Part 2. *Ab initio* Valence Bond

VB tutorial

<<< VB workshop program page

An Ab Initio Non-orthogonal Valence Bond Program

Four tutorials ("hands-on" labs) sessions are planned, where participants will learn to use the XMVB program, as well as the BLW and HuLis programs, and apply the methods and concepts on some chemical problems of progressive difficulty. Part of the «hands-on» sessions can as well be used by participants for questions/answers concerning the main lectures or book exercises. Rooms will also be at the disposal of participants during the «hands-on» time for free discussions.

Contents [hide]

The XMVB program

[edit]

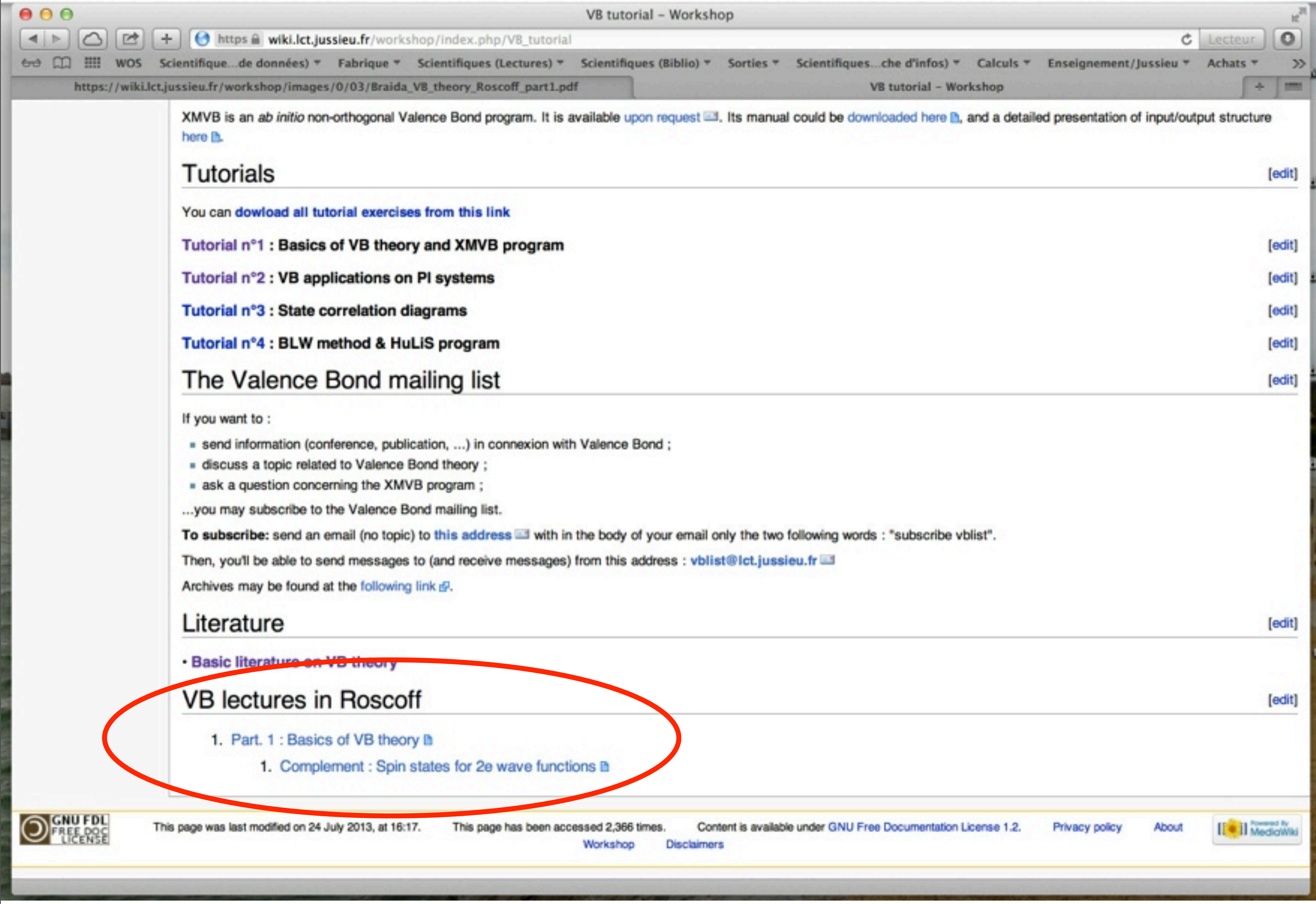
XMVB is an *ab initio* non-orthogonal Valence Bond program. It is available upon request. Its manual could be downloaded here, and a detailed presentation of input/output structure here.

Tutorials

[edit]

You can **dowload all tutorial exercises from this link**

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



XMVB is an *ab initio* non-orthogonal Valence Bond program. It is available upon request. Its manual could be downloaded here, and a detailed presentation of input/output structure here.

Tutorials

[edit]

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Tutorial n°1 : Basics of VB theory and XMVB program [edit]

Tutorial n°2 : VB applications on PI systems [edit]

Tutorial n°3 : State correlation diagrams [edit]

Tutorial n°4 : BLW method & HuLiS program [edit]

The Valence Bond mailing list

[edit]

If you want to :

- send information (conference, publication, ...) in connexion with Valence Bond ;
- discuss a topic related to Valence Bond theory ;
- ask a question concerning the XMVB program ;

...you may subscribe to the Valence Bond mailing list.

To subscribe: send an email (no topic) to **this address** with in the body of your email only the two following words : "subscribe vblist".

Then, you'll be able to send messages to (and receive messages) from this address : **vblist@lct.jussieu.fr**

Archives may be found at the following link.

Literature

[edit]

- **Basic literature on VB theory**

VB lectures in Roscoff

[edit]

1. Part. 1 : Basics of VB theory
    1. Complement : Spin states for 2e wave functions

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

Ab initio Valence Bond

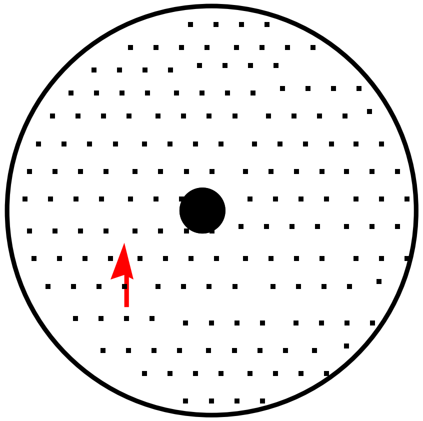
- Electron correlation
- VB methods including electron correlation
- VB computation in practice
- Illustrative application
- Limits of VB theory

Stop me at any time !

Electron correlation

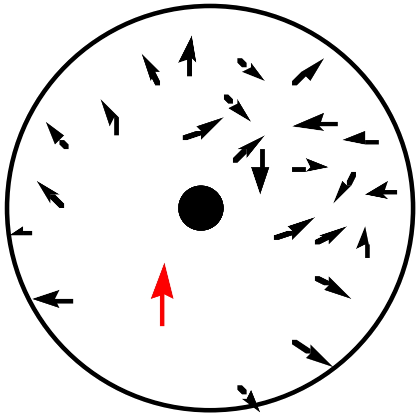
- Nature of electron correlation :
  - «Uncorrelated» (Ψ_{HF} or Ψ_{HL}) :

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



  - Correlated :

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

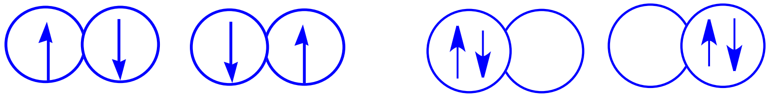


Electron correlation

- «Uncorrelated» methods :

$$\hat{H} = \hat{T} + \hat{V} \longrightarrow \hat{V}_{ee} + \hat{V}_{en}$$

Ψ_{HF} too much ionic :



50% covalent 50% ionic

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

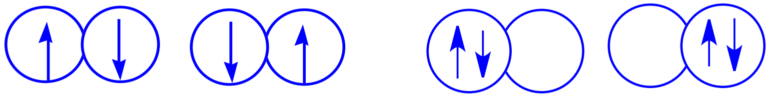
$\hat{V}_{ee}$ too large (ionic : high probability to find e⁻ in the same place)

Electron correlation

- «Uncorrelated» methods :

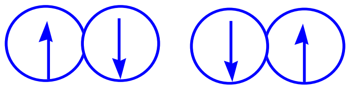
$$\hat{H} = \hat{T} + \hat{V} \rightarrow \hat{V}_{ee} + \hat{V}_{en}$$

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 (ionic : high probability to find e⁻ in the same place)

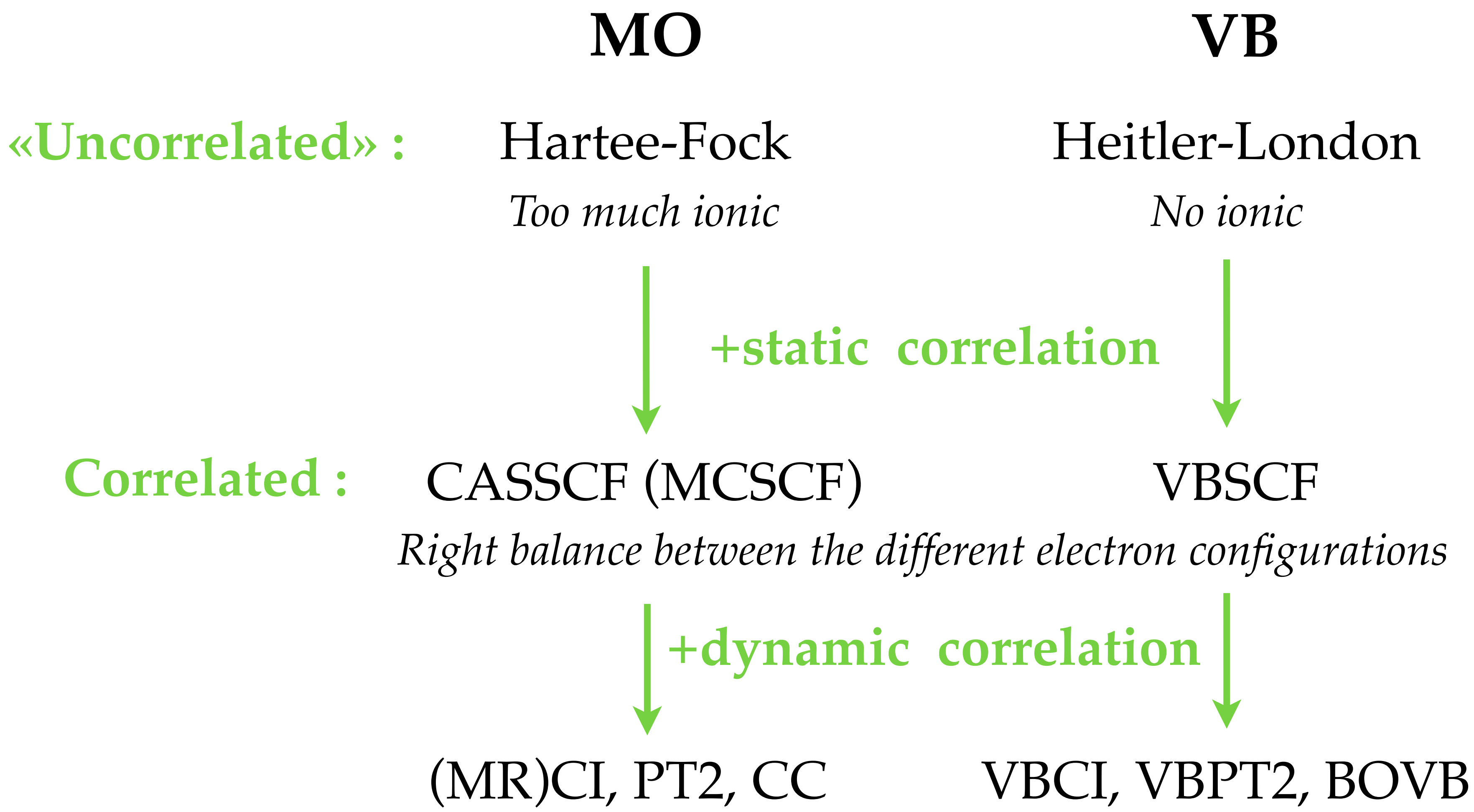
$\hat{T}$ too large (e⁻ visit a small box)

$\hat{V}_{ee}$ **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 :



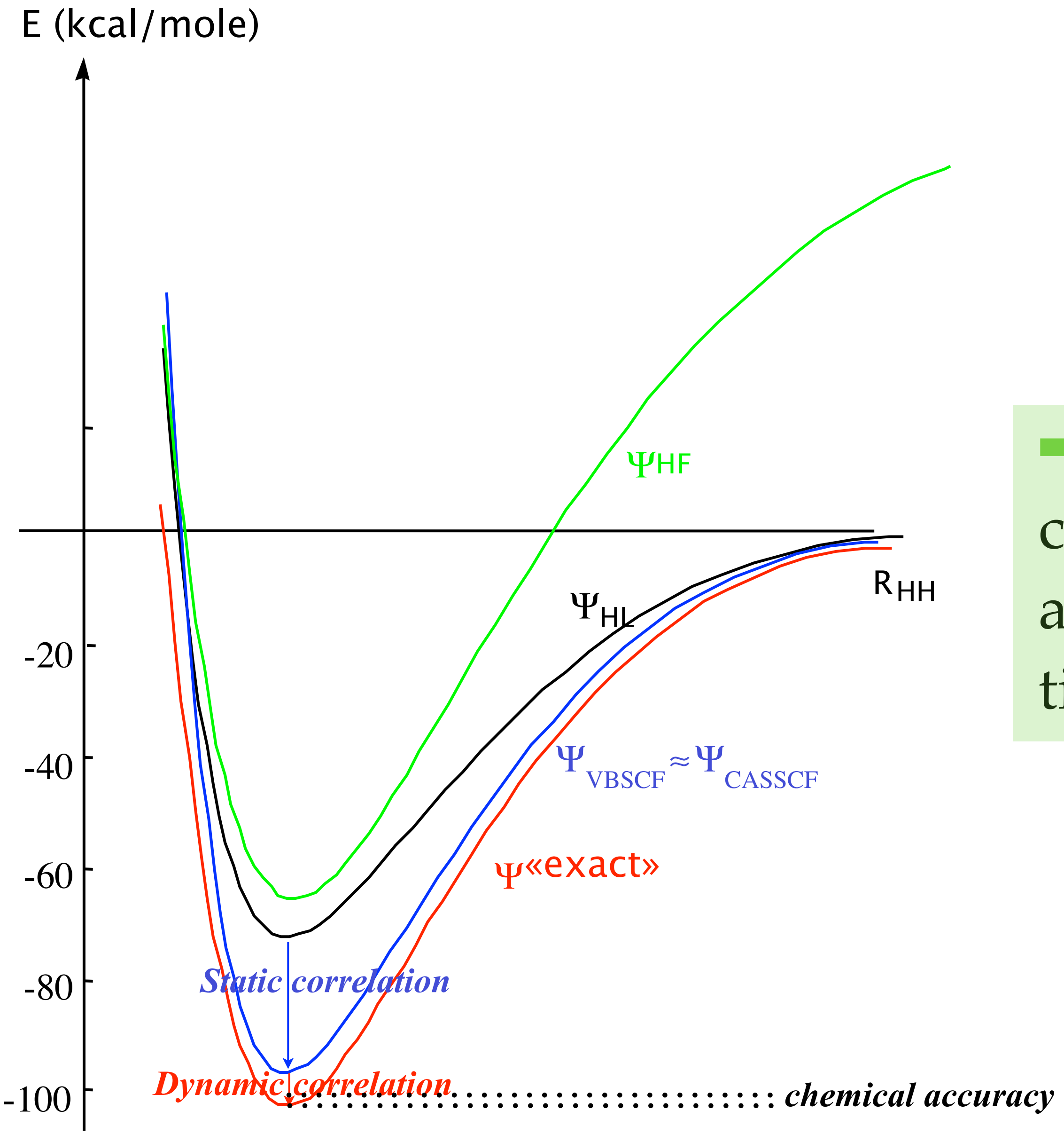
	MO	**VB**
«Uncorrelated» :	Hartee-Fock *Too much ionic*	Heitler-London *No ionic*
	+static correlation	
Correlated :	CASSCF (MCSCF)	VBSCF

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 :

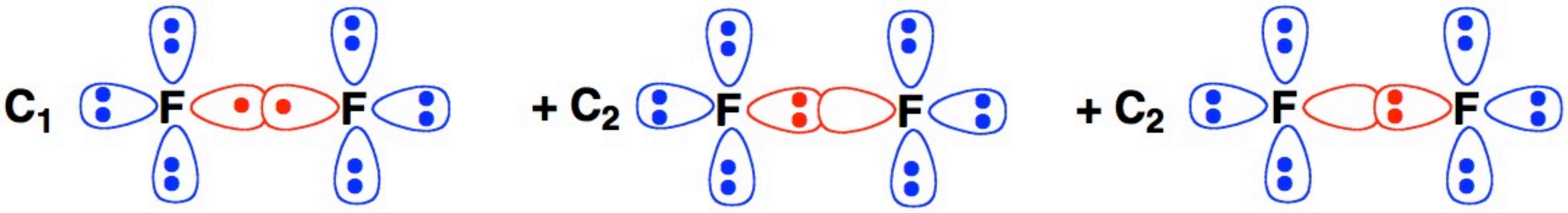
$$\boxed{\Psi_{VBSCF} = \sum_K C_K \Phi_K} \quad \text{with :} \begin{cases} \Phi_K(1,\ldots,N) = \hat{A}\{\prod_{i=1}^{N} \varphi_i(1)\Theta_K\} : \text{VB structures} \\ \{\varphi_i\} : \text{set of non-orthogonal localized orbitals} \\ \qquad \text{expanded onto a set of basis functions } \{\chi_m\}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

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 :**

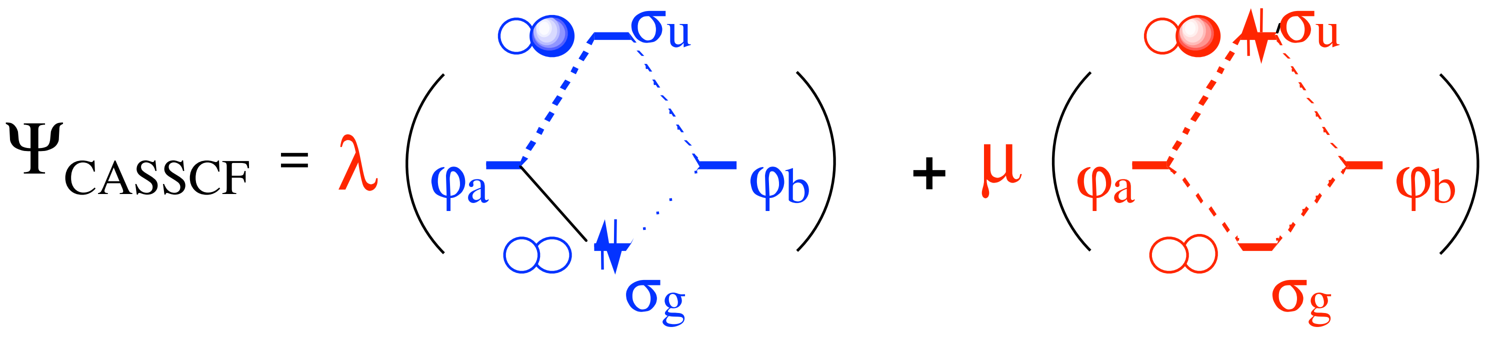


	F•—•F	F^-F^+	F^+F^-
HF :	50%	25%	25%
HL :	100%	0%	0%
VBSCF :	**80%**	**10%**	**10%**

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

VB methods including correlation

- **The VBSCF method :**
  - 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 :

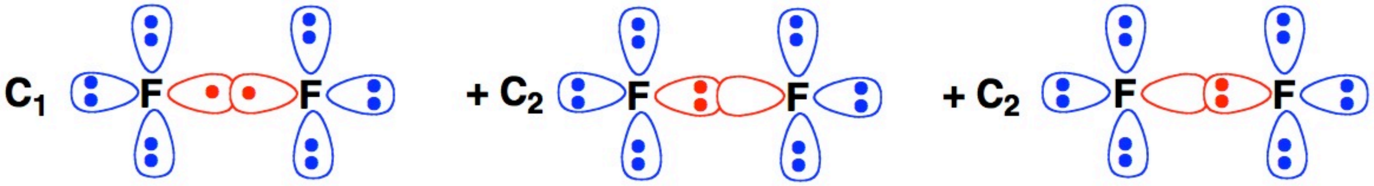
$$\mathbf{F{-}F} \xrightarrow{\Delta \mathrm{E}} \mathbf{F\bullet} + \mathbf{F\bullet}$$

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

Some important physical ingredient is missing...

VB methods including correlation

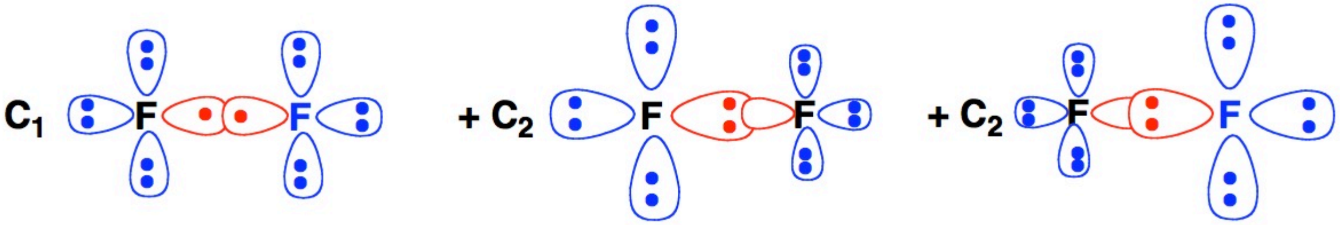
- **The VBSCF method :**
  - What the VBSCF method does :



F•—•F $\quad$ F^-F^+ $\quad$ 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 :

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

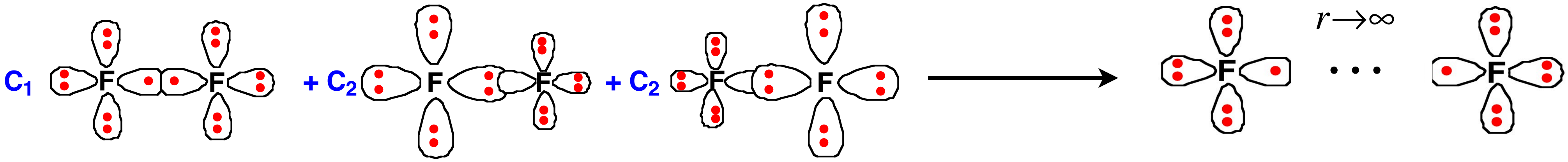
All w.f. parameters : structure coef. $\{C_K\}$ and orb. coef. **sets** $\{d^i_m\}^K$ are optimized simultaneously minimizing $\langle \Psi_{BOVB} | \hat{H} | \Psi_{BOVB} \rangle$

* *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

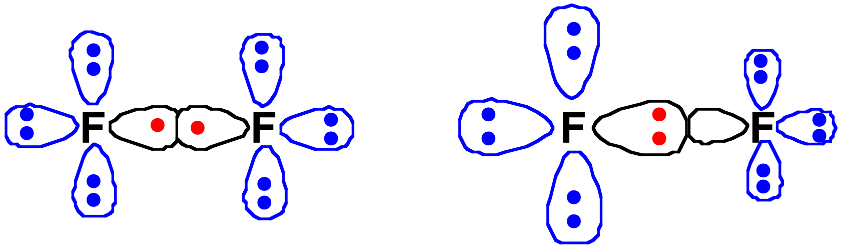
  - BOVB keeps the same **compacity** as the VBSCF wave function

  - BOVB provides a visual image of the role of electron correlation

VB methods including correlation

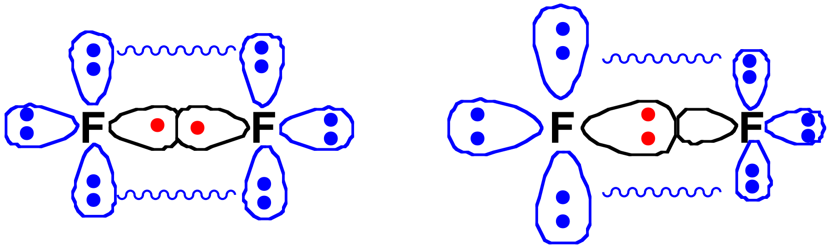
- **The BOVB method :**

- **L-BOVB :**



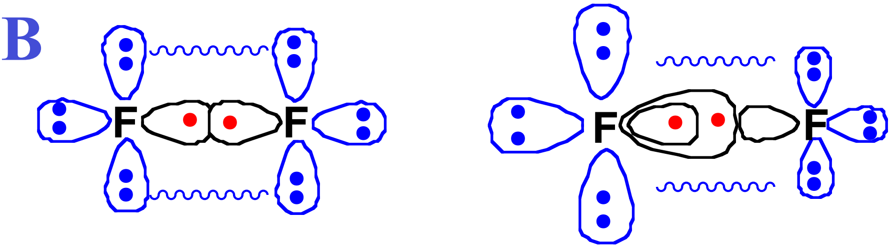
All orbitals are localized, ionics are closed-shell

- **D-BOVB :**



Spectator orbitals are delocalized in all structures

- **SD-BOVB**

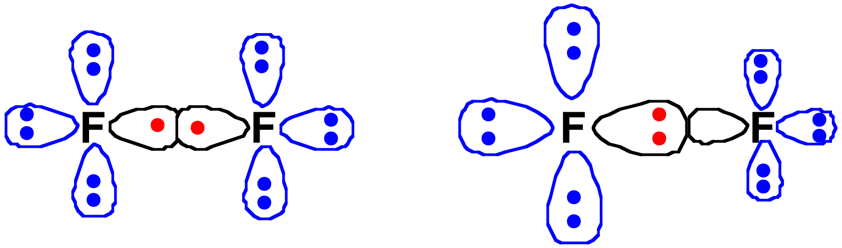


- Active orbitals are split in ionics
- Spectator orbitals are delocalized in all structures

VB methods including correlation

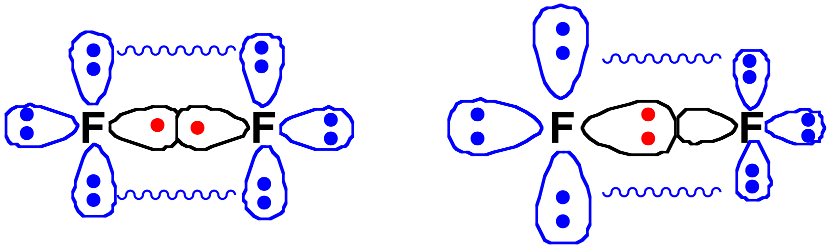
- **The BOVB method :**

- **L-BOVB :**



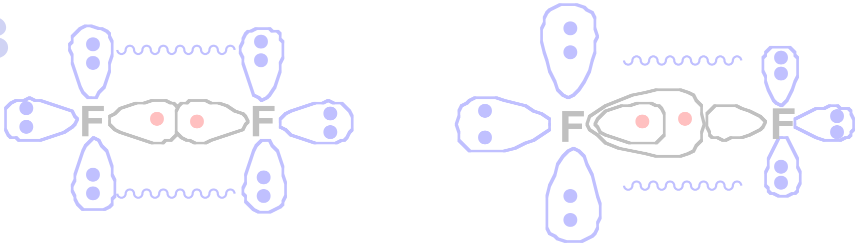
All orbitals are localized, ionics are closed-shell

- **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 :

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

	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 $\Phi^0{}_K$ are the fundamental structures (obtained from VBSCF)

- and $\Phi^i{}_K$ are excited structures, built from $\Phi^0{}_K$ by replacing an occupied by a virtual orbital, but having the **same physical meaning** as $\Phi^0{}_K$:

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

➡ 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 procedure to occupied orbitals on their own fragments :

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

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

VB methods including correlation

- **The VBCI method :**

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

- The energy is obtained by :

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

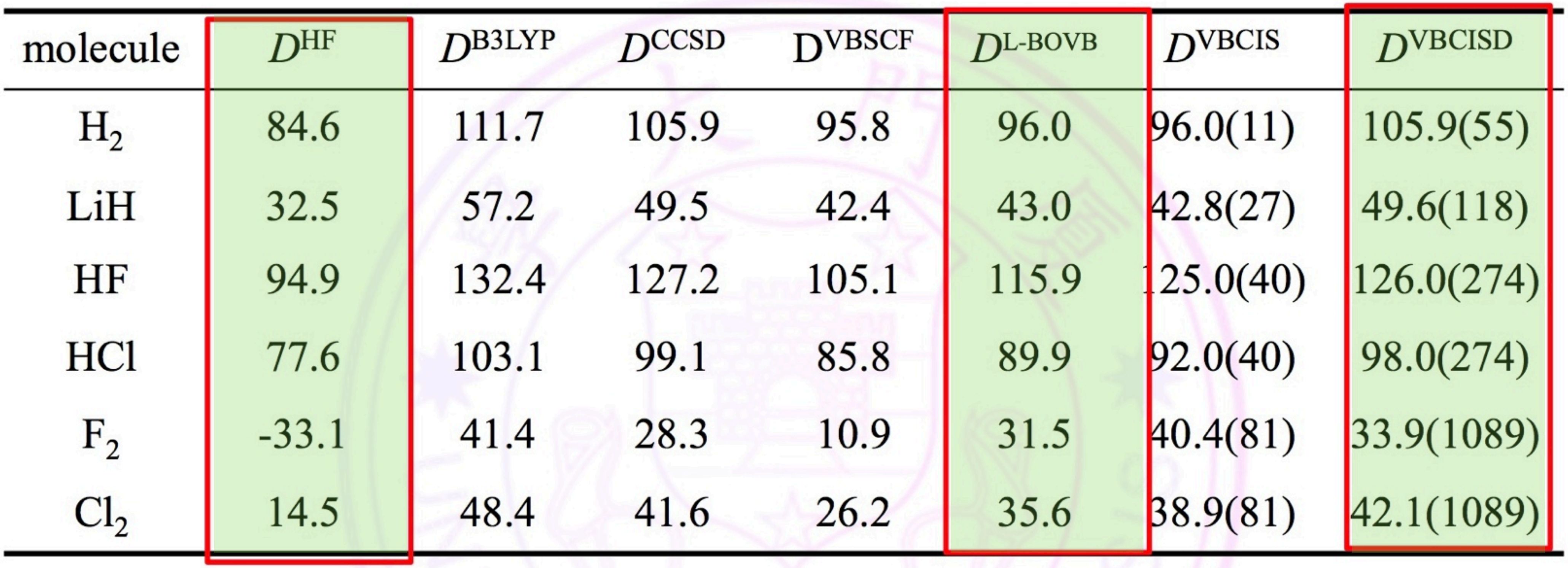
- A Davidson type of correction to the energy also exists :

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

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

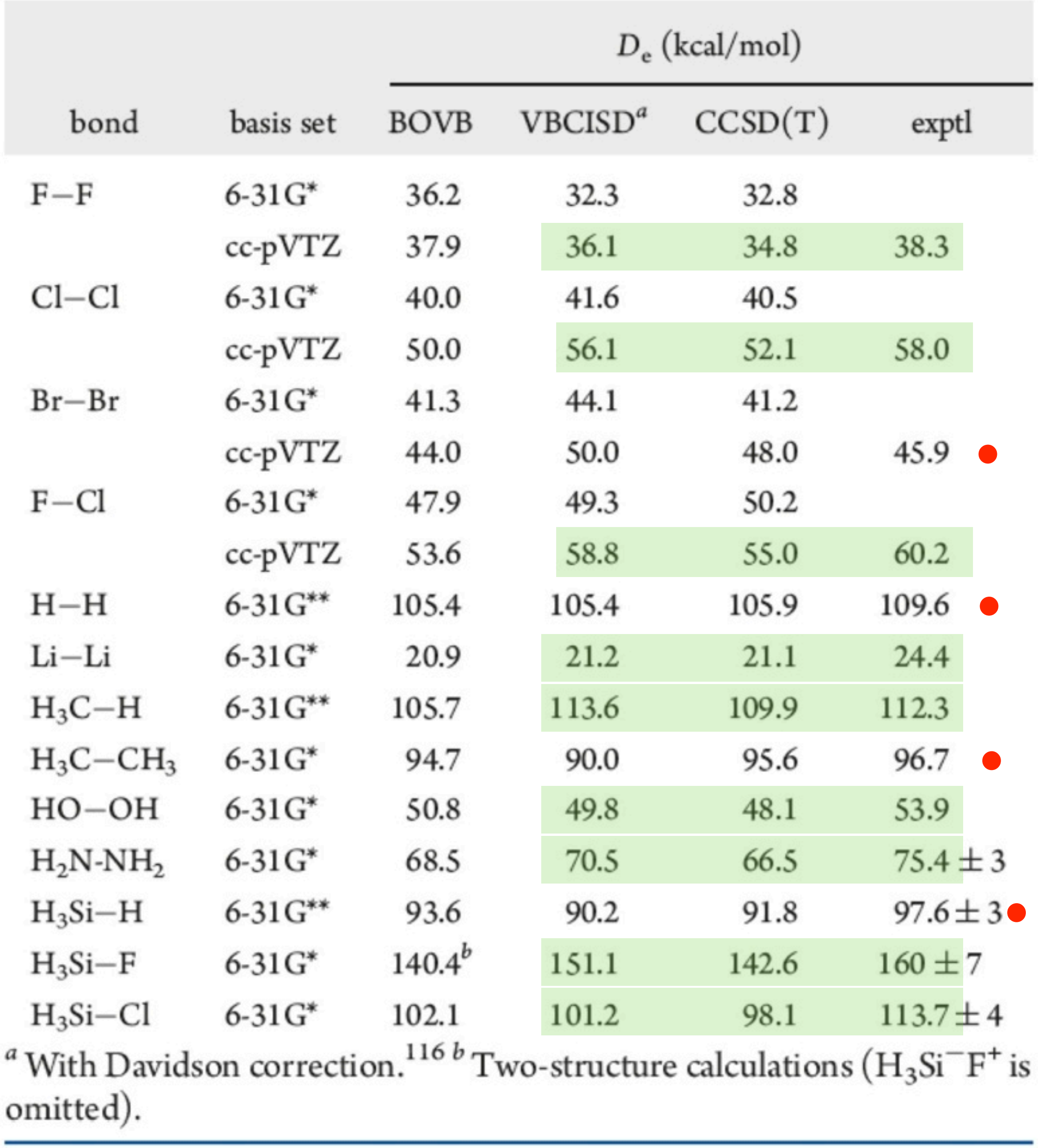
VB methods including correlation

- **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 :**

  - 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

➡ When pushed to their highest level, MO-based and VB-based methods ultimately converge to the same limit

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 :**

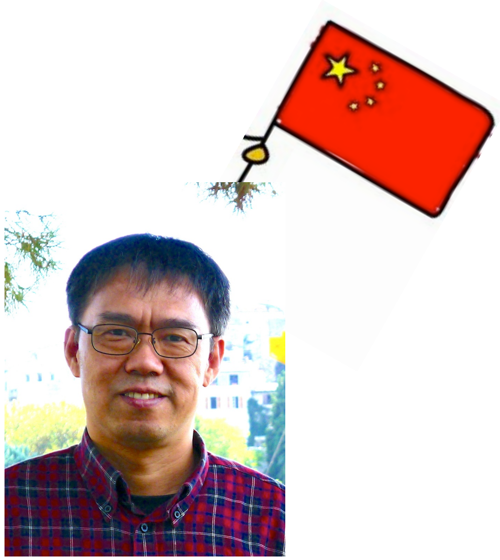
  - **(ic)VBPT2 :** very cheap, the interpretability of the VB w.f. is lost at the moment (delocalized virtual orbitals)...

  - **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 methods including correlation

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



VB computations in practice

What do you still have to know ?

VB computations in practice

- **Basis of structures :**

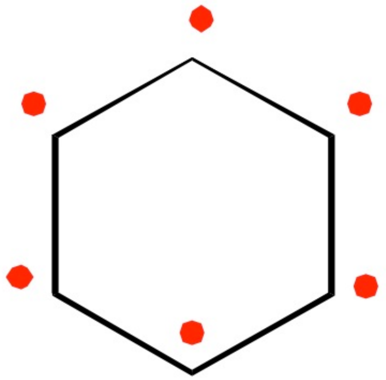
The VB w.f. is a superposition of structures (covalent, ionic,...) :

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

C_K : coefficients

Φ_K : VB structures

➡ *Which structures to choose ?*



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

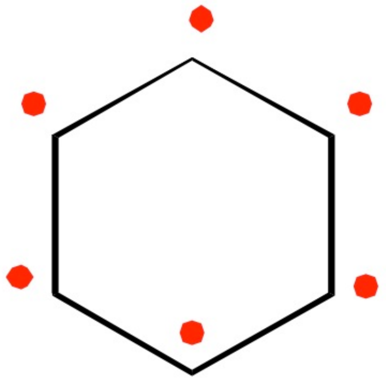
Three methods to generate a complete basis of structures :

- **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



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

VB computations in practice

- **Basis of structures / graphical Rumer's method :**
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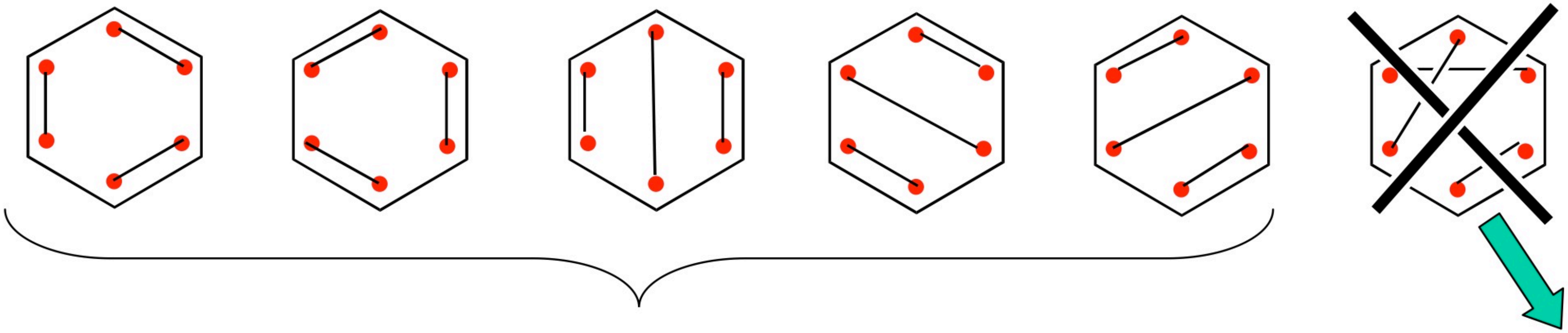

- Complete and non-redundant set of VB structures
- VB structures are «chemically meaningful»

- 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

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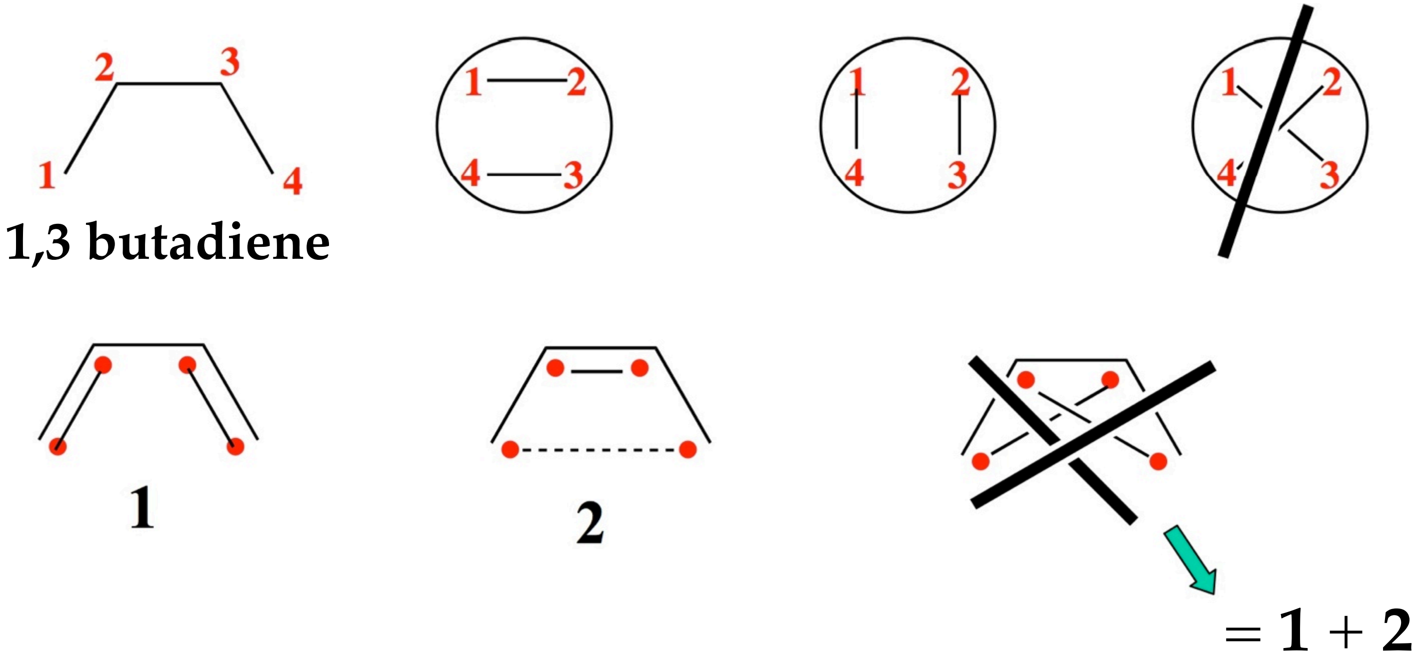


1,3 butadiene

1

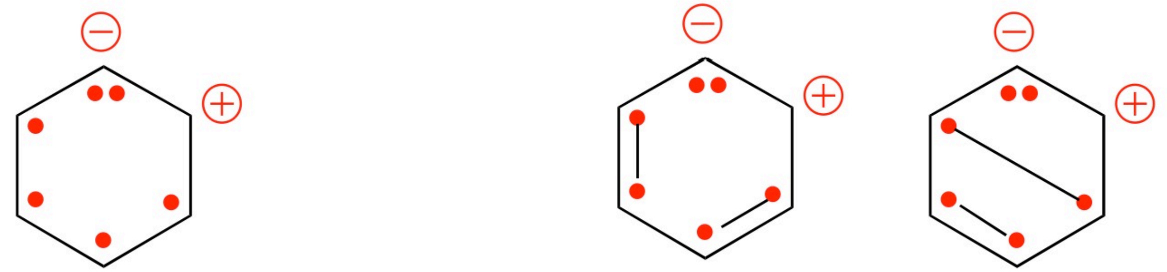
2

= **1** + **2**

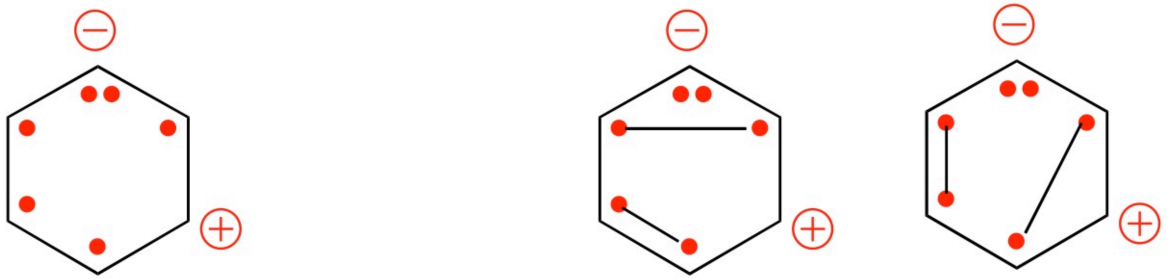
VB computations in practice

- **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	⋯

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**

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

VB computations in practice

- **Choice of an active space :**
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    - an **active space** of electrons/orbitals treated at the **VB level**
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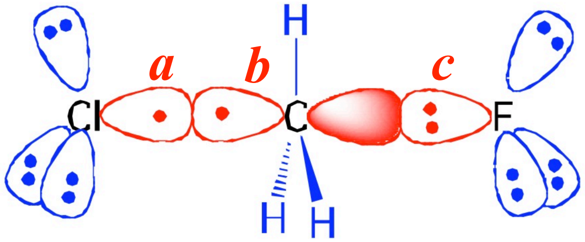
$$\Psi_{VB} = \sum_K C_K \Phi_K \text{ with: } \Phi_K = \left|\{inactives\}\{actives\}\right|$$

  - Active space chosen depending on the chemical problem :

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



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

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

➡ **Exercise 3 (answers) :**

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

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

- 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

What do you get out of the calculation ?

VB computations in practice

(good) numbers...

VB computations in practice

...but also insight !

VB computations in practice

- **Chemical insight / structure weights :**

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

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 % ($100W_K$)

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** :

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

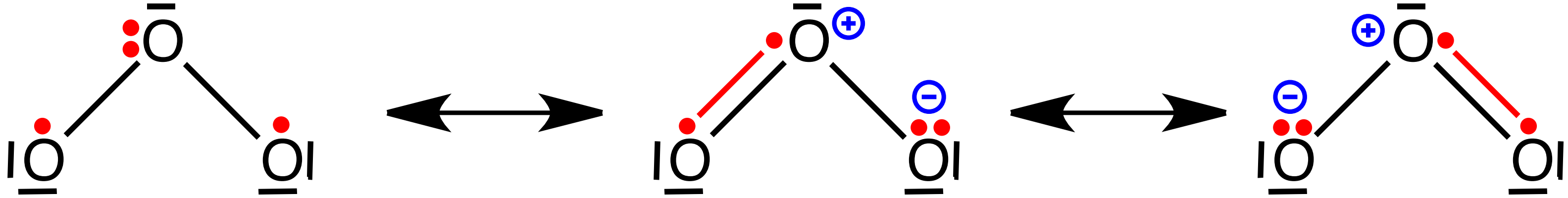
- Other options : Hiberty, Lowdin, Gallup (inverse) weights

VB computations in practice

- **Chemical insight / structure weights :**

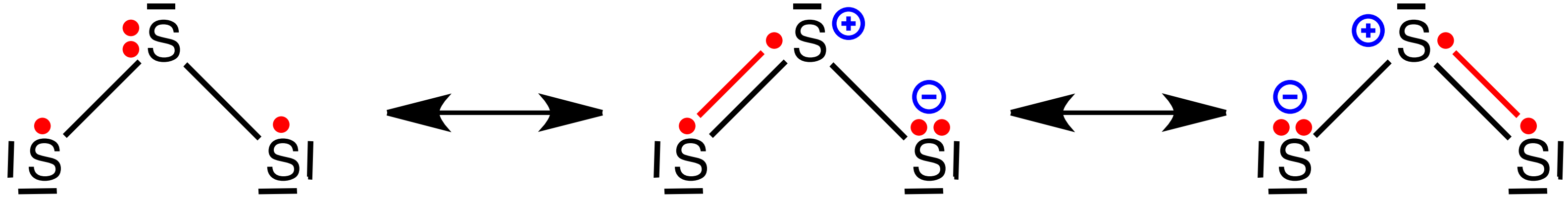
<u>Ex :</u> reactivity of ozone vs. trisulfur :

Very reactive



52% 24% 24%

Not reactive



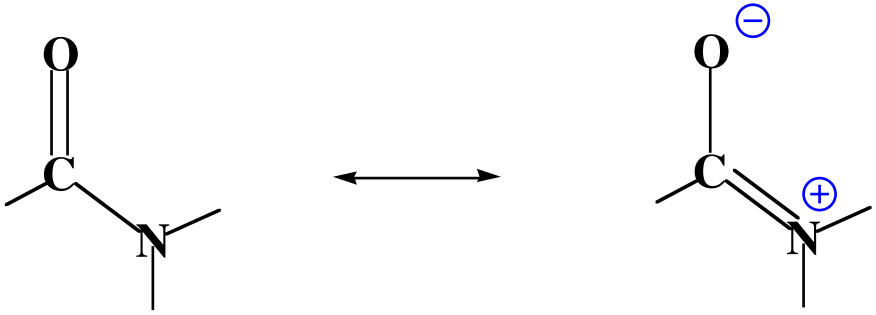
8% 46% 46%

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.) :



1 **2**

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

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

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

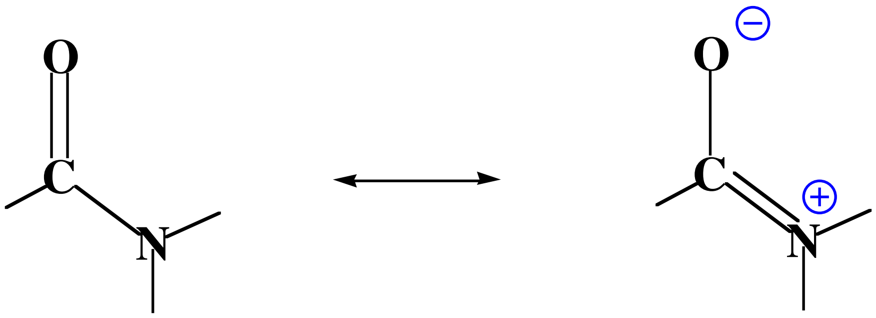
$$\Psi_{\mathbf{(1\leftrightarrow 2)}} = \mathrm{C}_1(\Psi_{\mathbf{1}}) + \mathrm{C}_2(\Psi_{\mathbf{2}})$$

VB computations in practice

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

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

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



1 **2**

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

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

2) Optimize Ψ_1 separately

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

R.E. = 37 kcal/mol

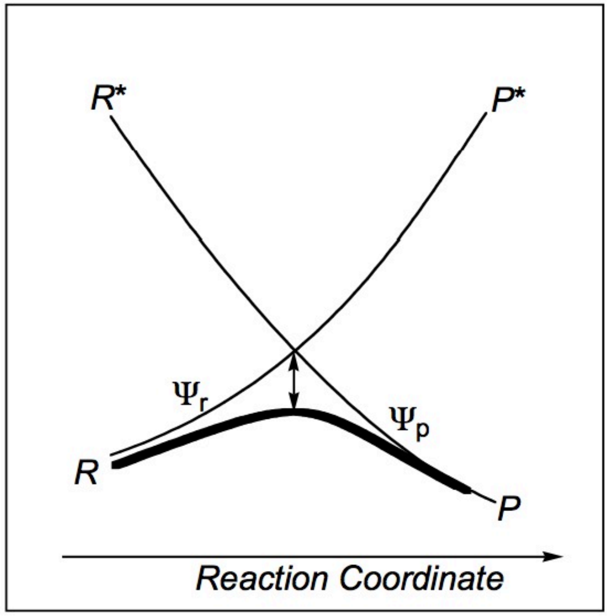
$\Rightarrow$ *formamide rotation barrier is due to* π *resonance energy*

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 :



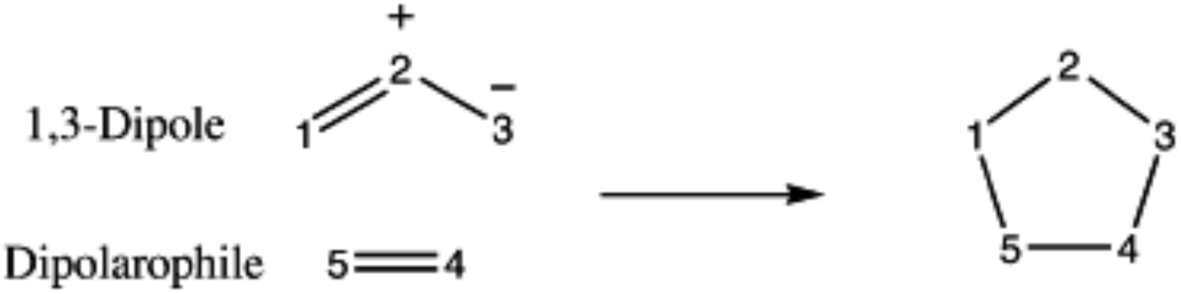
Part 4. lecture

Application

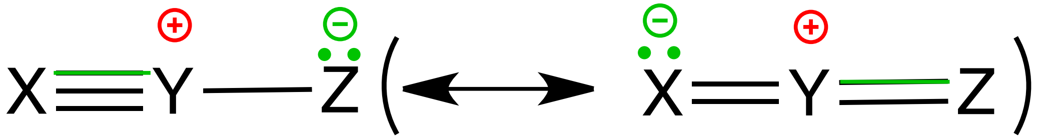
1,3-dipolar cycloadditions

1-3 dipolar cycloadditions

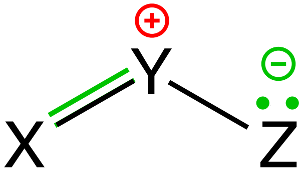
- Method for heterocyclic compounds synthesis :



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



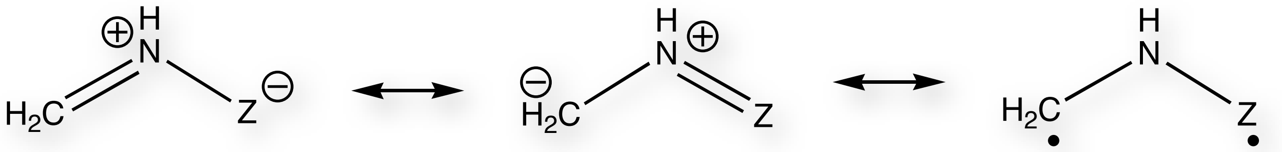
Propargylic (N_2O,...)



Allylic (O_3,...)

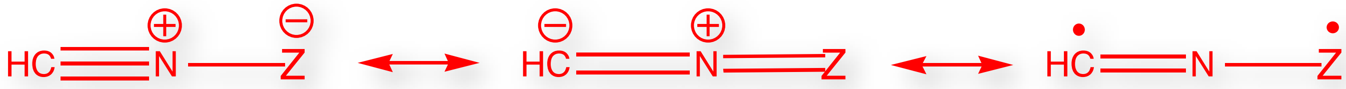
Some families of dipoles

Azomethine betaines :



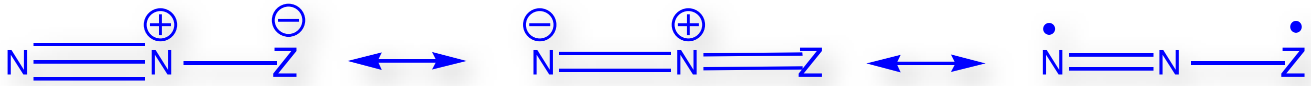
$Z = O, NH, CH_2$

Nitrilium betaines :



$Z = O, NH, CH_2$

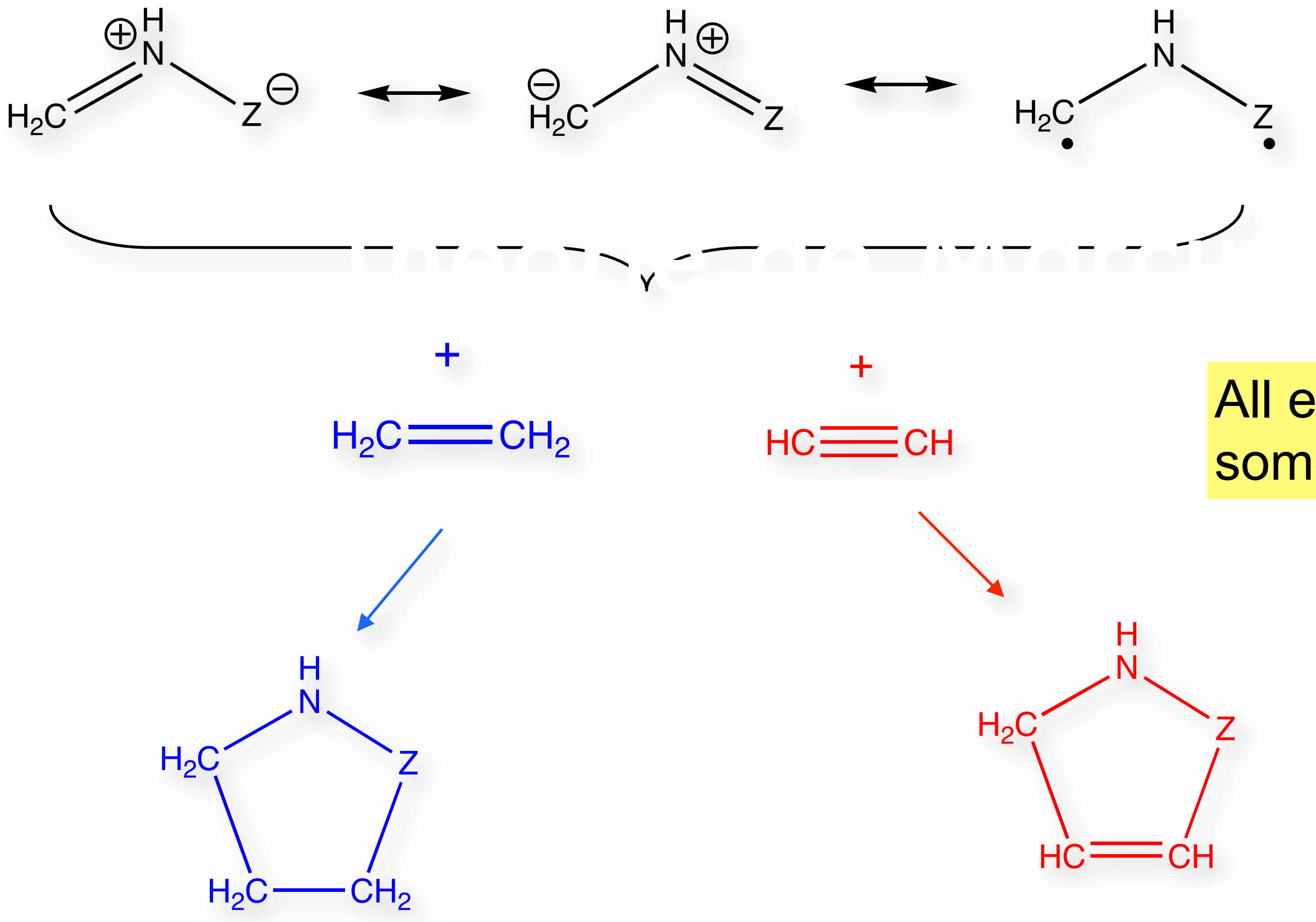
Diazonium betaines :



$Z = O, NH, CH_2$

Reactions studied

- Dipolarophiles : ethylene et acetylene :

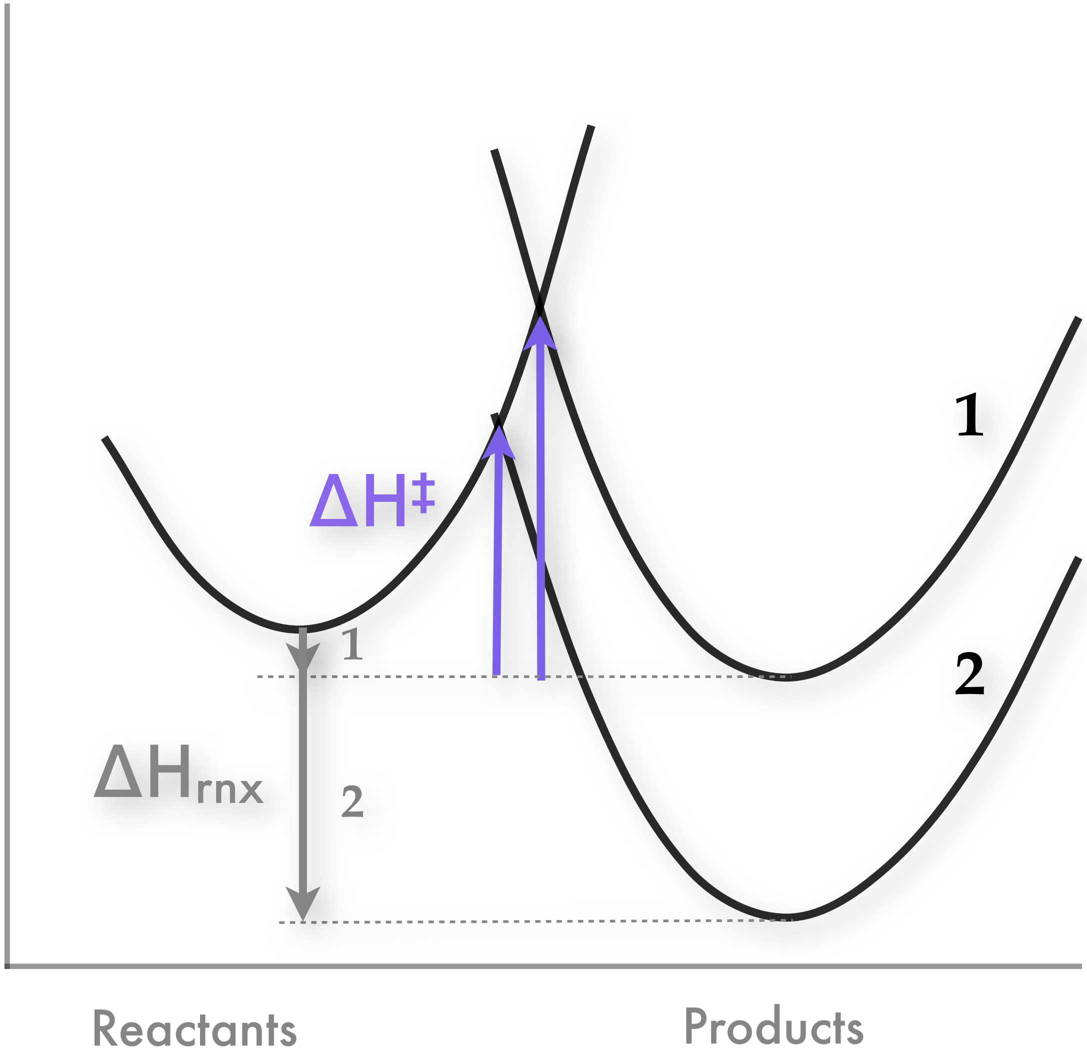


Z = O, NH, CH_2

All exothermic, but something funny…

Marcus theory ?

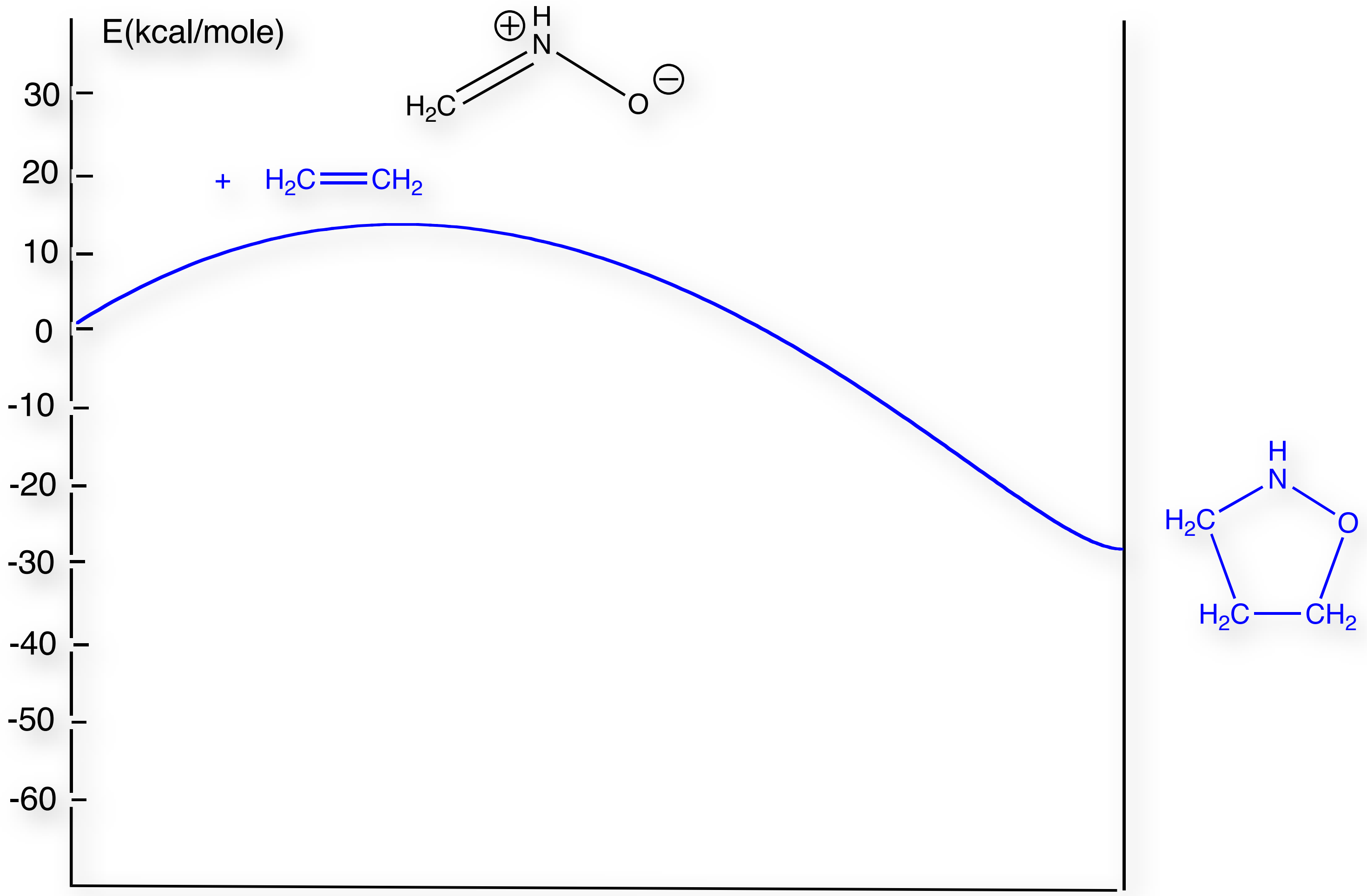
- Marcus : correlation between **barriers** and **enthalpies** :



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

Marcus theory ?

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



Marcus theory ?

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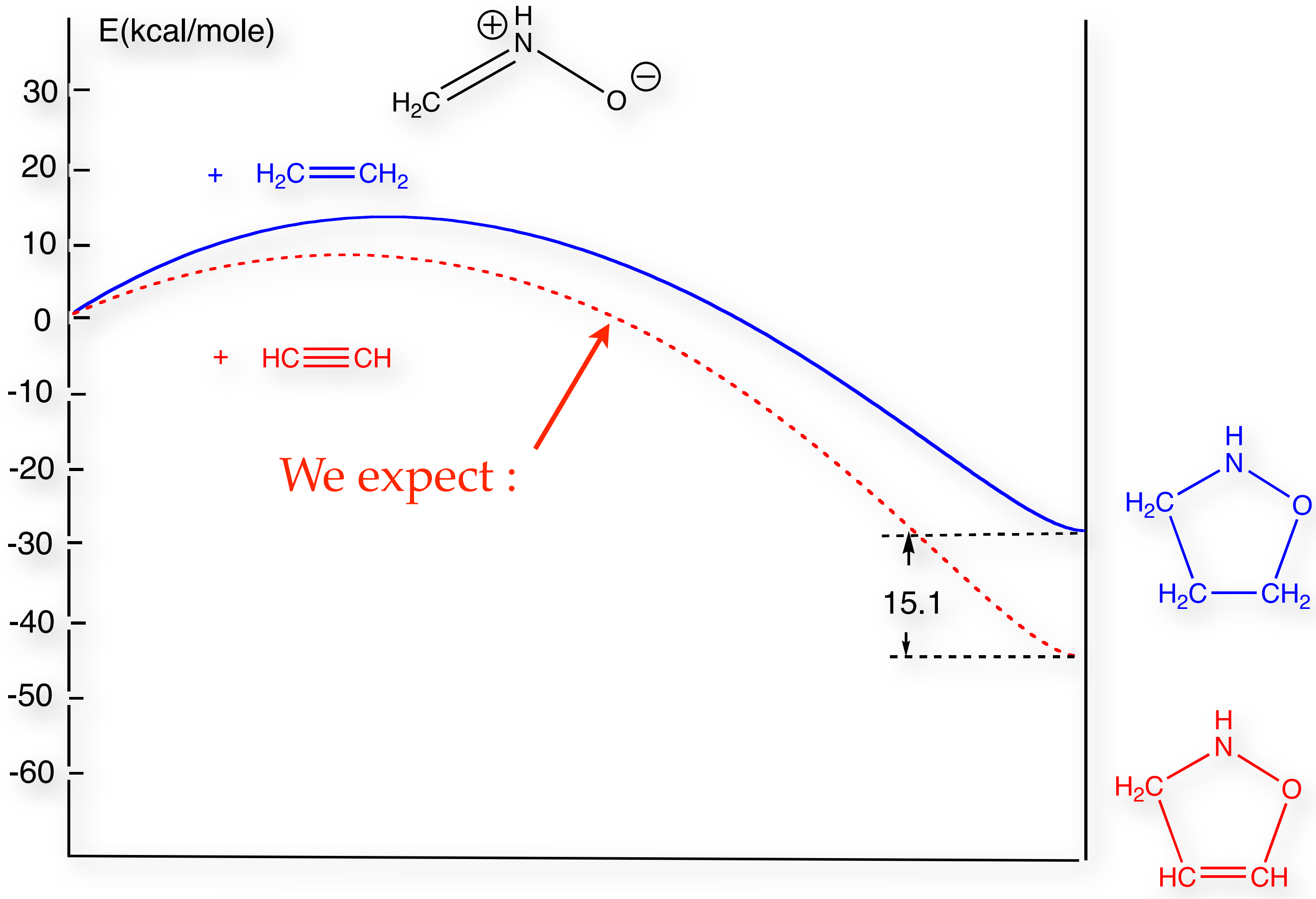

Marcus theory ?

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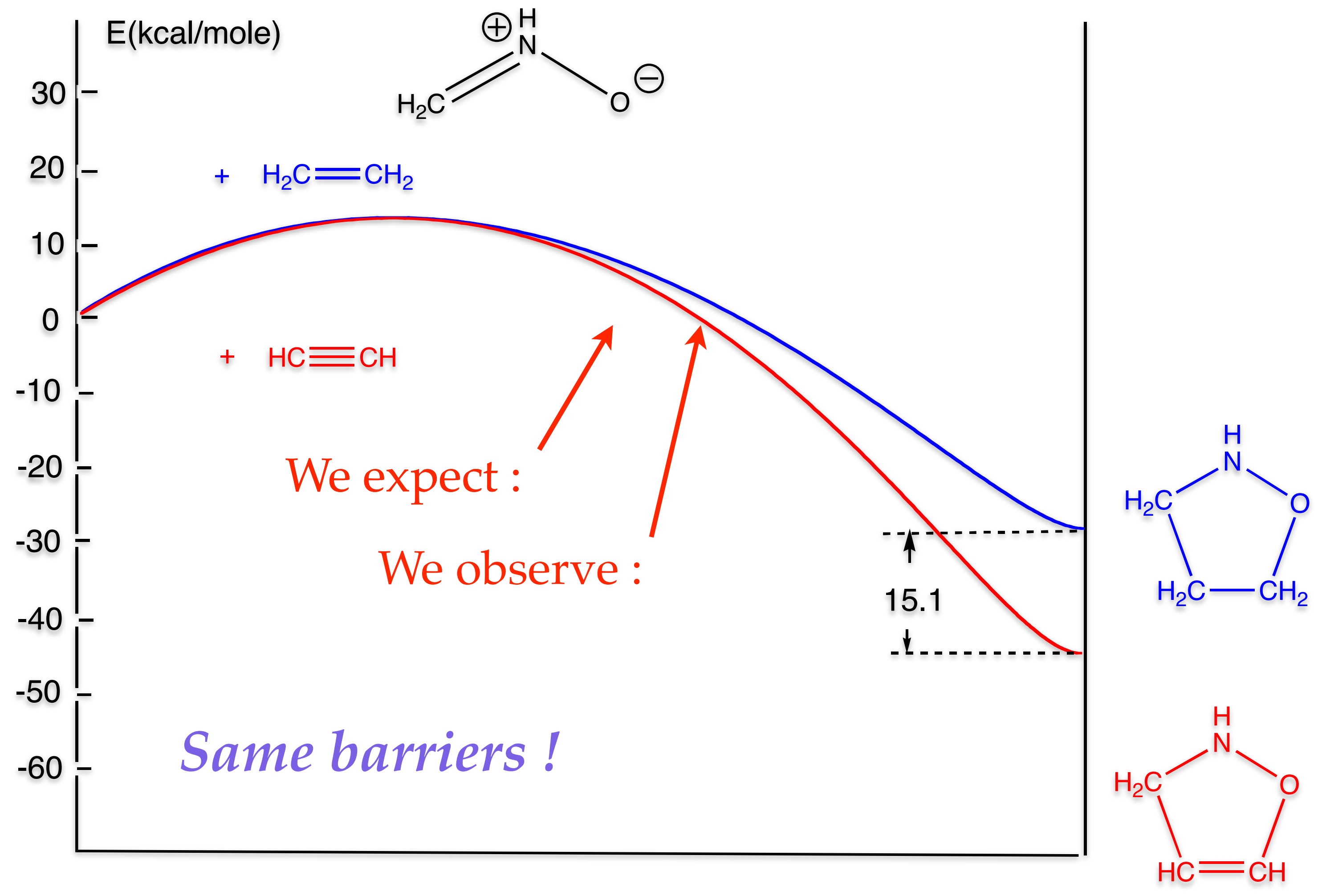


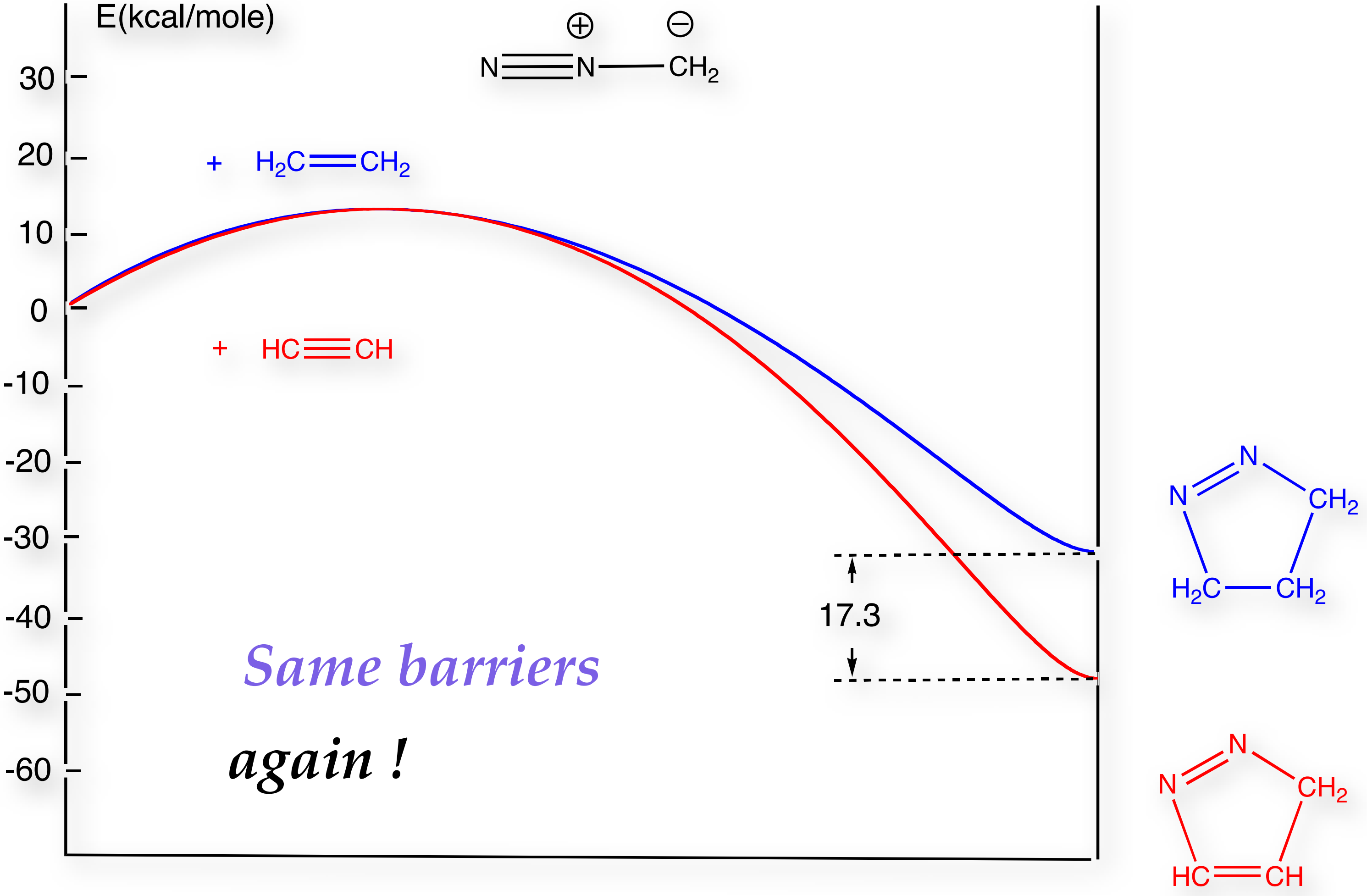
We expect :

We observe :

Same barriers !

Marcus theory ?

- **Propargylic** dipole

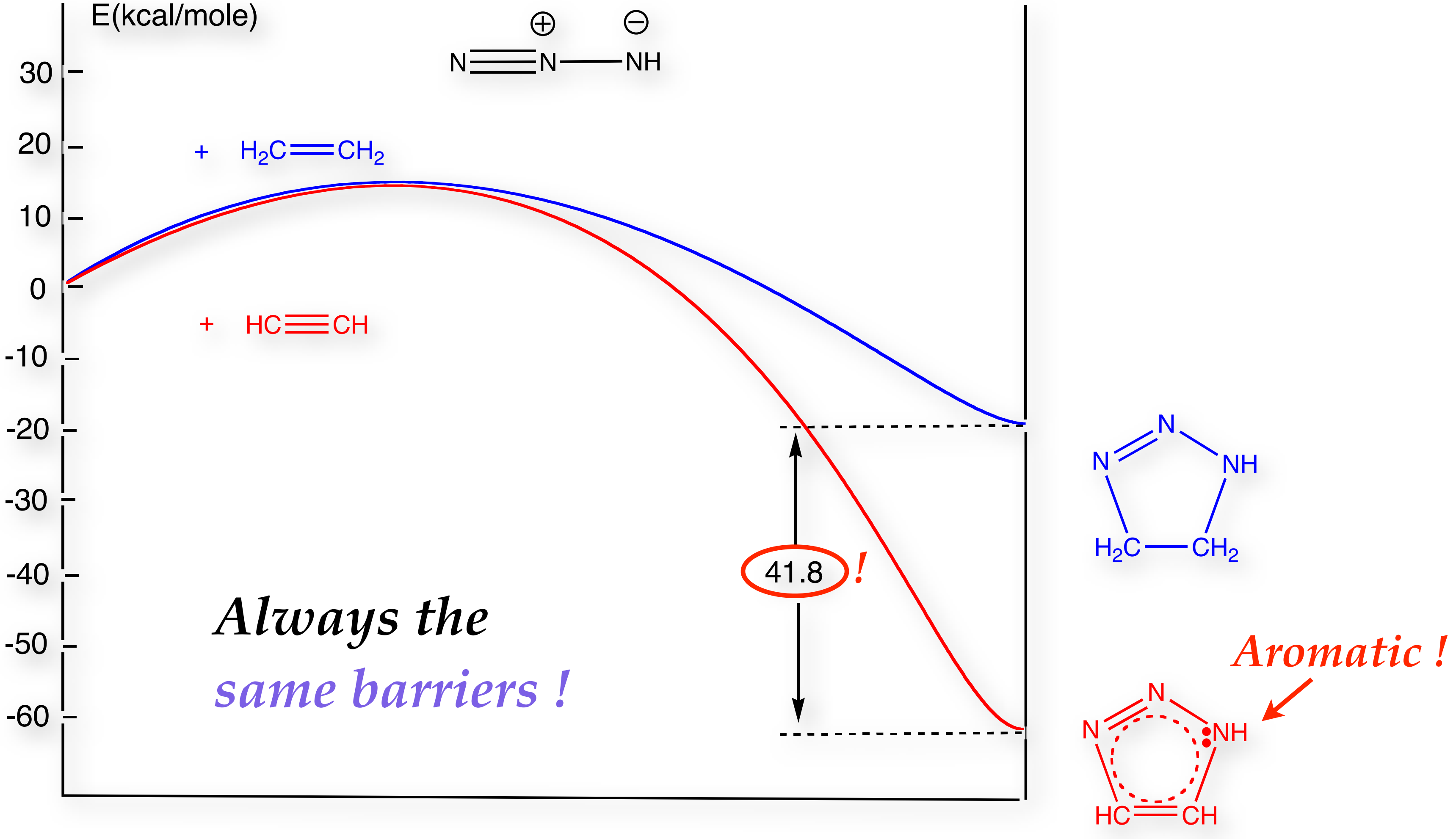


Same barriers

again !

Marcus theory ?

- **Propargylic** dipole

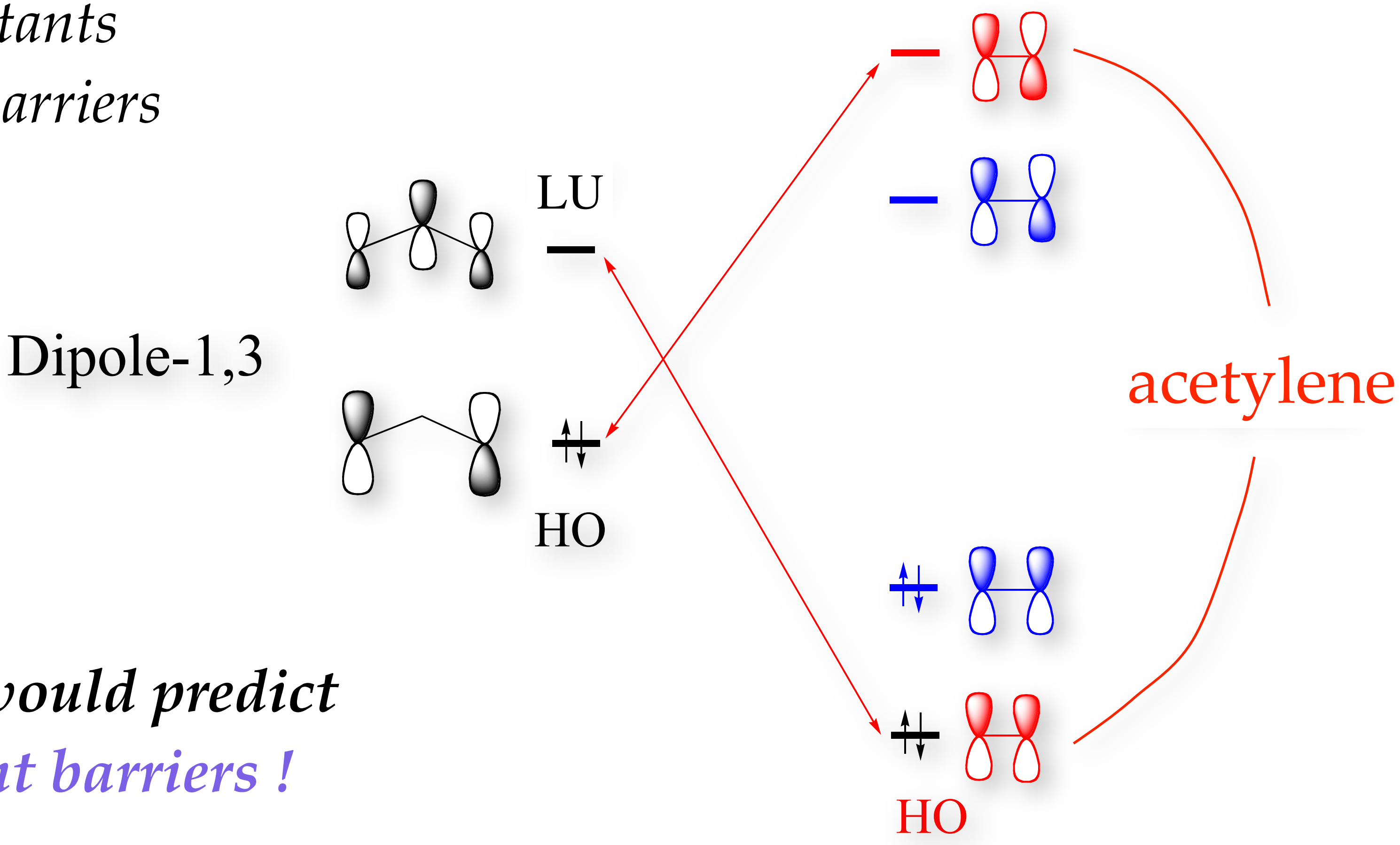


Always the
same barriers !

FMO theory ?

Small HOMO-LUMO energy difference between reactants

=> small barriers

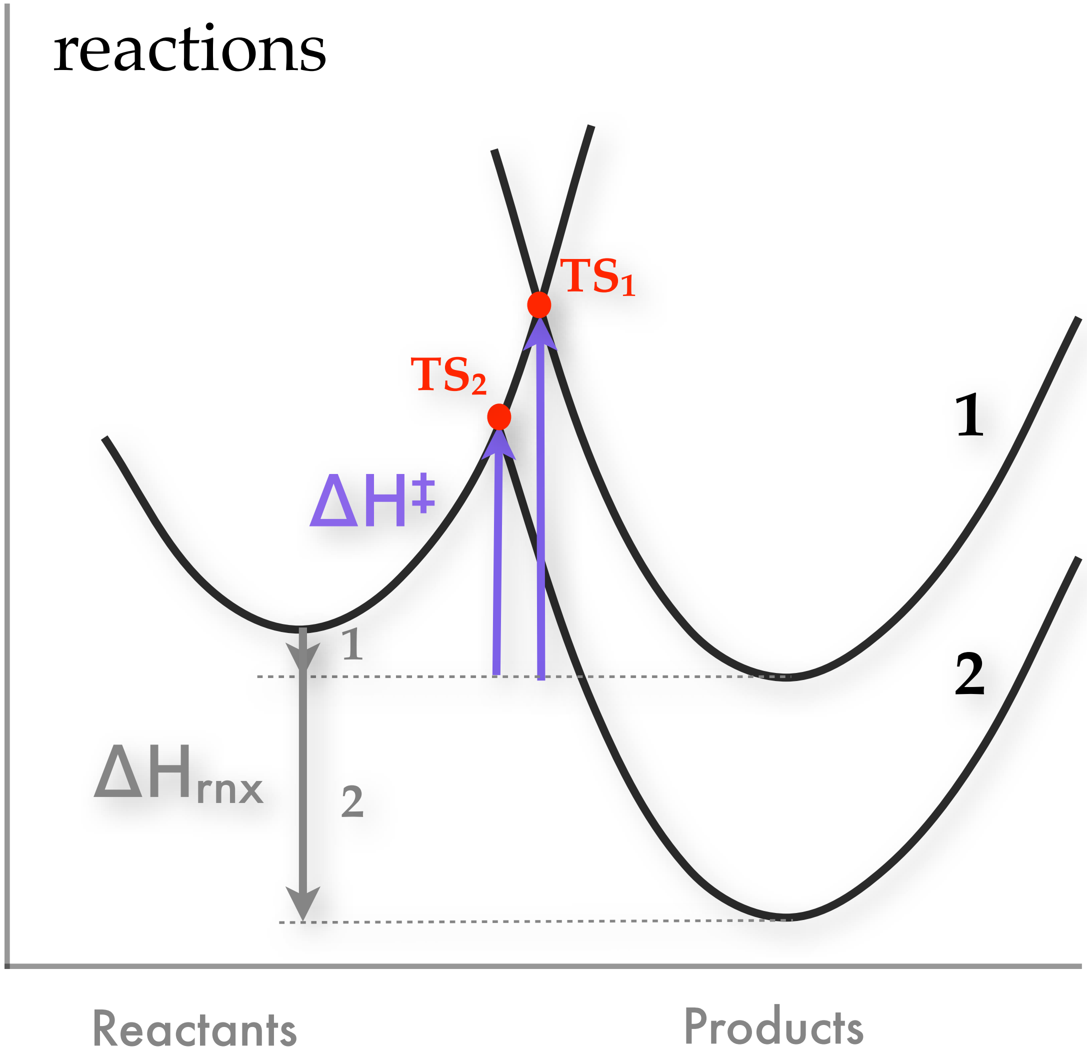


***FMO** would predict*

different barriers !

Hammond postulate ?

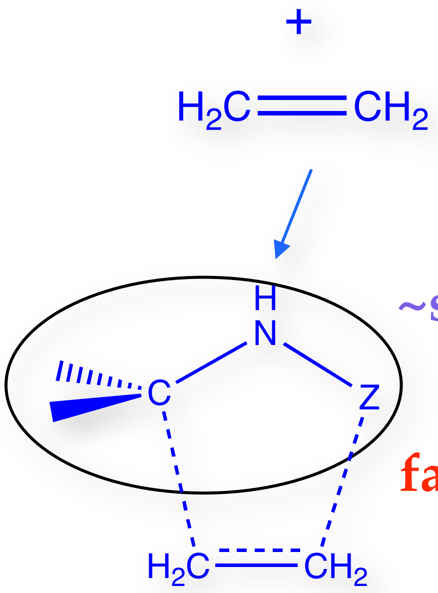
- Hammond : TS is more reactant-like for more exothermic reactions



Different enthalpies, different **TS geometries**

Hammond principle ?

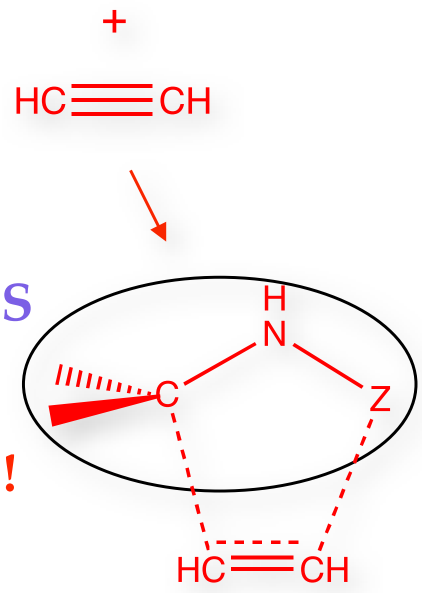
- All dipoles **distort** when going to TS :



~same dipole geometries at TS

(systematic)

falsifies Hammond principle !



Hammond principle ?

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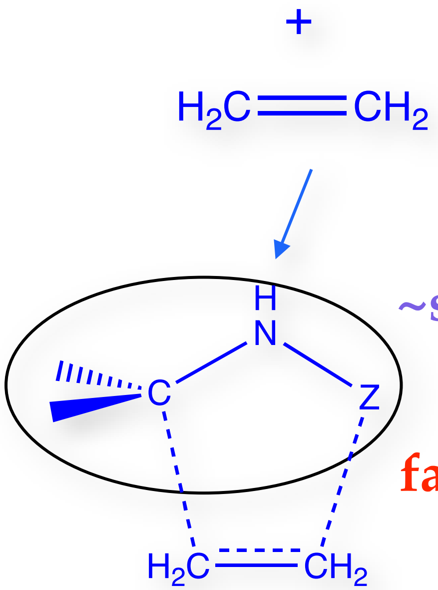

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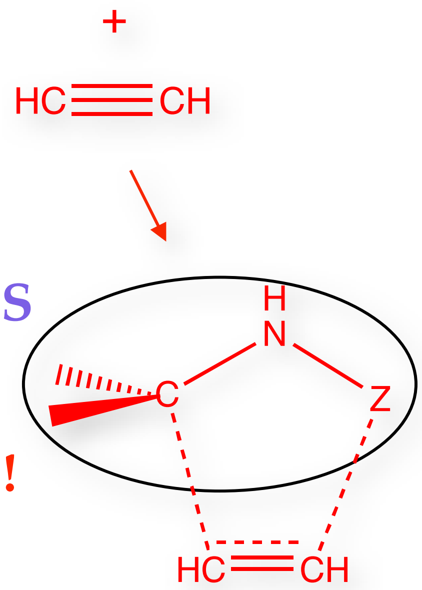


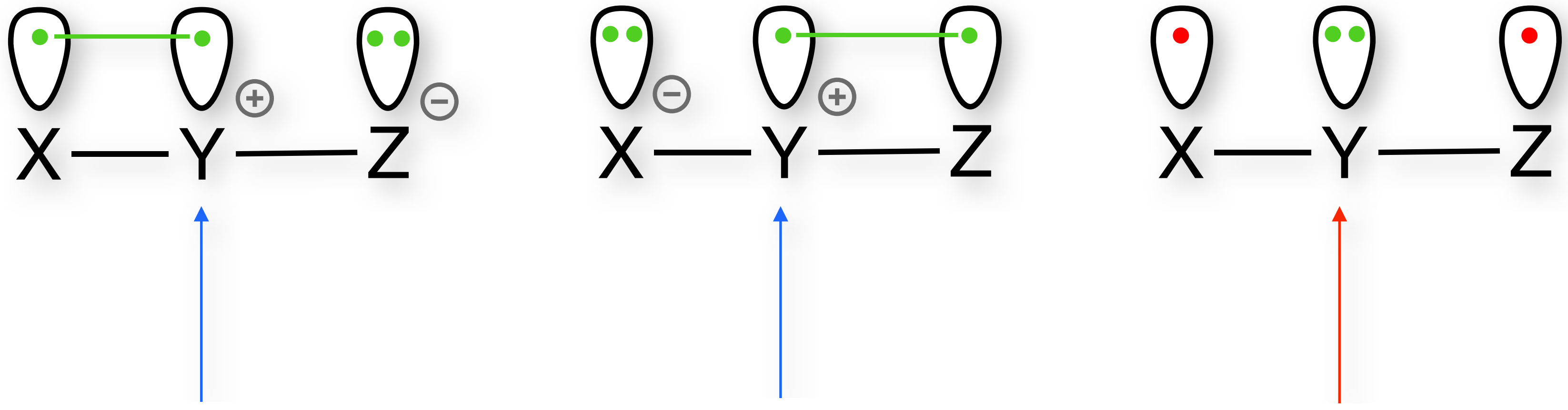
Ess & Houk* : barriers only depend on dipole distortion energies

… but why ?…

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

Ab initio VB calculations

- VB description :



Non reactive

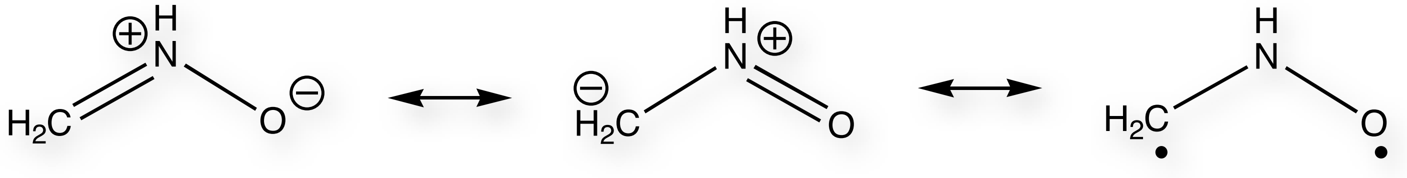
Non reactive

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) :



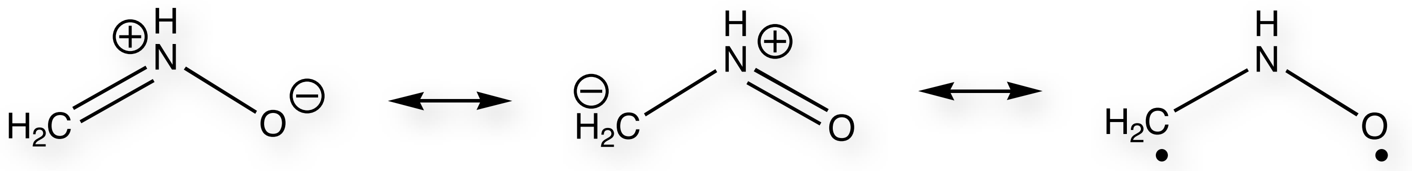
Reactants :	48,4%	18,0%	33,7%

- 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%

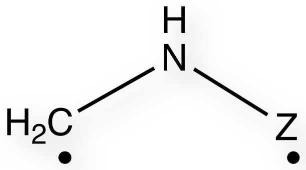
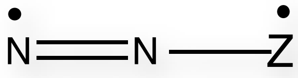
- Diradical character is important !

- 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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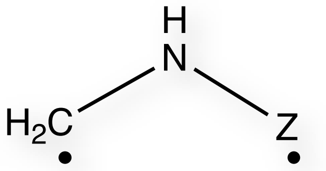

	Reactants :	TS :
Z = O	33.7	38.6
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	Reactants :	TS :
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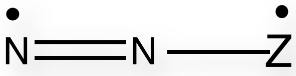
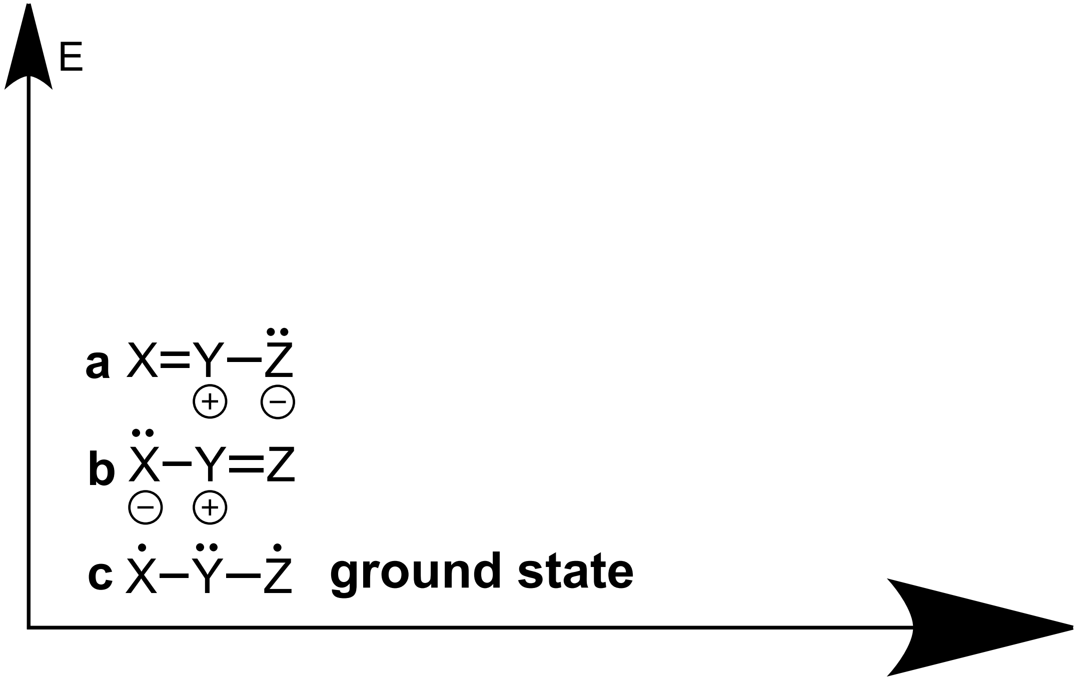


	Reactants :	TS :
Z = O	21.6	31.6
Z = NH	25.1	34.4
Z= CH_2	27.7	36.4

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

Ab initio VB calculations



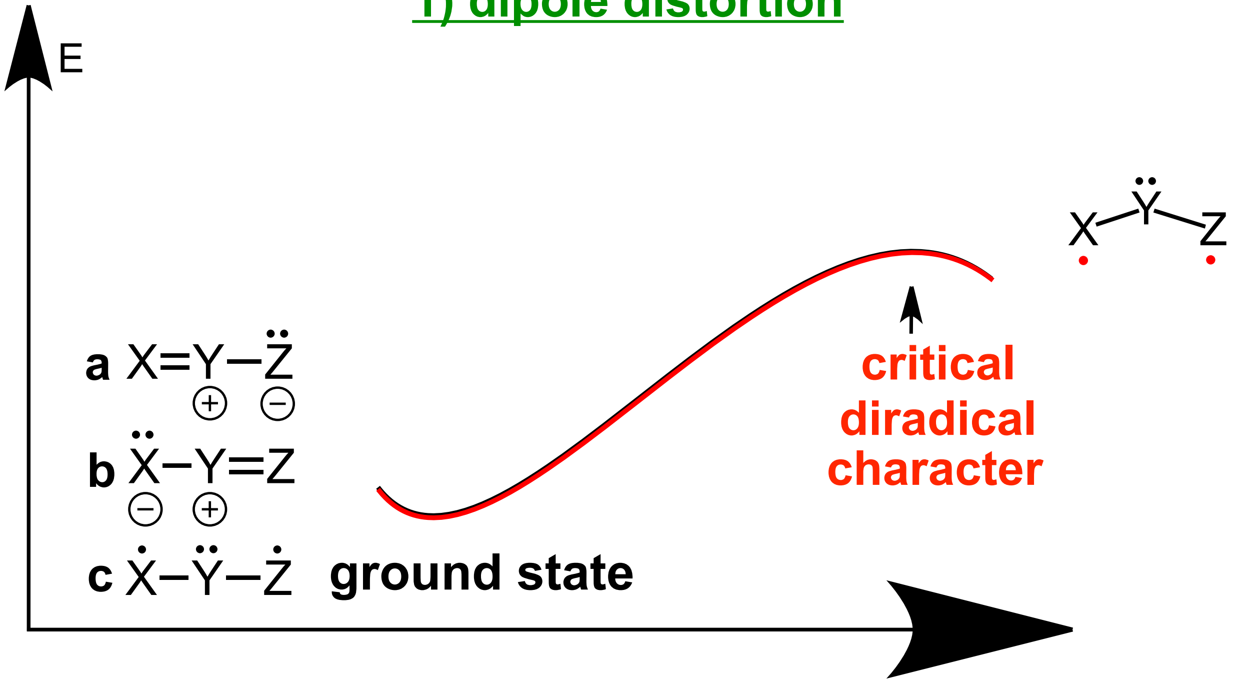
a $X=\underset{\oplus}{Y}-\underset{\ominus}{\ddot{Z}}$

b $\underset{\ominus}{\ddot{X}}-\underset{\oplus}{Y}=Z$

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

Ab *initio* VB calculations

1) dipole distortion

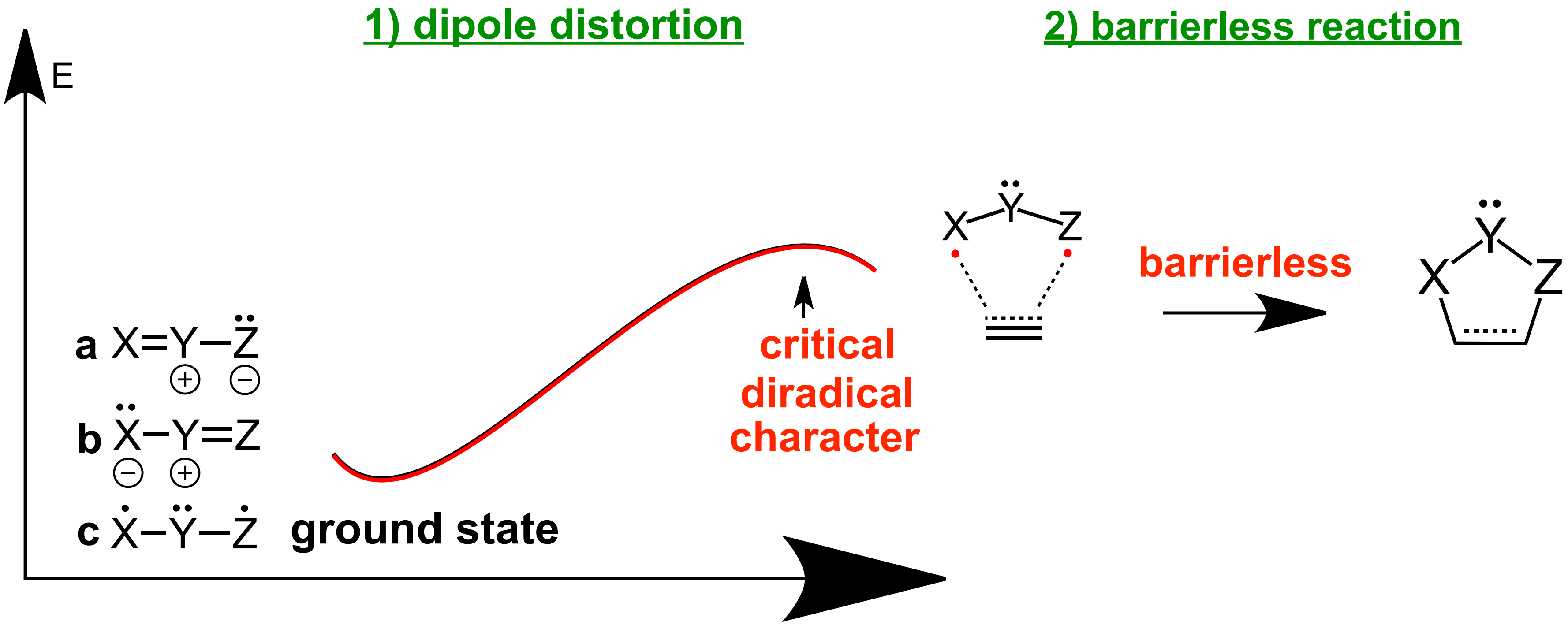


ground state

critical diradical character

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

Ab initio VB calculations

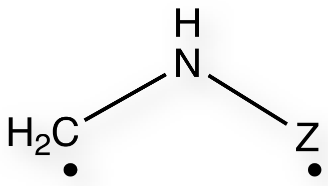


1) Dipole distortion → reach a **«critical» diradical character**

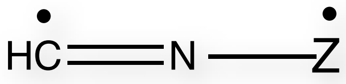
2) Dienophile attack (almost barrierless) !

Ab initio VB calculations

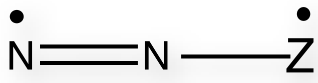
1) If our postulated mechanism is correct :



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



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



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

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

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

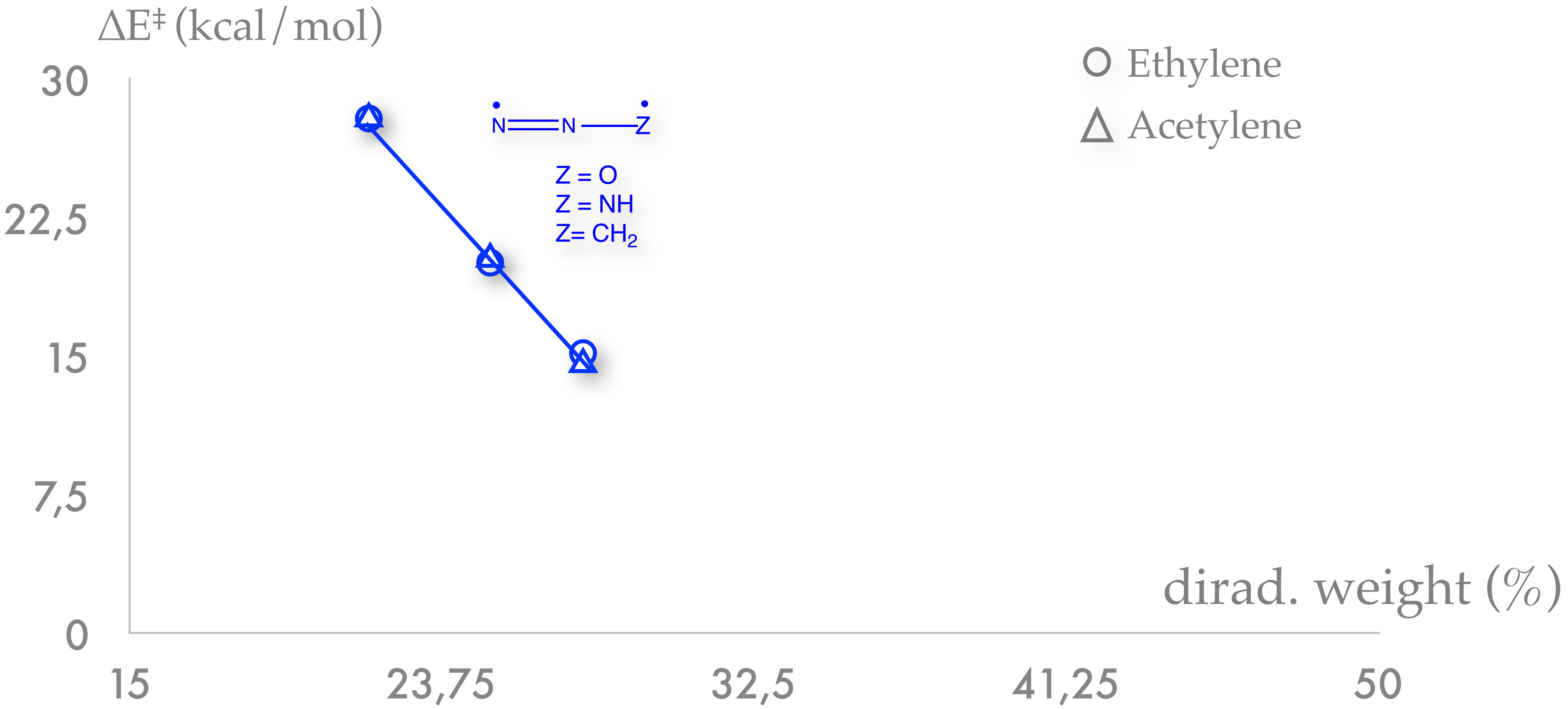
=> ***Inverse correlation***

between diradical ***weights***

and reaction ***barriers***

Ab initio VB calculations

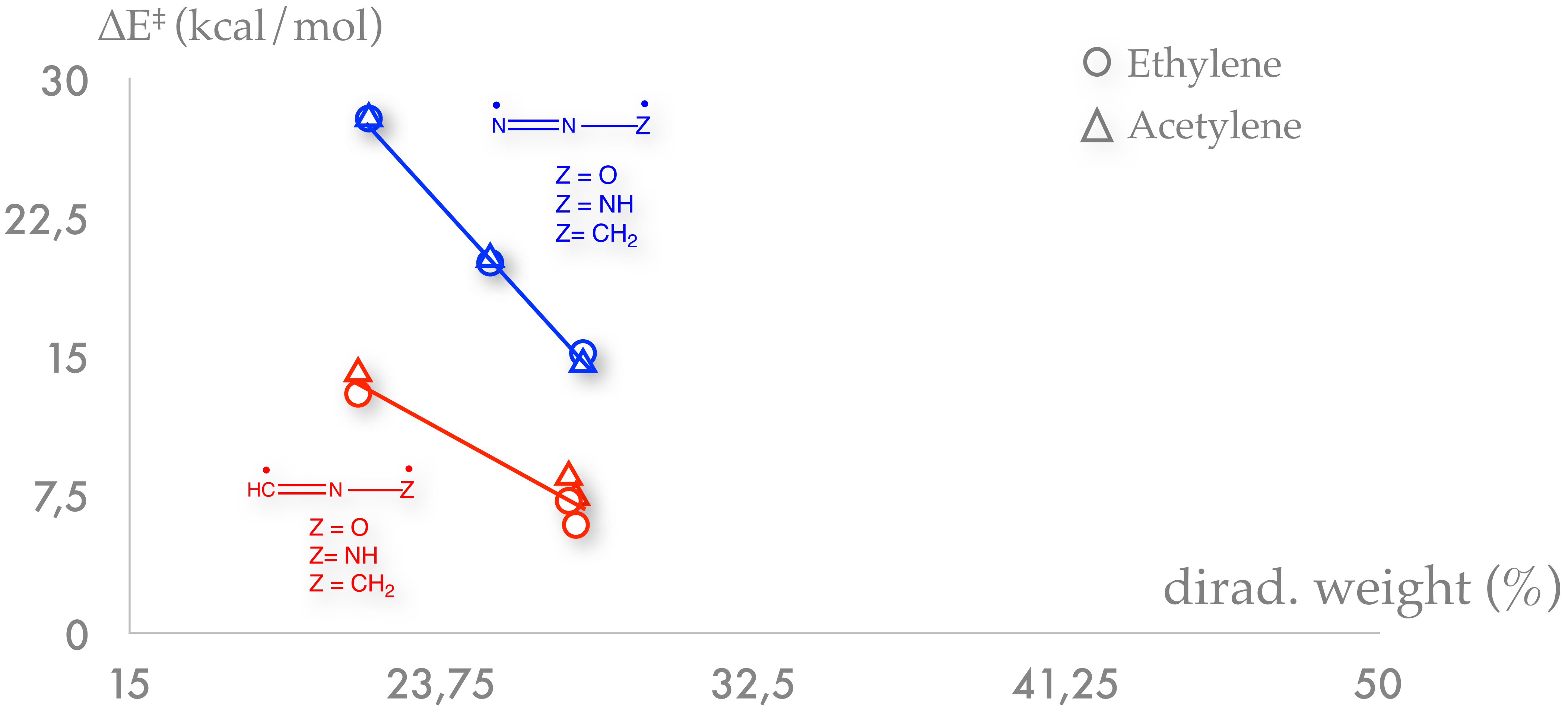
1) Correlation diradical **weights** / **barriers**



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

Ab initio VB calculations

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



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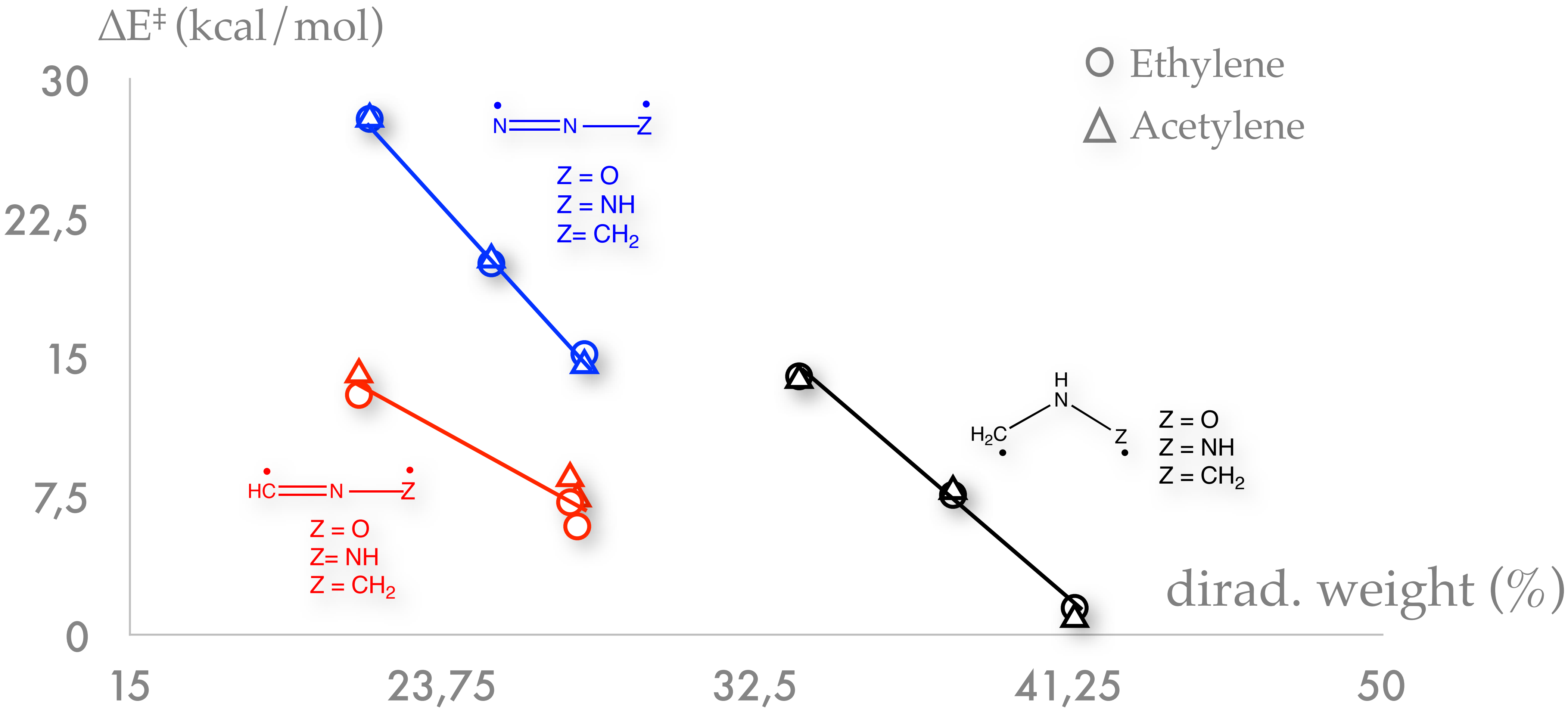

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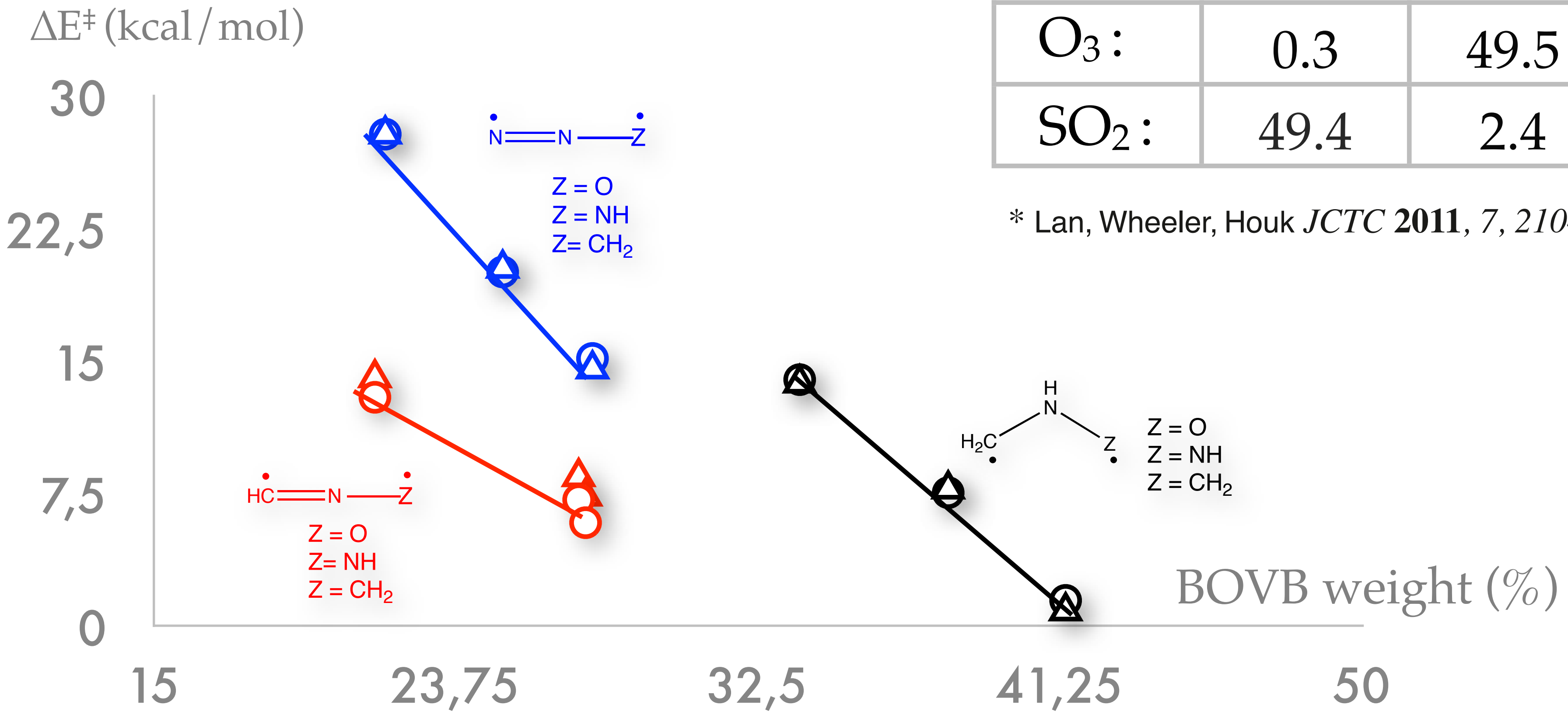
Ab initio VB calculations

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

Two extreme cases :*

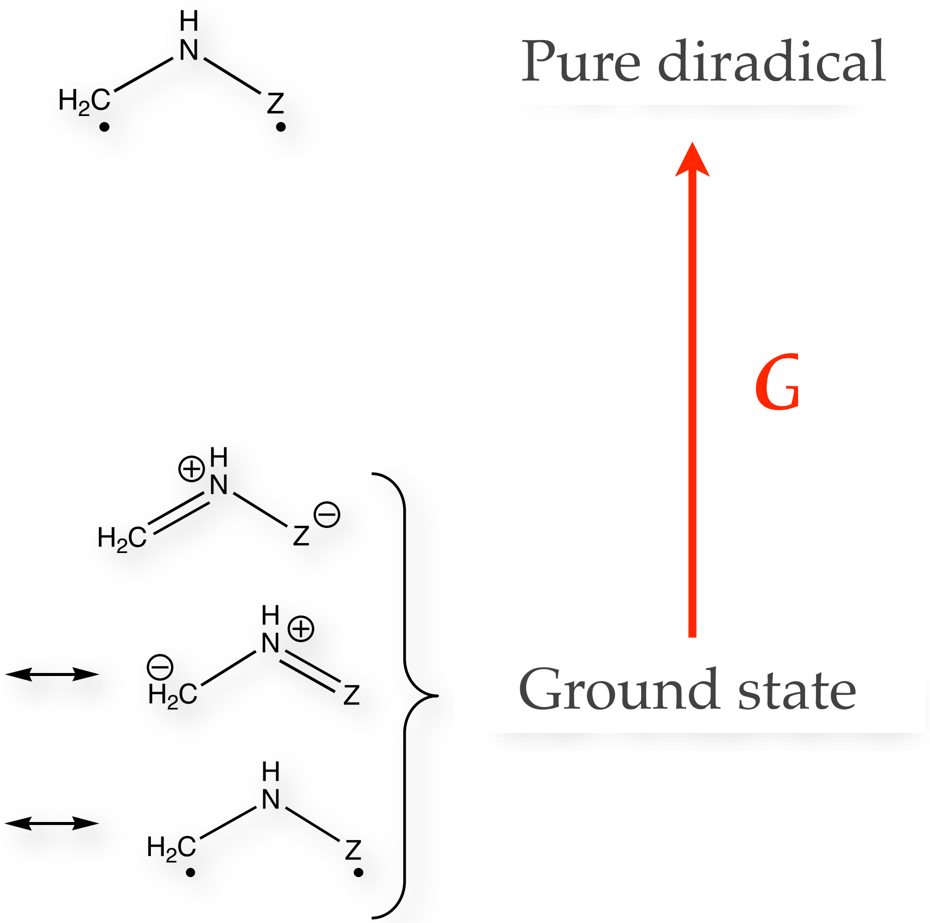
	$\Delta E^{\ddagger}$	w (%)
O_3 :	0.3	49.5
SO_2 :	49.4	2.4

* 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 :

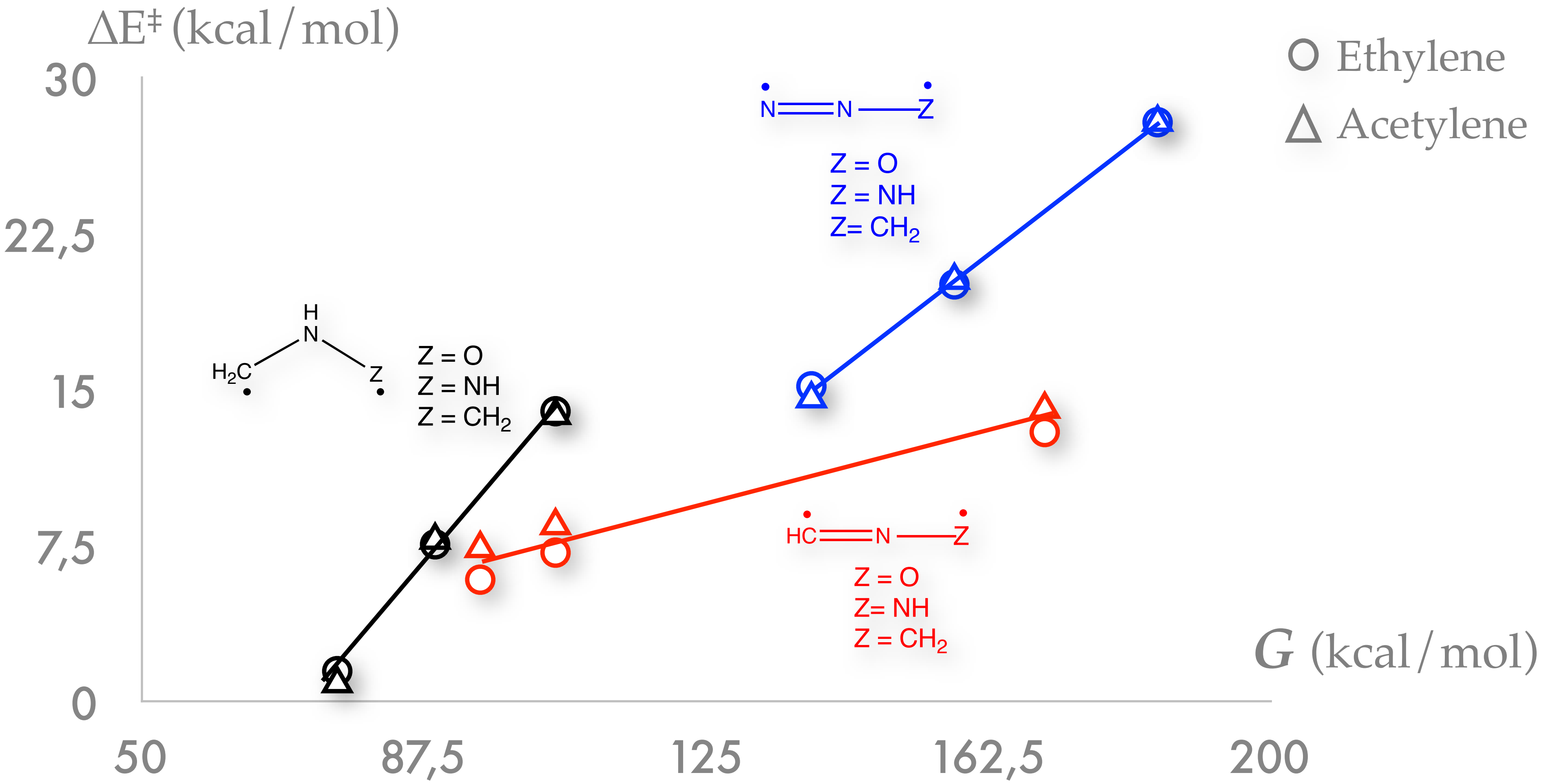
→ small G

→ small $\Delta H^\ddagger$

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

Ab initio VB calculations

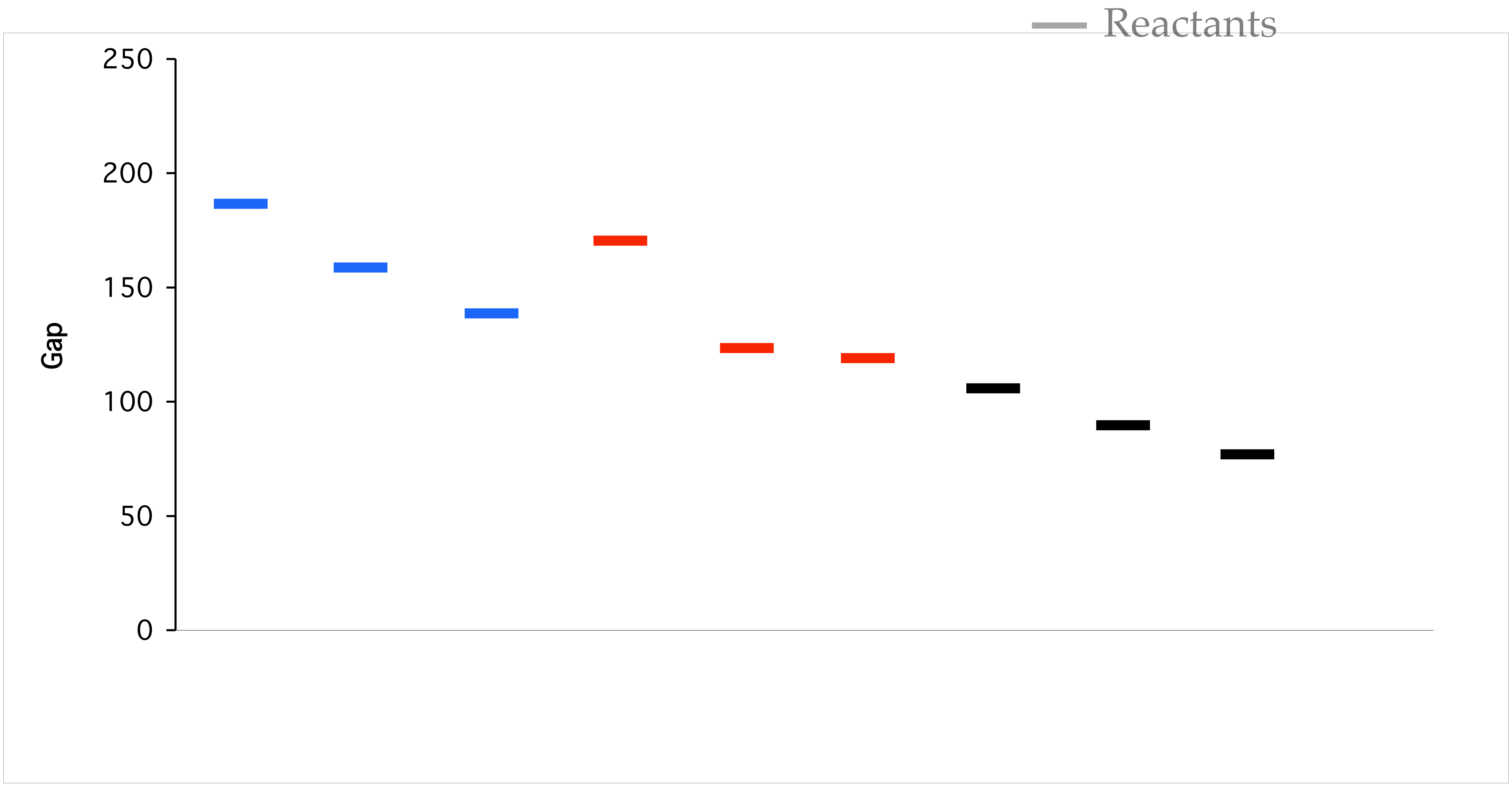
2) Correlation *G* / $\Delta H^{\ddagger}$:



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

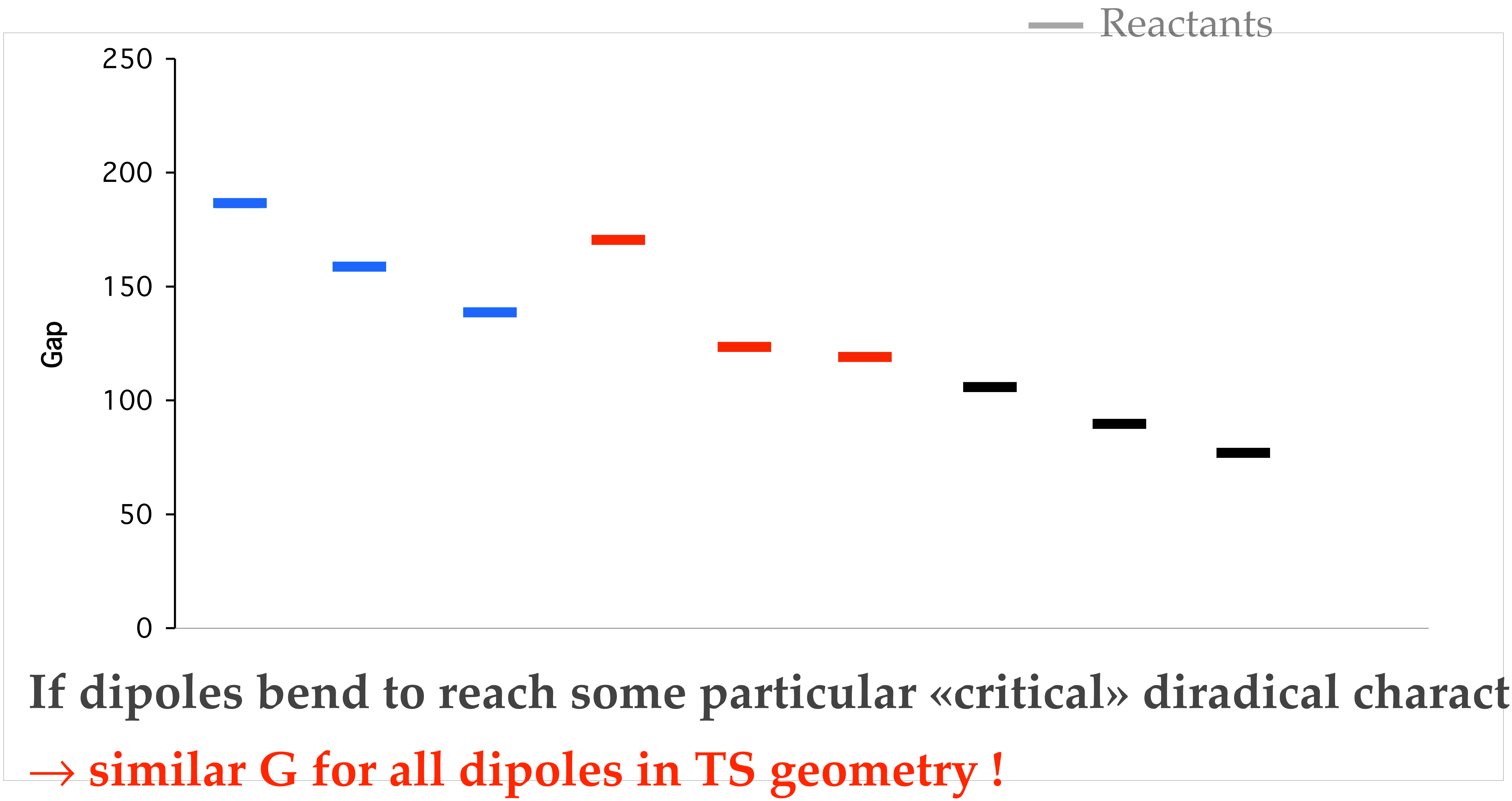
Ab initio VB calculations

- *G* : reactants :



Ab initio VB calculations

- *G* : reactants vs. TS :

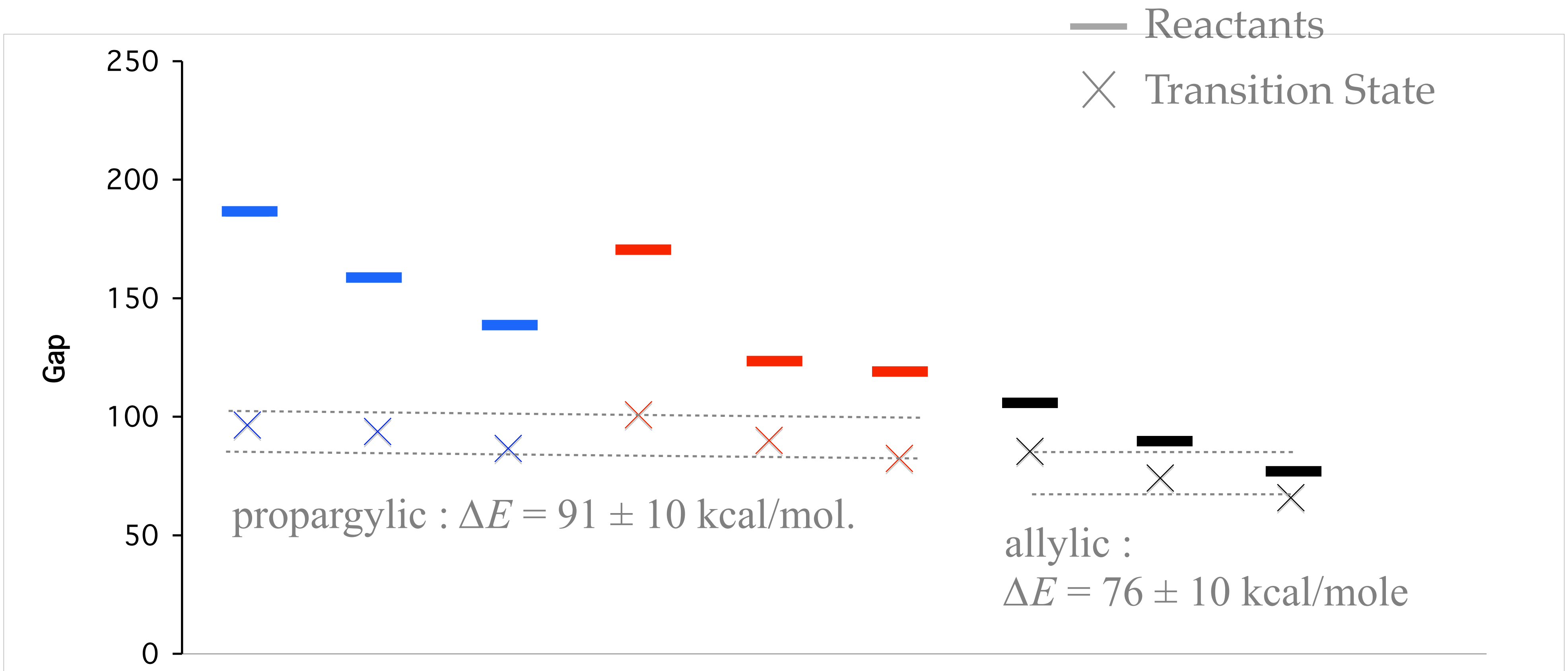


If dipoles bend to reach some particular «critical» diradical character

→ similar G for all dipoles in TS geometry !

Ab initio VB calculations

- *G* : reactants vs. TS :

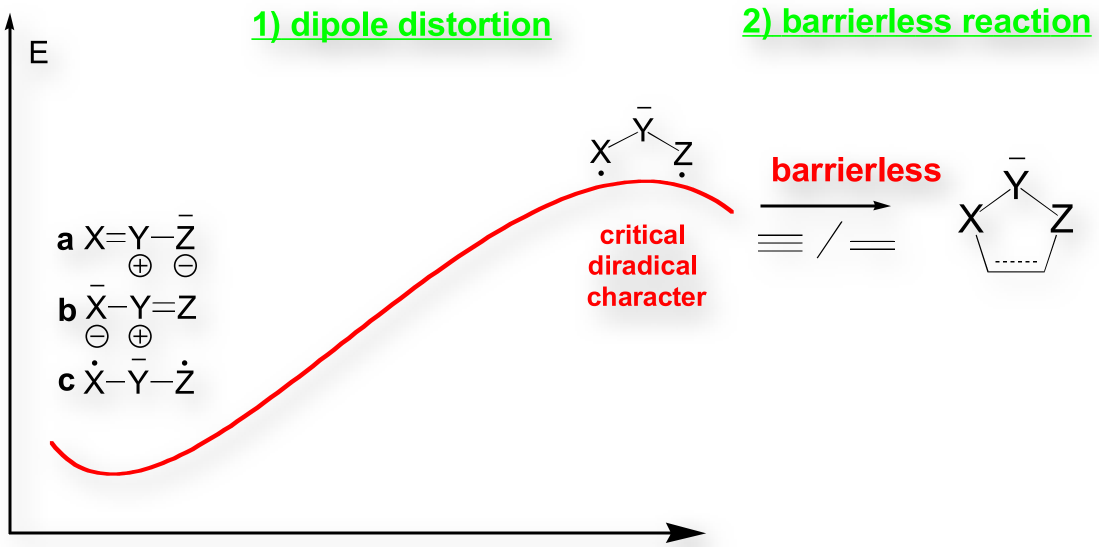


If dipoles bend to reach some particular «critical» diradical character

→ 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



Bernd Engels & Christof Walter

Philippe Hiberty

Würzburg University

Univ. Paris Sud

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

Conclusions

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

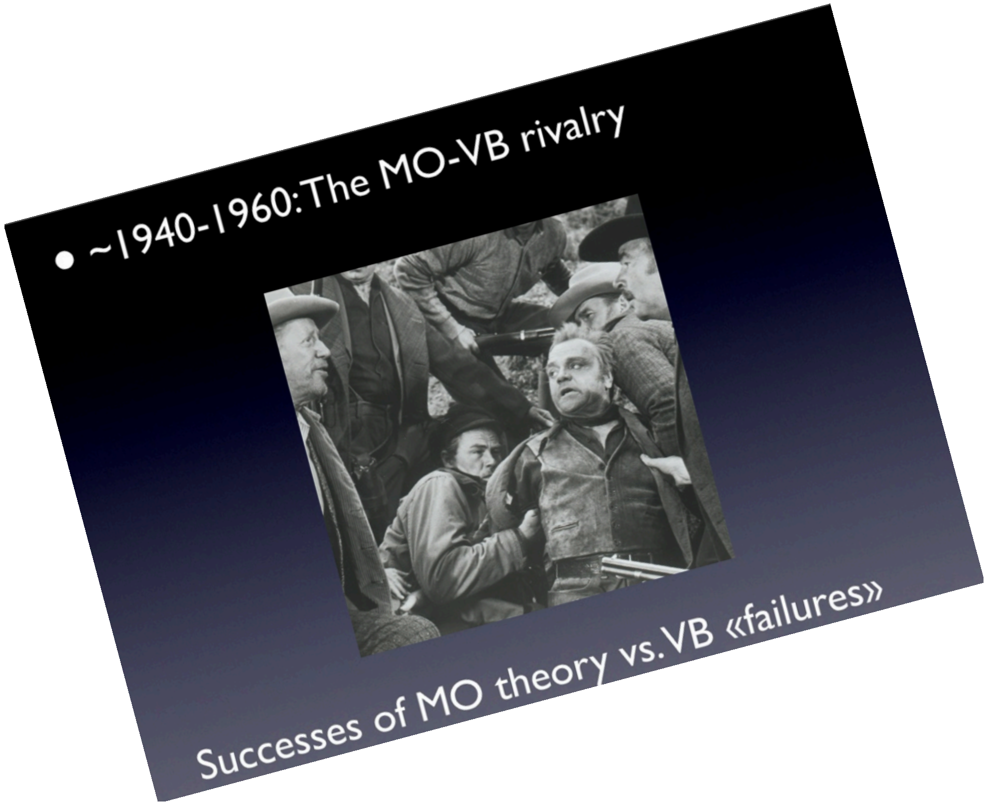

(Prof. Keating, Dead Poets Society)

Limits of VB theory

So, why everybody has not been doing VB ?

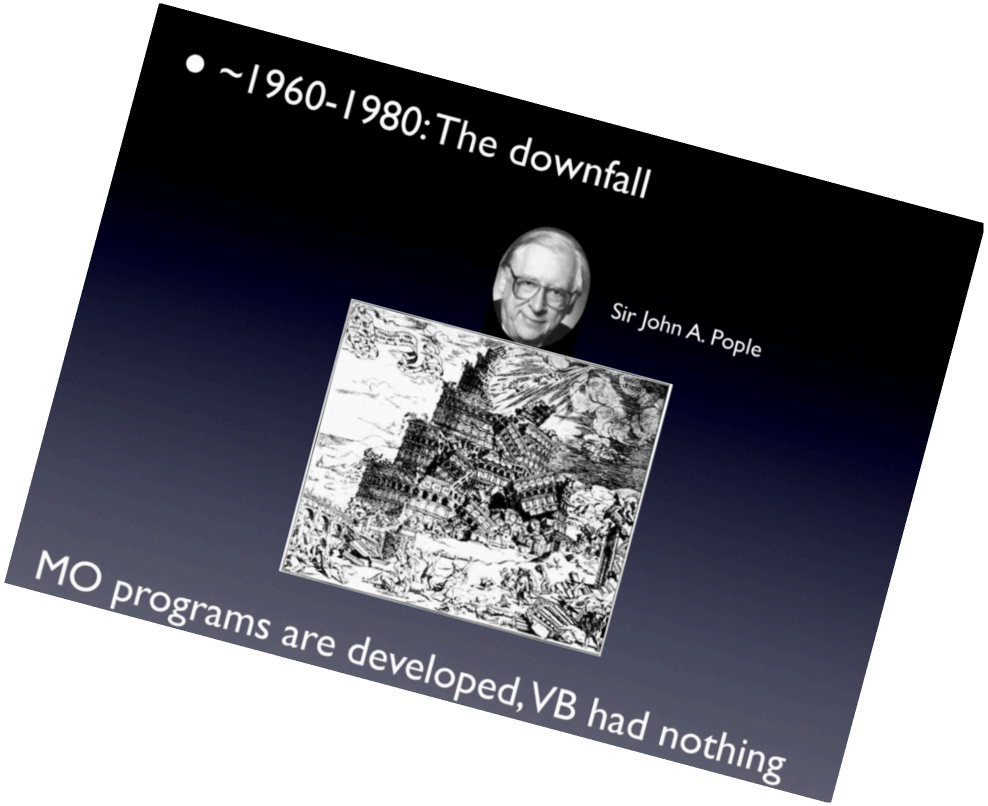
Limits of VB theory

- **Historical reasons :**



- ~1940-1960: The MO-VB rivalry

Successes of MO theory vs. VB «failures»



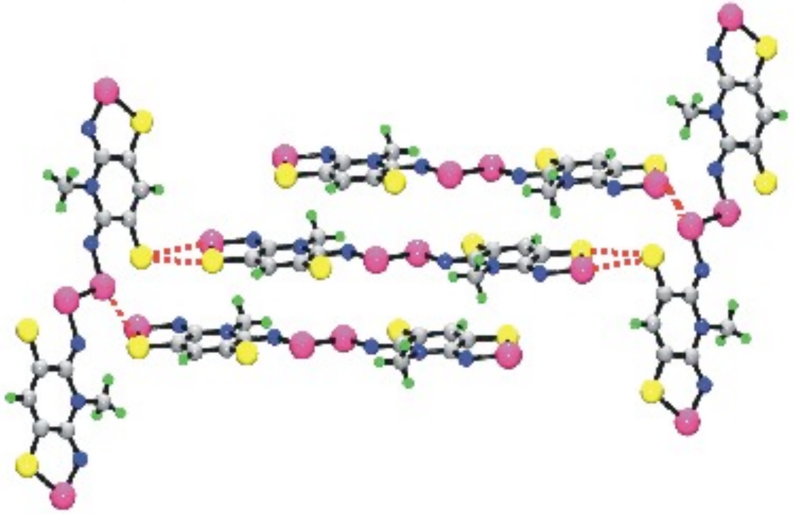
- ~1960-1980: The downfall

Sir John A. Pople

MO programs are developed, VB had nothing

Limits of VB theory

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



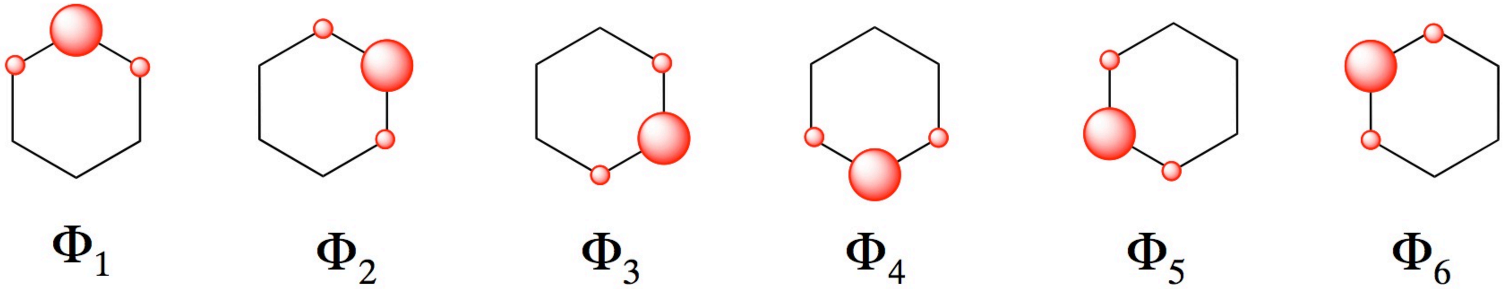
No way !

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

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

Limits of VB theory

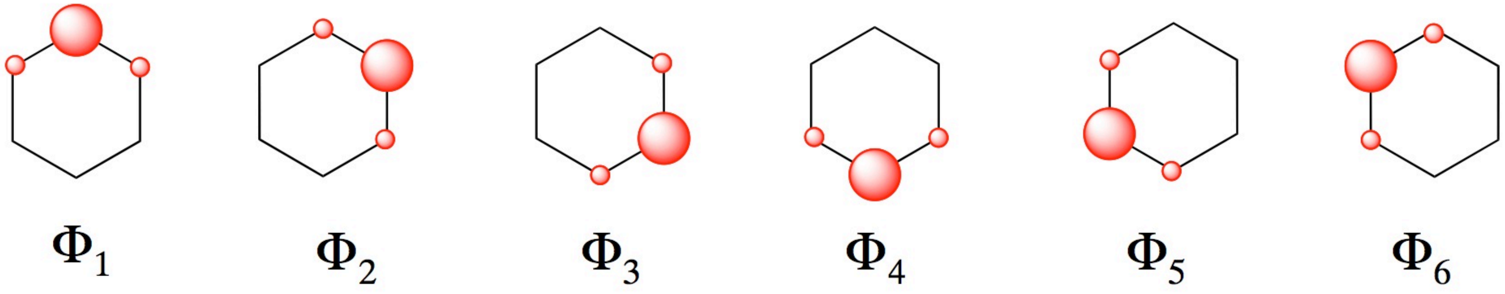
- **Nonorthogonality :**
  - Orthogonal orbitals cannot be strictly localized :



← Delocalization tails

Limits of VB theory

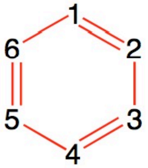
- **Nonorthogonality :**
  - Orthogonal orbitals cannot be strictly localized :

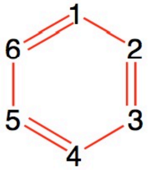


←Delocalization tails

$$\Psi^{GVB} \propto \left|(\Phi_1\overline{\Phi}_2 + \Phi_2\overline{\Phi}_1)(\Phi_3\overline{\Phi}_4 + \Phi_4\overline{\Phi}_3)(\Phi_5\overline{\Phi}_6 + \Phi_6\overline{\Phi}_5)\right|$$
$$+ \left|(\Phi_2\overline{\Phi}_3 + \Phi_3\overline{\Phi}_2)(\Phi_4\overline{\Phi}_5 + \Phi_5\overline{\Phi}_4)(\Phi_6\overline{\Phi}_1 + \Phi_1\overline{\Phi}_6)\right|$$

Orbitals are delocalized on 3 centers

The relationship to 

and 

is less obvious

➡ To get strictly localized orbitals we need to use nonorthogonal orb

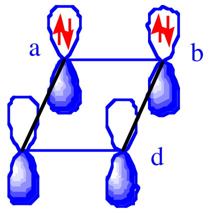
Limits of VB theory

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

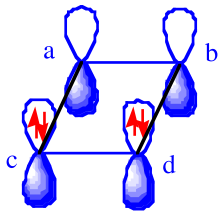
$$\hat{H} = \sum_{i} \hat{h}_{i} + \sum_{i,j} \frac{1}{r_{ij}}$$

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

Ex : a 4e/4o pb :



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



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

...

Limits of VB theory

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

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

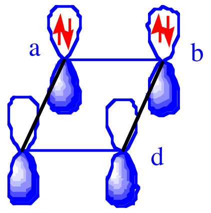
MO theory :

(orthogonal orbs.)

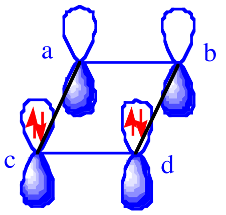
$$\bar{\bar{S}}$$

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

Ex : a 4e/4o pb :



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



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

...

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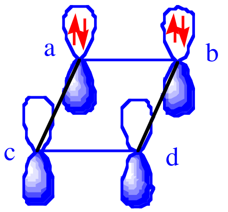
$$\bar{\bar{H}}$$

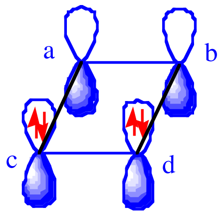
$$\begin{array}{c} |a\bar{a}b\bar{b}| \\ |a\bar{a}c\bar{c}| \\ \\ \vdots \\ \\ |c\bar{c}d\bar{d}| \end{array} \begin{pmatrix} \times & \times & \times & \times & \times & 0 \\ \times & \times & \times & \times & 0 & \times \\ \times & \times & \times & 0 & \times & \times \\ \times & \times & 0 & \times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

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

Ex : a 4e/4o pb :



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



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

...

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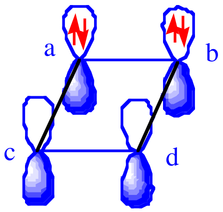
VB theory :

(nonorthogonal orbs.)

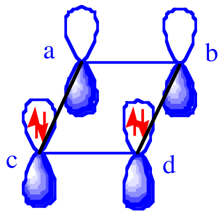
$$\bar{\bar{S}}$$

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

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

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

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

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

VB theory :

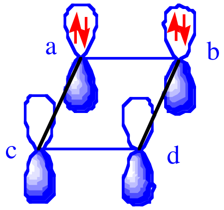
(nonorthogonal orbs.)

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

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

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

Ex : a 4e/4o pb :



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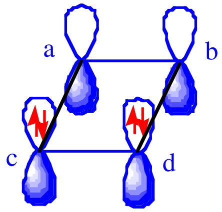


$|c\bar{c}d\bar{d}|$

Limits of VB theory

- **Nonorthogonality :**

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

  Ex 2 : (ic)VBPT2 formulas :

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

Limits of VB theory

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

But :

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

    1) Second Quantization Technique for non-orthogonal orbitals ;

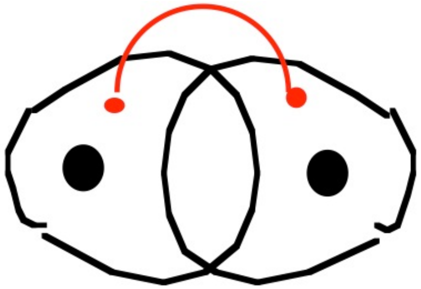
    2) Tensor Analysis ;

    3) Automatic Formula/Code Generator

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

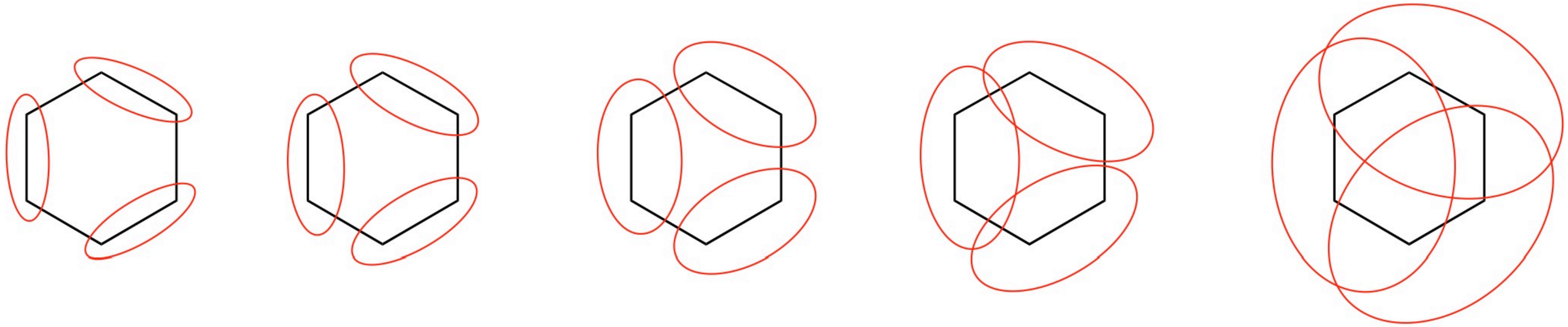
H_2/LiH : $S \approx 0.8$!

☝

basically the only two
really pathologic cases

Limits of VB theory

- **Moderate overlap between active orbitals :**



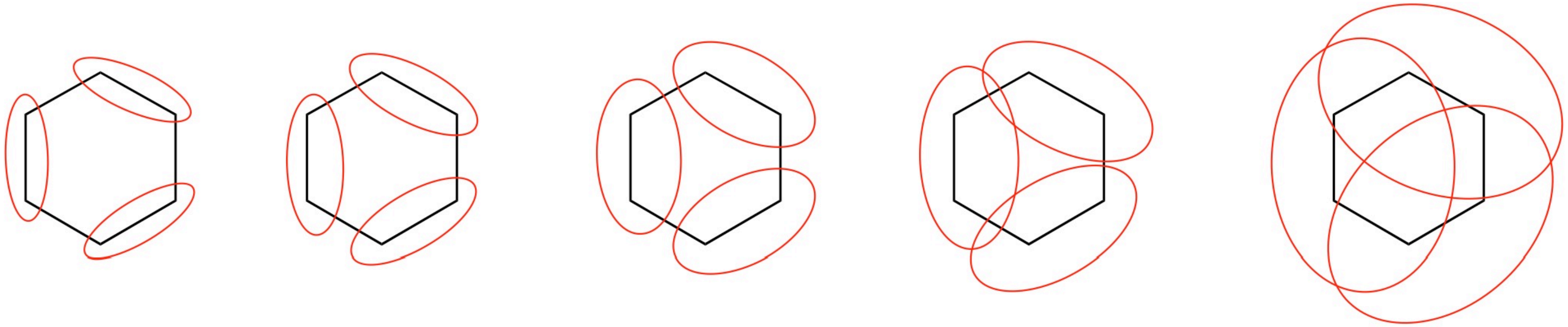
DZ+P TZ+P aug-TZ+P aug-QZ+P aug-5Z+P

• 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

An Ab Initio Non-orthogonal Valence Bond Program

It's up to you (tutorials) !

- Tutoriel 1 (Thurs. 15h-18h) : Basics of XMVB computations

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