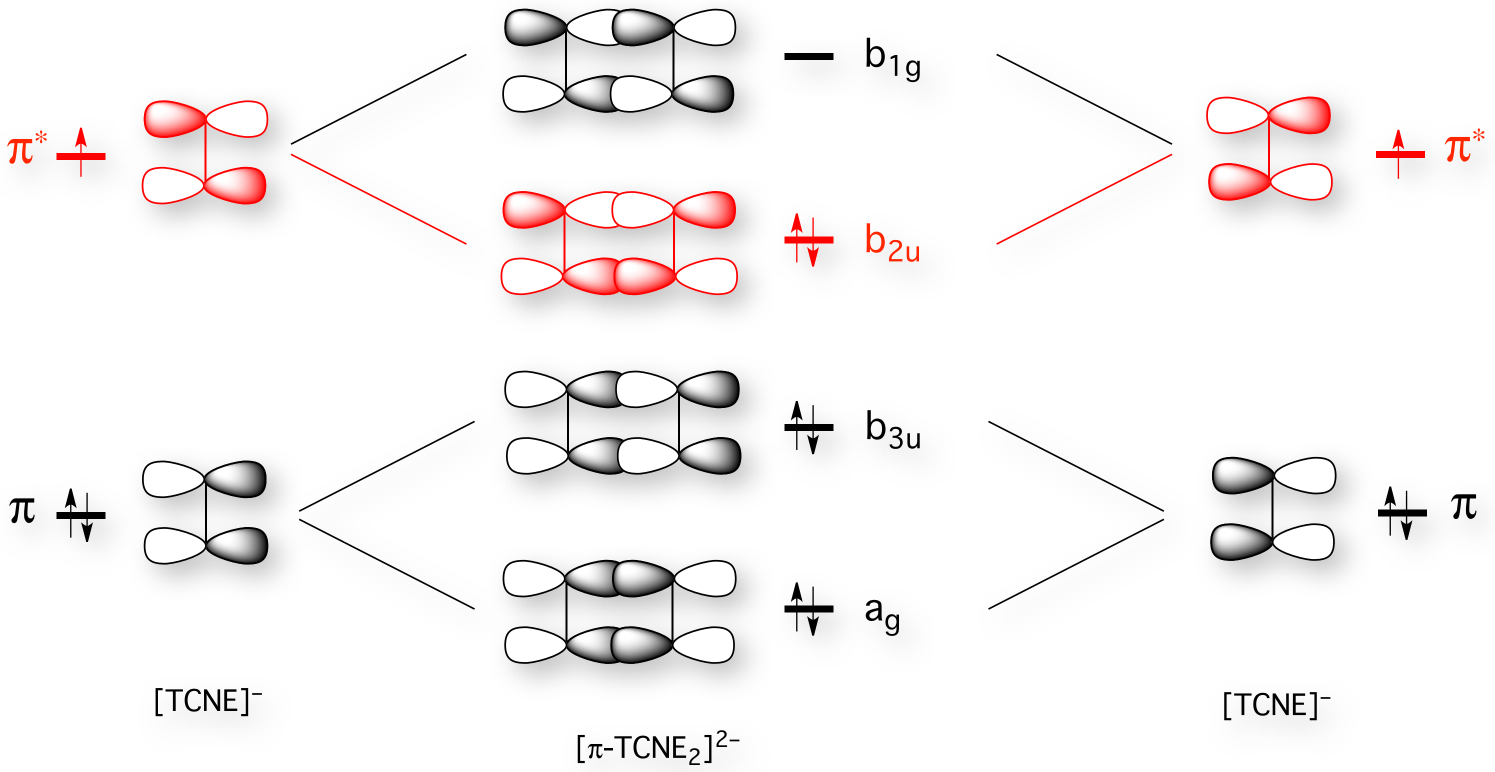
Qualitative MO analysis



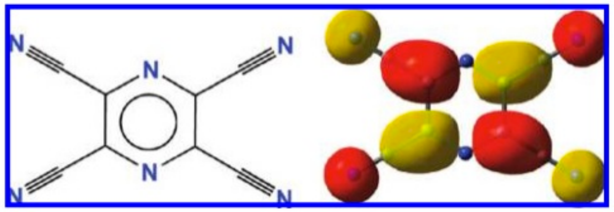
⇒ a simple **4 centers / 2 electrons bond ?**

Qualitative MO analysis

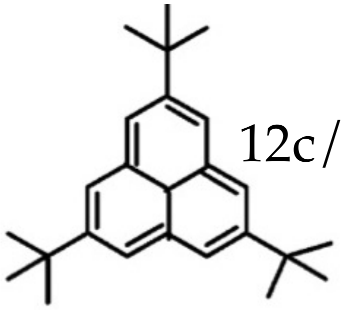




Other «pancake bonding» systems : **n center / 2e⁻ bonds**



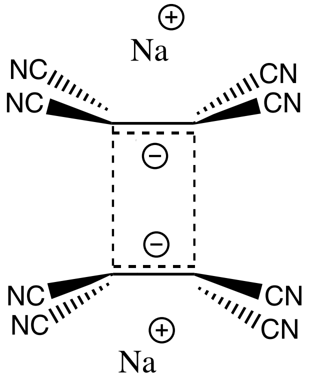
8c/2e⁻

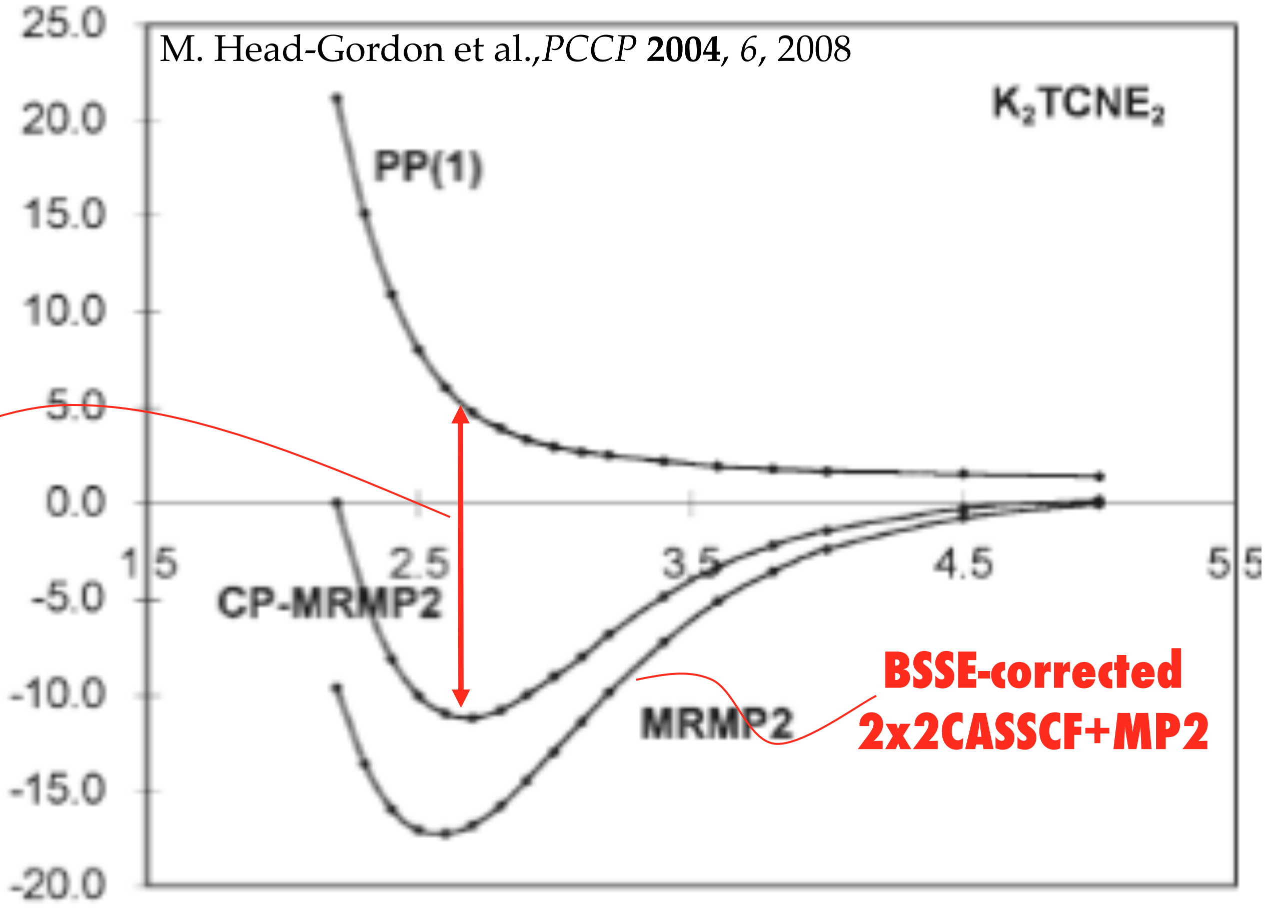


12c/2e⁻

Quantitative MO computations

- GVB calculations of the axial conformation :





M. Head-Gordon et al.,*PCCP* **2004**, *6*, 2008

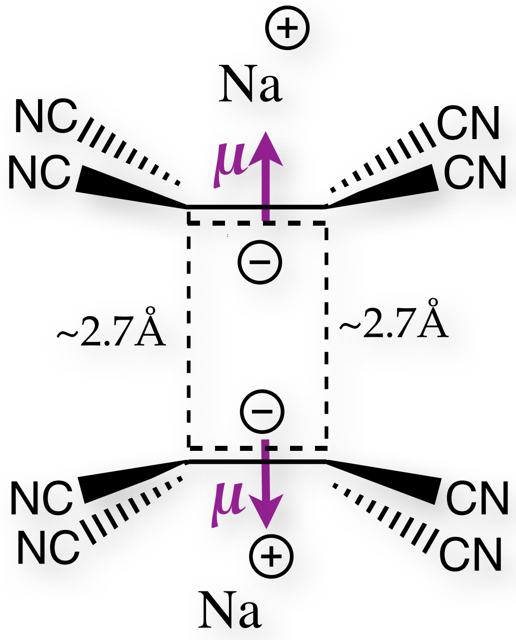
BSSE-corrected
2x2CASSCF+MP2

Contribution of
dynamic correlation
to bonding:
> 23 kcal/mol !

- 2x2 CASSCF describes well 2e bonds (particularly stretched...) : not the case here !
- Contribution of dynamical correlation energy huge !

Situation

- What kind of bonding in $DTCNE_2^{2-}$?



!

$D_e \approx 11.\ kcal/mol$

- Same bonding distance whatever the counter-ion, the environment, the system...

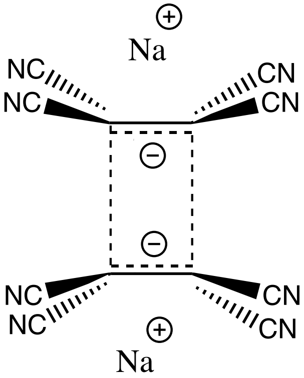
- MO analysis propose a 4c/2e bond, but GVB-PP fails to account for any bonding...

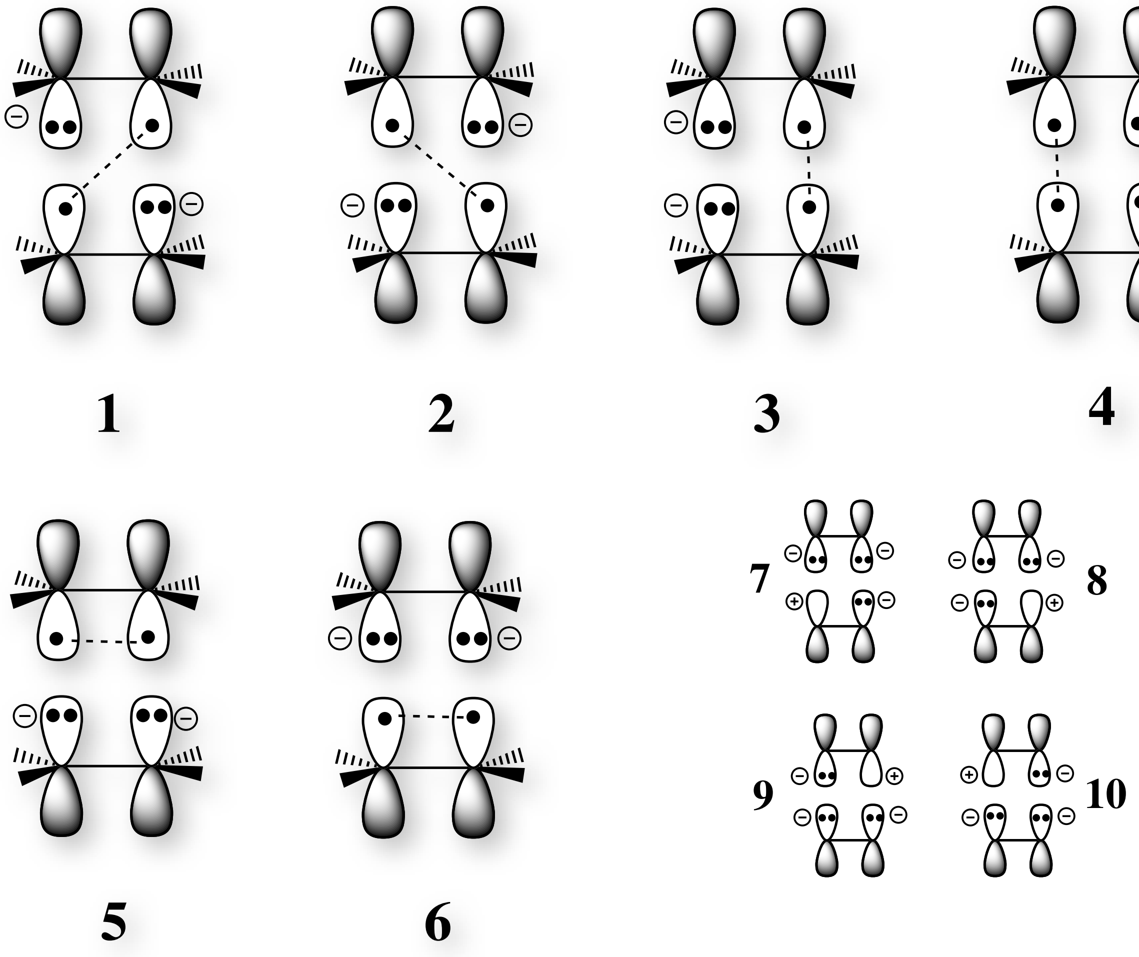
- Distance too short, bond energy too strong to be dispersion...

⇒ try a different perspective... with VB theory !

Qualitative VB analysis

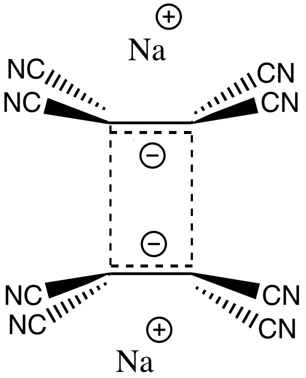
- VB set of structures for DTCNE$_2^{2-}$:

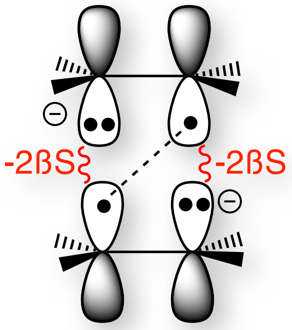




Qualitative VB analysis

- VB set of structures for DTCNE$_2^{2-}$:





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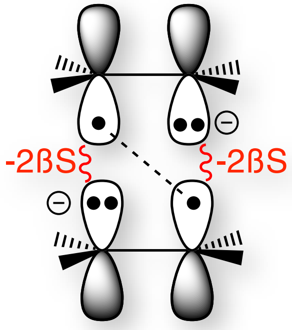

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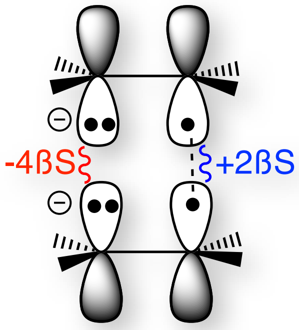

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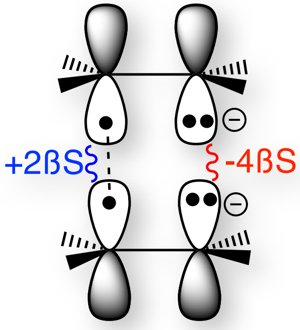

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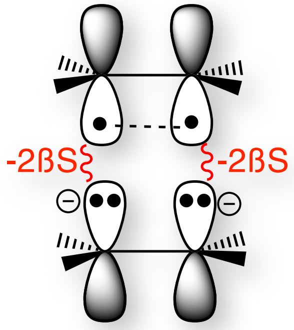

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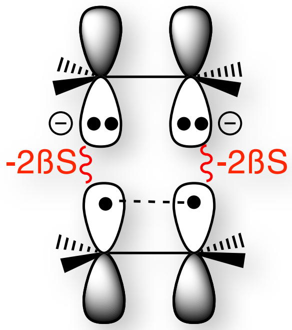

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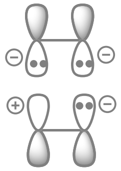

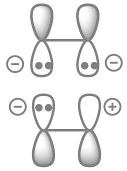

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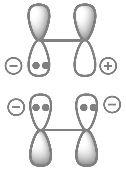
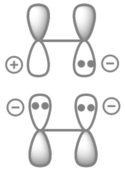


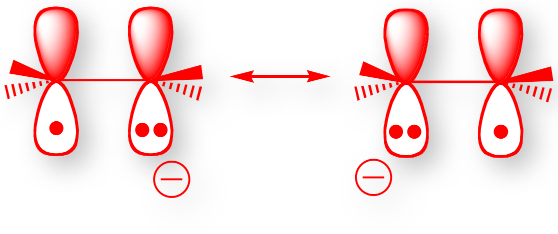


10

⟹ No structure is bonding by itself, **all the bonding comes from the resonance !**

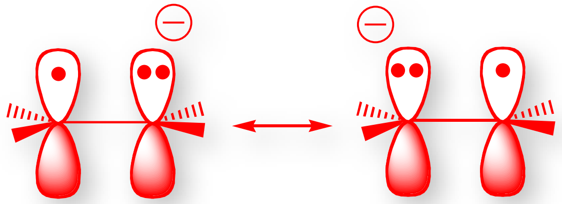
Qualitative VB analysis

- What about three-electron bonding ?...

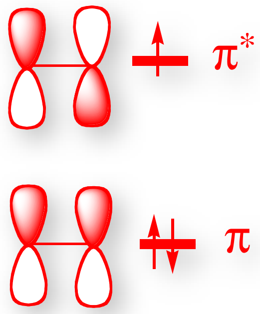


At infinite distance, each fragment displays a **3e$^-$ π bond** :

∞

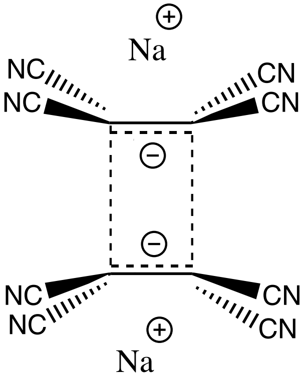


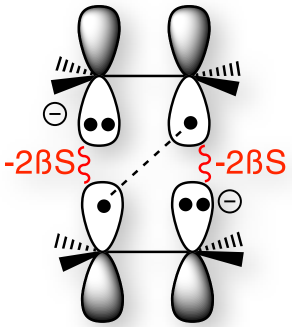
Left-right exchange of the negative charge, equivalent to:



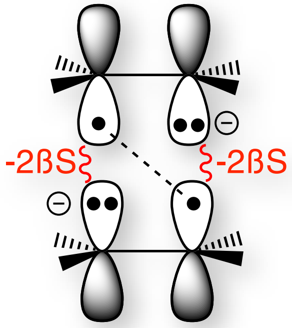
Qualitative VB analysis

- VB set of structures for DTCNE$_2^{2-}$:





1



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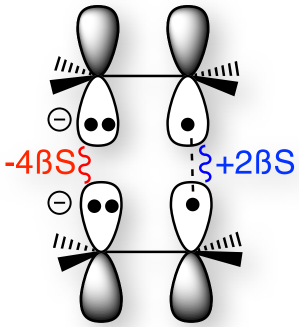

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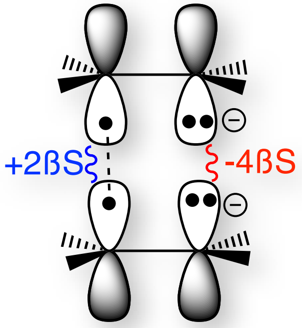

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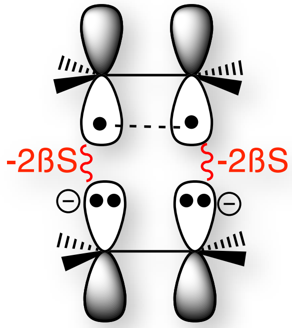

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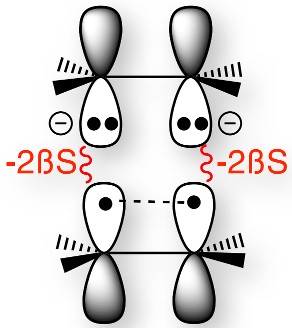
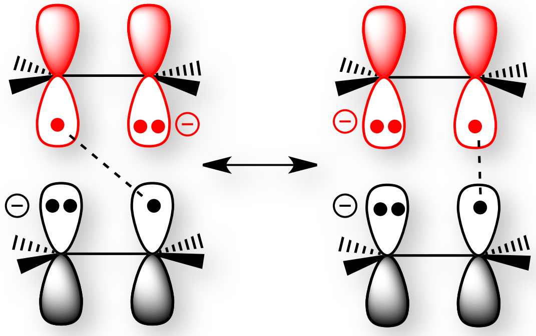


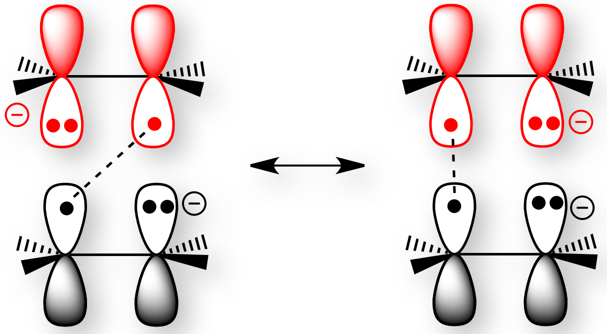
6

Qualitative VB analysis

- 2↔3 and 1↔4 : **intra-fragment $3e^-$ π bond** (upper fragment) :



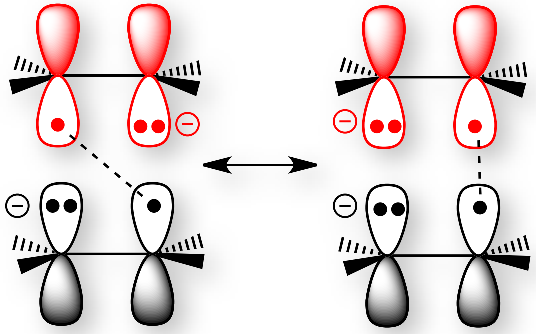
2 **3**



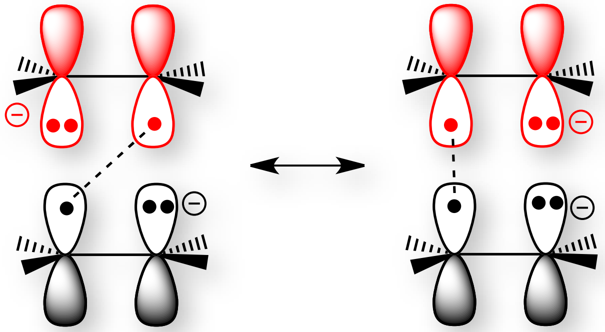
1 **4**

Qualitative VB analysis

- 2↔3 and 1↔4 : **intra-fragment $3e^-$ π bond** (upper fragment) :

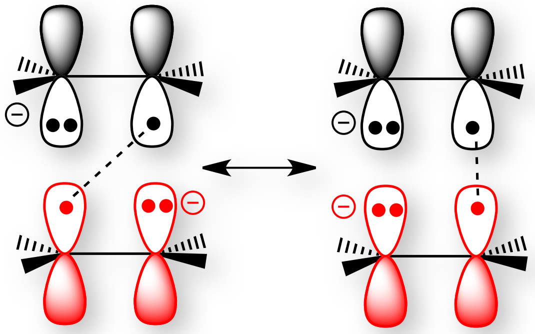


2 **3**

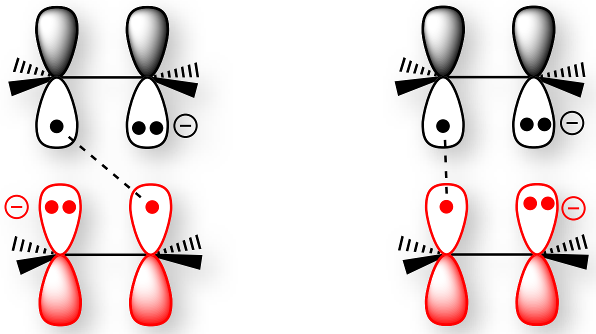


1 **4**

- 1↔3 and 2↔4 : **intra-fragment $3e^-$ π bond** (lower fragment) :



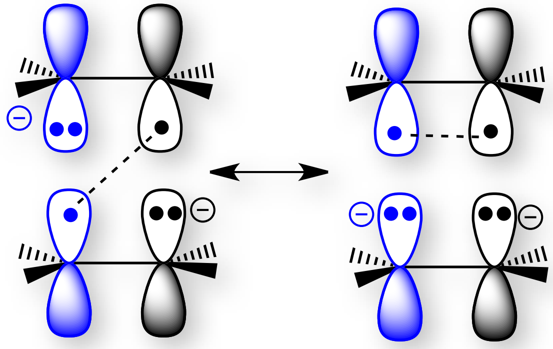
1 **3**



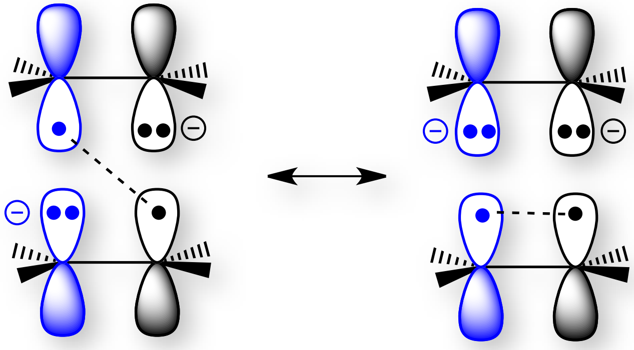
2 **4**

Qualitative VB analysis

- 1↔5 and 2↔6 : **inter-fragment 3e$^-$ π bond** (left-hand side) :

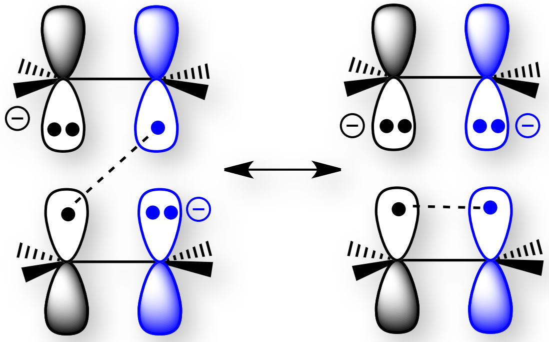


1 **5**

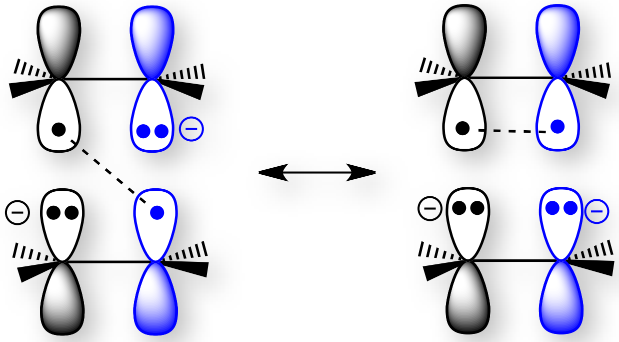


2 **6**

- 2↔5 and 1↔6 : **inter-fragment 3e$^-$ π bond** (right-hand side) :

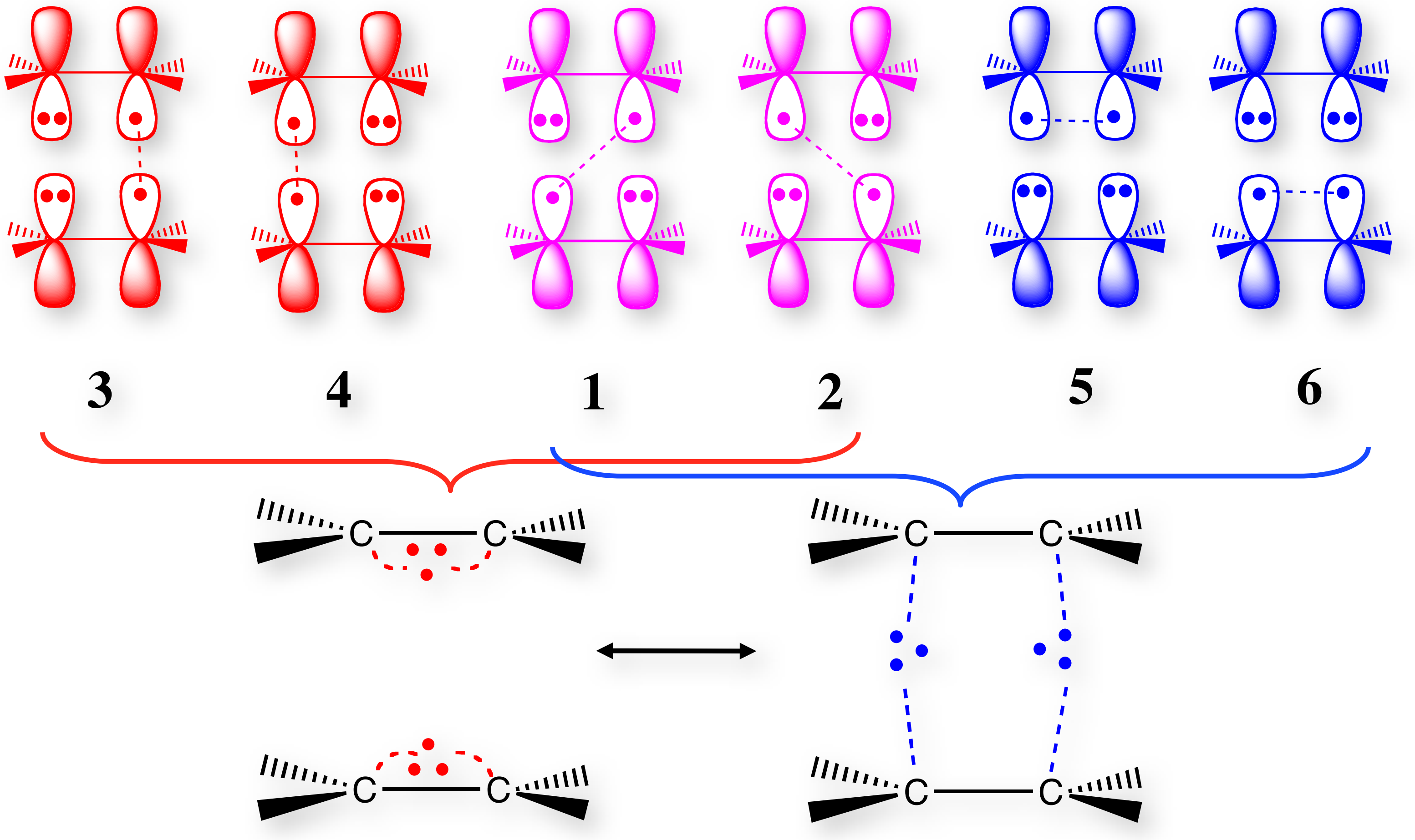


1 **6**



2 **5**

Qualitative VB analysis



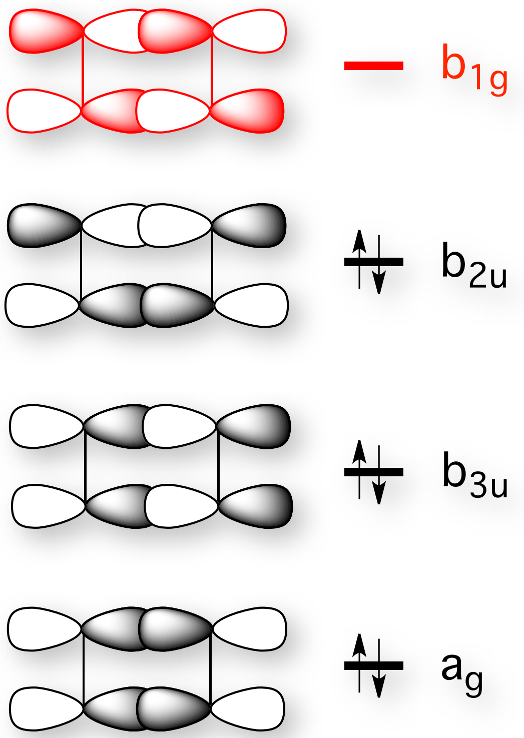
Intra-fragment 3-e π bond Inter-fragment 3-e σ bond

⇒ bonding in DTCNE : two inter-fragment 3e bonds ?

Qualitative VB analysis

- MO/VB mapping :

Development of the HF determinant in the VB basis of structures :

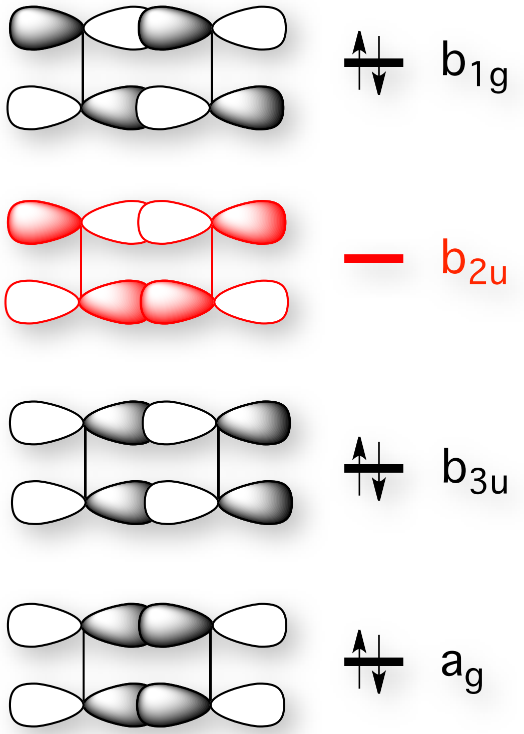


$$\Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = \ominus \Psi_1^{VB} \ominus \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} \ominus \Psi_5^{VB} \ominus \Psi_6^{VB}$$

Qualitative VB analysis

- MO/VB mapping :

Development of the 1st excited det. in the VB basis of structures :

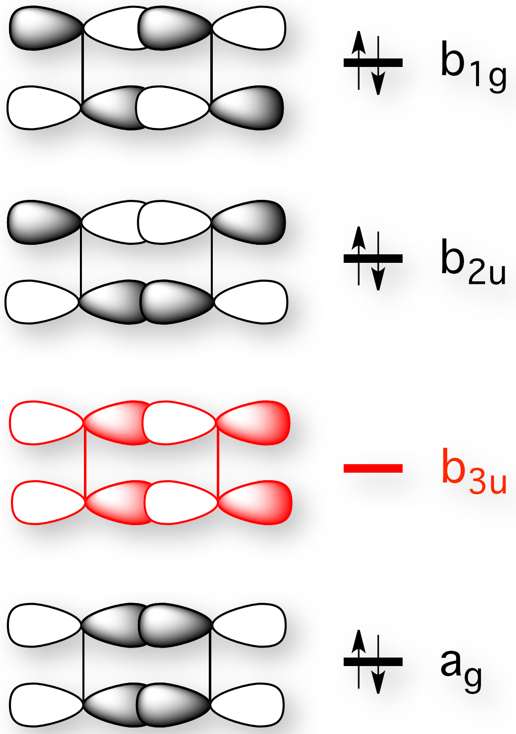


$$\Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} \ominus \Psi_3^{VB} \ominus \Psi_4^{VB} \ominus \Psi_5^{VB} \ominus \Psi_6^{VB}$$

Qualitative VB analysis

- MO/VB mapping :

Development of the 2nd excited det. in the VB basis of structures :

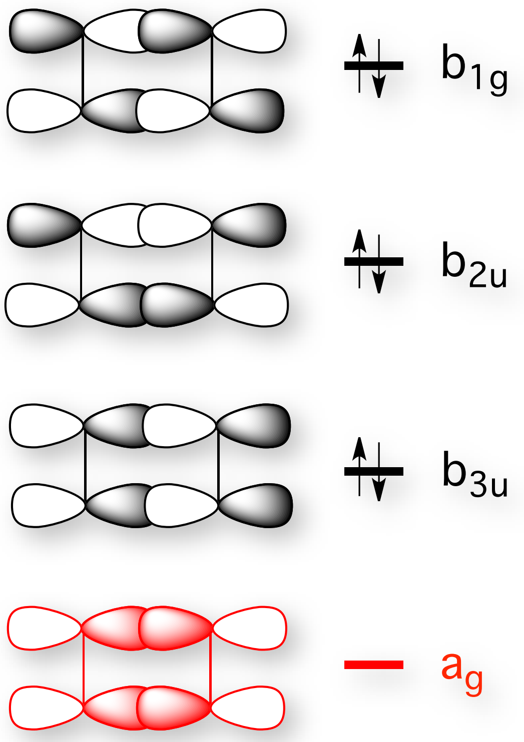


$$\Psi_{2-ext} = \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB}$$

Qualitative VB analysis

- MO/VB mapping :

Development of the 3rd excited det. in the VB basis of structures :



$$\Psi_{3-ext} = \left| b_{3u}\bar{b}_{3u}b_{2u}\bar{b}_{2u}b_{1g}\bar{b}_{1g} \right| = \ldots = -\Psi_1^{VB} - \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB}$$

Qualitative VB analysis

- MO/VB mapping :

CAS(4,4) ⇔ 6 VB structures mixing :

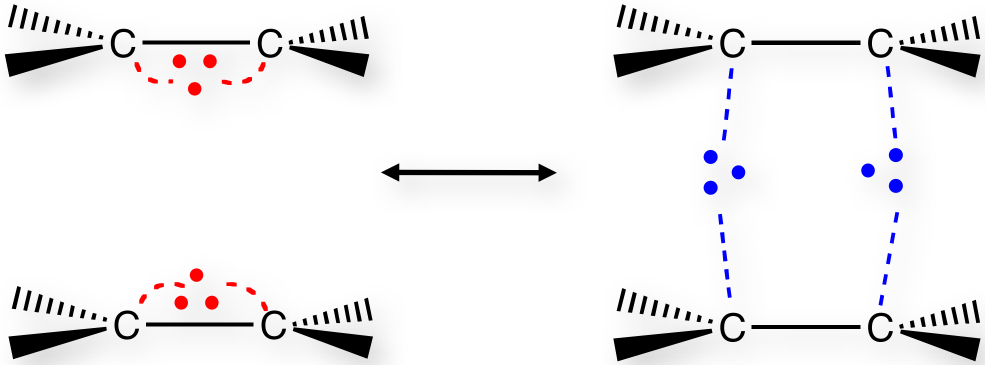
$$\begin{cases} \Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\ \Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB} \\ \Psi_{2-ext} = \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\ \Psi_{3-ext} = \left| b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB} \end{cases}$$

MO (4x4) description = VB description, but...

the VB analysis which reveals the 3e-bond nature

Qualitative VB analysis

- Conclusion of the qualitative VB analysis :



Intra-fragment 3-e π bond

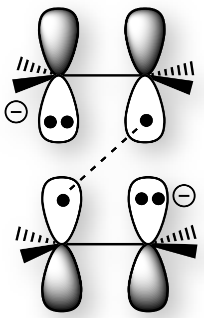
Inter-fragment 3-e σ bond

Bonding in DTCNE :

two inter-fragment 3e bonds ?...

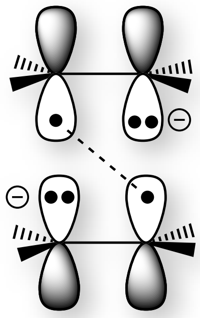
Ab initio VB calculations

- $DTCNE_2^{2-}$: computed weights (J-VB) :



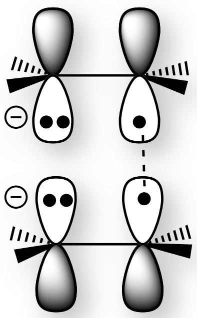
1

20.2%



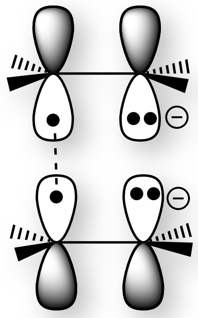
2

20.2%



3

16.1%



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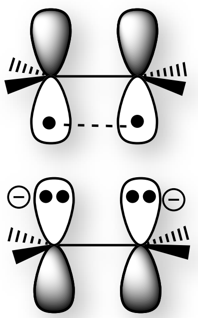
16.1%



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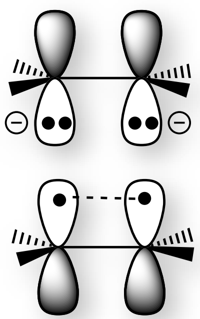
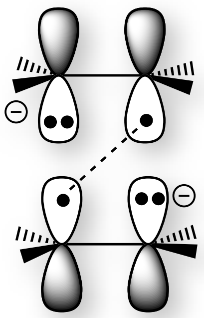


6

10.1%

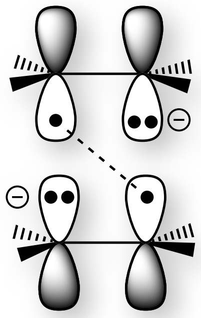
Ab initio VB calculations

- $DTCNE_2^{2-}$: computed weights (J-VB) :



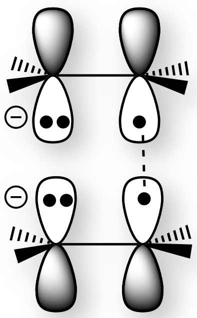
1

20.2%



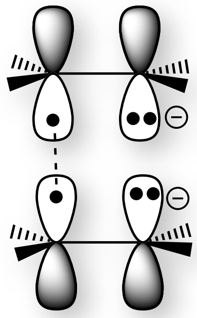
2

20.2%



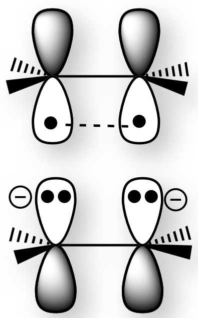
3

16.1%



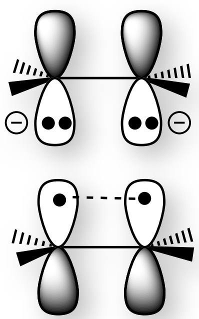
4

16.1%



5

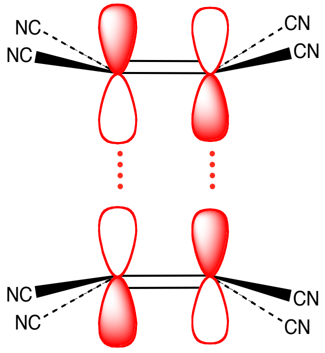
10.1%



6

10.1%

- Interfragment 2e bond ?



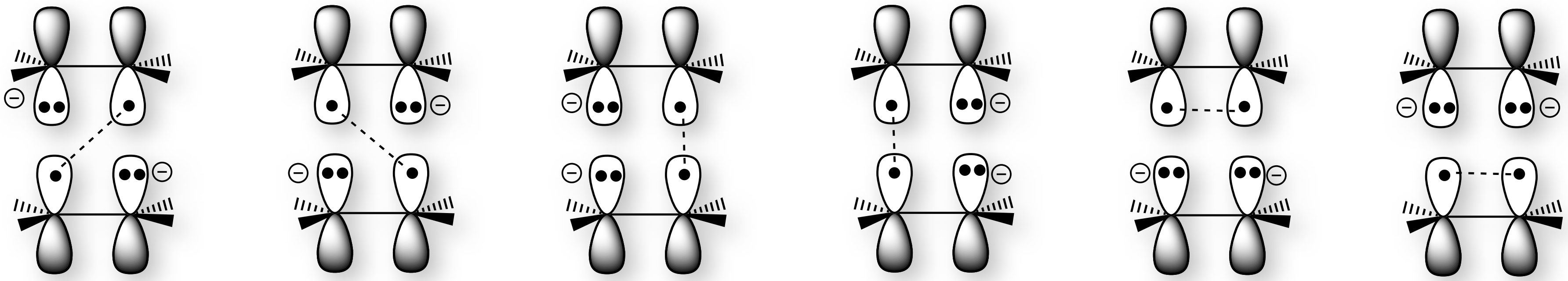
MO/VB maping :

Purely covalent π*-π* 2-e bond =

1 + **2** + **3** + **4** (equal weights)

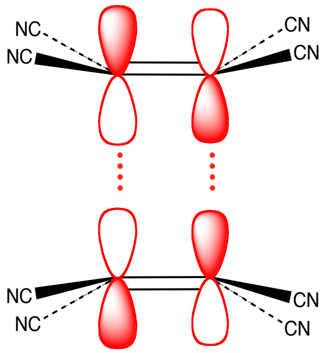
Ab initio VB calculations

- DTCNE$_2^{2-}$: computed weights (J-VB) :



1	**2**	**3**	**4**	**5**	**6**
20.2%	20.2%	16.1%	16.1%	**10.1%**	**10.1%**

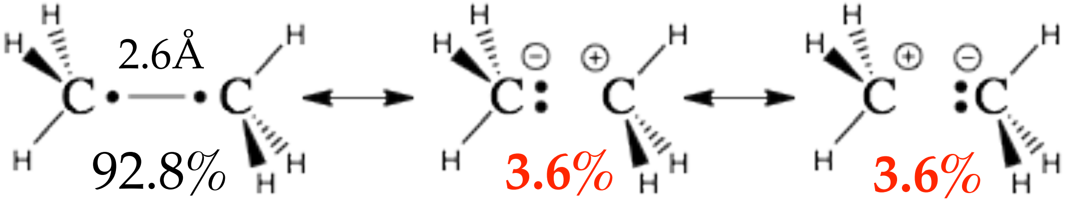
- Interfragment 2e bond ?



(covalent + ε ionic) π-π* 2-e bond =

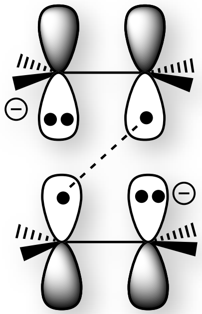
1 + **2** + **3** + **4** + ε (**5** + **6**)

However, ε = 3.6% in a stretched C-C bond:



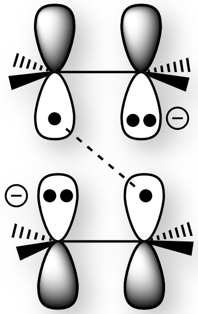
Ab initio VB calculations

- $DTCNE_2^{2-}$: computed weights (J-VB) :



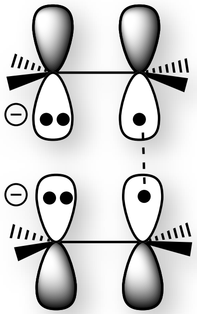
1

20.2%



2

20.2%



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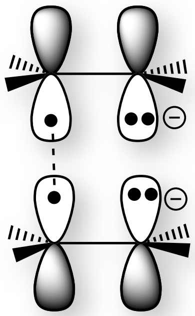
16.1%



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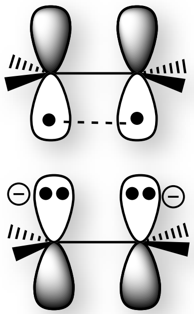
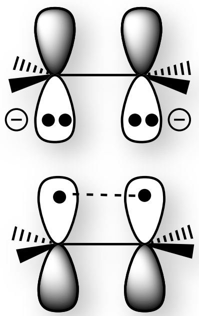


5

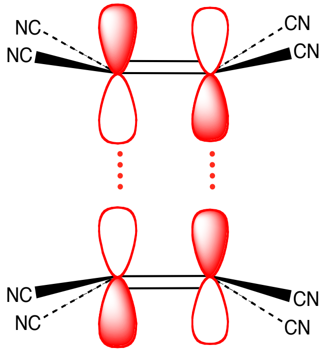
10.1%



6

10.1%

- Interfragment 2e bond ?



(covalent + ε ionic) π-π* 2-e bond =

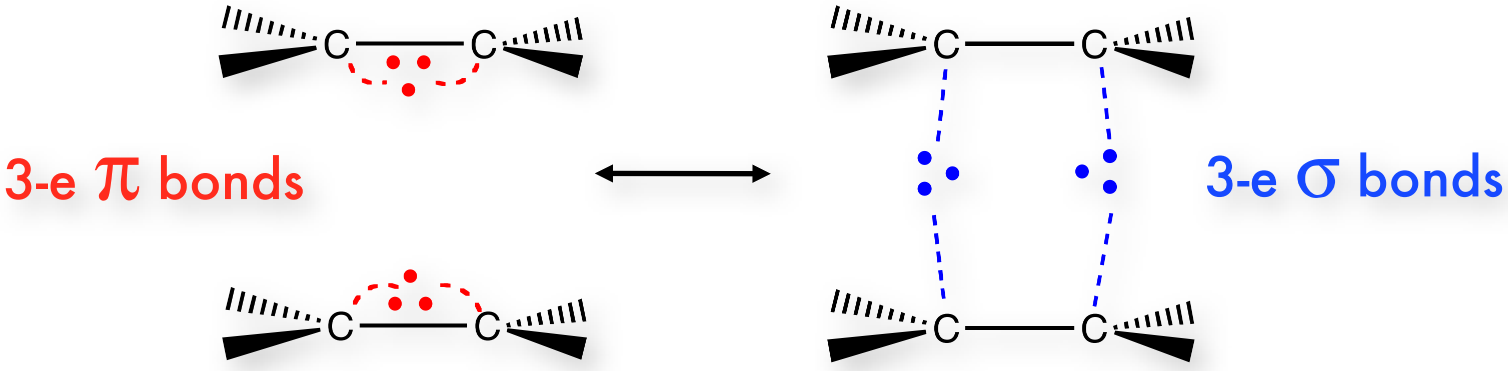
$\mathbf{1} + \mathbf{2} + \mathbf{3} + \mathbf{4} + \varepsilon\,(\mathbf{5} + \mathbf{6})$

However, $\varepsilon = 3.6\%$ in a stretched C-C bond:

⇒ The inter-fragment bond cannot be a simple π-π* 2-e bond

Ab *initio* VB calculations

- Some tests of credibility :



3-e π bonds

3-e σ bonds

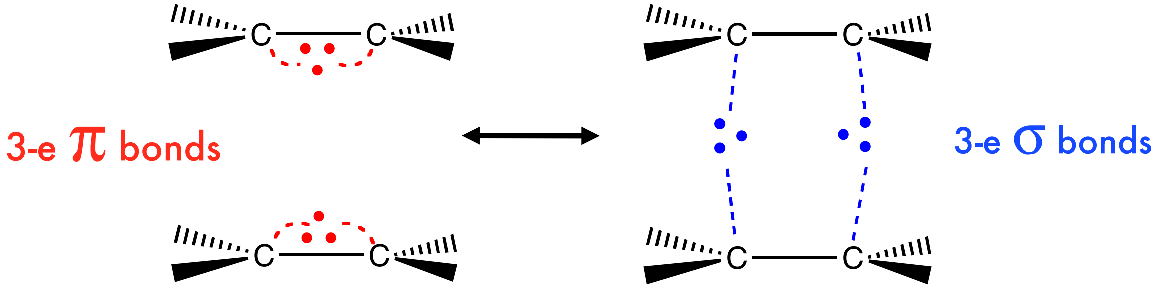
Characteristics of 3e bonds :

1) Large equilibrium distances : $d(S—S) \approx 2.0$ Å ; $d(S \therefore S^-) \approx 2.8$ Å

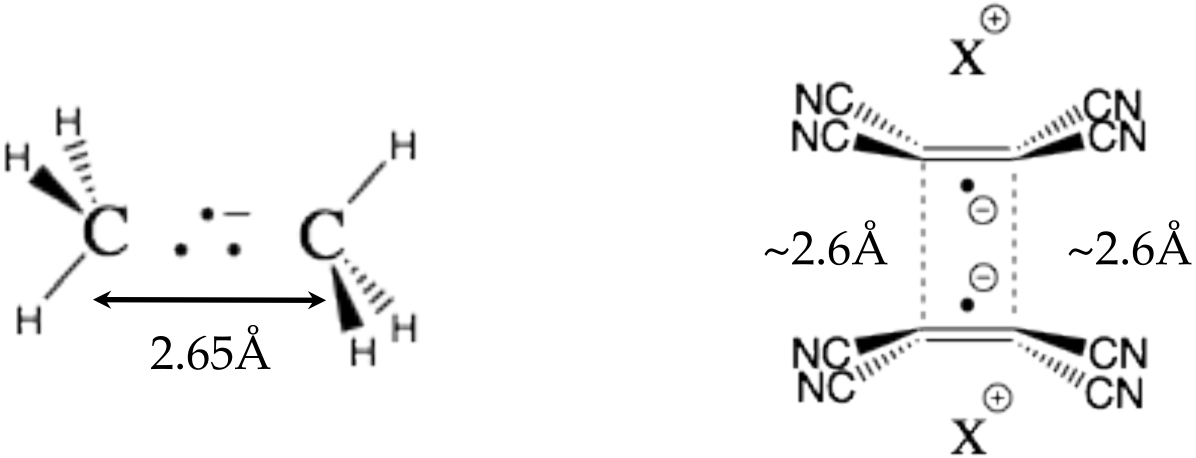
2) Small overlap $(S_{opt} \approx 0.17)$

3) Importance of dynamical correlation

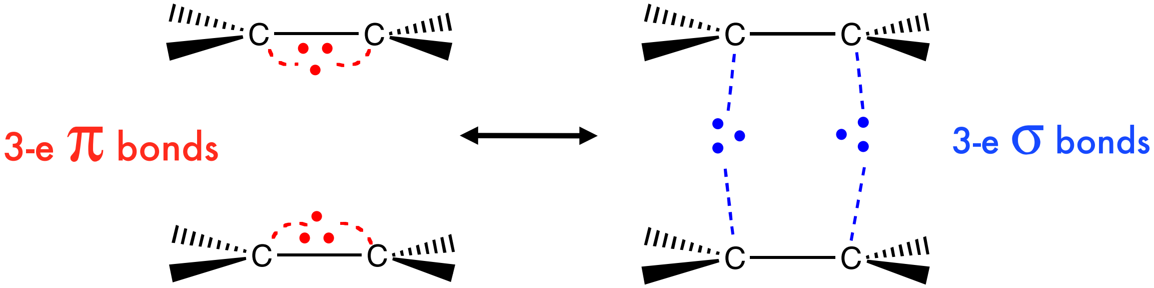
Ab *initio* VB calculations



1) Interfragment bond length close to 3e$^-$ bonded ethane anion :



Ab initio VB calculations



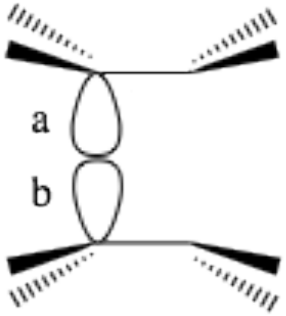
2) Interfragment orbital overlaps close to optimal 3e$^-$ bond value :

$$S_{opt} \approx 0.17$$

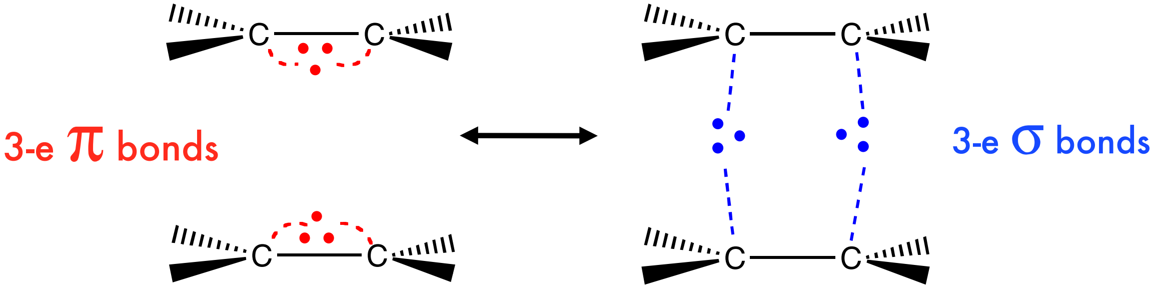
for any 3-e bond
(demonstrated in
qualitative VB theory
as well as Extended Hückel theory)

$$S_{ab} = 0.15$$

(computed)



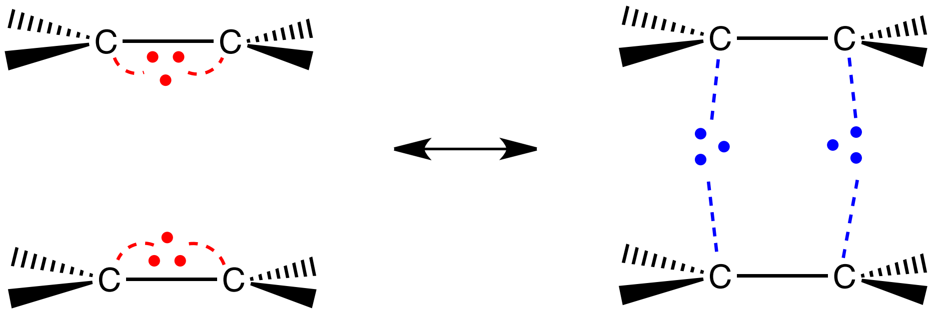
Ab initio VB calculations



3) Contribution of dynamic correlation to bonding:

- In **$[F\therefore F]^-$**, dynamic correlation contributes ~ 30 kcal/mol to bonding
- In **$[TCNE]_2^{2-}$**, dynamic correlation contributes > 30 kcal/mol to bonding

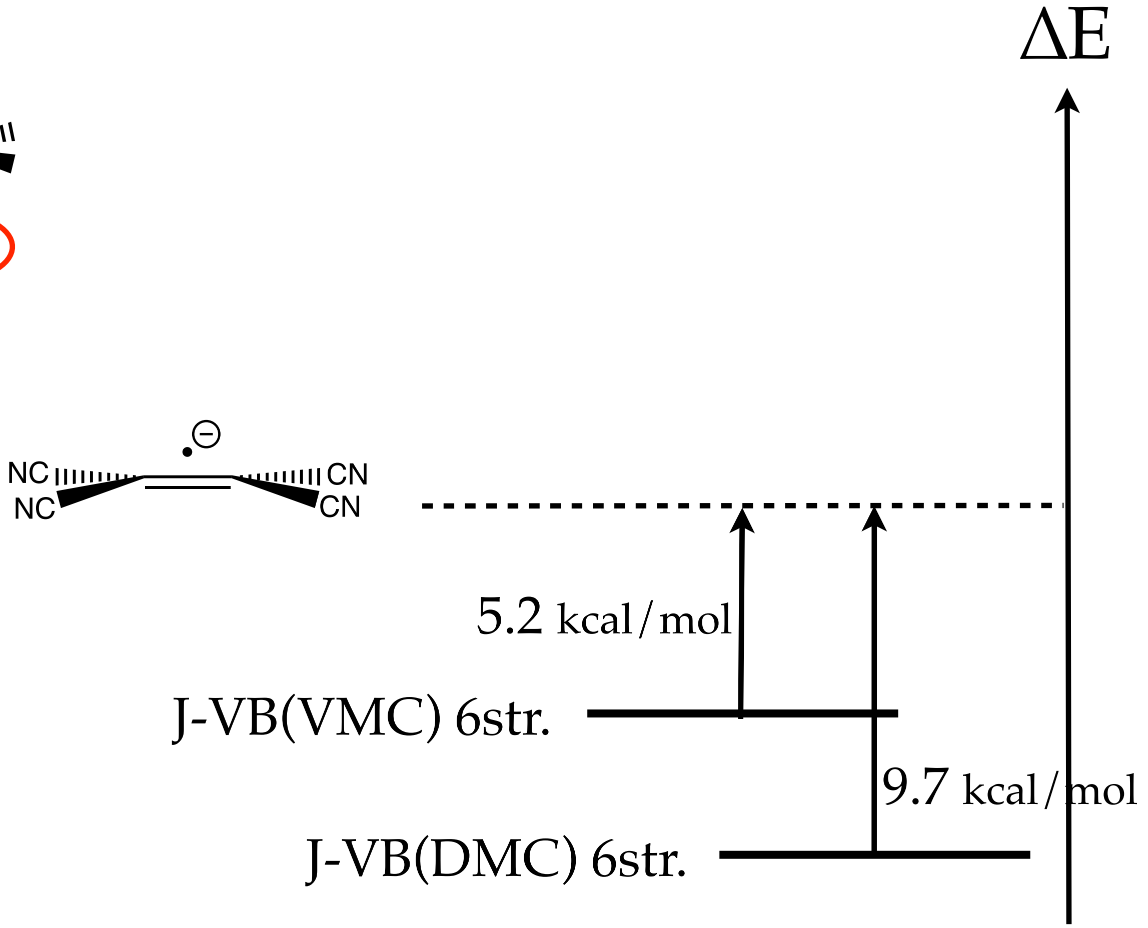
Ab initio VB calculations



1↔2↔3↔4

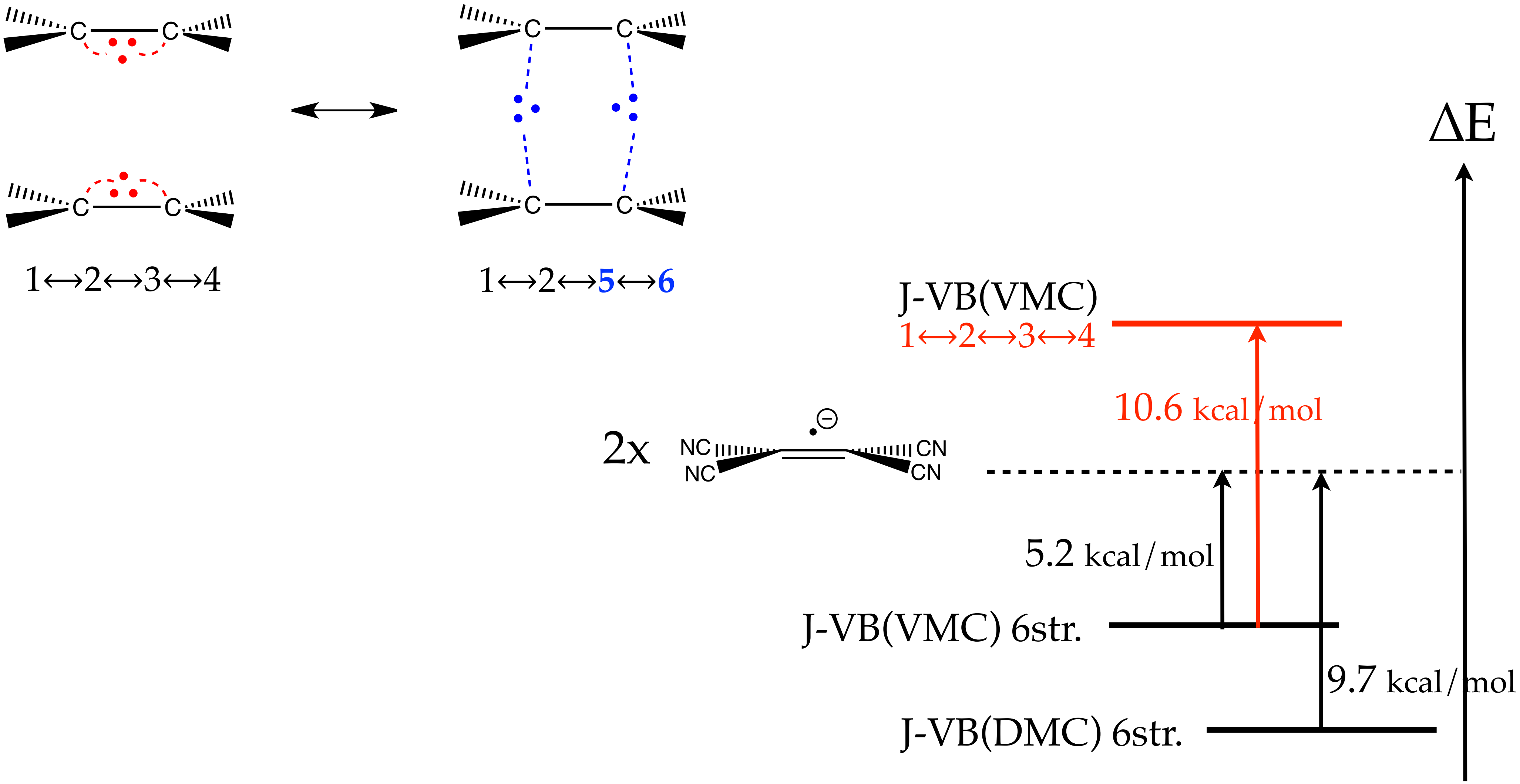
1↔2↔**5↔6**

2x



ΔE(«reference») ≈ 11. kcal/mol

Ab initio VB calculations



1↔2↔3↔4

1↔2↔**5**↔**6**

2x

J-VB(VMC)
1↔2↔3↔4

10.6 kcal/mol

5.2 kcal/mol

J-VB(VMC) 6str.

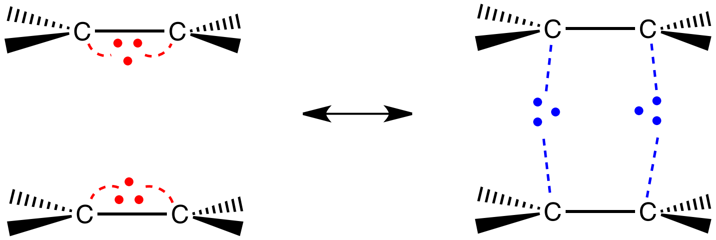
9.7 kcal/mol

J-VB(DMC) 6str.

⟹ Without str. 5-6, DTCNE becomes repulsive !

Conclusion

- About $[TCNE]_2^{2-}$:



- A simple VB wave function in terms of only 6 VB structures accurately describes the electronic structure of $[TCNE]_2^{2-}$

- Even when electrostatic interaction is repulsive (axial conformation), the two fragment anions are directly bonded by **a pair of 3-e bonds**

- This simple picture explains at once :

  1) the unusual bond length,
  2) the interfragment overlap,
  3) the importance of dynamic correlation