

# Part 3. Qualitative Valence Bond

**Stop me at any time !**

# Qualitative VB

- Basic ingredients :

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

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

# Qualitative VB

- Basic ingredients :

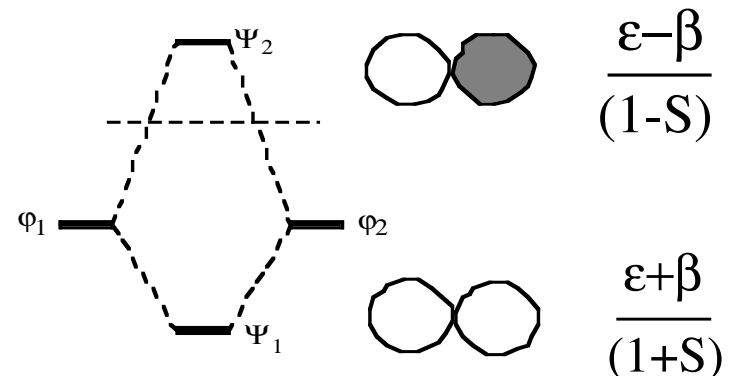
1) Effective Hamiltonian :  $\mathbf{H}^{\text{eff}} = \mathbf{h}^{\text{eff}}(1) + \mathbf{h}^{\text{eff}}(2) + \mathbf{h}^{\text{eff}}(3) + \dots$

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

2) Parametrization :  $\epsilon, \beta, S$

$\left\{ \begin{array}{l} \epsilon_i : \text{orbital } i \text{ self-energy} \\ \beta : \text{resonance integral} \\ S : \text{overlap integral} \end{array} \right.$

Same as in Hückel theory :



# Qualitative VB

- General calculus rules :

Reminder :

$$h_{aa} = \int a(1)h(1)a(1)d\tau_1$$

$$h_{ab} = \int a(1)h(1)b(1)d\tau_1$$

$$S_{ab} = \int a(1)b(1)d\tau_1$$

# Qualitative VB

- General calculus rules :

What we have to calculate :

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

H matrix elements

Overlaps S

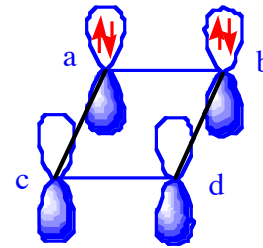
# Qualitative VB

- General calculus rules :

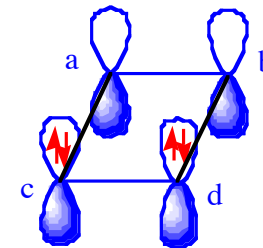
- 1) Rule for calculating determinant overlaps :

Generate permutations :

- between identical spins
- only one side



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



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

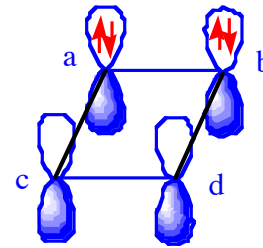
# Qualitative VB

- General calculus rules :

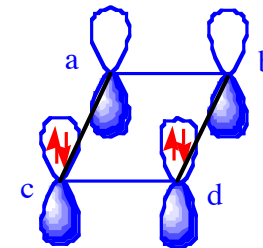
## 1) Rule for calculating determinant overlaps :

Generate permutations :

- between identical spins
- only one side



$$\frac{1}{\sqrt{4}} |a\bar{a}b\bar{b}|$$



$$\frac{1}{\sqrt{4}} |c\bar{c}d\bar{d}|$$

$$\begin{aligned} \frac{1}{4} \langle |a\bar{a}b\bar{b}| | |c\bar{c}d\bar{d}| \rangle &= \langle a(1)\bar{a}(2)b(3)\bar{b}(4) | c(1)\bar{c}(2)d(3)\bar{d}(4) \rangle \\ &\quad - \langle a(1)\bar{a}(2)b(3)\bar{b}(4) | \textcolor{red}{d}(1)\bar{c}(2)\textcolor{red}{c}(3)\bar{d}(4) \rangle + \dots \\ &= S_{ac}^2 S_{bd}^2 - S_{ad} S_{ac} S_{bc} S_{bd} - S_{ac} S_{ad} S_{bd} S_{bc} + S_{ad}^2 S_{bc}^2 \end{aligned}$$

$$\langle |a\bar{a}b\bar{b}| | |a\bar{a}b\bar{b}| \rangle = 1 - 2S_{ab}^2 + 4S_{ab}^4$$



# Qualitative VB

- **General calculus rules :**

- 2) Rule for calculating Hamiltonian matrix elements :**

Generate permutations :

- between identical spins
  - only one side
- $$\langle \Omega | H^{eff} | \Omega' \rangle = \langle \Omega | h(1) + h(2) + h(3) + h(4) | \Omega' \rangle$$

# Qualitative VB

- General calculus rules :

## 2) Rule for calculating Hamiltonian matrix elements :

Generate permutations :

- between identical spins  $\langle \Omega | H^{eff} | \Omega' \rangle = \langle \Omega | h(1) + h(2) + h(3) + h(4) | \Omega' \rangle$
- only one side

$$\begin{aligned}
 \frac{1}{4} \langle (|a\bar{a}b\bar{b}|) | \hat{h}_1 | (|c\bar{c}d\bar{d}|) \rangle &= \langle a(1)\bar{a}(2)b(3)\bar{b}(4) | \hat{h}_1 | c(1)\bar{c}(2)d(3)\bar{d}(4) \rangle \\
 &\quad - \langle a(1)\bar{a}(2)b(3)\bar{b}(4) | \hat{h}_1 | d(1)\bar{c}(2)c(3)\bar{d}(4) \rangle \\
 &\quad - \langle a(1)\bar{a}(2)b(3)\bar{b}(4) | \hat{h}_1 | c(1)\bar{d}(2)d(3)\bar{c}(4) \rangle \\
 &\quad + \langle a(1)\bar{a}(2)b(3)\bar{b}(4) | \hat{h}_1 | d(1)\bar{d}(2)c(3)\bar{c}(4) \rangle \\
 &= h_{ac} S_{ac} S_{bd}^2 - h_{ad} S_{ac} S_{bc} S_{bd} - h_{ac} S_{ad} S_{bd} S_{bc} + h_{ad} S_{ad} S_{bc}^2
 \end{aligned}$$

# Qualitative VB

- General calculus rules :

## 2) Rule for calculating Hamiltonian matrix elements :

Generate permutations :

- between identical spins  $\langle \Omega | H^{eff} | \Omega' \rangle = \langle \Omega | h(1) + h(2) + h(3) + h(4) | \Omega' \rangle$
- only one side

$$\frac{1}{4} \langle (|a\bar{a}b\bar{b}|) | \hat{h}_1 | (|c\bar{c}d\bar{d}|) \rangle = \dots = h_{ac} S_{ac} S_{bd}^2 - h_{ad} S_{ac} S_{bc} S_{bd} - h_{ac} S_{ad} S_{bd} S_{bc} + h_{ad} S_{ad} S_{bc}^2$$

Then repeat :  $\frac{1}{4} \langle (|a\bar{a}b\bar{b}|) | \hat{h}_2 | (|c\bar{c}d\bar{d}|) \rangle = \dots$

$$\frac{1}{4} \langle (|a\bar{a}b\bar{b}|) | \hat{h}_3 | (|c\bar{c}d\bar{d}|) \rangle = \dots$$

Rather tedious...

$$\frac{1}{4} \langle (|a\bar{a}b\bar{b}|) | \hat{h}_4 | (|c\bar{c}d\bar{d}|) \rangle = \dots$$

# Qualitative VB

- **Simplified expressions :**

1) Choice of an origin of energies (shift) :

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

$$\left\{ \begin{array}{l} \varepsilon_i = h_{ii} - \frac{1}{n} \sum_{i=1}^n h_{ii} \\ \beta_{ij} = h_{ij} - \frac{1}{n} \sum_{i=1}^n h_{ii} \end{array} \right.$$

# Qualitative VB

- **Simplified expressions :**

1) Choice of an origin of energies (shift) :

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

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

# Qualitative VB

- **Simplified expressions :**

1) Choice of an origin of energies (shift) :

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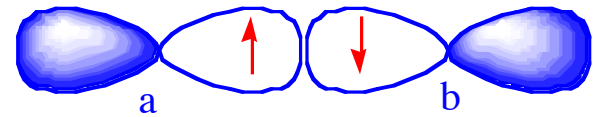
2) Approximation :

– Neglect  $S_{ac}$  and  $h_{ac}$  if **a** and **c** are not nearest neighbours

# Qualitative VB

- Elementary interactions energies :

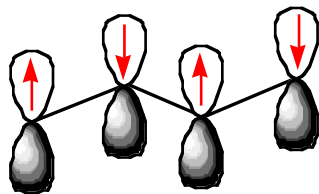
- 1) The QC state :



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

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

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

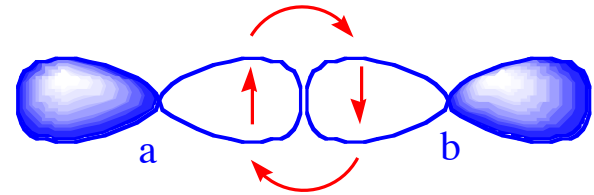


$$E=0$$

# Qualitative VB

- Elementary interactions energies :

- 2) The two electron bond :



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

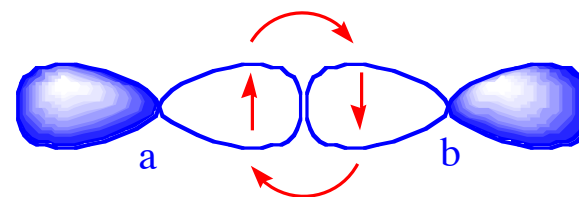
$$\begin{aligned} \langle \Psi | \hat{H}^{eff} | \Psi \rangle \Rightarrow & \begin{cases} \text{Diagonal terms (two)} : \langle (|a\bar{b}|) | \hat{h}_1 + \hat{h}_2 | (|a\bar{b}|) \rangle = \varepsilon_1 + \varepsilon_2 = 0 \\ \text{Off-diag. terms (two)} : \langle (|a\bar{b}|) | \hat{h}_1 + \hat{h}_2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



# Qualitative VB

- Elementary interactions energies :

## 2) The two electron bond :

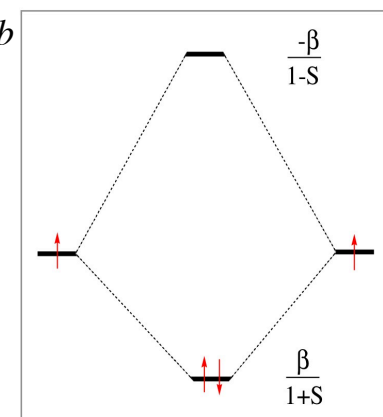


$$\Psi_{2e} = \frac{|a\bar{b}| + |b\bar{a}|}{\sqrt{2(1 + S^2)}}$$

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

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

*Different in MO-Hückel theory :*

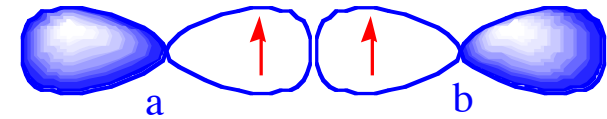


$$D_e = 2\beta/(1+S)$$

# Qualitative VB

- Elementary interactions energies :

### 3) The triplet repulsion :

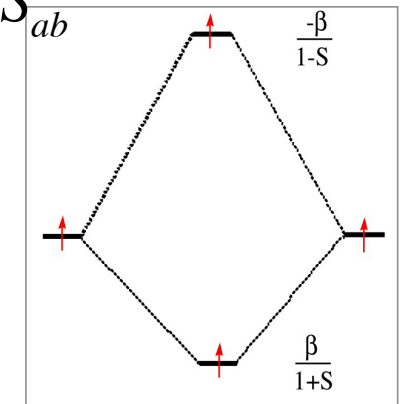


$$\Psi_T = \frac{|a\bar{b}| - |b\bar{a}|}{\sqrt{2(1-S^2)}}$$

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

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

Same in MO-Hückel theory :



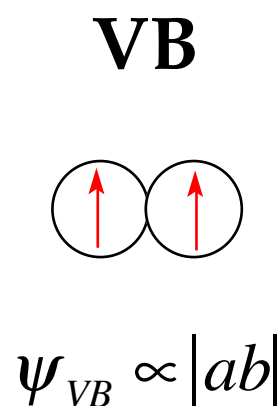
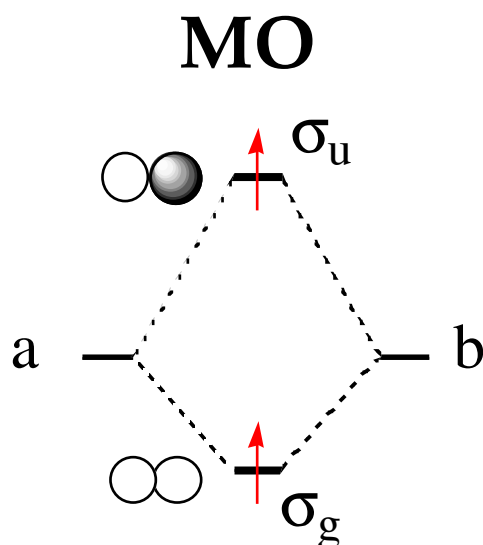
$$E = \frac{\beta}{1+S} + \frac{-\beta}{1-S} = \frac{-2\beta S}{1-S^2}$$

# Qualitative VB

- Elementary interactions energies :

## 3) The triplet repulsion :

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



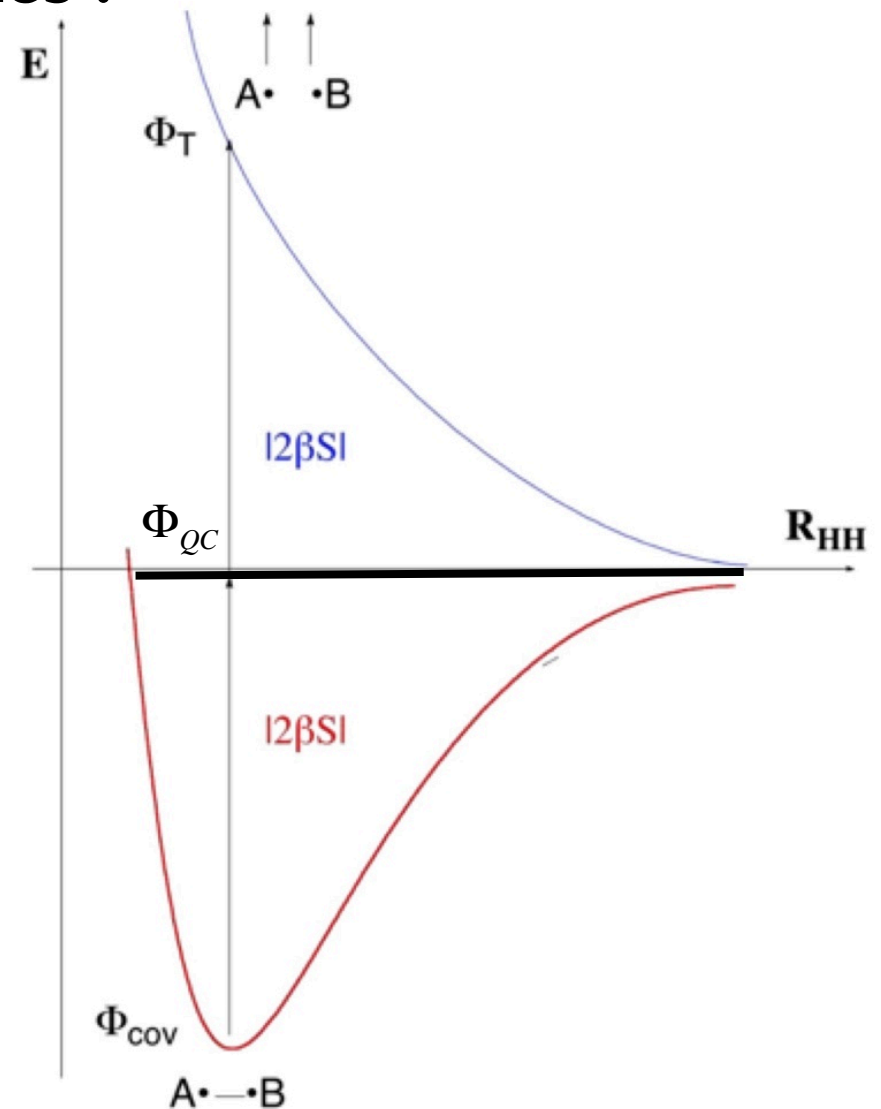
$$\psi_{MO} \propto |\sigma_g \sigma_u| = |(a+b)(a-b)| = |\cancel{aa}| + |\cancel{bb}| + |ba| - |ab| \propto \psi_{VB}$$

# Qualitative VB

- Elementary interactions energies :



• Lecture 1 :  
 $\Delta E_{ST} \approx 2De$

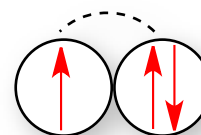


# Qualitative VB

- Elementary interactions energies :

## 4) All repulsions :

- 3e repulsion : **same** as triplet :



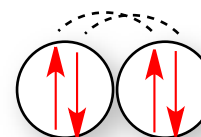
VB

$$\frac{-2\beta S}{1 - S^2}$$

MO

**Same**

- 4e repulsion : **two times** triplet :

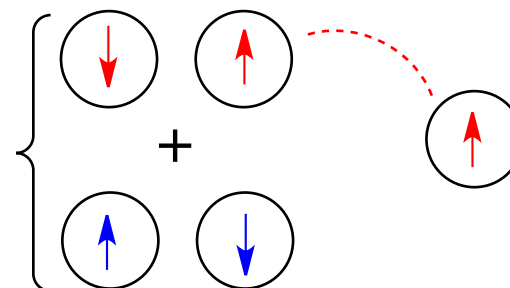


$$\frac{-4\beta S}{1 - S^2}$$

**Same**

- NCI : **half time** triplet :

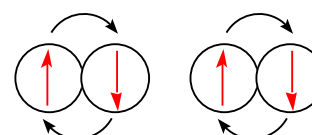
bond... single electron



$$\frac{-\beta S}{1 - S^2}$$

/

bond... bond



$$\frac{-\beta S}{1 - S^2}$$

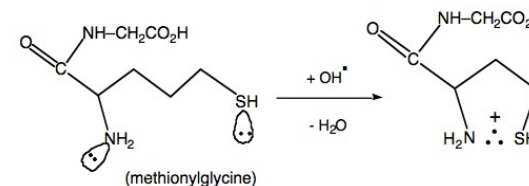
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# Qualitative VB

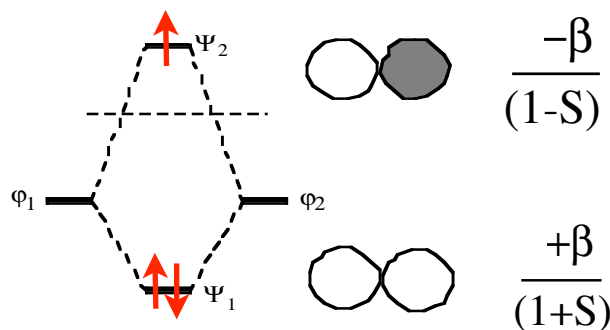
- Elementary interactions energies :

## 5) The 3e bond :

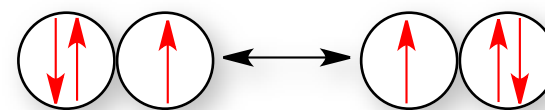
Examples :  $\text{He}_2^+$ ,  $\text{RS}^\ominus \cdots \text{SR}'$ ,  
radical intermediates :



### MO



### VB



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

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

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

**Remind for later use !**

# Qualitative VB


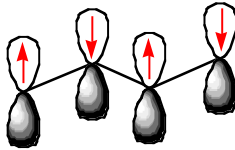
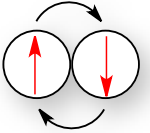
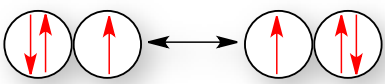
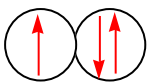
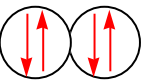
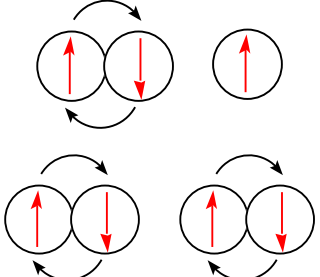
- Elementary interactions energies :

Energy of a determinant with *n pairs of interacting  $e^-$*  :  $\frac{\sigma 2n\beta S}{1+\sigma S^2}$   
 $\sigma$  sign : + if attractive, – if repulsion



Work for all but 3e bond

# Qualitative VB

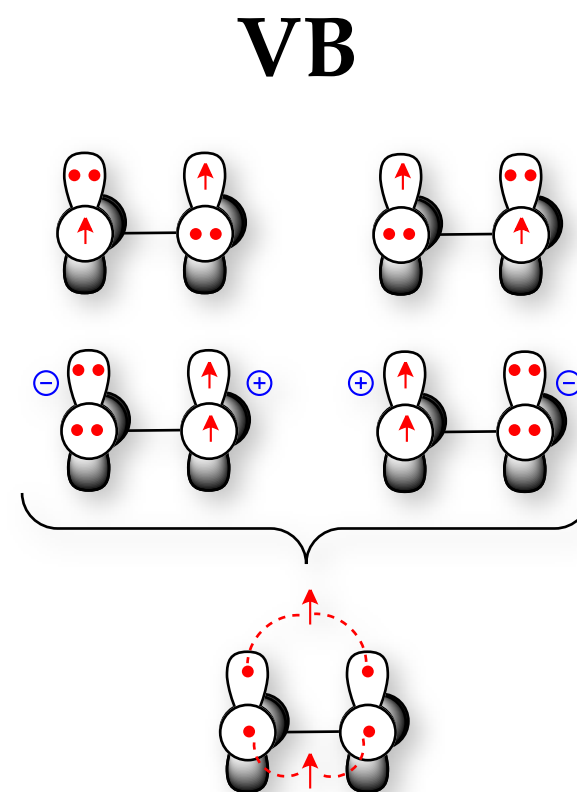
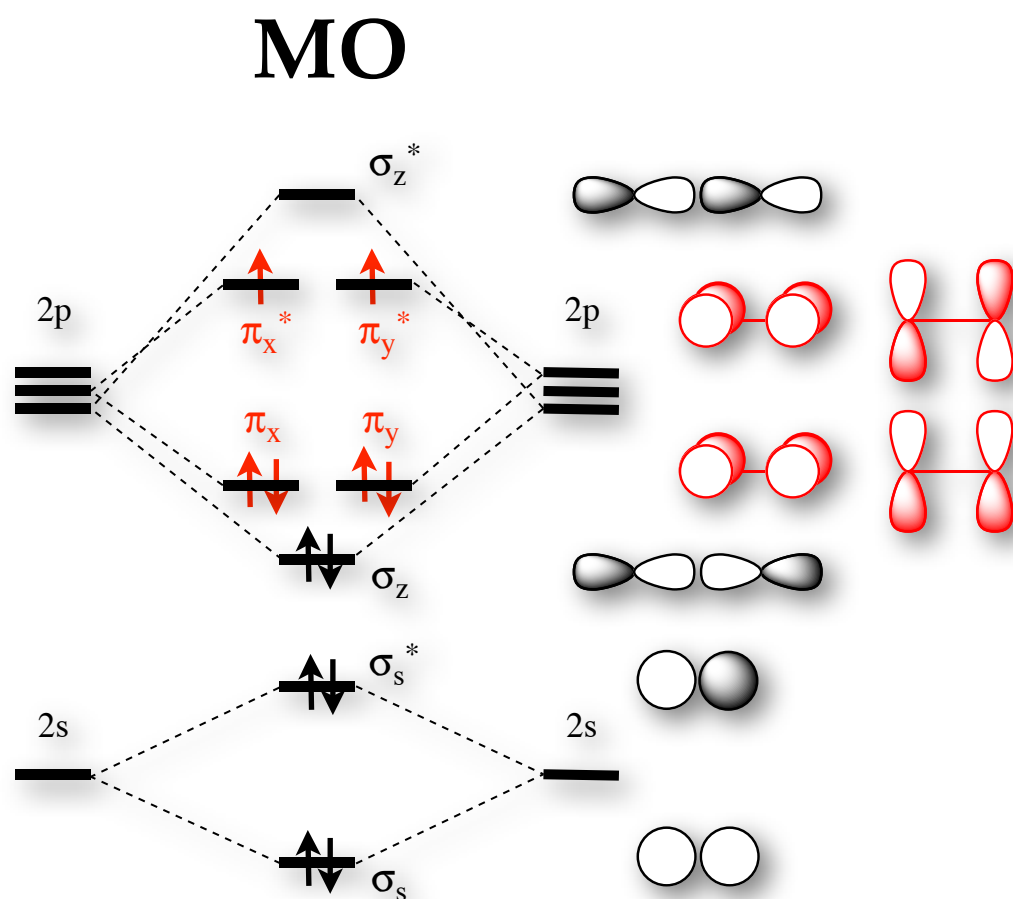
	VB	MO	$\frac{\sigma 2n\beta S}{1+\sigma S^2}$ 
spin-alternated det.			
	0	(VB only)	
2-e bond (A-B) =		$2\beta S/(1+S^2)$	$2\beta/(1+S)$
3-e bond(A:B) =		$\beta(1-3S)/(1-S^2)$	Same as VB
triplet=3-e repulsion		$-2\beta S/(1-S^2)$	Same as VB
4-e repulsion		$-4\beta S/(1-S^2)$	Same as VB
bond...single e <sup>-</sup> and bond...bond		$-\beta S/(1-S^2)$	(VB only)



# Qualitative VB

## ➔ Exercise 4 : ground state of $O_2$ :

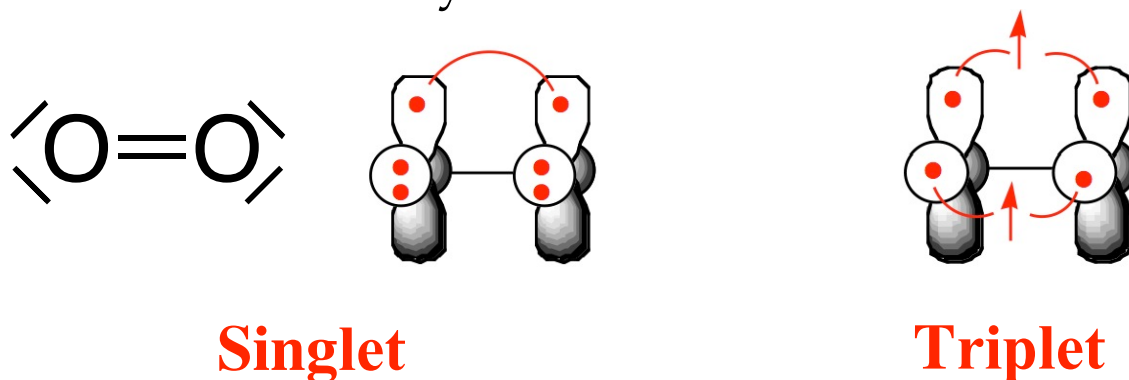
Dioxygen triplet ground state : two  $\pi$ -type 3e-bonds :



# Qualitative VB

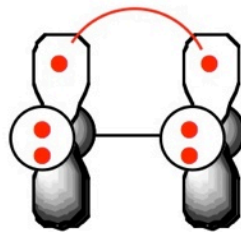
## ➔ Exercise 4 : ground state of $O_2$ :

- 1) Calculate the energy expression for the  $\pi$  system of the lowest triplet state of the dioxygen molecule, at the qualitative VB level (using the complete expressions with denominators)
- 2) Same question for the closed-shell singlet state, corresponding to the usual Lewis structure used for this molecule.
- 3) Take the difference, and conclude which state is predicted to be the lowest at the qualitative VB level of theory.

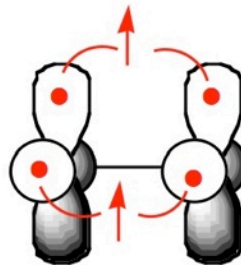


# Qualitative VB

➔ Exercise 4 : ground state of O<sub>2</sub> (answer) :



$$E(S) = 2\beta S / (1+S^2) - 4\beta S / (1-S^2)$$



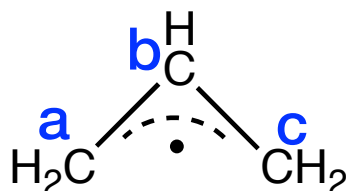
$$E(T) = 2\beta (1 - 3S) / (1-S^2)$$

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

➔ *The triplet state is always the lower*

# Qualitative VB

## ➔ Exercise 5 : spin polarization in allyl radical :



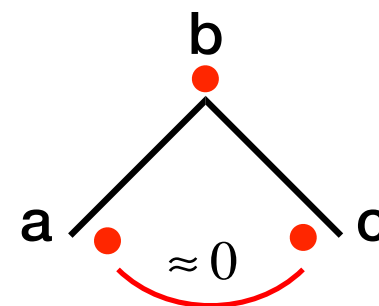
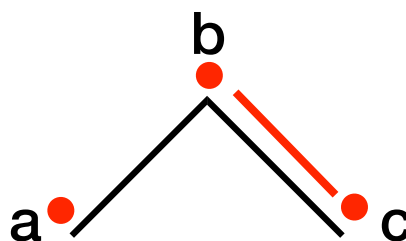
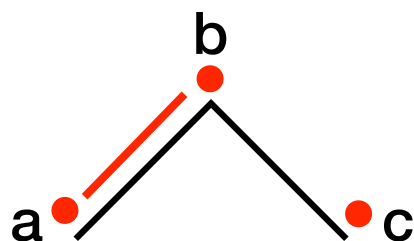
*The allyl radical is a planar molecule with three electrons in its  $\pi$  system (in 3  $p_C$  orbitals).*

- 1) What are the three possible covalent structures for the allyl radical ? Express their energy at the qualitative VB level, and show that two of them are degenerate.
- 2) Show that the third structure can be expressed as a linear combination of the first two structures, and thus that only two of the three covalent structures form a complete basis of non-redundant structures (Rumer basis).
- 3) EPR measurements show that the spin density on the central atom is  $-0.2$  (ie : excess of down spin electron), whereas  $-1$ . value of is predicted at the UHF level. Express the HL w.f. corresponding to the ground state, and calculate the predicted spin density.

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

# Qualitative VB

## ➔ Exercise 5 : spin polarization in allyl radical :



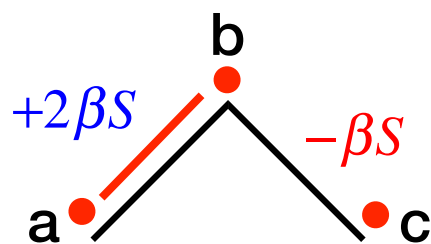
$$\psi(I) = \frac{1}{\sqrt{2}} (|a\bar{b}c| + |b\bar{a}c|)$$

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

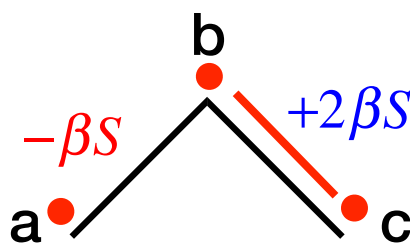
$$\psi(III) = \frac{1}{\sqrt{2}} (|ab\bar{c}| + |cb\bar{a}|) = \psi(I) + \psi(II)$$

# Qualitative VB

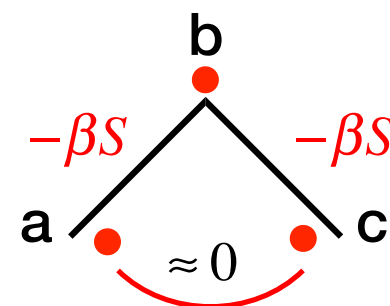
## ➔ Exercise 5 : spin polarization in allyl radical :



$$\Rightarrow E(I) = +\beta S < 0$$



$$\Rightarrow E(II) = +\beta S < 0$$

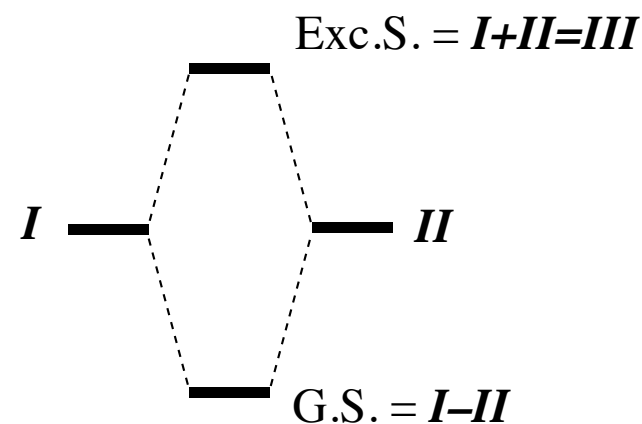


$$\Rightarrow E(III) = -2\beta S$$

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

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

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



# Qualitative VB

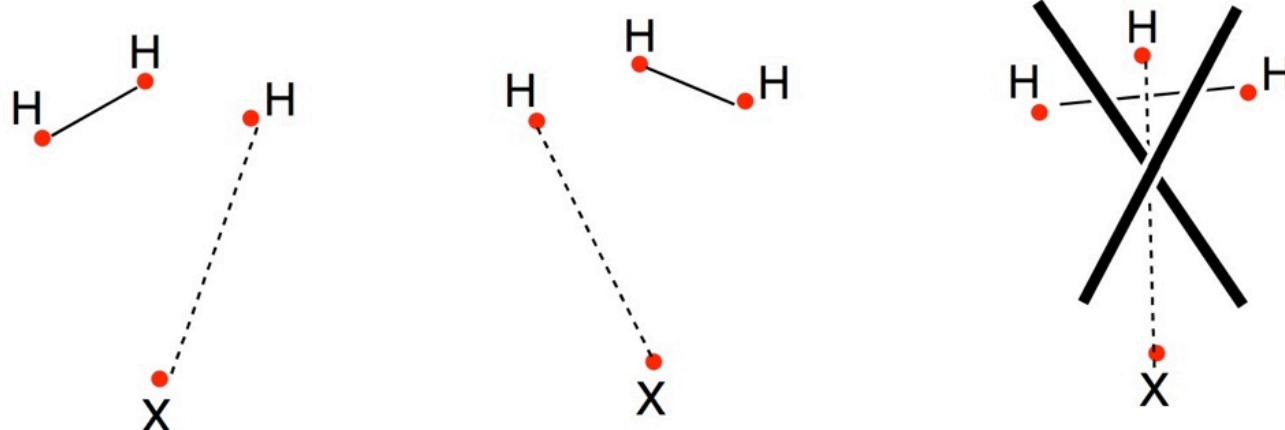
## ➔ Exercise 5 : spin polarization in allyl radical :

- We could also have applied **Rumers' graphical method for a radical** to get a complete basis of («chemically meaningful») structures :

*1) Add a fictitious center with one electron*

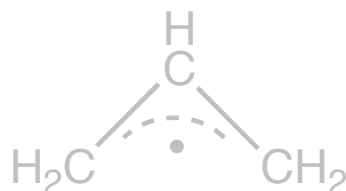
*2) Apply to this new system Rumer's rules for a singlet*

Exemple :  $\text{H}_3$  radical



# Qualitative VB

## ➔ Exercise 5 : spin polarization in allyl radical :



*The allyl radical is a planar molecule with three electrons in its  $\pi$  system (in 3  $p_C$  orbitals).*

1) What are the three possible covalent structures for the allyl radical ? Express their energy at the qualitative VB level, and show that two of them are degenerate.

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

3) EPR measurements show that the spin density on the central atom is  $-0.2$  (ie : excess of down spin electron), whereas  $-1$ . value of is predicted at the UHF level. Express the HL w.f. corresponding to the ground state, and calculate the predicted spin density.

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



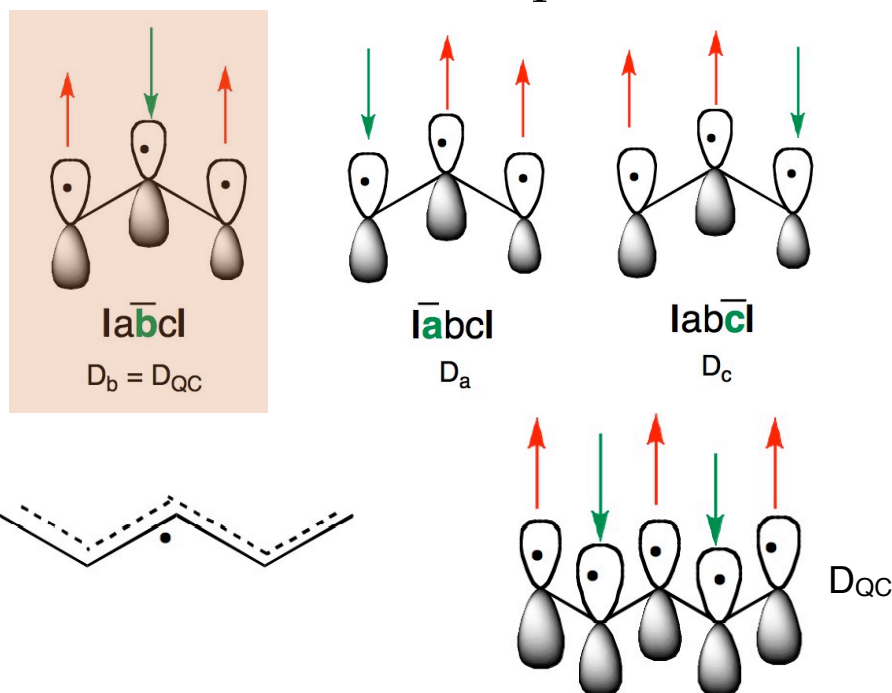
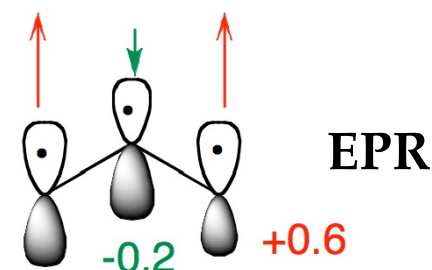
# Qualitative VB

## ➔ Exercise 5 : spin polarization in allyl radical :

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

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

⇒ much closer to experiment than UHF



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

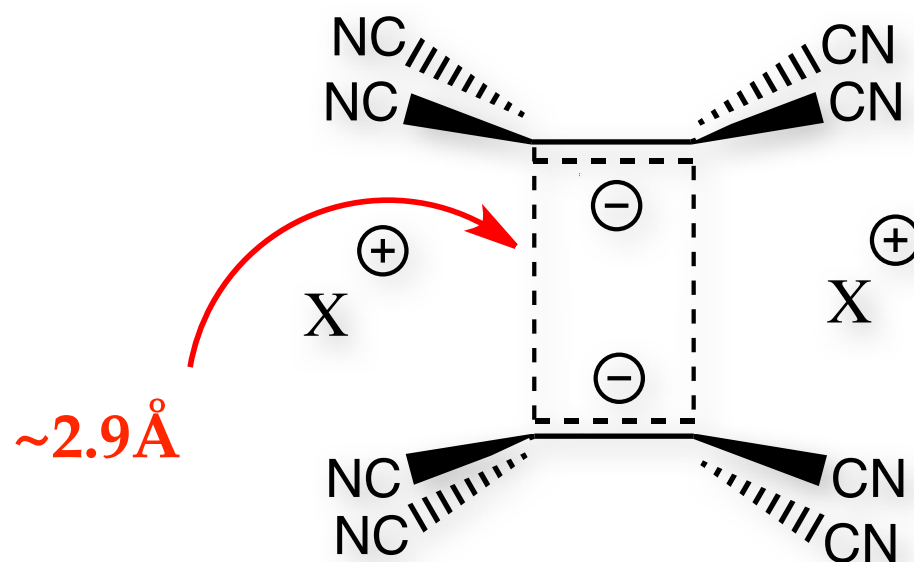
➔ General rule, works for all polyenes

# Application

## Electronic structure of the DTCNE dimer

# «Pancake bonding»

- $\text{DTCNE}_2^{2-}$  :



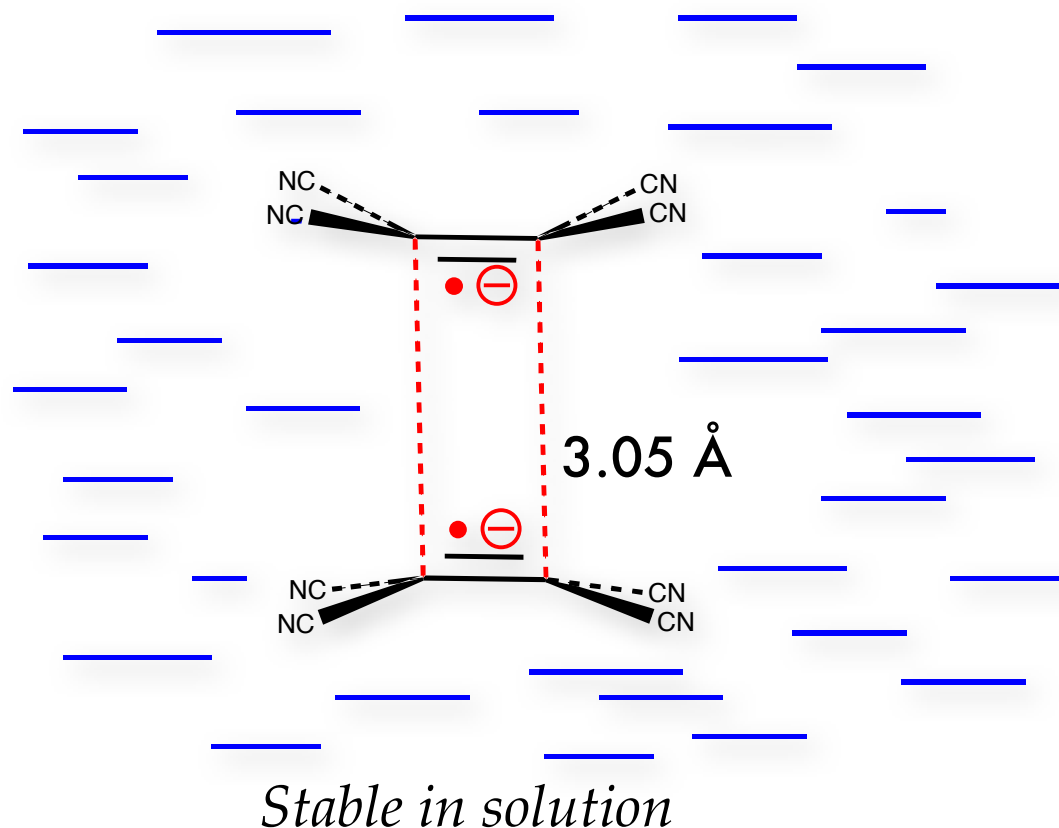
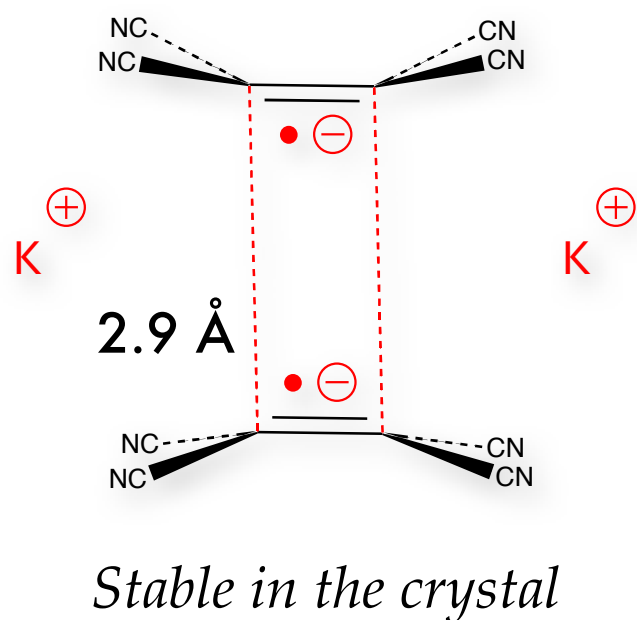
$\text{X}^+ : \text{Na}^+, \text{Cs}^+, [\text{iPr}_4\text{N}]^+, [\text{Cr}(\text{C}_6\text{Me}_3\text{H}_3)_2]^+, \dots$

**Electrostatic complex ?...**

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

# «Pancake bonding»

- $\text{DTCNE}_2^{2-}$  :

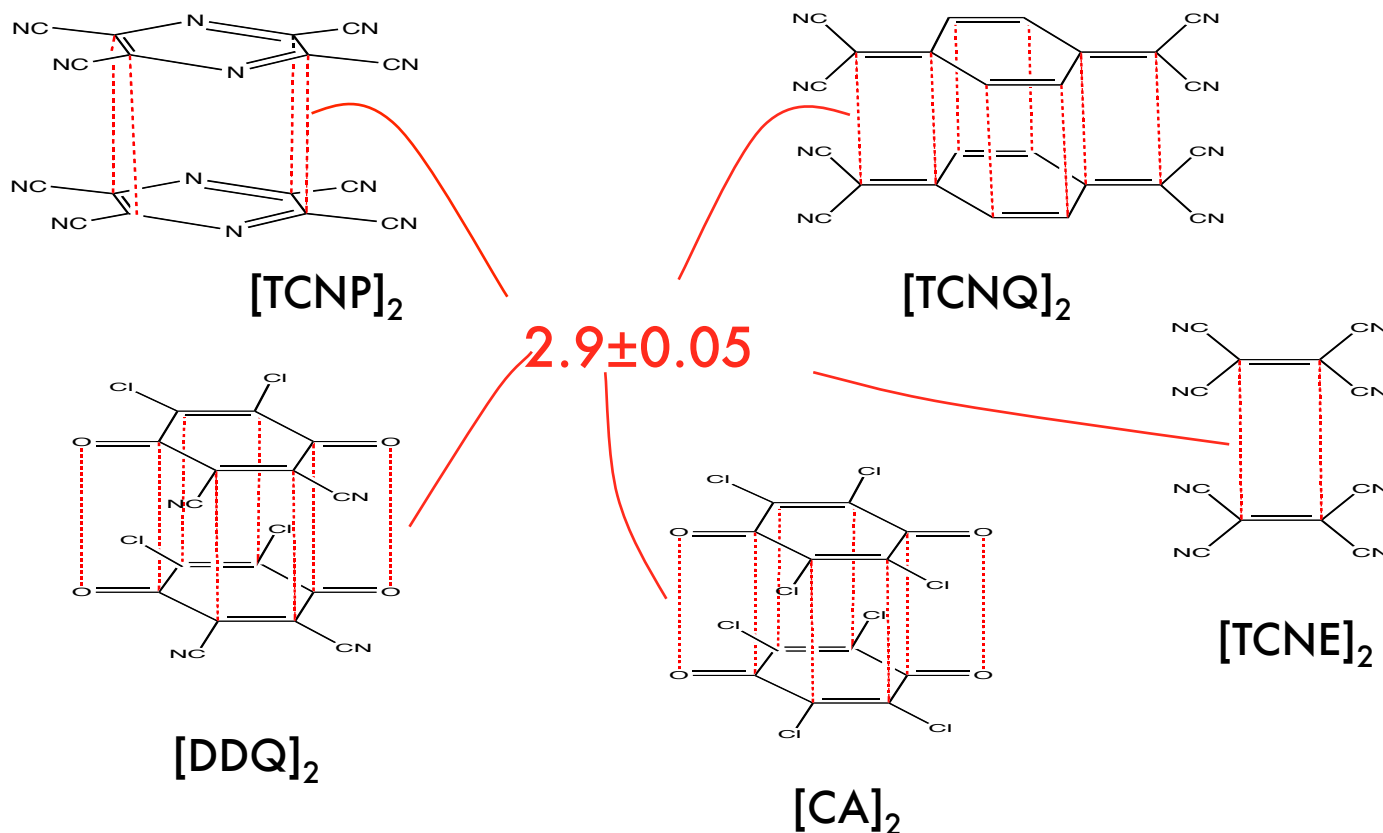


- Same bonding distance whatever the environment !

**$\Rightarrow$  not only electrostatic... also an interfragment bond**

# «Pancake bonding»

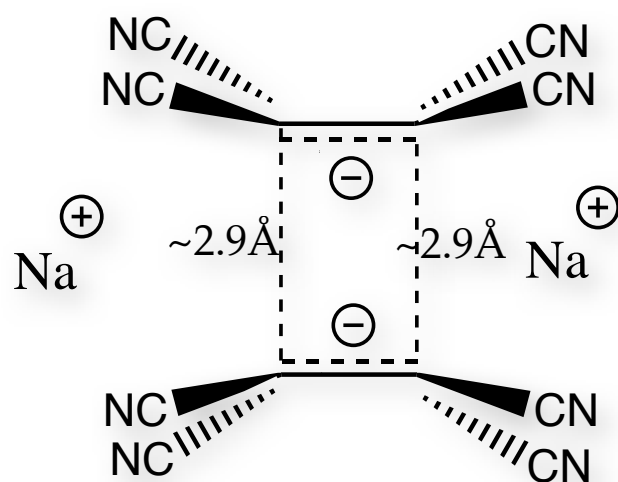
- Other «pancake bonding» systems :



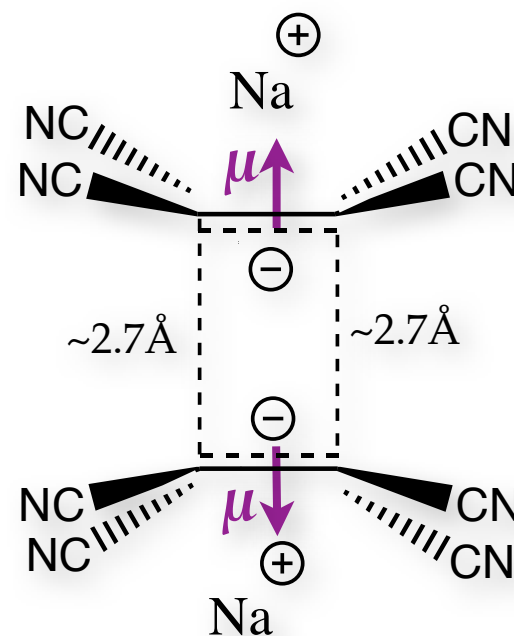
- Same bonding distance whatever the system !
- $d_{C...C} < \text{sum of vdW radii } (3.45 \text{ \AA})$  , but much longer than C-C 2e bonds ( $1.54 \text{ \AA}$ )

# «Pancake bonding»

- What kind of bonding in  $\text{DTCNE}_2^{2-}$  ?



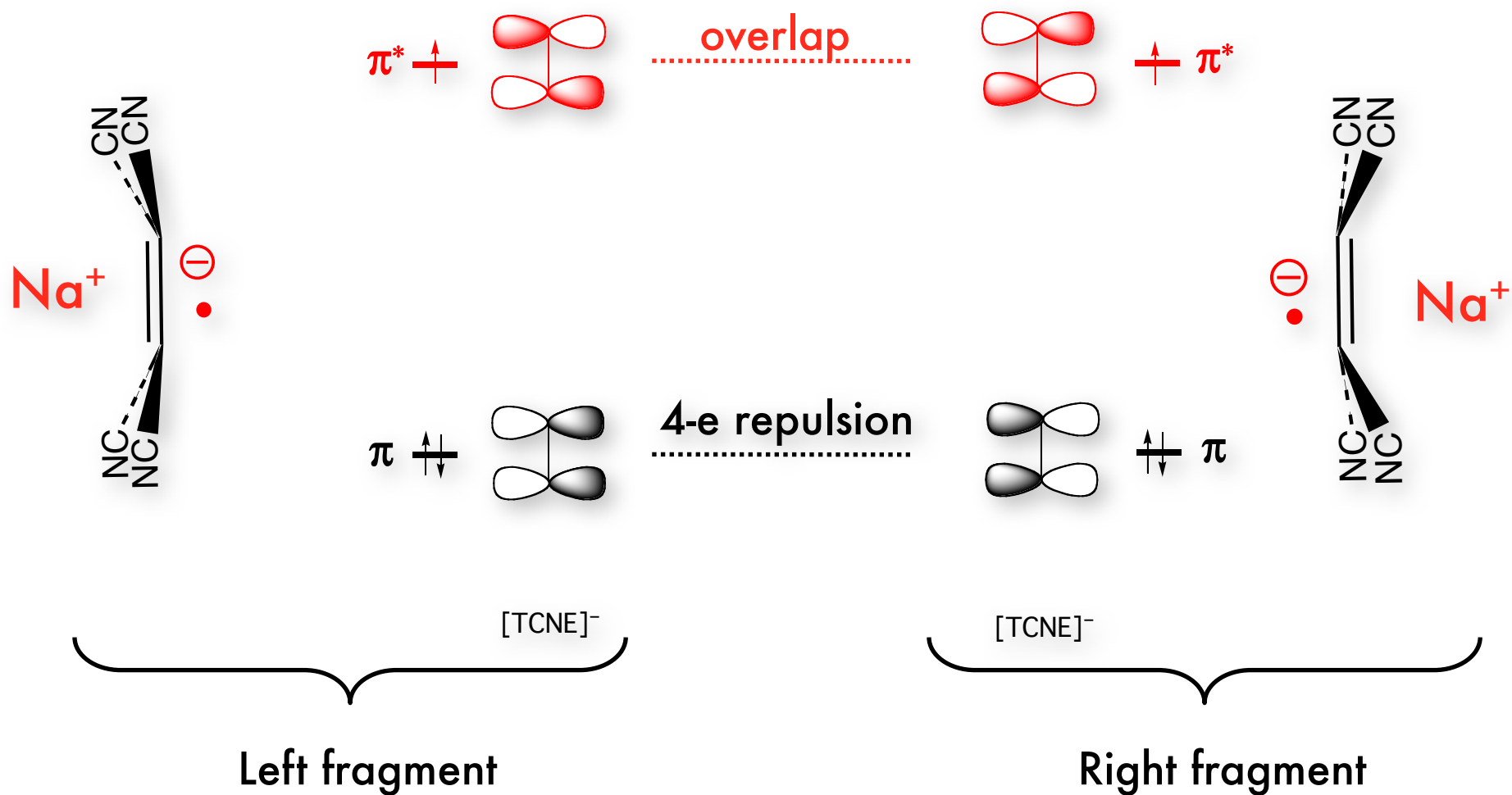
$$D_e \approx 80. \text{ kcal/mol}$$



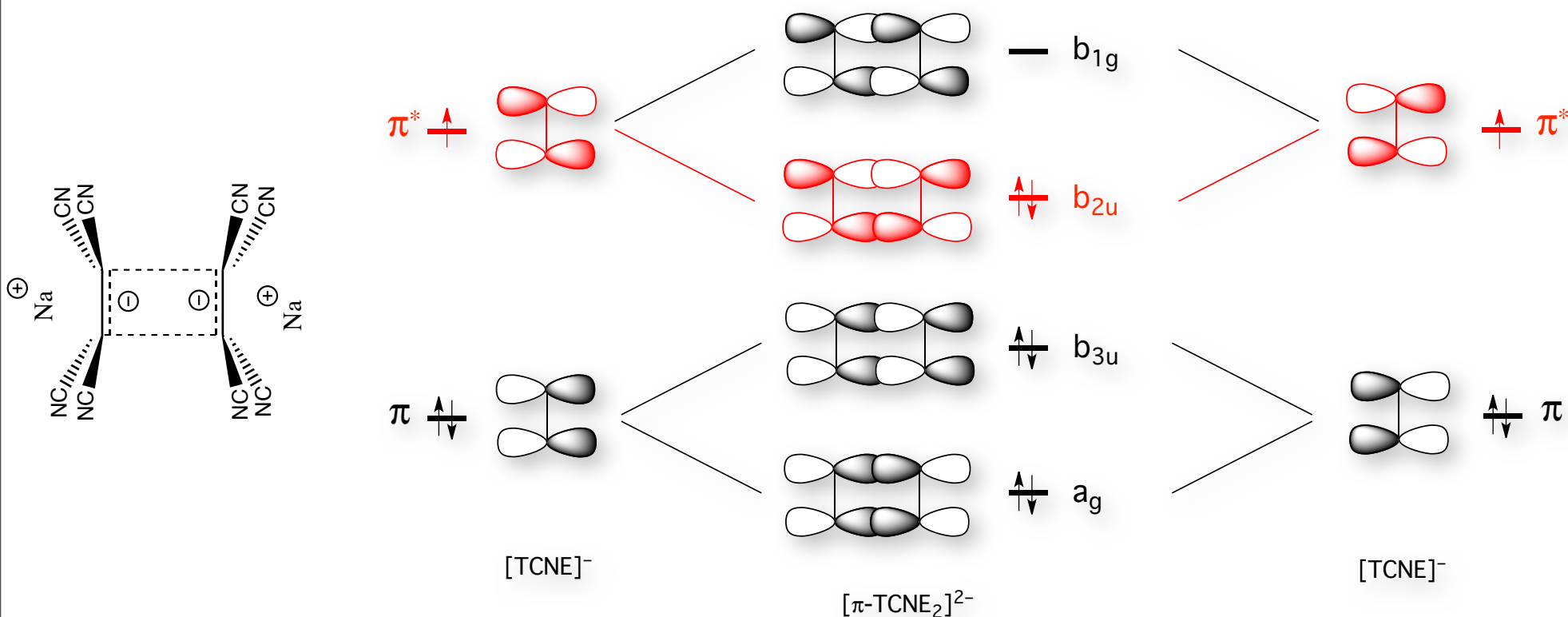
$$D_e \approx 11. \text{ kcal/mol} !$$

Right geom : significant bonding force overcome repulsive electrostatics !

# Qualitative MO analysis



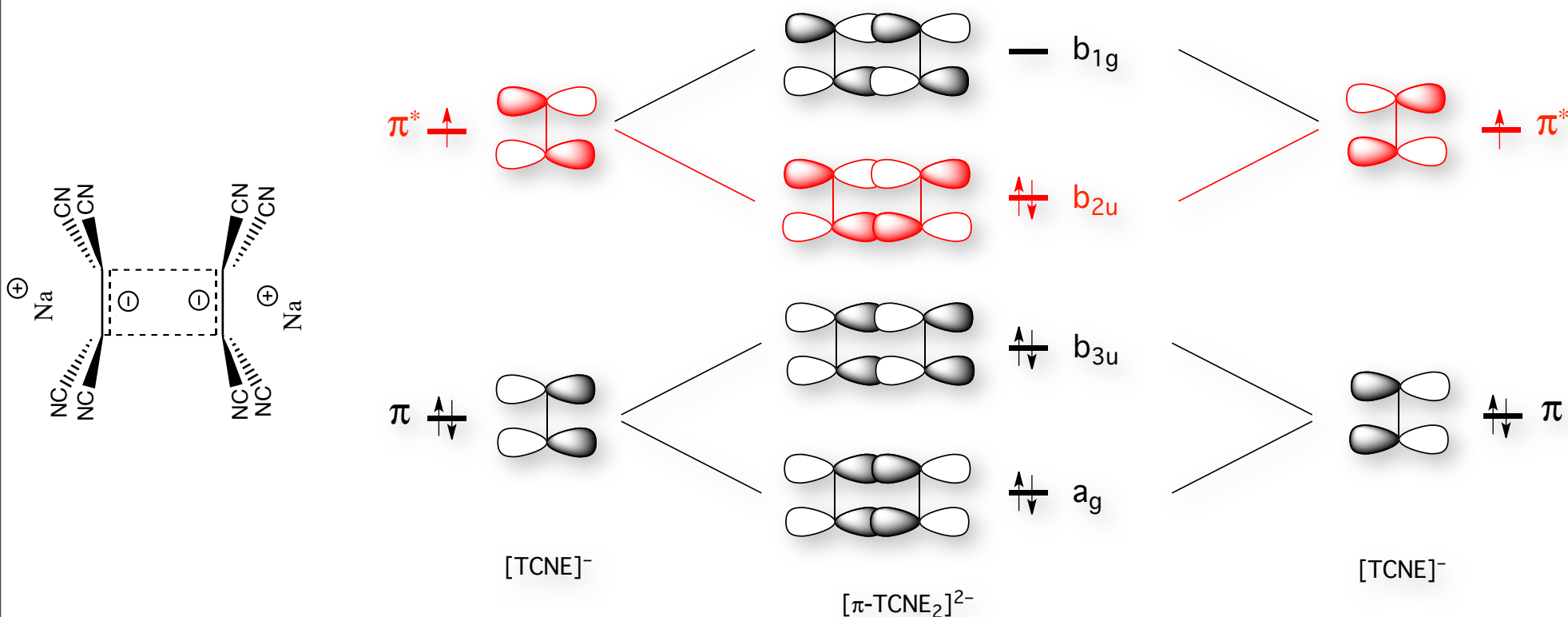
# Qualitative MO analysis



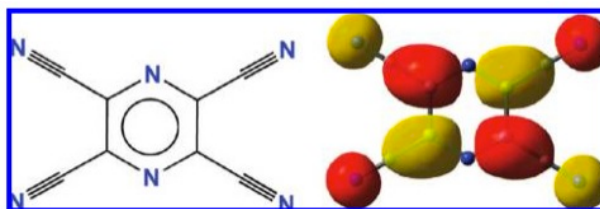
$\Rightarrow$  a simple **4 centers / 2 electrons bond** ?



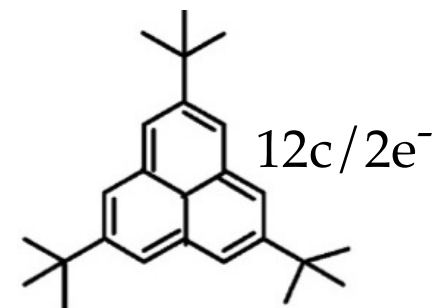
# Qualitative MO analysis



Other «pancake bonding»  
systems : **n center /  $2e^-$  bonds**



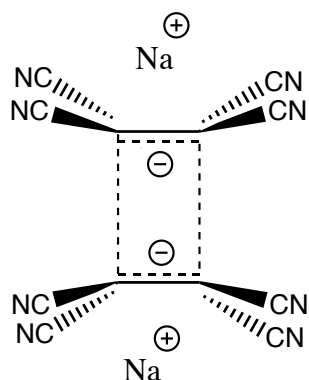
$8c/2e^-$



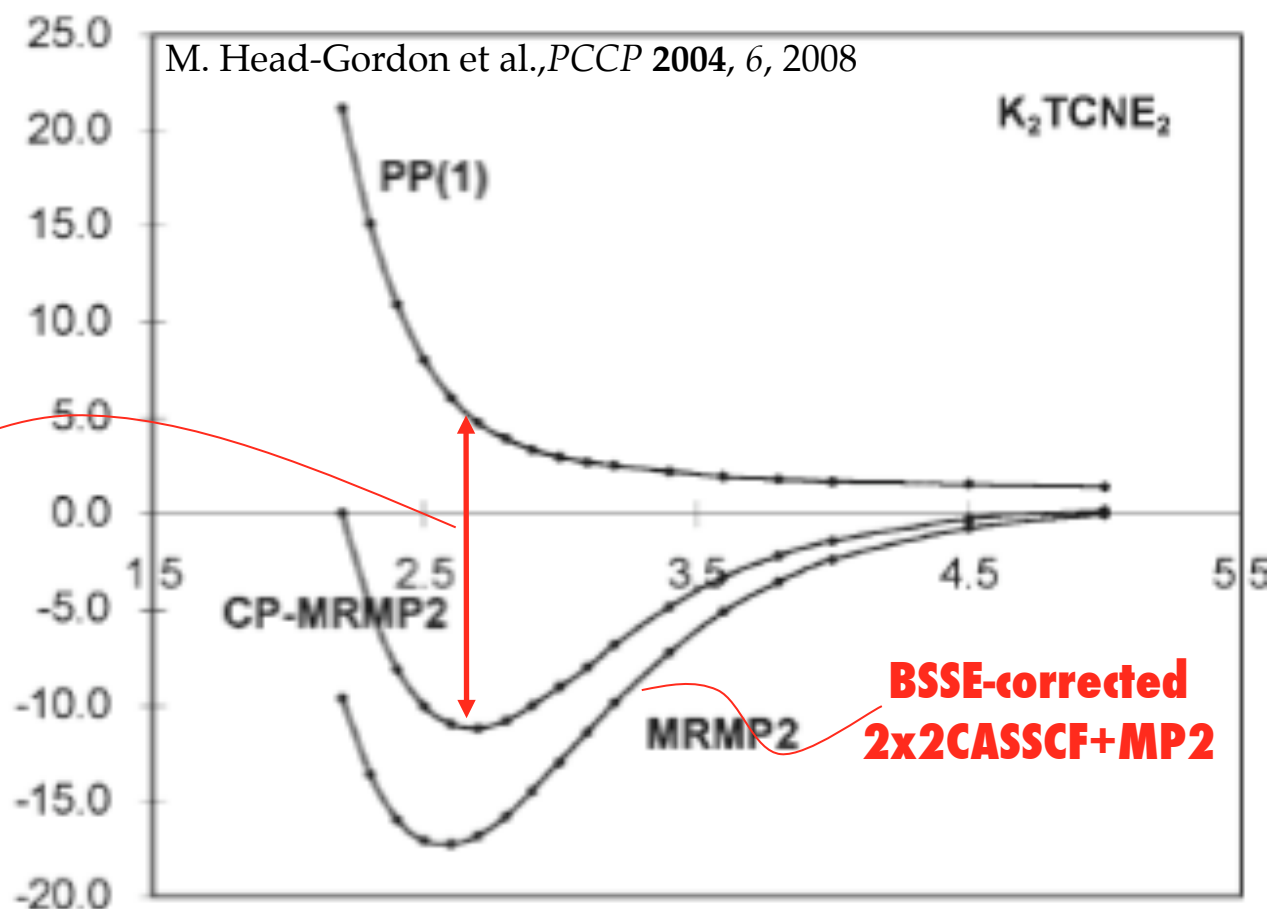
$12c/2e^-$

# Quantitative MO computations

- GVB calculations of the axial conformation :



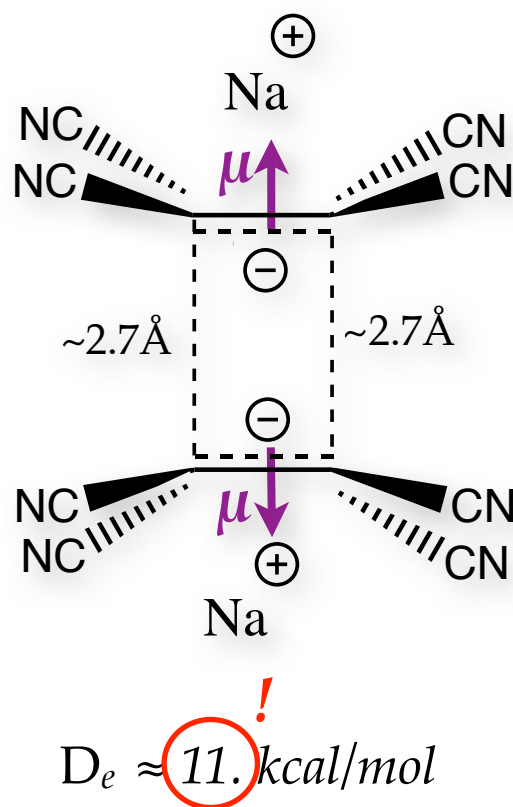
Contribution of  
dynamic correlation  
to bonding:  
**> 23 kcal/mol !**



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

# Situation

- What kind of bonding in  $\text{DTCNE}_2^{2-}$  ?

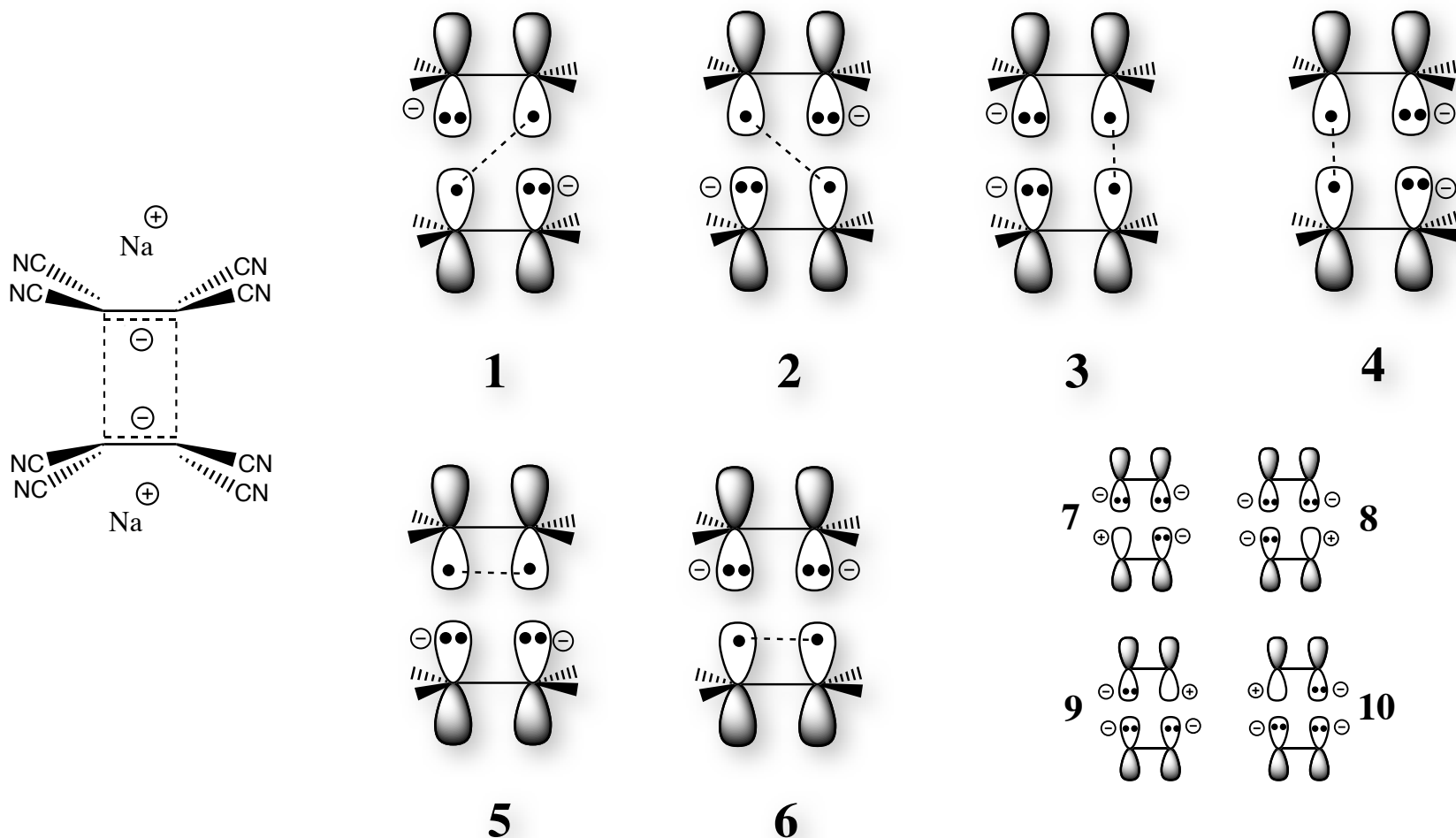


- Same bonding distance whatever the counter-ion, the environment, the system...
- MO analysis propose a  $4c/2e$  bond, but GVB-PP fails to account for any bonding...
- Distance too short, bond energy too strong to be dispersion...

**$\Rightarrow$  try a different perspective... with VB theory !**

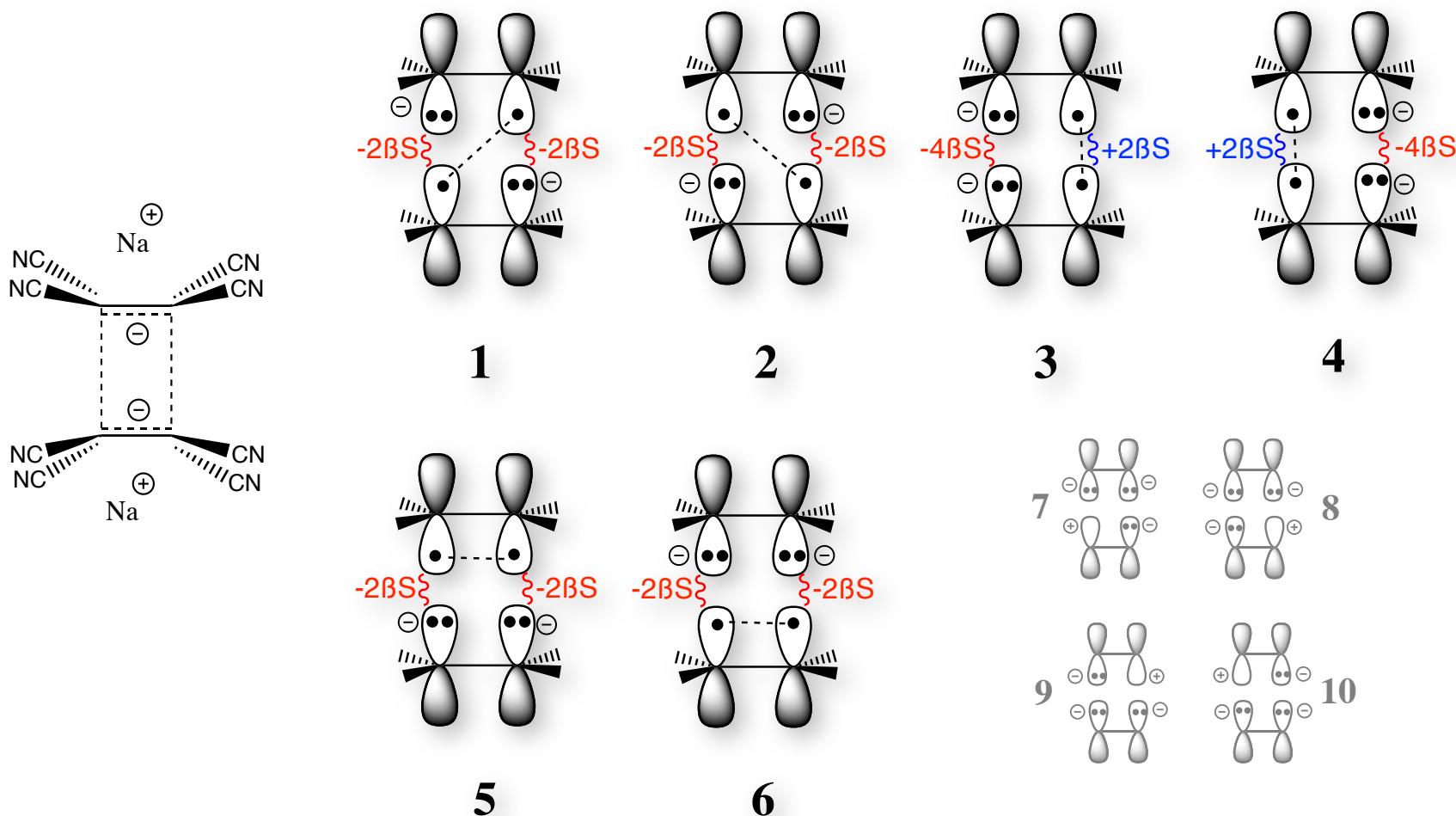
# Qualitative VB analysis

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



# Qualitative VB analysis

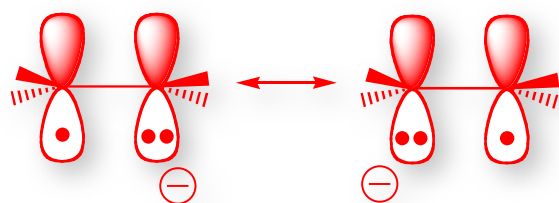
- VB set of structures for  $\text{DTCNE}_2^{2-}$  :



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

# Qualitative VB analysis

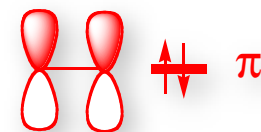
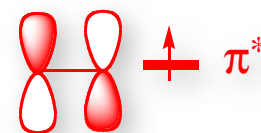
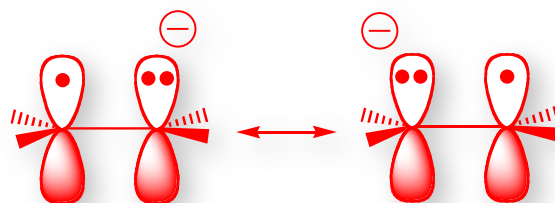
- What about three-electron bonding ?...



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

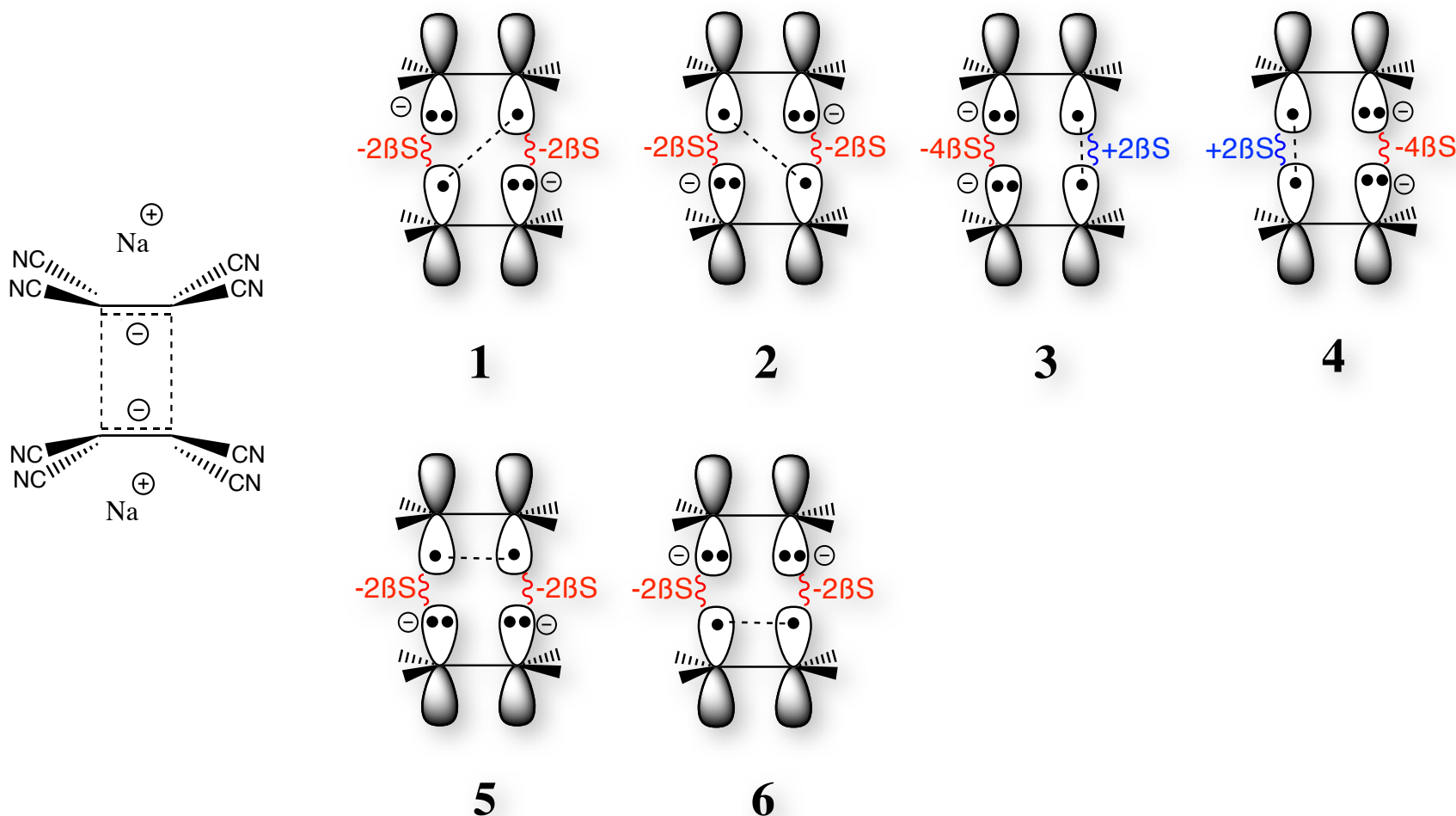
At infinite distance, each fragment displays a  **$3e^- \pi$  bond** :

$\infty$



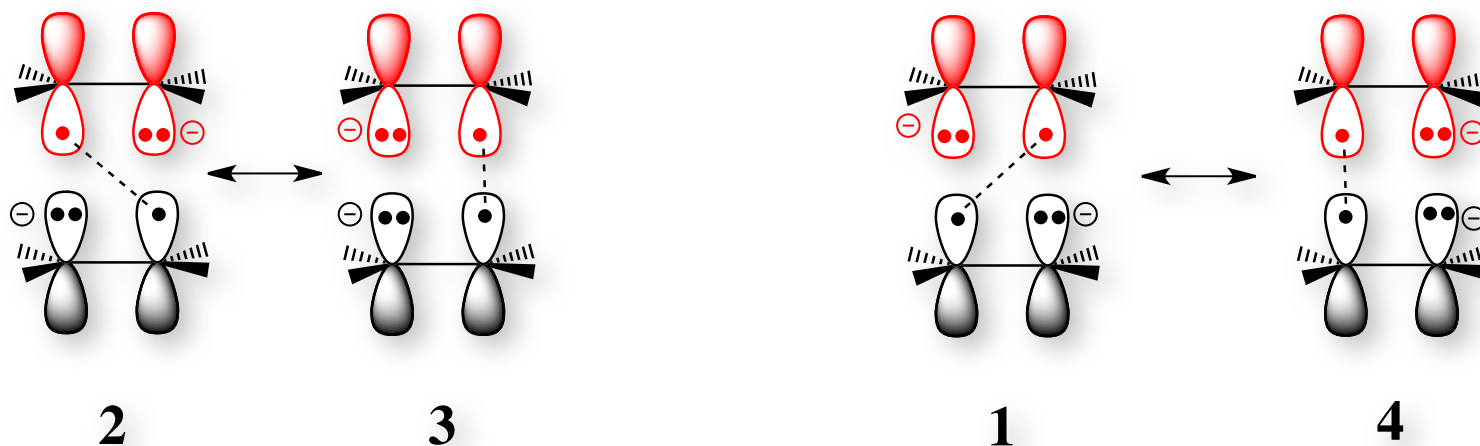
# Qualitative VB analysis

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



# Qualitative VB analysis

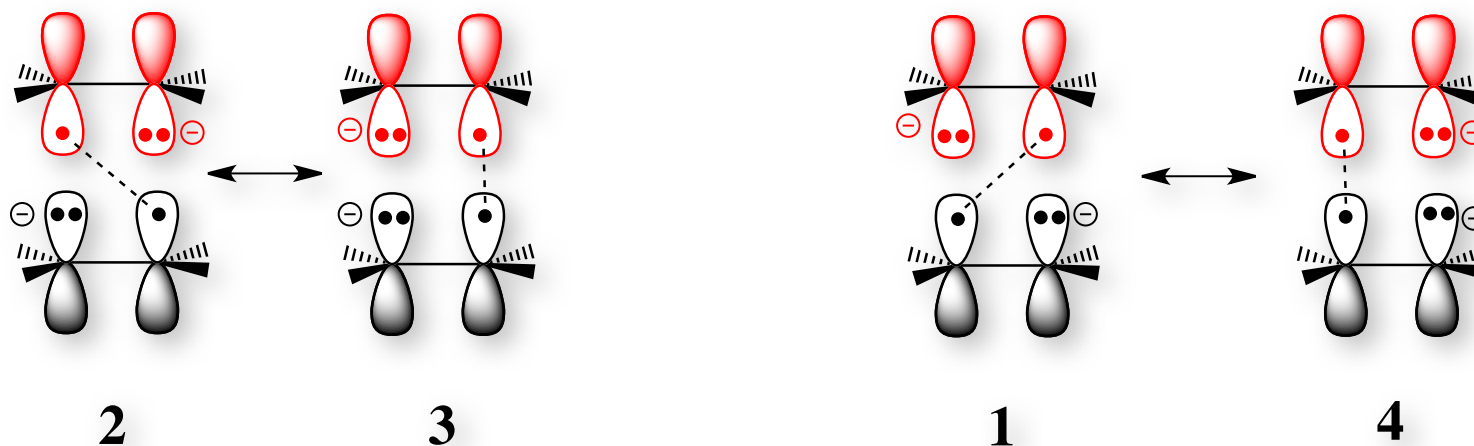
- $2 \leftrightarrow 3$  and  $1 \leftrightarrow 4$  : **intra-fragment  $3e^- \pi$  bond** (upper fragment) :



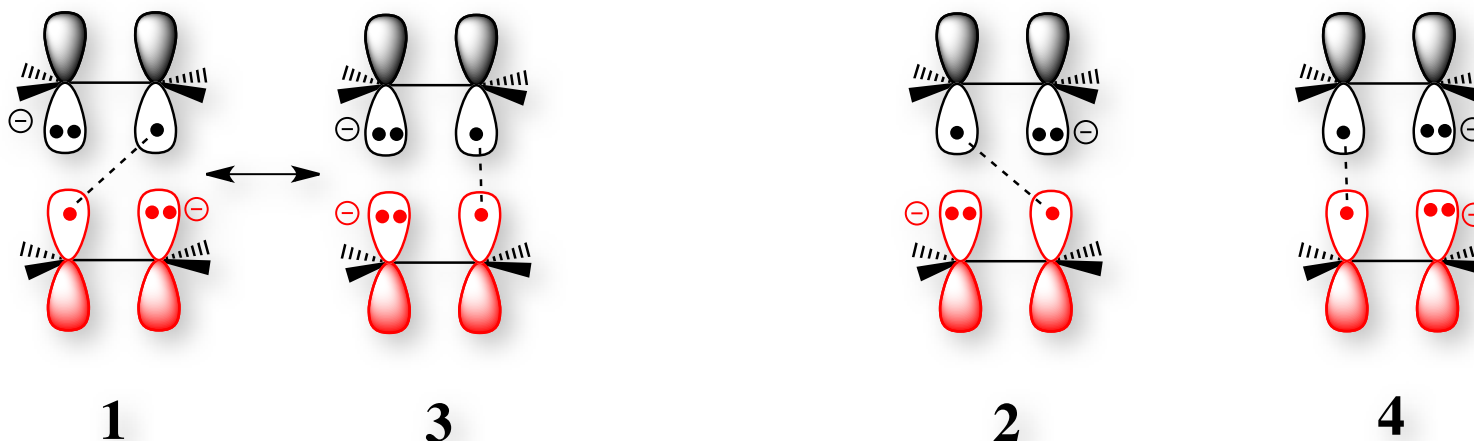


# Qualitative VB analysis

- $2 \leftrightarrow 3$  and  $1 \leftrightarrow 4$  : **intra-fragment  $3e^- \pi$  bond** (upper fragment) :

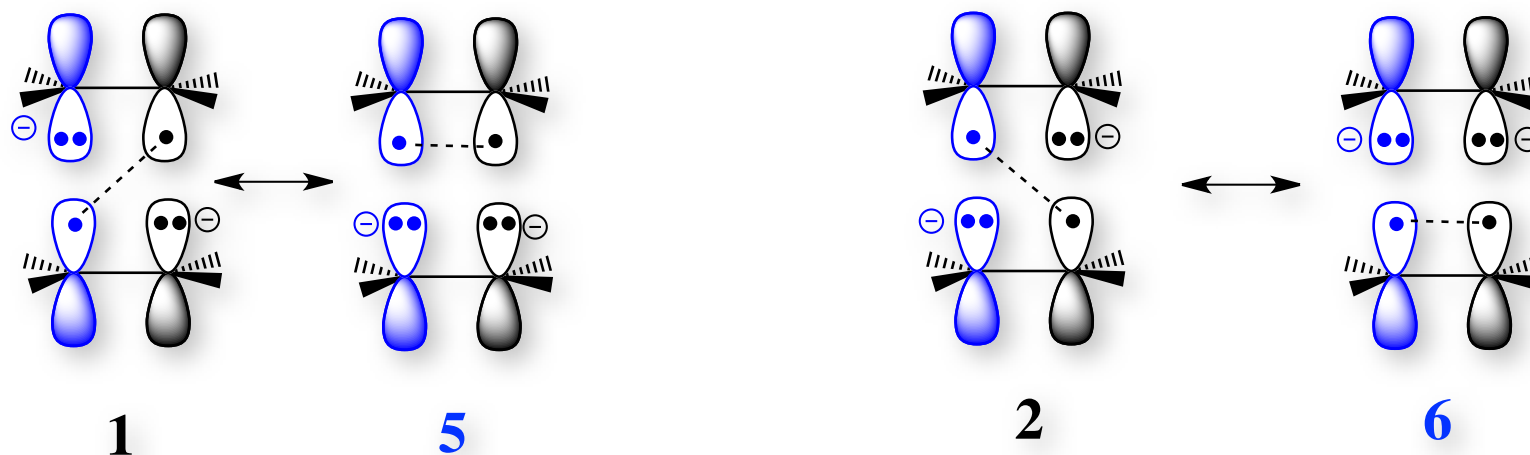


- $1 \leftrightarrow 3$  and  $2 \leftrightarrow 4$  : **intra-fragment  $3e^- \pi$  bond** (lower fragment) :

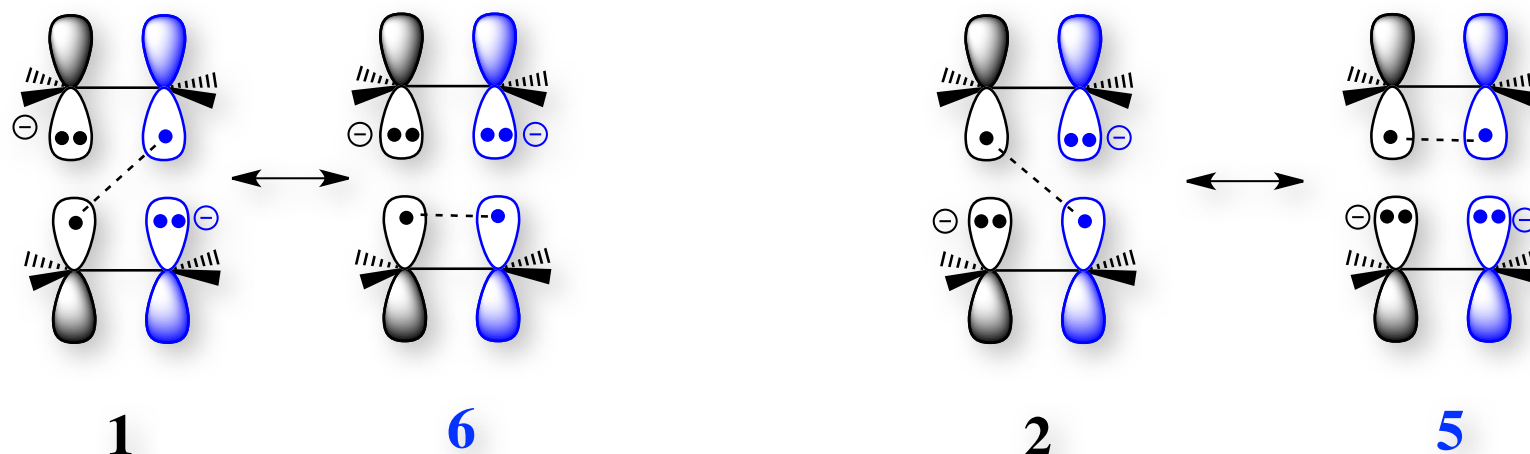


# Qualitative VB analysis

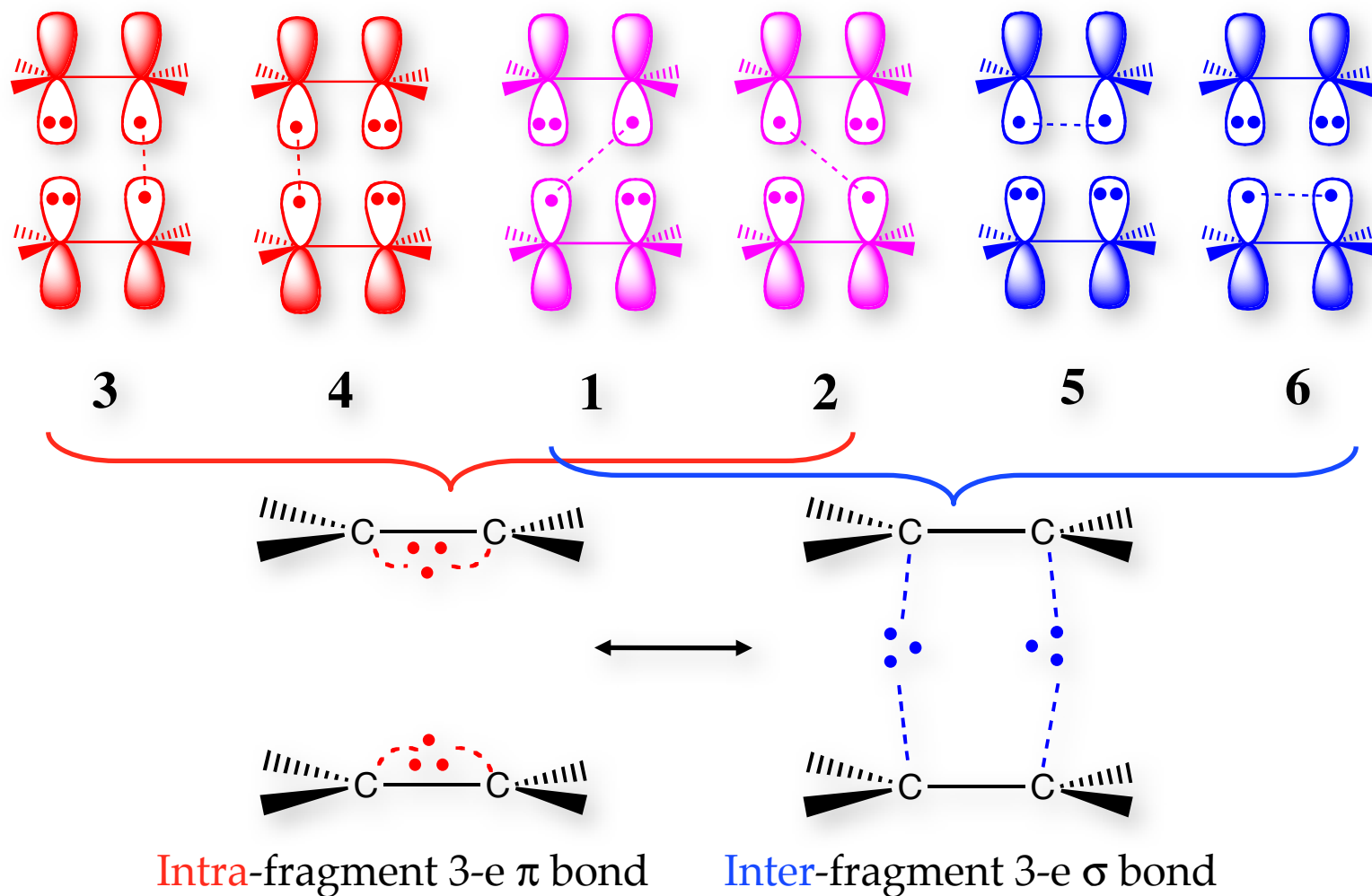
- $1 \leftrightarrow 5$  and  $2 \leftrightarrow 6$  : **inter-fragment  $3e^- \pi$  bond** (left-hand side) :



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



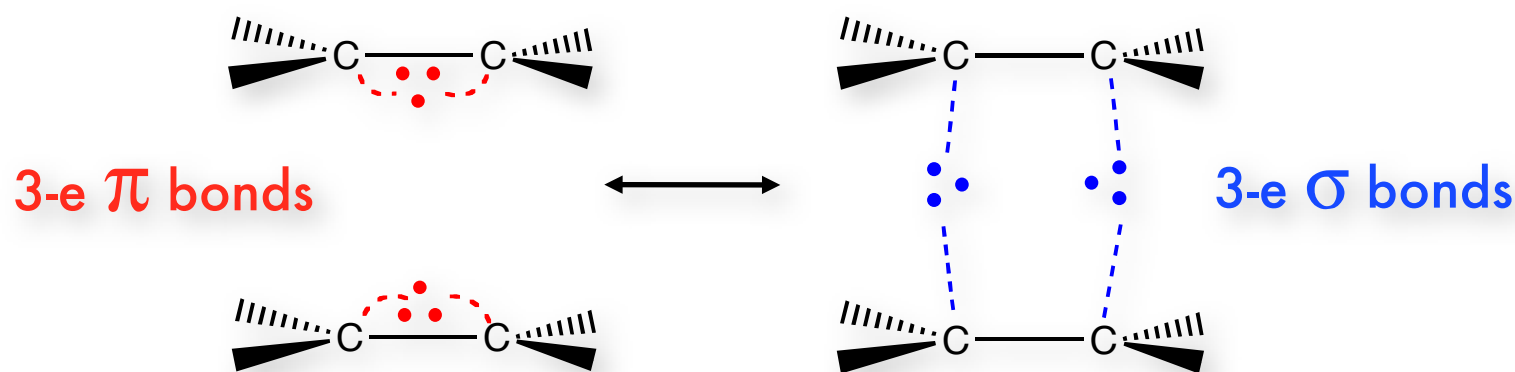
# Qualitative VB analysis



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

# Ab initio VB calculations

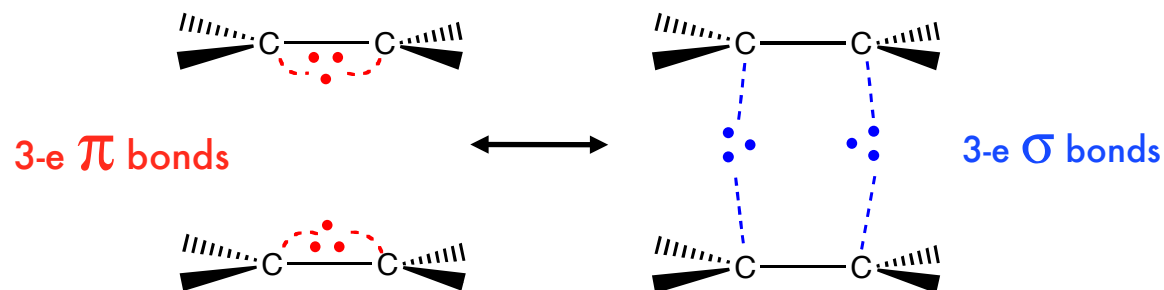
- Some tests of credibility :



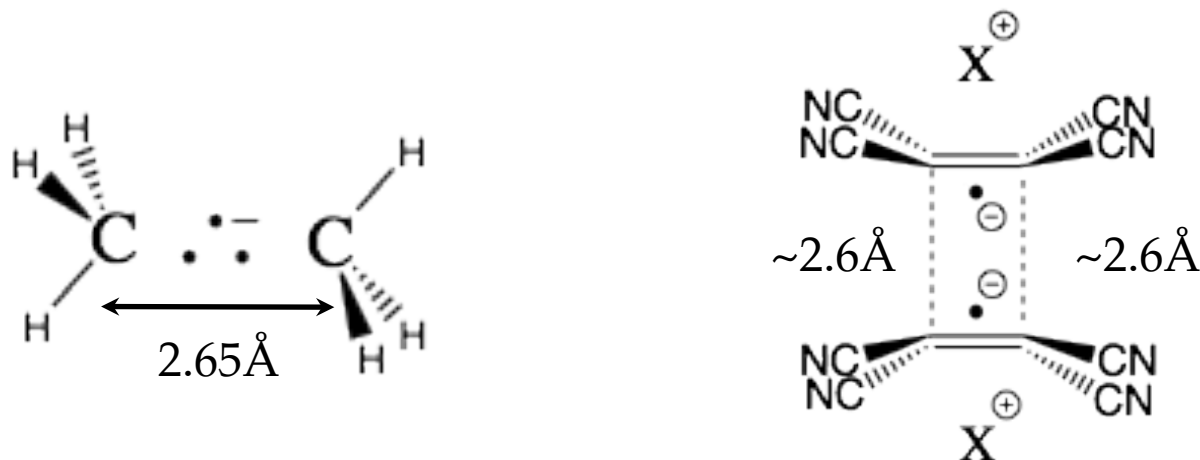
Characteristics of 3e bonds :

- 1) Large equilibrium distances :  $d(\text{S}—\text{S}) \approx 2.0 \text{ \AA}$  ;  $d(\text{S} \cdot \cdot \text{S}^-) \approx 2.8 \text{ \AA}$
- 2) Small overlap ( $S_{opt} \approx 0.17$ )
- 3) Importance of dynamical correlation

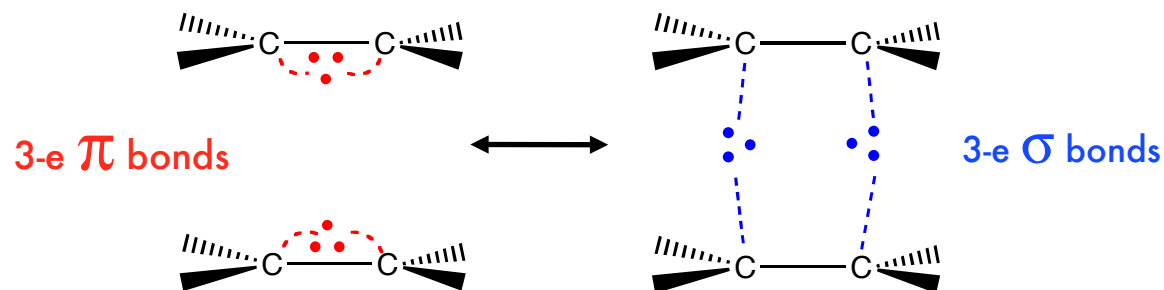
# Ab initio VB calculations



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



# Ab initio VB calculations



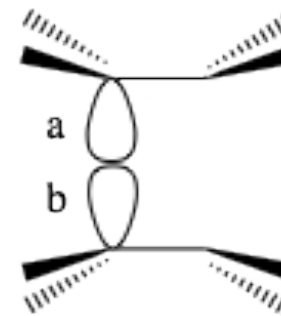
2) Interfragment orbital overlaps close to optimal 3e<sup>-</sup> bond value :

$$S_{opt} \approx 0.17$$

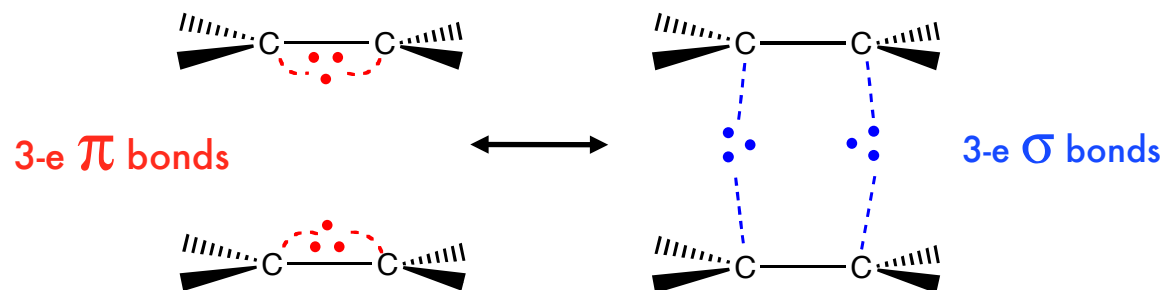
for any 3-e bond  
(demonstrated in  
qualitative VB theory  
as well as Extended Hückel theory)

$$S_{ab} = 0.15$$

(computed)



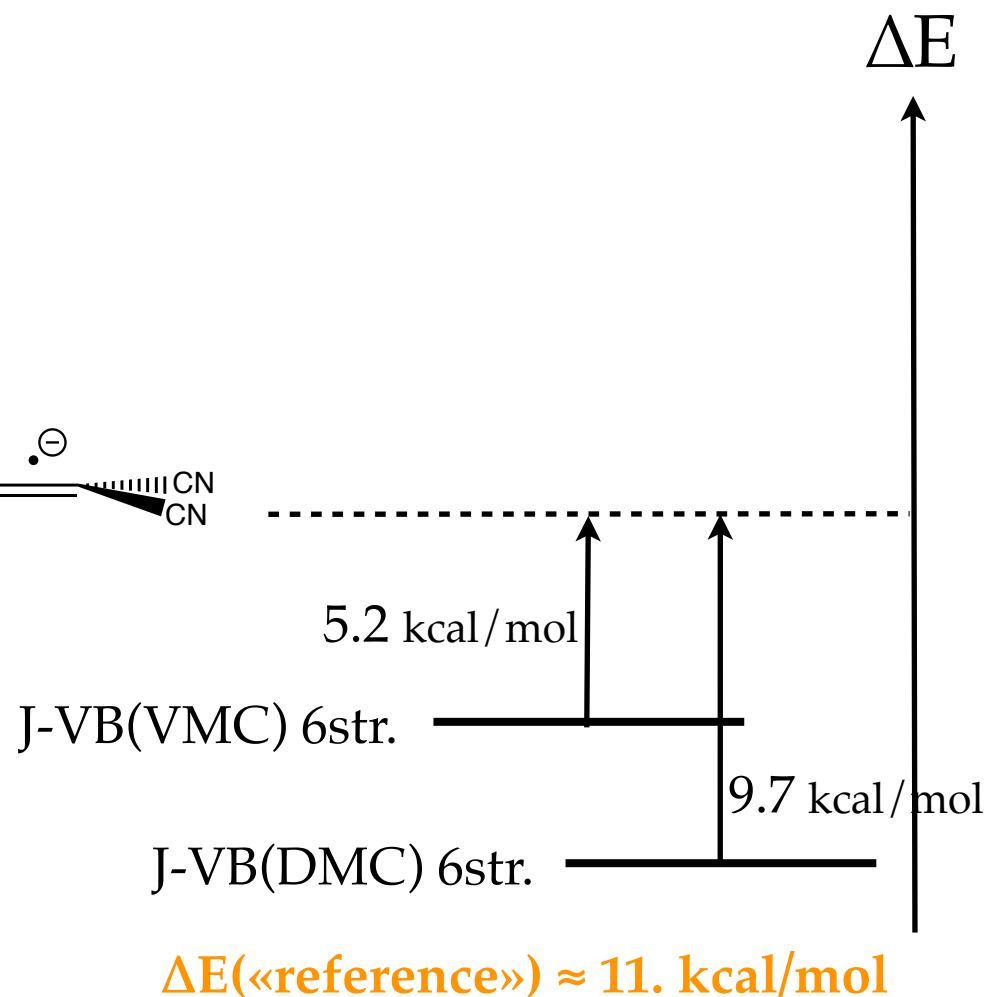
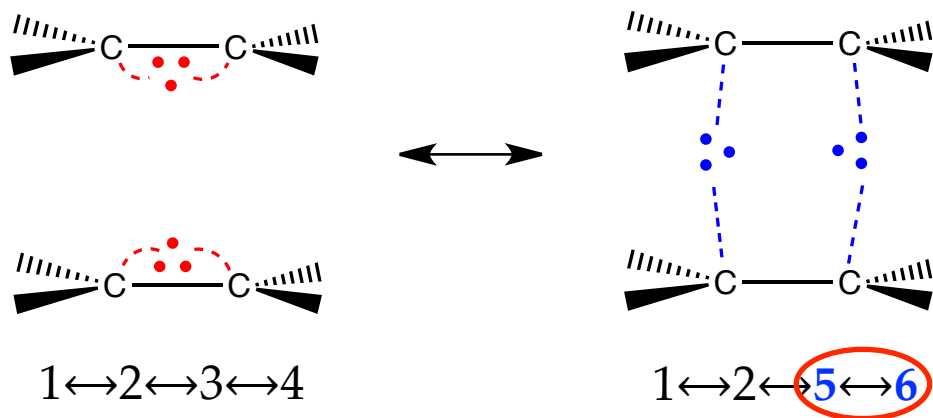
# *Ab initio* VB calculations



## 3) Contribution of dynamic correlation to bonding:

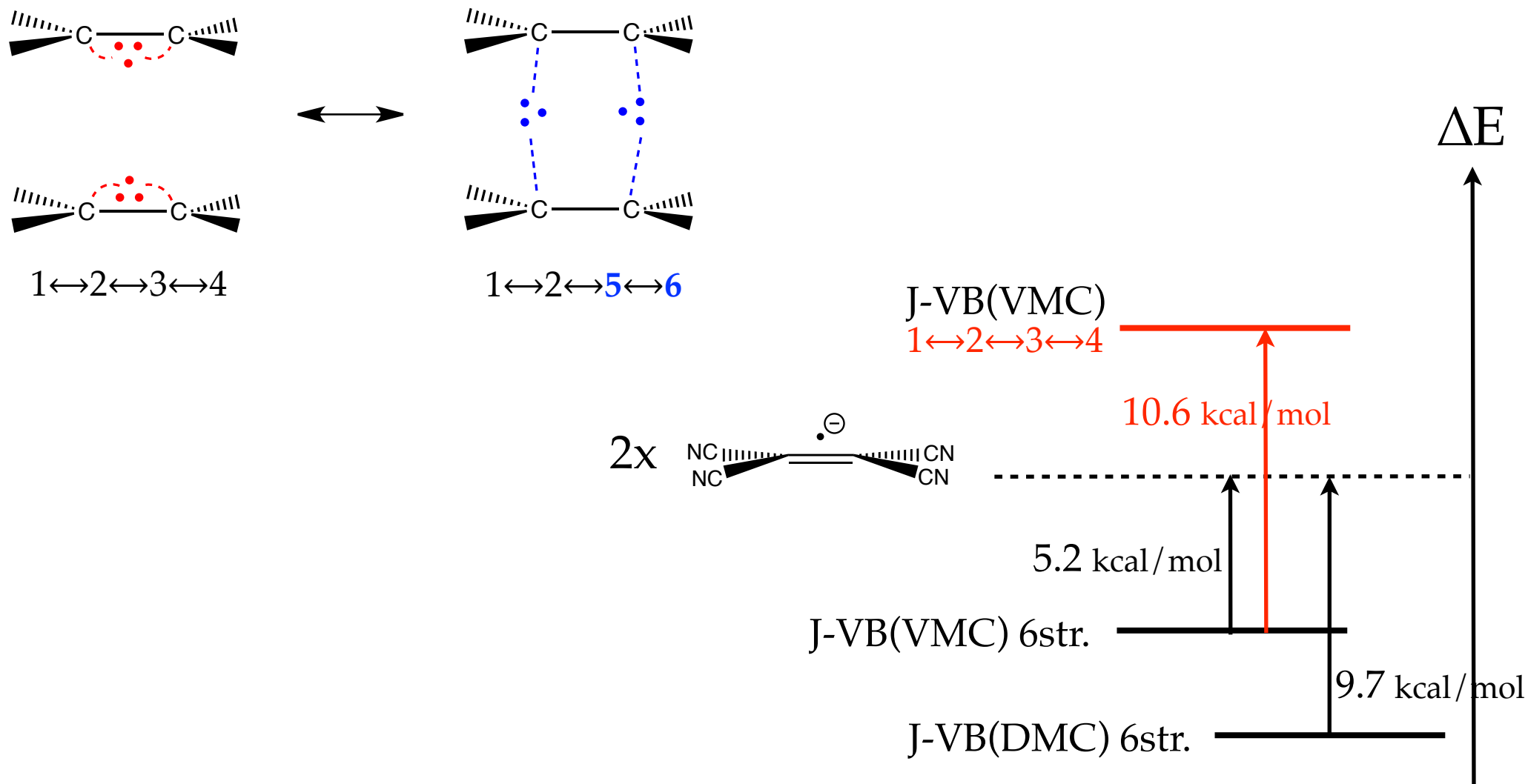
- In  $[\text{F} \cdot \cdot \text{F}]^-$ , dynamic correlation contributes  $\sim 30$  kcal/mol to bonding
- In  $[\text{TCNE}]_2^{2-}$ , dynamic correlation contributes  $> 30$  kcal/mol to bonding

# Ab initio VB calculations





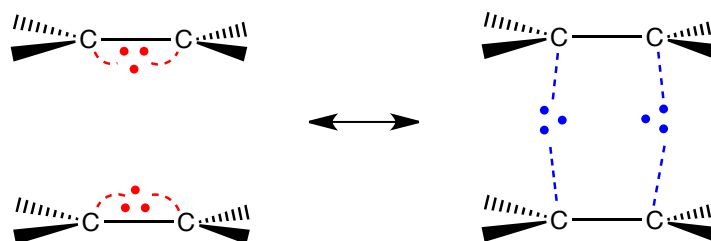
# Ab initio VB calculations



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

# Conclusion

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



- 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
- Qualitative VB analysis already reveal the 3e bond nature of the interfragment interaction, then *ab initio* VB quantitatively support it.