

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 :**

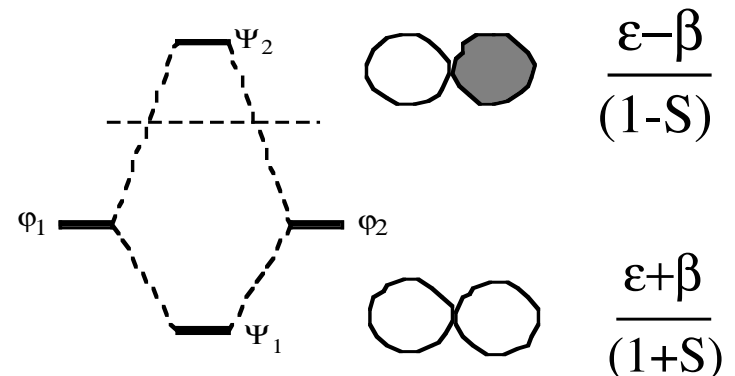
1) **Effective Hamiltonian :** $\mathbf{H}^{\text{eff}} = \mathbf{h}^{\text{eff}}(1) + \mathbf{h}^{\text{eff}}(2) + \mathbf{h}^{\text{eff}}(3) + \dots$

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

2) **Parametrization :** ϵ, β, 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 want 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 :**

Rule for calculating H and S terms :

Start with the determinants diagonal product

Then generate permutations :

- between identical spins
- only one side

Qualitative VB

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- only one side

Ex 1 : $|a\bar{b}|$

$$\langle (|a\bar{b}|) | (|a\bar{b}|) \rangle$$

$$= \langle (a(1)\bar{b}(2) - \bar{b}(1)a(2)) | (a(1)\bar{b}(2) - \bar{b}(1)a(2)) \rangle$$

$$= \underbrace{\langle a(1)\bar{b}(2) | a(1)\bar{b}(2) \rangle + \langle \bar{b}(1)a(2) | \bar{b}(1)a(2) \rangle}_{\text{Same value (differ by a permutation of coordinates } 1 \leftrightarrow 2)} \quad -2 \underbrace{\langle a(1)\bar{b}(2) | \bar{b}(1)a(2) \rangle}_{=0 \text{ as 1 and 2 are integrated over different spin functions}}$$

$$\Rightarrow \langle (|a\bar{b}|) | (|a\bar{b}|) \rangle = 2 \langle a(1)\bar{b}(2) | a(1)\bar{b}(2) \rangle$$

Qualitative VB

- **General calculus rules :**

- Rule for calculating H and S terms :**

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Then generate permutations :

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- only one side

Ex 2 : $|ab\bar{b}|$

$$\langle (|ab\bar{b}|) | (|ab\bar{b}|) \rangle$$

$$= \langle (a(1)b(2)\bar{b}(3) + b(1)\bar{b}(2)a(3) + \bar{b}(1)a(2)b(3) - a(1)\bar{b}(2)b(3) - \bar{b}(1)b(2)a(3) - b(1)a(2)\bar{b}(3)) |$$

$$(a(1)b(2)\bar{b}(3) + b(1)\bar{b}(2)a(3) + \bar{b}(1)a(2)b(3) - a(1)\bar{b}(2)b(3) - \bar{b}(1)b(2)a(3) - b(1)a(2)\bar{b}(3)) \rangle$$

Qualitative VB

- **General calculus rules :**

Rule for calculating H and S terms :

Start with the determinants diagonal product

Then generate permutations :

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Ex 2 : $|ab\bar{b}|$

$$\begin{aligned} & \langle (|ab\bar{b}|) | (|ab\bar{b}|) \rangle \\ &= \langle (a(1)b(2)\bar{b}(3) + b(1)\bar{b}(2)a(3) + \bar{b}(1)a(2)b(3) - a(1)\bar{b}(2)b(3) - \bar{b}(1)b(2)a(3) - b(1)a(2)\bar{b}(3)) | \\ & \quad | (a(1)b(2)\bar{b}(3) + b(1)\bar{b}(2)a(3) + \bar{b}(1)a(2)b(3) - a(1)\bar{b}(2)b(3) - \bar{b}(1)b(2)a(3) - b(1)a(2)\bar{b}(3)) \rangle \\ &= \langle a(1)b(2)\bar{b}(3) | a(1)b(2)\bar{b}(3) \rangle - \langle a(1)b(2)\bar{b}(3) | b(1)a(2)\bar{b}(3) \rangle + \dots \end{aligned}$$

Qualitative VB

- **General calculus rules :**

- Rule for calculating H and S terms :**

Start with the determinants diagonal product

Then generate permutations :

- between identical spins
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$$\text{Ex 2 : } |ab\bar{b}|$$

$$\langle (|ab\bar{b}|) | (|ab\bar{b}|) \rangle$$

$$= \langle (a(1)b(2)\bar{b}(3) + b(1)\bar{b}(2)a(3) + \bar{b}(1)a(2)b(3) - a(1)\bar{b}(2)b(3) - \bar{b}(1)b(2)a(3) - b(1)a(2)\bar{b}(3)) |$$

$$(a(1)b(2)\bar{b}(3) + b(1)\bar{b}(2)a(3) + \bar{b}(1)a(2)b(3) - a(1)\bar{b}(2)b(3) - \bar{b}(1)b(2)a(3) - b(1)a(2)\bar{b}(3)) \rangle$$

$$= \langle a(1)b(2)\bar{b}(3) | a(1)b(2)\bar{b}(3) \rangle - \langle a(1)b(2)\bar{b}(3) | b(1)a(2)\bar{b}(3) \rangle + \dots$$

$$\Rightarrow \langle (|ab\bar{b}|) | (|ab\bar{b}|) \rangle = 6 \langle a(1)b(2)\bar{b}(3) | a(1)b(2)\bar{b}(3) \rangle - \langle a(1)b(2)\bar{b}(3) | b(1)a(2)\bar{b}(3) \rangle$$

Qualitative VB

- **General calculus rules :**

Rule for calculating H and S terms :

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- between identical spins
- only one side

Ex 2 : $|ab\bar{b}|$

And thus :

$$E(|ab\bar{b}|) = \frac{\langle |ab\bar{b}| | \hat{H} | |ab\bar{b}| \rangle}{\langle |ab\bar{b}| | |ab\bar{b}| \rangle} = \frac{\cancel{\langle a(1)b(2)\bar{b}(3) | \hat{H} | a(1)b(2)\bar{b}(3) \rangle} - \langle a(1)b(2)\bar{b}(3) | \hat{H} | b(1)a(2)\bar{b}(3) \rangle}{\cancel{\langle a(1)b(2)\bar{b}(3) | a(1)b(2)\bar{b}(3) \rangle} - \langle a(1)b(2)\bar{b}(3) | b(1)a(2)\bar{b}(3) \rangle}$$

Qualitative VB

- **General calculus rules :**

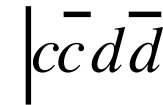
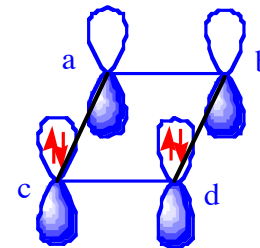
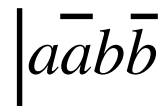
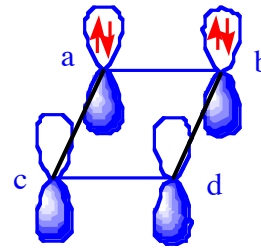
Rule for calculating H and S terms :

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Ex 3 :



Qualitative VB

- **General calculus rules :**

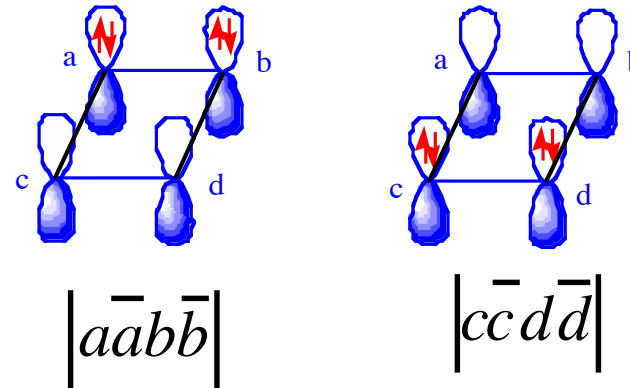
Rule for calculating H and S terms :

Start with the diagonal product

Then generate permutations :

- between identical spins
- only one side

Ex 3 :



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

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

Qualitative VB

- **General calculus rules :**

Rule for calculating H and S terms :

Start with the diagonal product

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

- between identical spins
- only one side

Qualitative VB

- **General calculus rules :**

Rule for calculating H and S terms :

Start with the diagonal product

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

- between identical spins

- only one side

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

Qualitative VB

- **General calculus rules :**

Rule for calculating H and S terms :

Start with the diagonal product

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

- between identical spins

- only one side

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

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

$$\langle (|a\bar{a}b\bar{b}\rangle) | \hat{h}_3 | (|c\bar{c}d\bar{d}\rangle) \rangle \propto \dots$$

Rather tedious...

$$\langle (|a\bar{a}b\bar{b}\rangle) | \hat{h}_4 | (|c\bar{c}d\bar{d}\rangle) \rangle \propto \dots$$

Qualitative VB

- **Simplified expressions :**

- Two orbitals case :

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

⇒ new energy scale where : $\epsilon_a + \epsilon_b = 0$

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

Qualitative VB

- **Simplified expressions :**

- General case :

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 :**

- General case :

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

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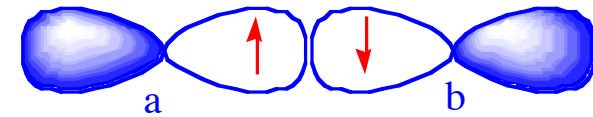
2) Approximation :

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

Qualitative VB

- Elementary interactions energies :

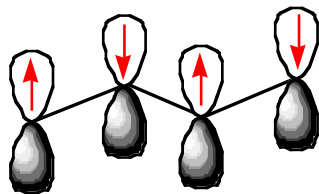
1) The QC state :



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

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

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

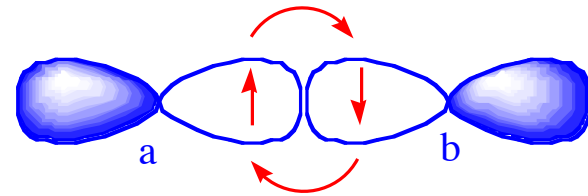


$$E=0$$

Qualitative VB

- Elementary interactions energies :

2) The two electron bond :



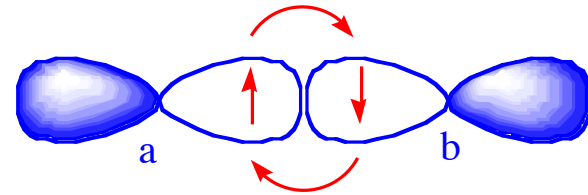
$$\Psi_{2e} \propto |a\bar{b}| + |b\bar{a}|$$

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

Qualitative VB

- Elementary interactions energies :

2) The two electron bond :

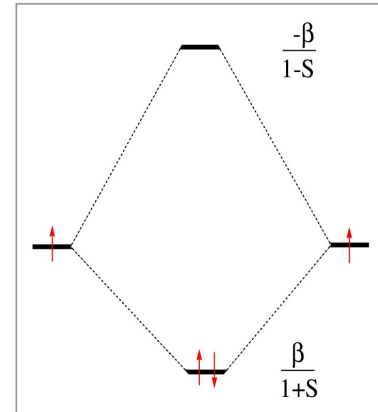


$$\Psi_{2e} \propto |a\bar{b}| + |b\bar{a}|$$

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

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

Different in MO-Hückel theory :

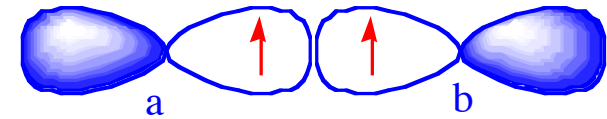


$$D_e = 2\beta/(1+S)$$

Qualitative VB

- Elementary interactions energies :

3) The triplet repulsion :

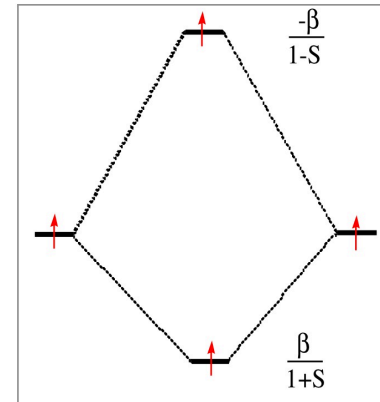


$$\Psi_T \propto |a\bar{b}| - |b\bar{a}|$$

$$\langle \Psi | \hat{H}^{eff} | \Psi \rangle \Rightarrow \begin{cases} \text{Symmetric terms (two)} : \langle (|a\bar{b}|) | \hat{h}_1 + \hat{h}_2 | (|a\bar{b}|) \rangle = \epsilon_1 + \epsilon_2 = 0 \\ \text{Disymmetric terms (two)} : - \langle (|a\bar{b}|) | \hat{h}_1 + \hat{h}_2 | (|b\bar{a}|) \rangle = -2\beta_{ab}S_{ab} \end{cases}$$

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

Same in MO-Hückel theory :



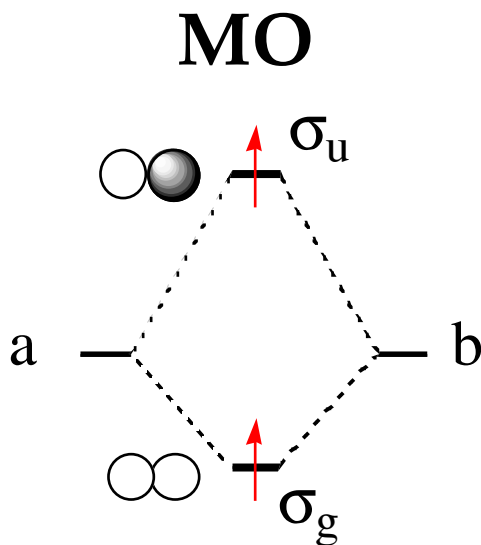
$$E = \frac{\beta}{1+S} + \frac{-\beta}{1-S} = \frac{-2\beta S}{1-S^2}$$

Qualitative VB

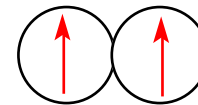
- Elementary interactions energies :

3) The triplet repulsion :

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



VB



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

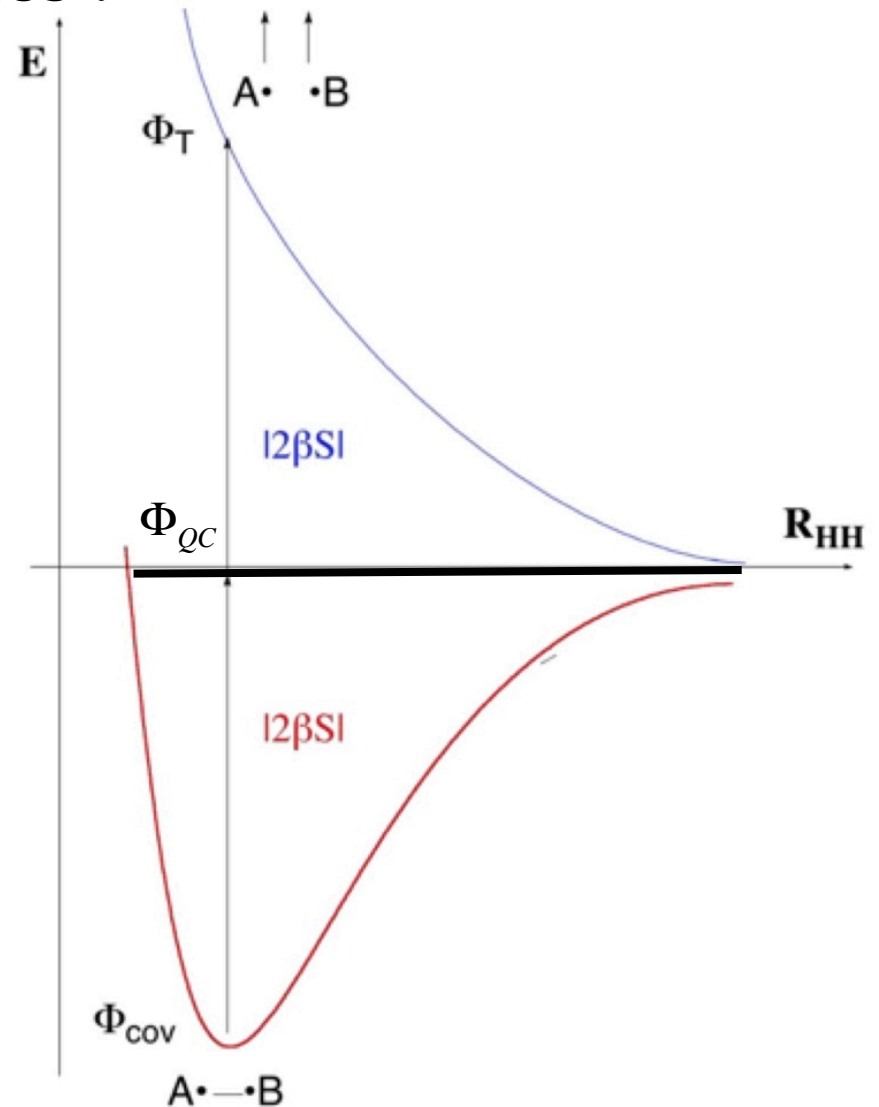
$$\psi_{MO} \propto |\sigma_g \sigma_u| = |(a+b)(a-b)| = |\cancel{aa} + |\cancel{bb} + |ba| - |ab| \propto \psi_{VB}$$

Qualitative VB

- Elementary interactions energies :



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

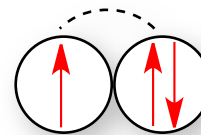


Qualitative VB

- Elementary interactions energies :

4) All repulsions :

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

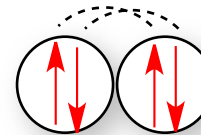


VB

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

MO
Same

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



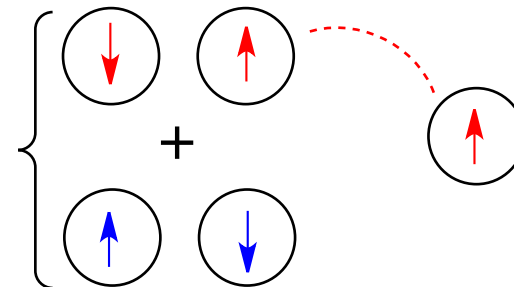
VB

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

MO
Same

- NCI : **half time** triplet :

bond... single electron

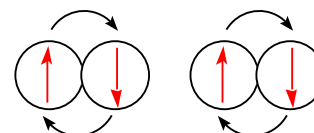


VB

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

/

bond... bond



VB

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

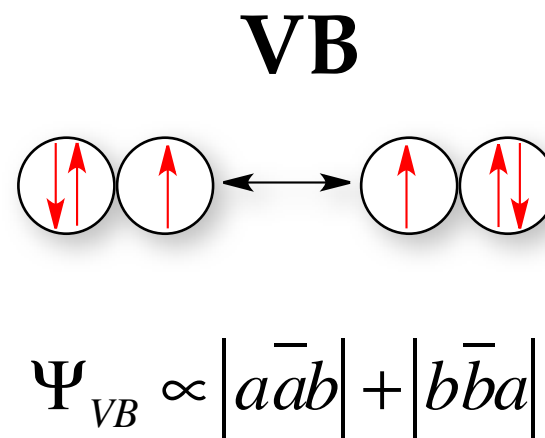
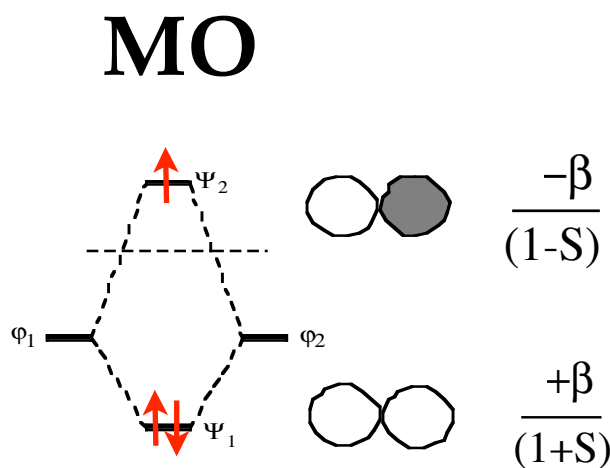
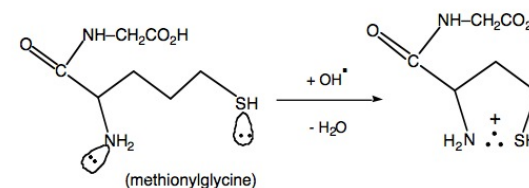
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Qualitative VB

- Elementary interactions energies :

5) The 3e bond :

Examples : He_2^+ , $\text{RS} \cdot \text{SR}'$,
radical intermediates :



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

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

Remind for later use !

Qualitative VB


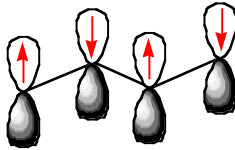
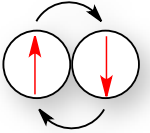
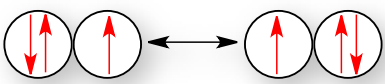
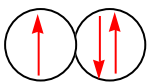
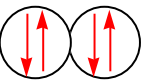
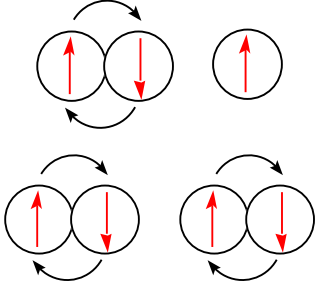
- Elementary interactions energies :

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


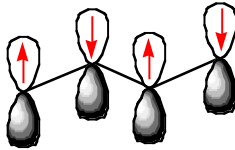
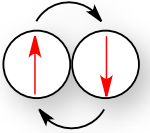
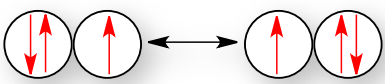
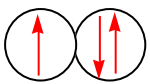
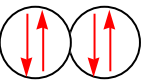
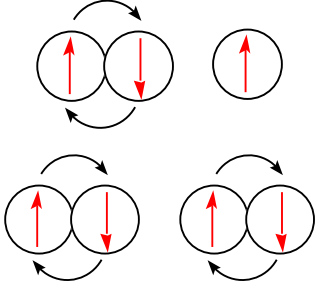


Work for all but 3e bond

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 ⁻ and bond...bond |  | $-\beta S/(1-S^2)$ | (VB only) |

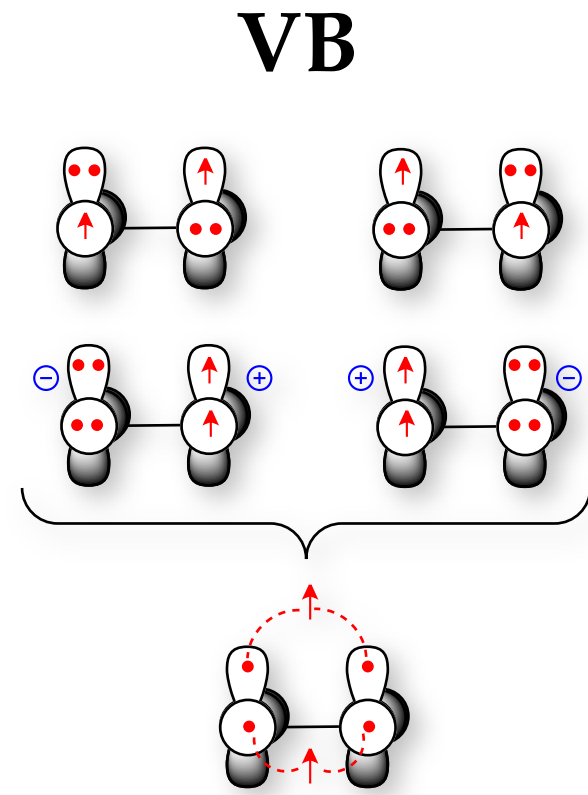
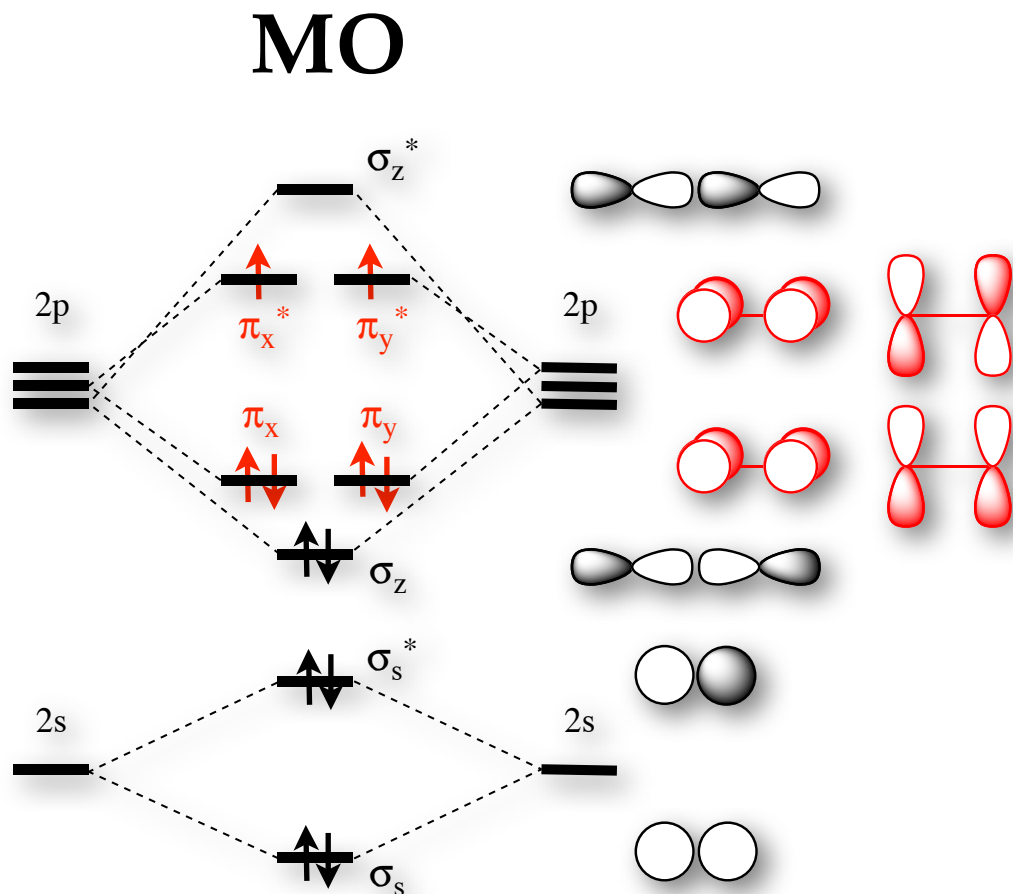
Qualitative VB

| | 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 ⁻ and bond...bond |  | $-\beta S/(1-S^2)$ | (VB only) |

Qualitative VB

➔ Exercise 4 : ground state of O₂ :

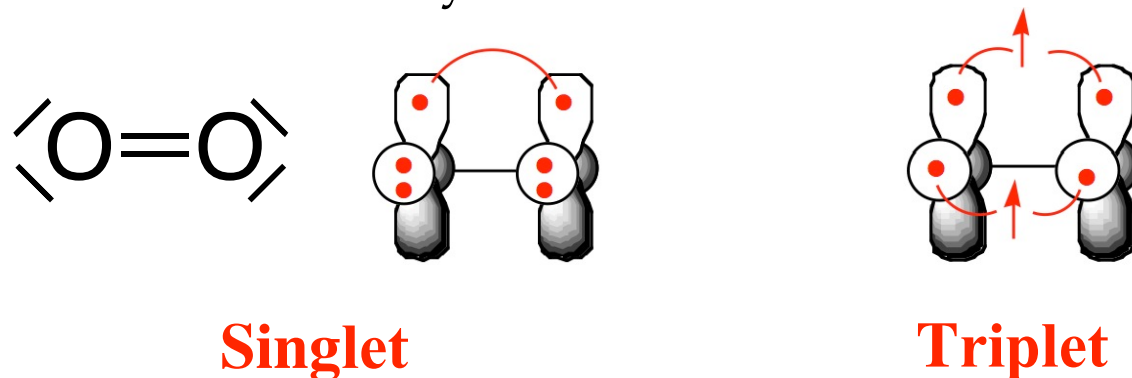
Dioxygen triplet ground state : two π -type 3e-bonds :



Qualitative VB

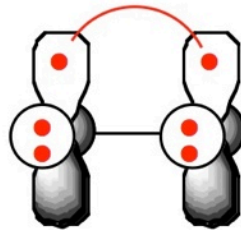
→ Exercise 4 : ground state of O₂ :

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

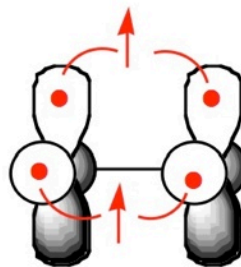


Qualitative VB

➔ Exercise 4 : ground state of O₂ (answer) :



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



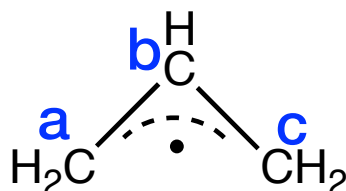
$$E(T) = 2\beta (1 - 3S) / (1-S^2)$$

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

➔ *The triplet state is always the lower*

Qualitative VB

→ Exercise 5 : spin polarization in allyl radical :



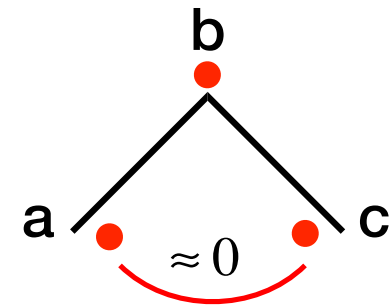
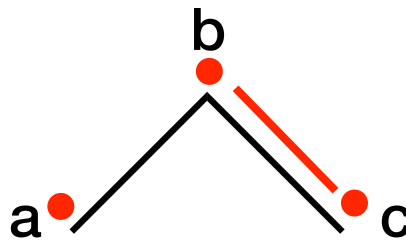
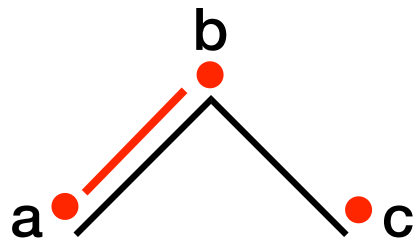
The allyl radical is a planar molecule with three electrons in its π system (in 3 p_C orbitals).

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

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

Qualitative VB

→ Exercise 5 : spin polarization in allyl radical :



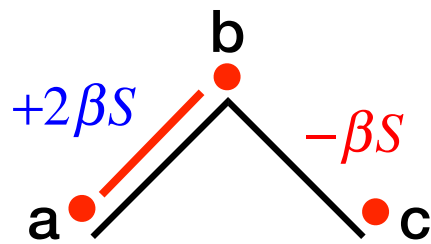
$$\psi(I) = \frac{1}{\sqrt{2}} (|a\bar{b}c| + |b\bar{a}c|)$$

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

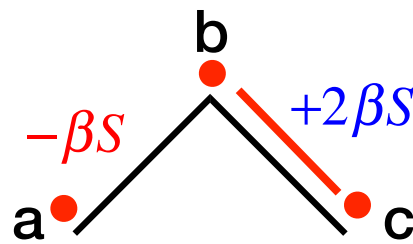
$$\psi(III) = \frac{1}{\sqrt{2}} (|abc\bar{c}| + |cb\bar{a}|) = \psi(I) + \psi(II)$$

Qualitative VB

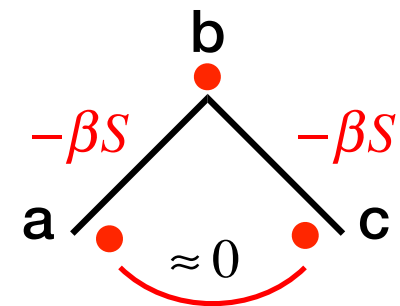
→ Exercise 5 : spin polarization in allyl radical :



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



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

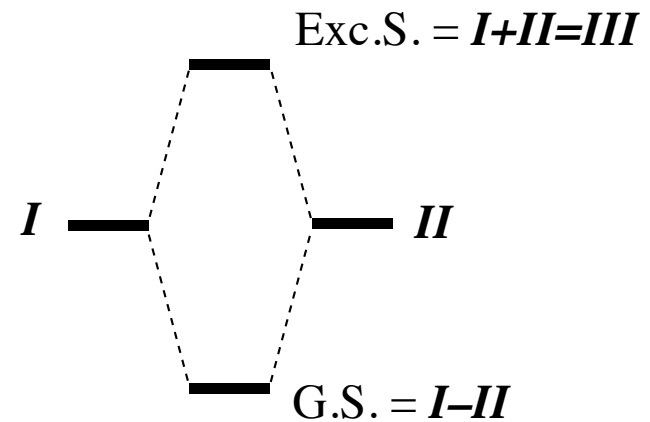


$$\Rightarrow E(III) = -2\beta S$$

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

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

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



Qualitative VB

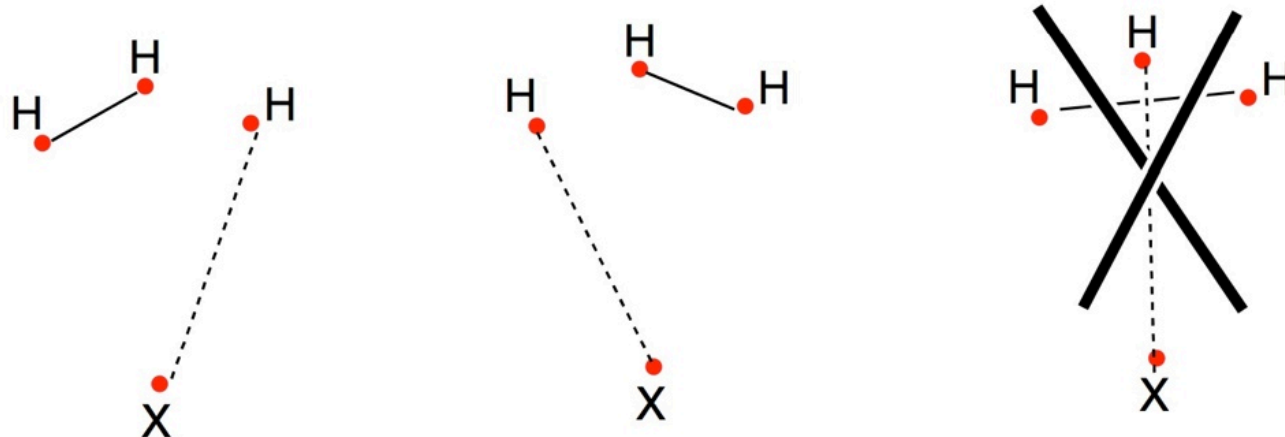
➔ Exercise 5 : spin polarization in allyl radical :

- 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

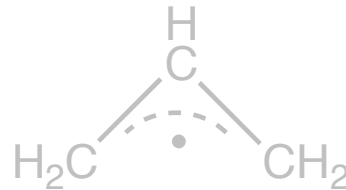
2) Apply to this new system Rumer's rules for a singlet

Exemple : H₃ radical



Qualitative VB

→ Exercise 5 : spin polarization in allyl radical :



The allyl radical is a planar molecule with three electrons in its π system (in 3 p_C orbitals).

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

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

3) EPR measurements show that the spin density on the central atom is -0.2 (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.

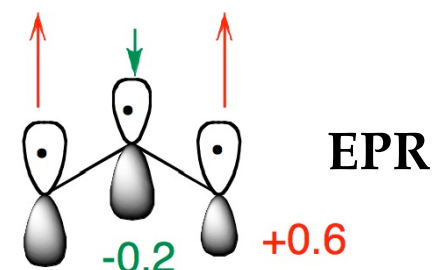
Continuation of the exercise : <https://wiki.lct.jussieu.fr/workshop/index.php/VBTutorial2>

Qualitative VB

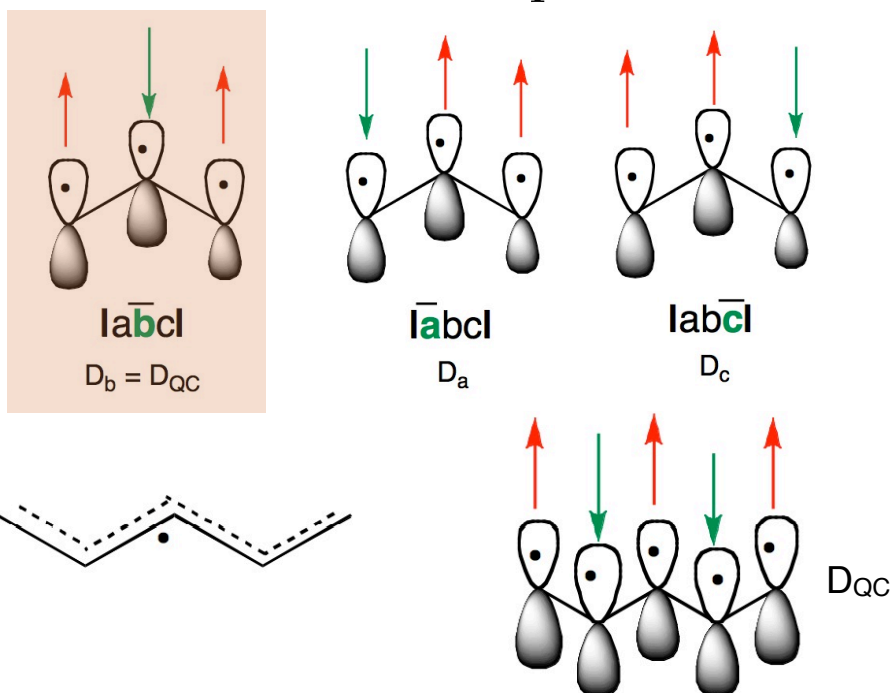
→ Exercise 5 : spin polarization in allyl radical :

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

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



⇒ much closer to experiment than UHF



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



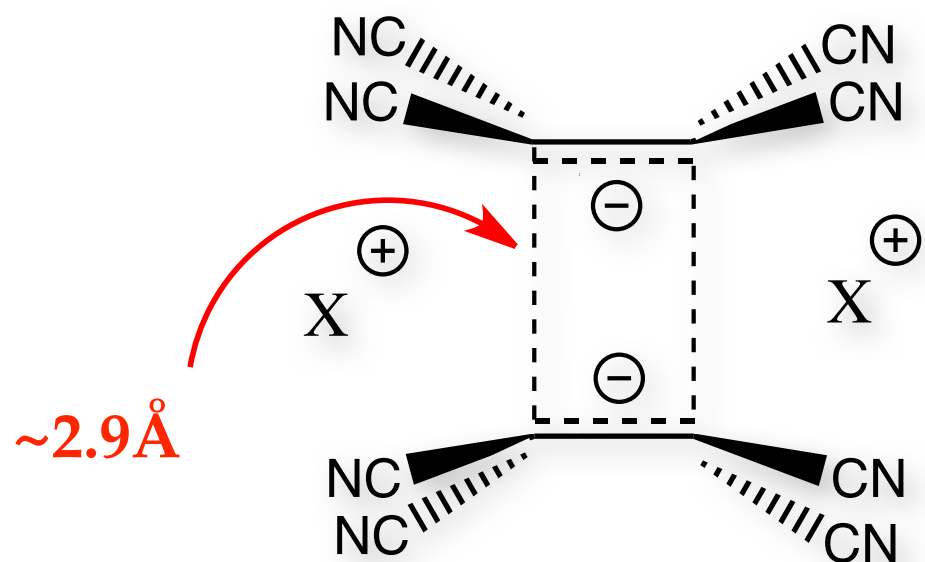
General rule, works for all polyenes

Application

Electronic structure of the DTCNE dimer

«Pancake bonding»

- DTCNE_2^{2-} :



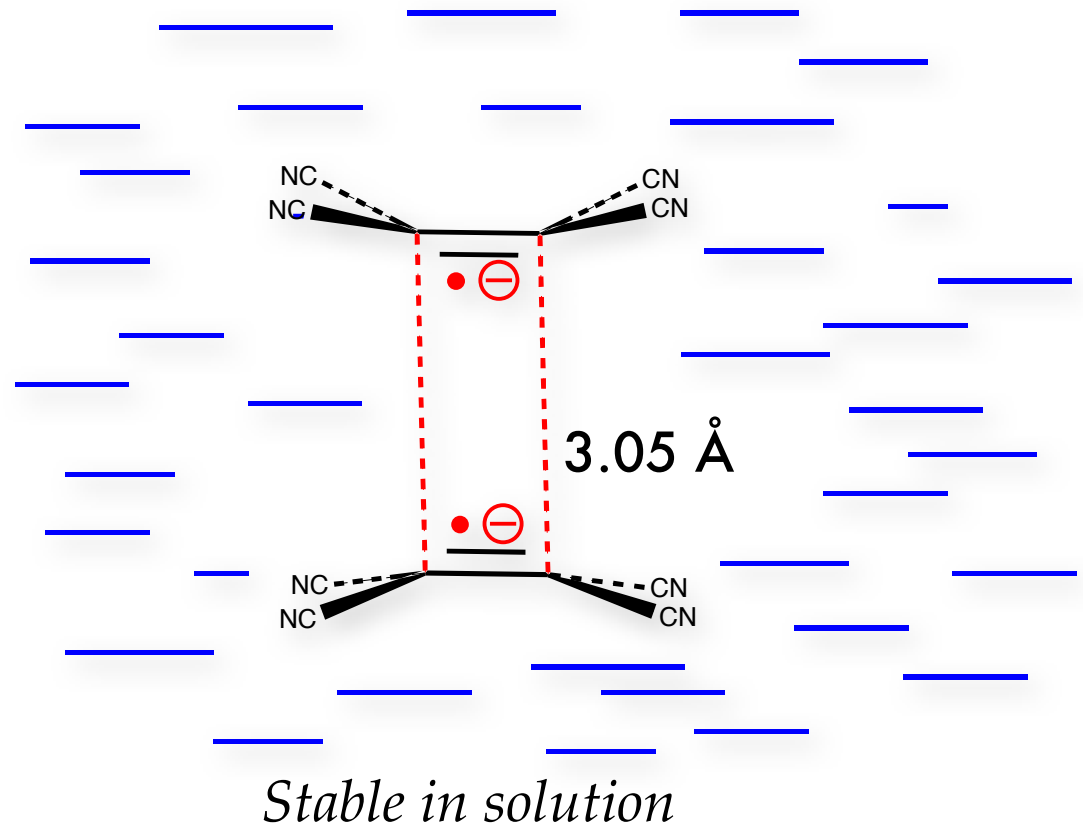
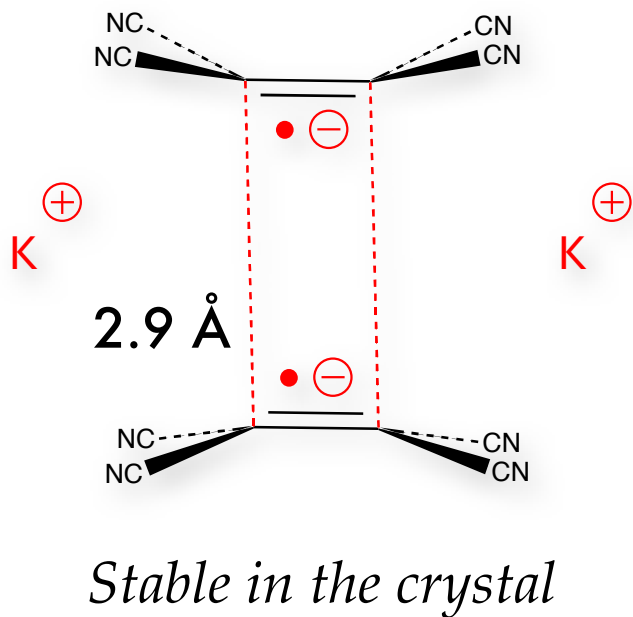
$X^+ : \text{Na}^+, \text{Cs}^+, [\text{iPr}_4\text{N}]^+, [\text{Cr}(\text{C}_6\text{Me}_3\text{H}_3)_2]^+, \dots$

Electrostatic complex ?...

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

«Pancake bonding»

- DTCNE_2^{2-} :

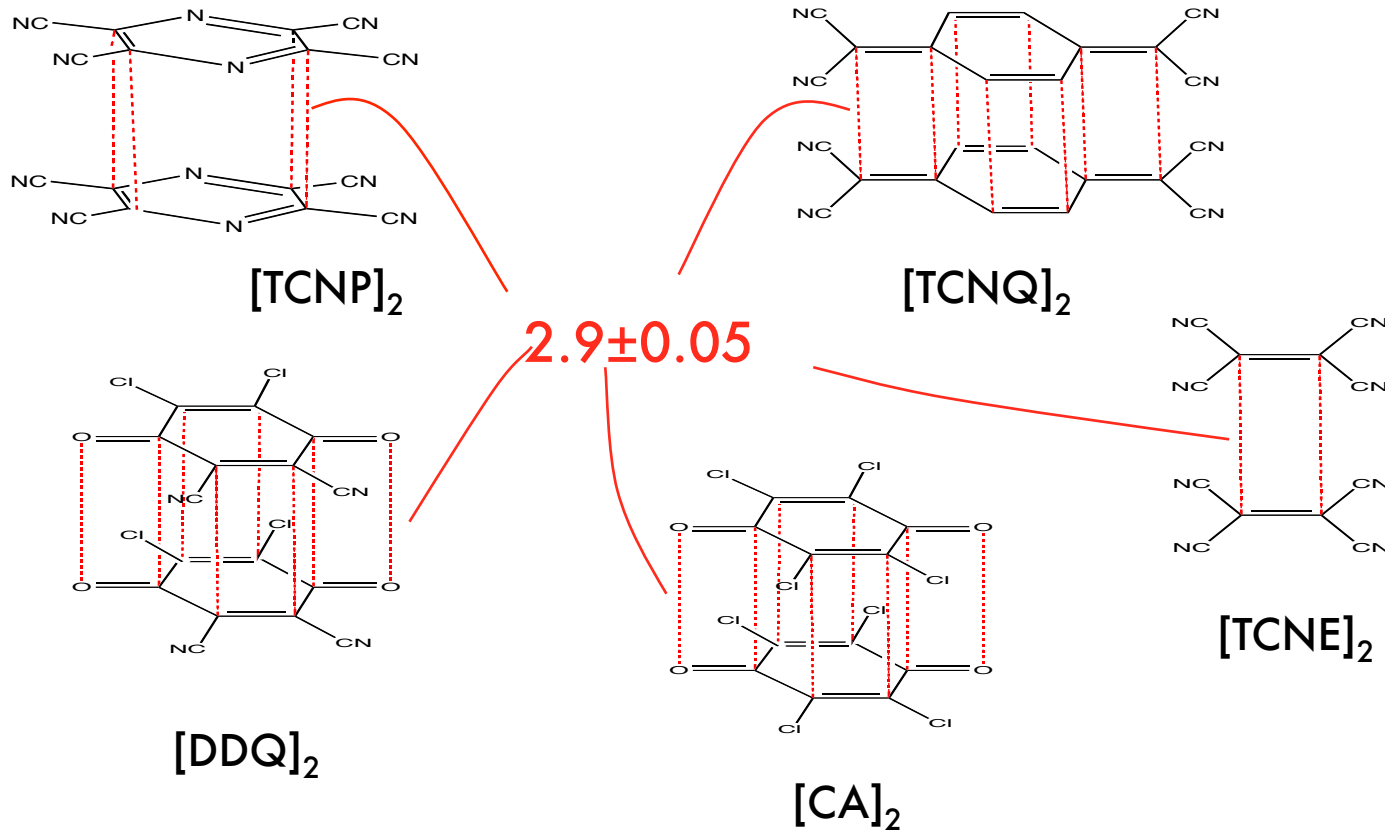


- Same bonding distance whatever the environment !

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

«Pancake bonding»

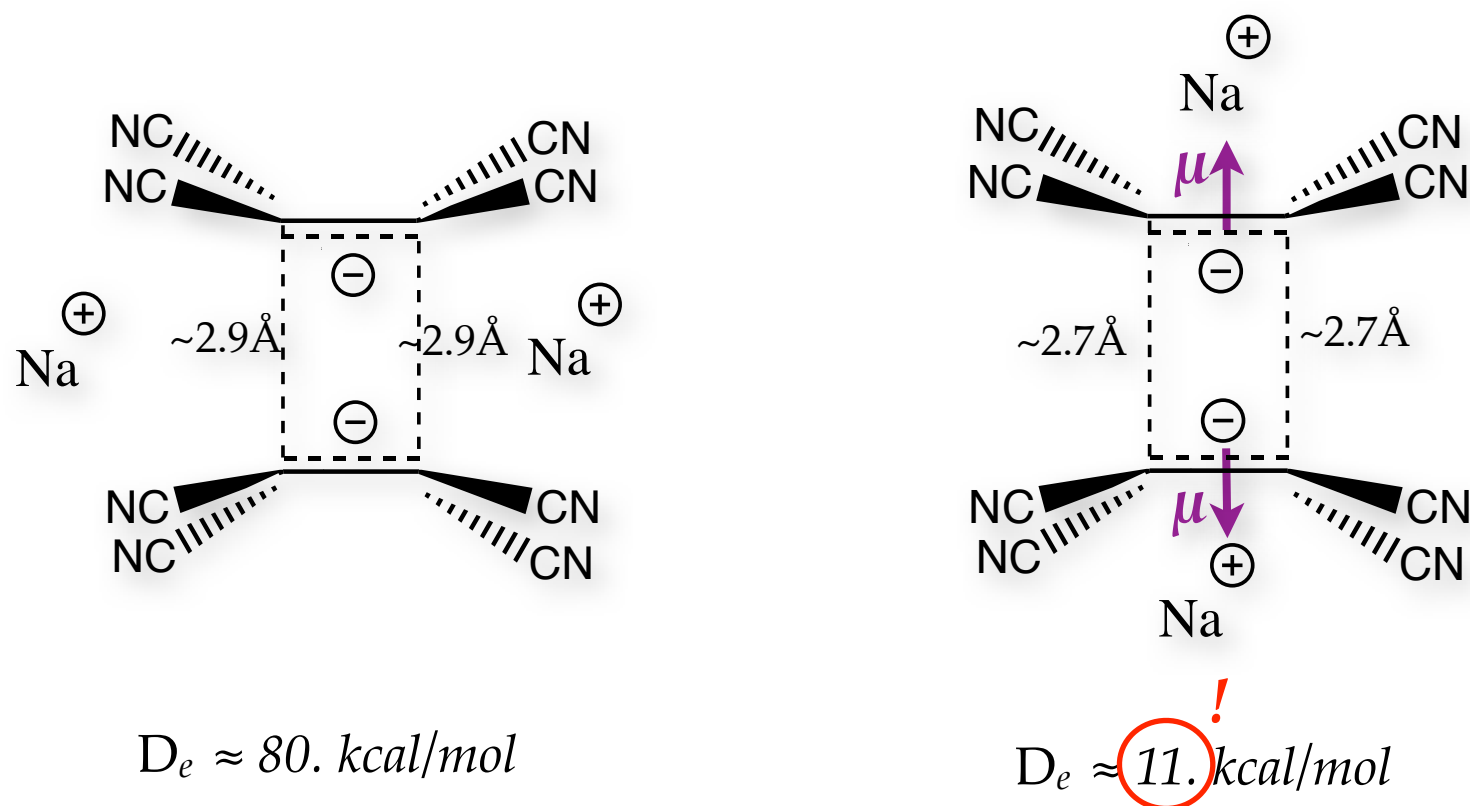
- Other «pancake bonding» systems :



- 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})

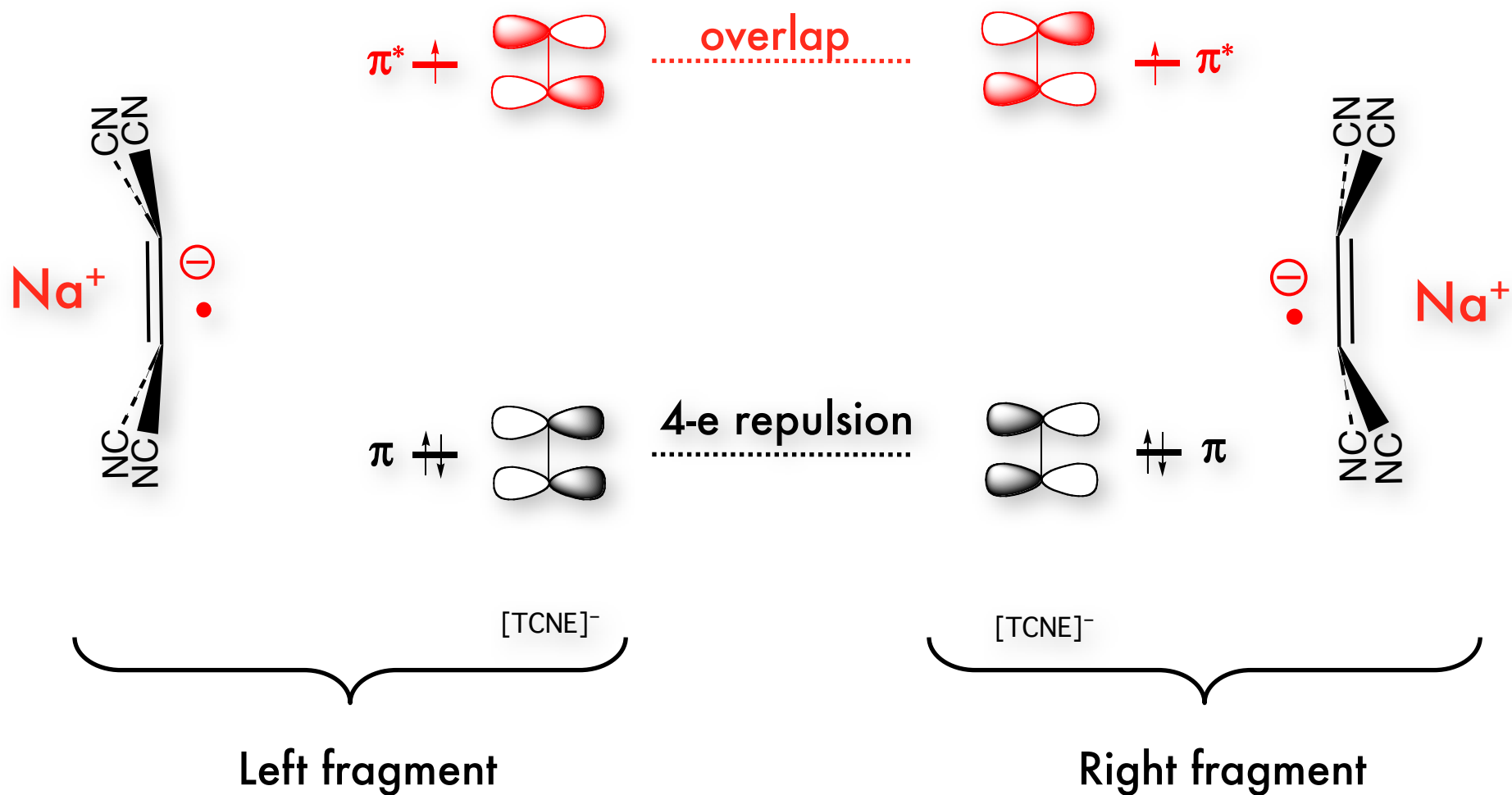
«Pancake bonding»

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

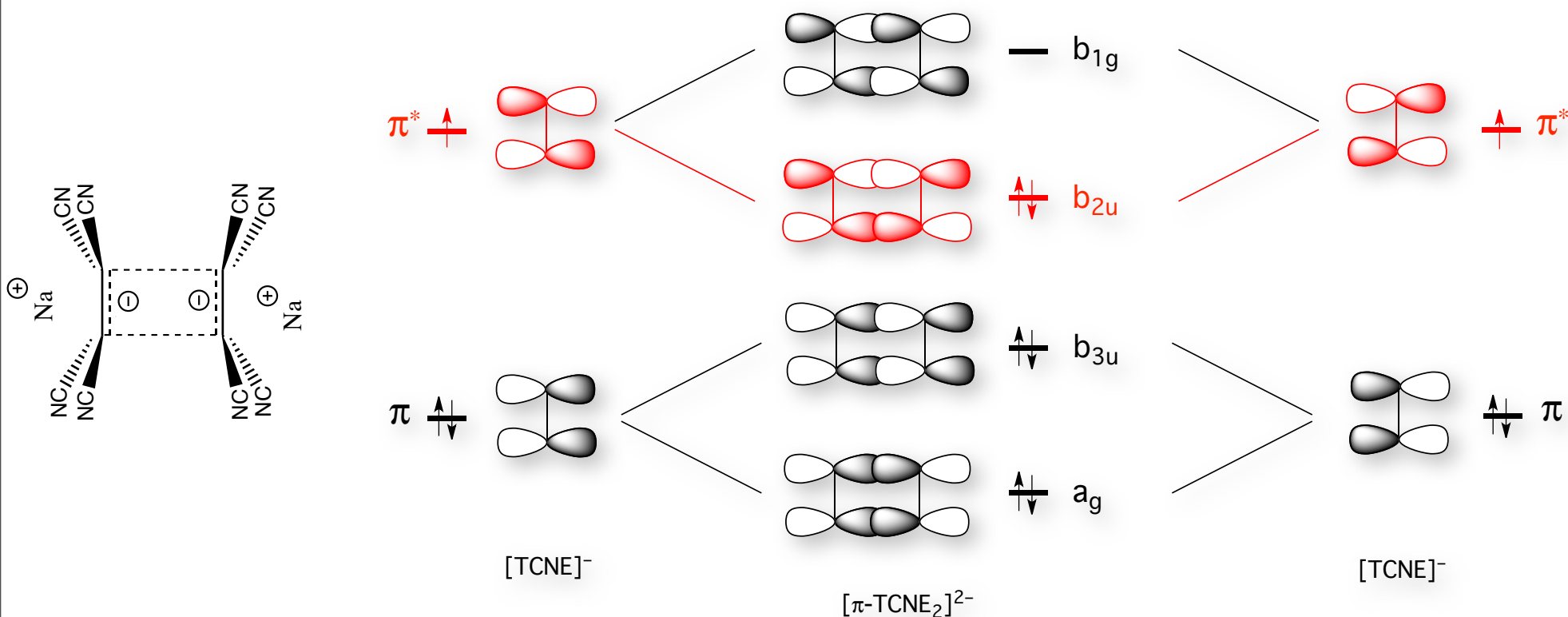


Right geom : significant bonding force overcome repulsive electrostatics !

Qualitative MO analysis

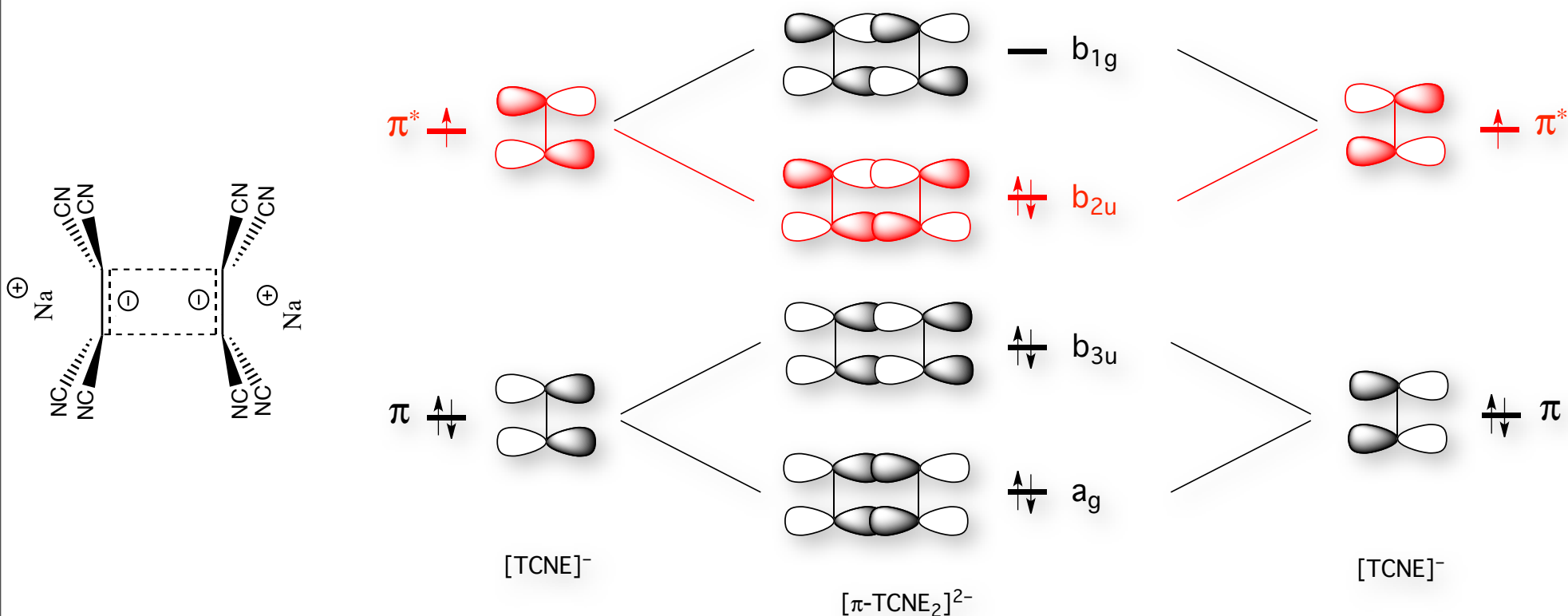


Qualitative MO analysis

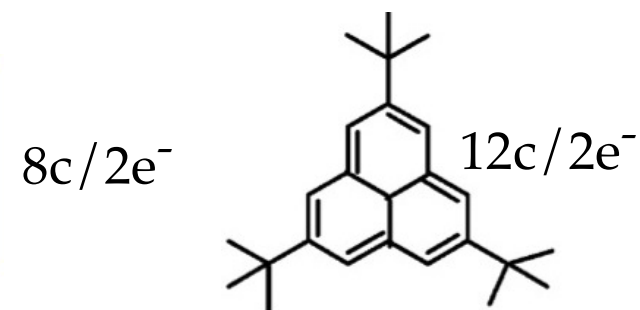
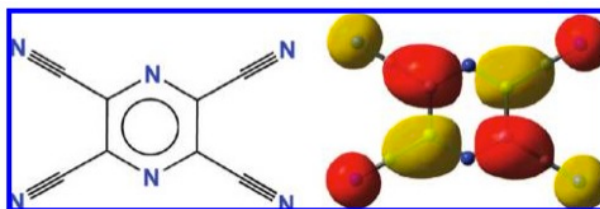


\Rightarrow a simple **4 centers / 2 electrons bond** ?

Qualitative MO analysis

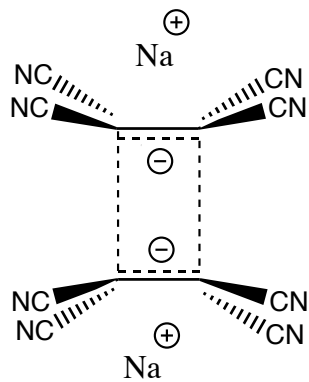


Other «pancake bonding»
systems : **n center / 2e⁻ bonds**

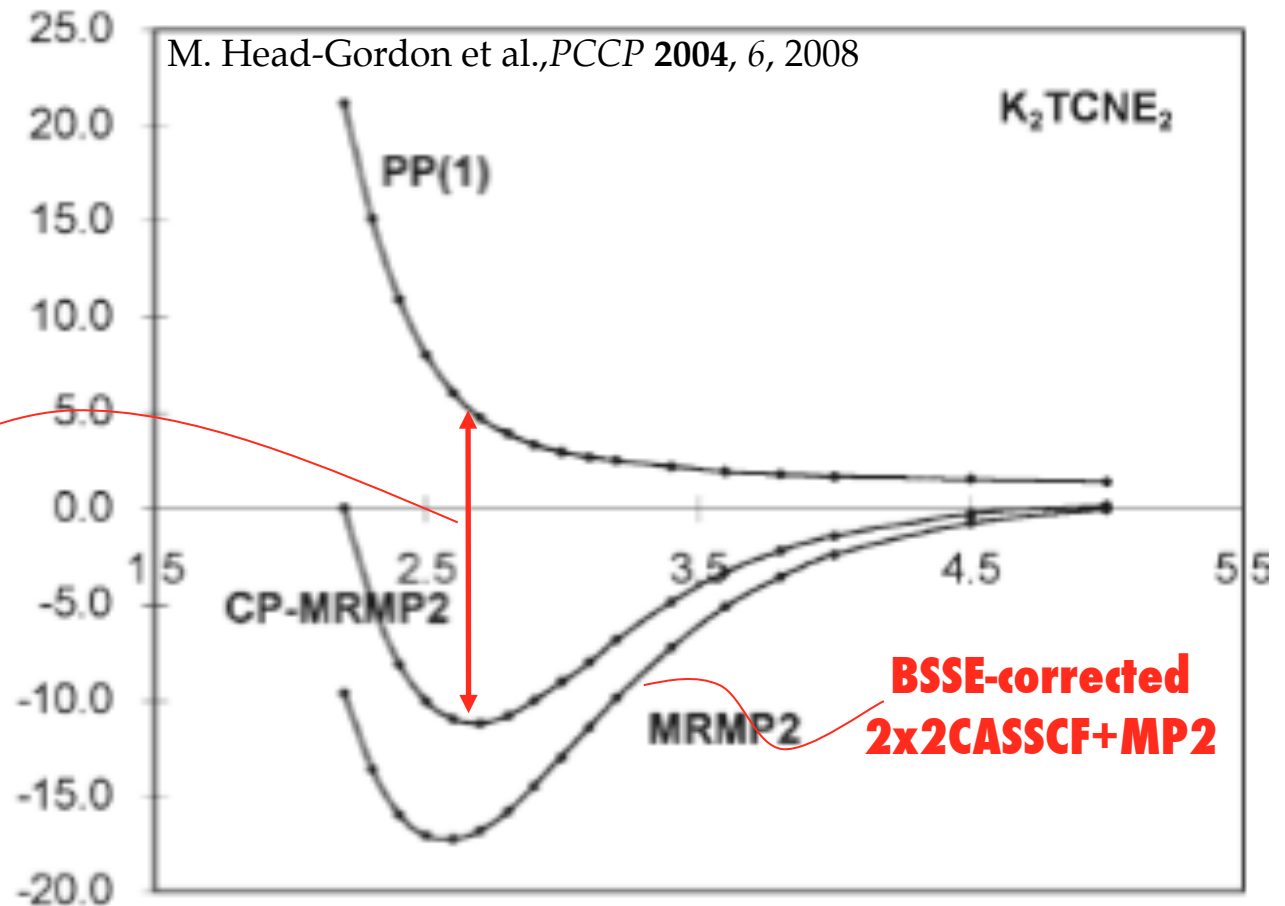


Quantitative MO computations

- GVB calculations of the axial conformation :



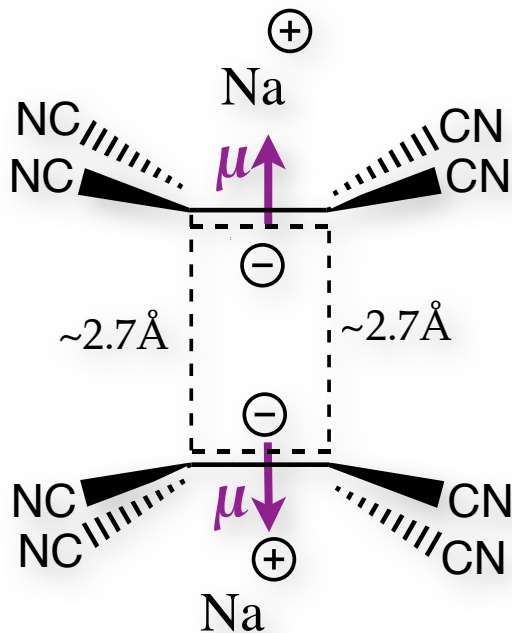
Contribution of
dynamic correlation
to bonding:
> 23 kcal/mol !



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

Situation

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



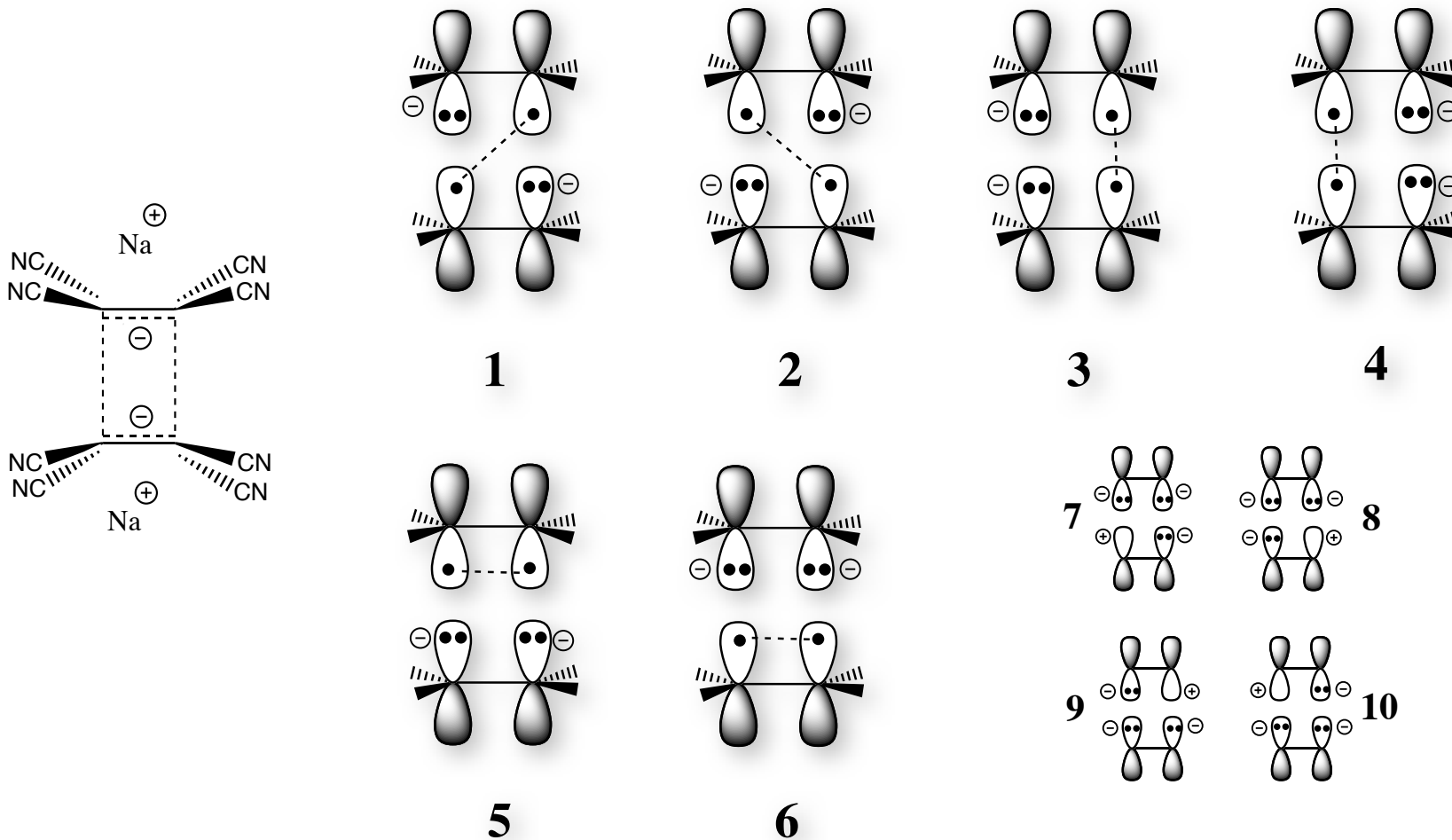
$$D_e \approx \textcircled{11.} \text{ kcal/mol} !$$

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

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

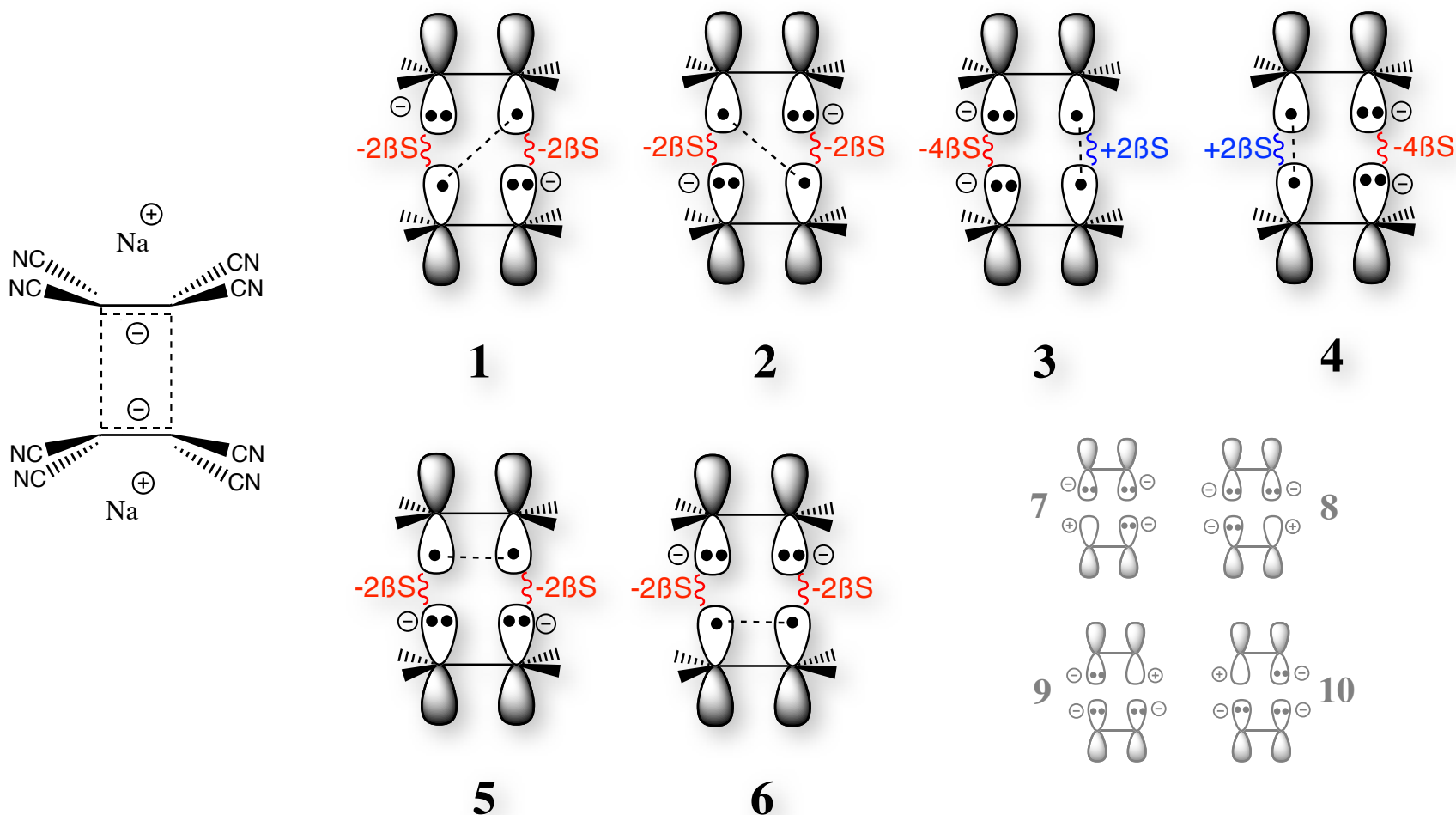
Qualitative VB analysis

- VB set of structures for DTCNE_2^{2-} :



Qualitative VB analysis

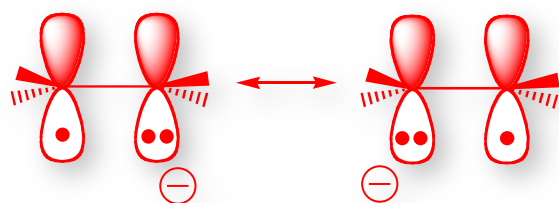
- VB set of structures for DTCNE_2^{2-} :



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

Qualitative VB analysis

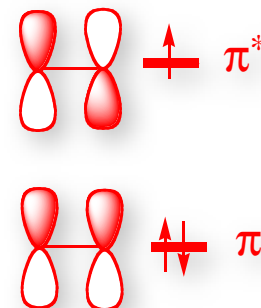
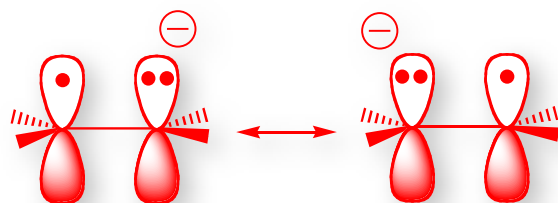
- What about three-electron bonding ?...



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

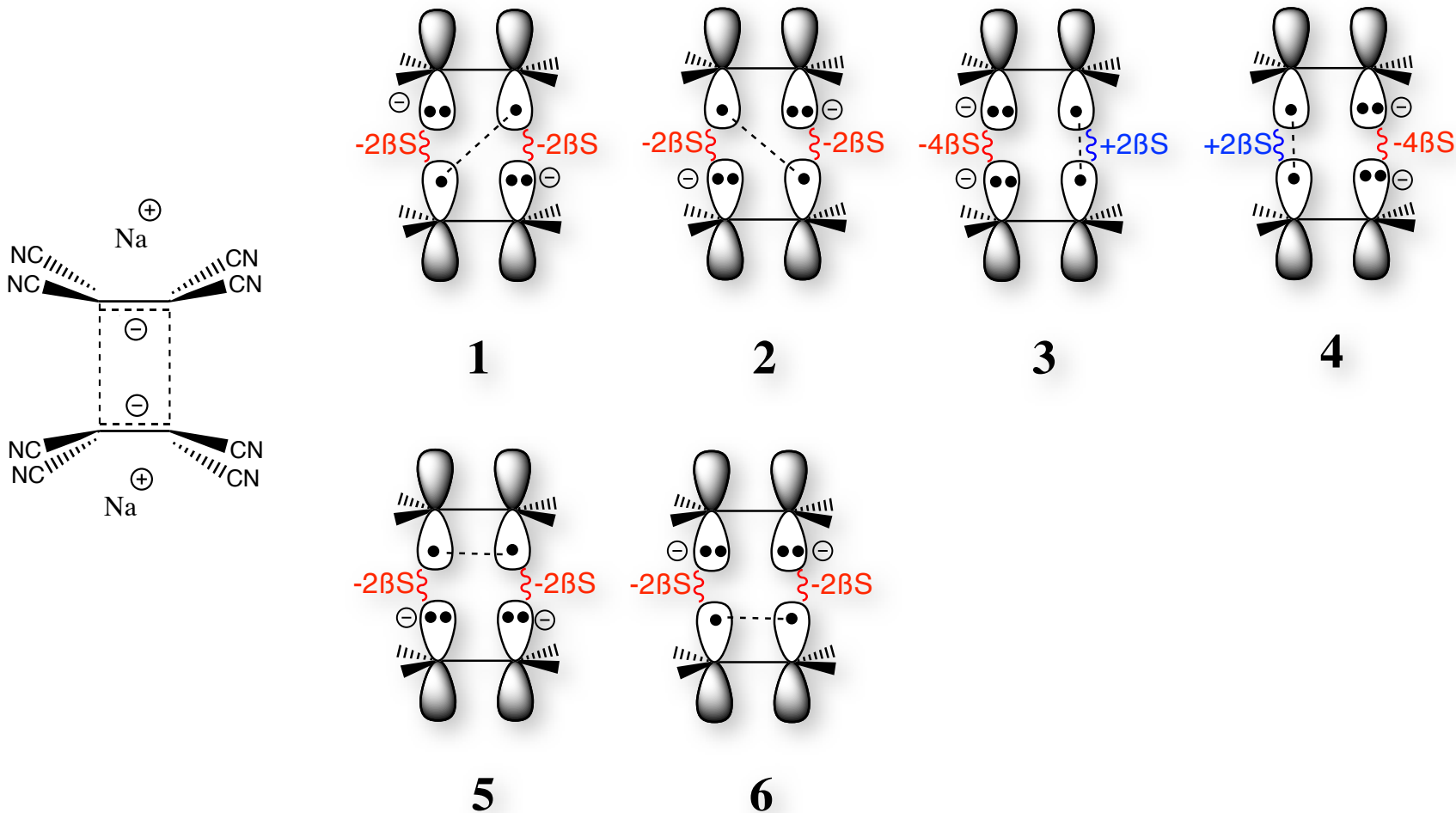
At infinite distance, each fragment displays a **3e⁻ π bond** :

∞



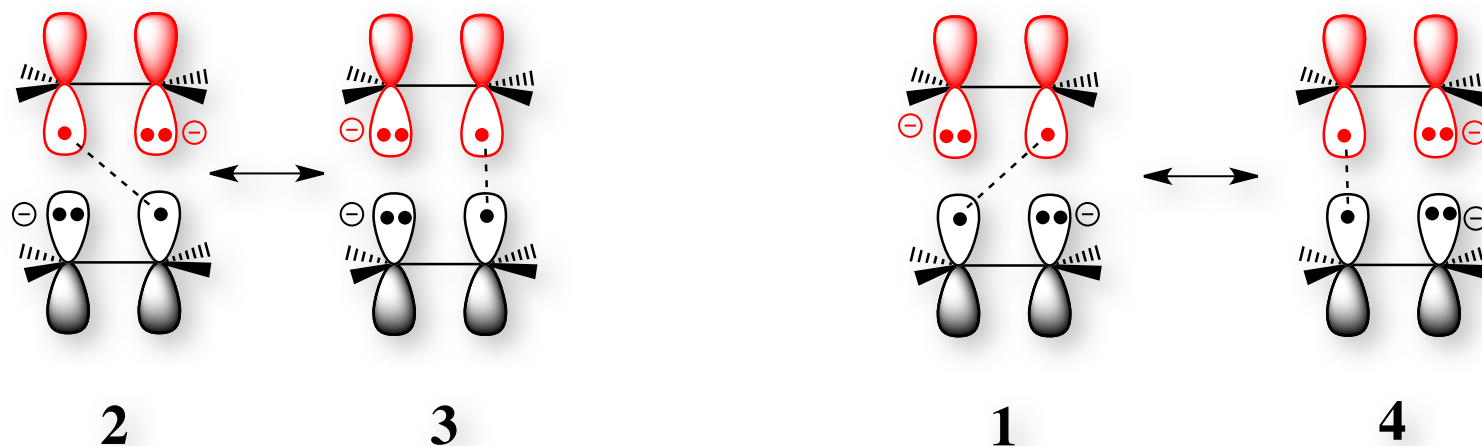
Qualitative VB analysis

- VB set of structures for DTCNE_2^{2-} :



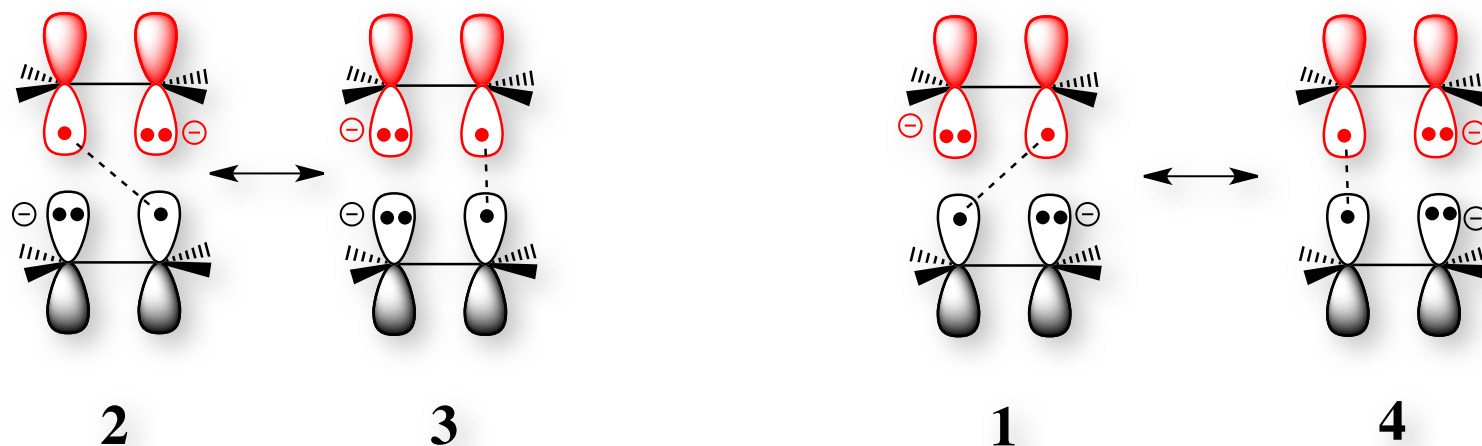
Qualitative VB analysis

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

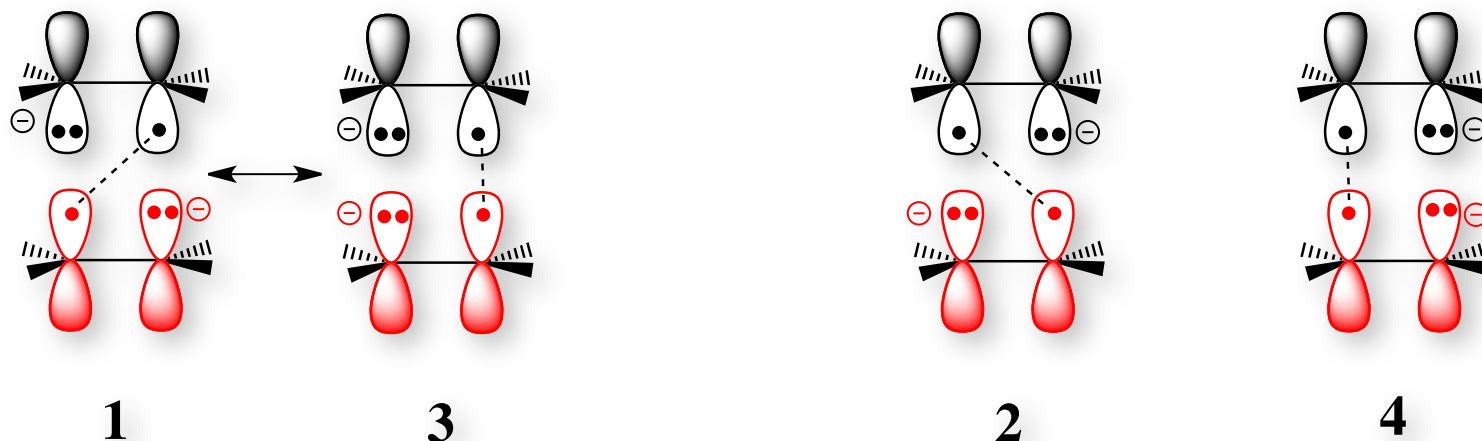


Qualitative VB analysis

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

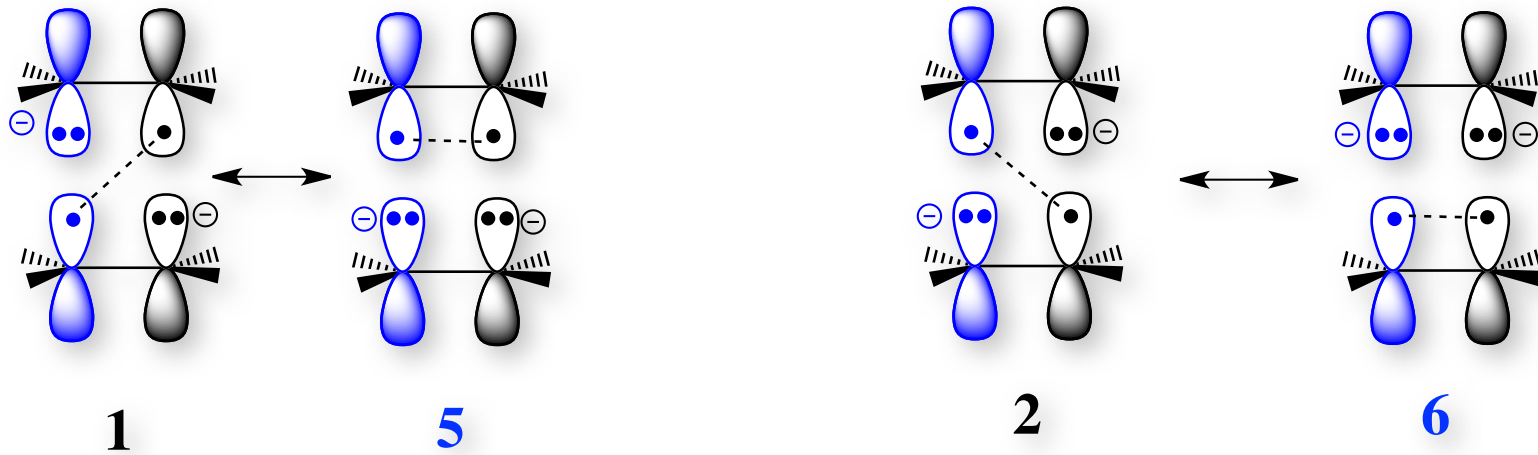


- $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$: **intra-fragment $3e^- \pi$ bond** (lower fragment) :

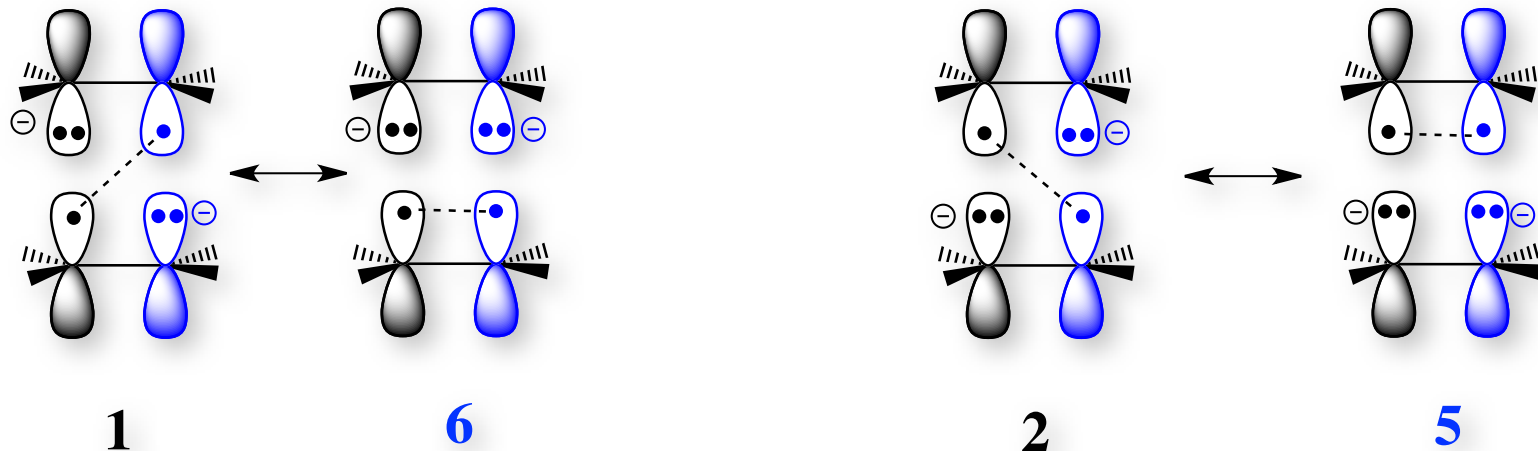


Qualitative VB analysis

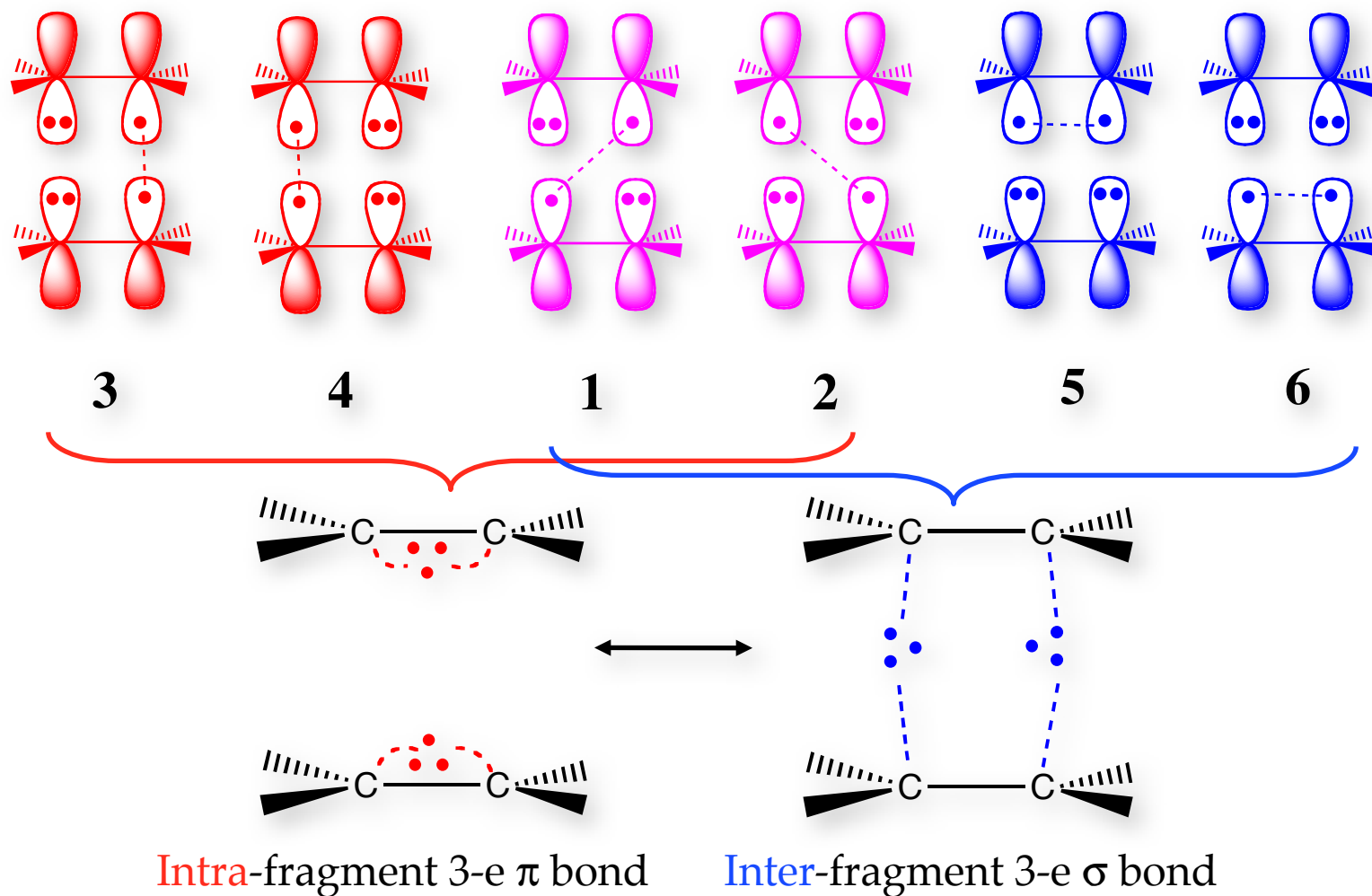
- $1 \leftrightarrow 5$ and $2 \leftrightarrow 6$: **inter-fragment $3e^- \pi$ bond** (left-hand side) :



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



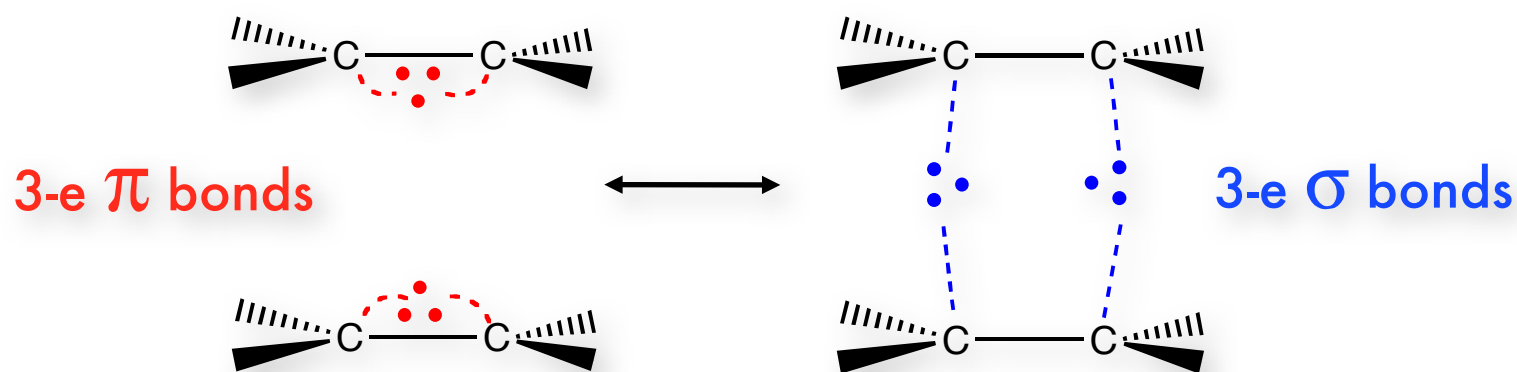
Qualitative VB analysis



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

Ab initio VB calculations

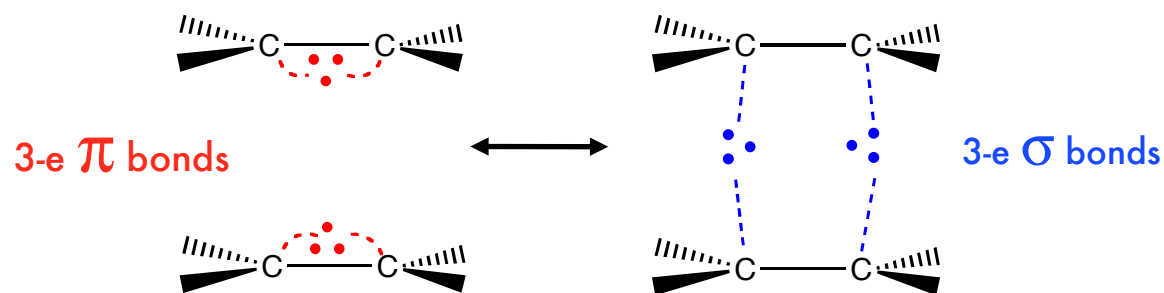
- Some tests of credibility :



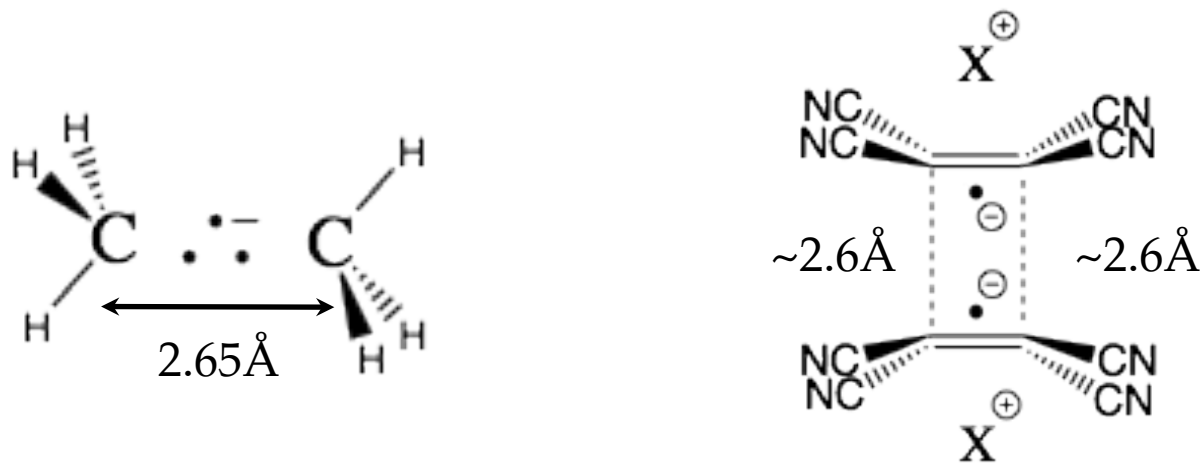
Characteristics of 3e bonds :

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

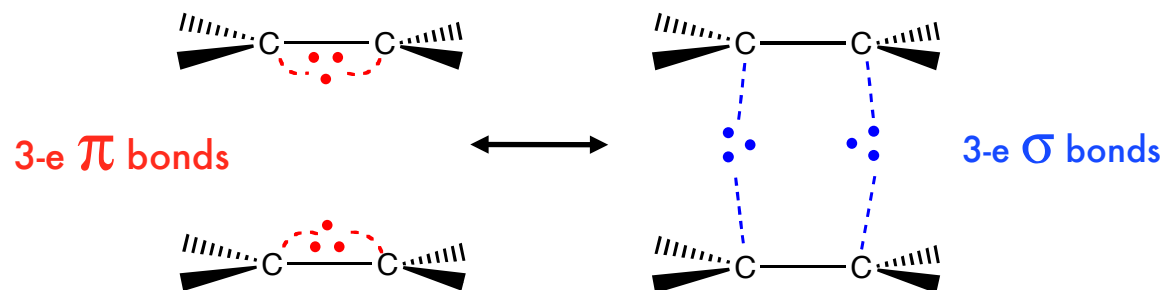
Ab initio VB calculations



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



Ab initio VB calculations



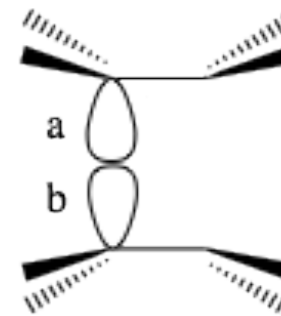
2) Interfragment orbital overlaps close to optimal 3e⁻ bond value :

$$S_{opt} \approx 0.17$$

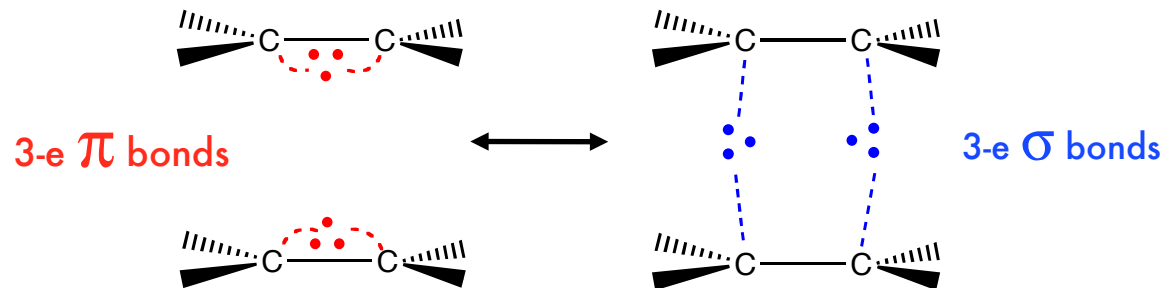
for any 3-e bond
(demonstrated in
qualitative VB theory
as well as Extended Hückel theory)

$$S_{ab} = 0.15$$

(computed)



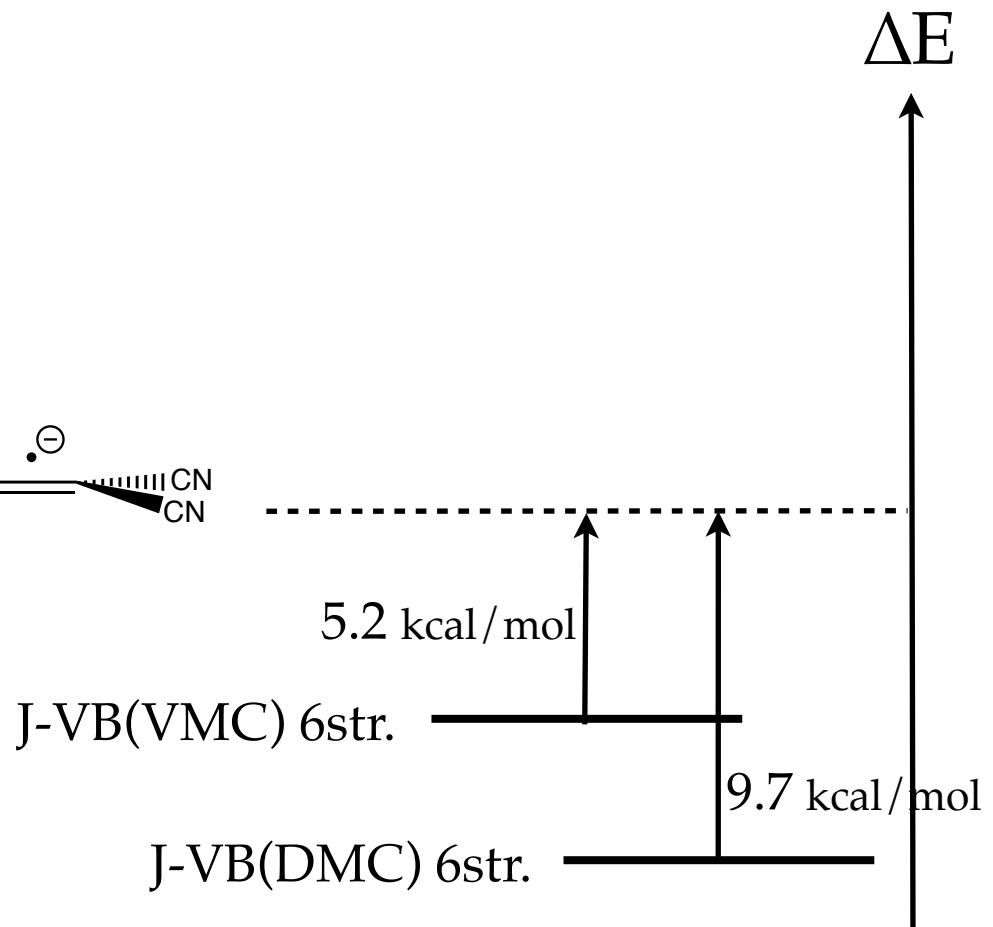
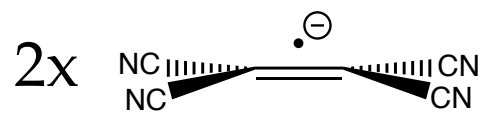
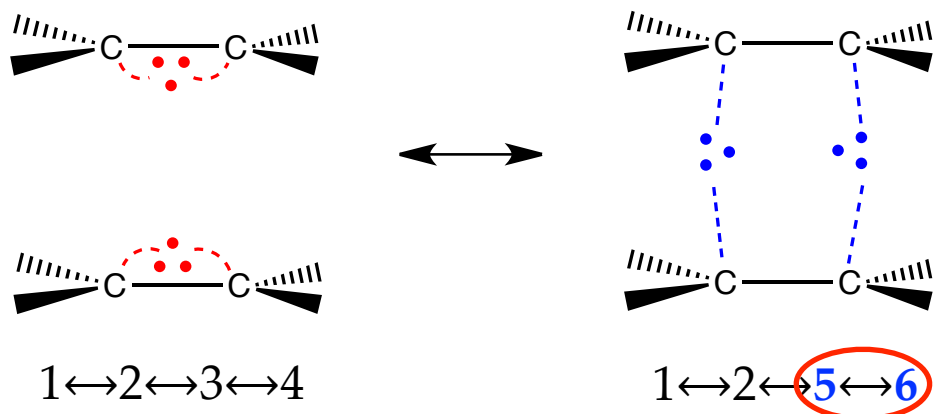
Ab initio VB calculations



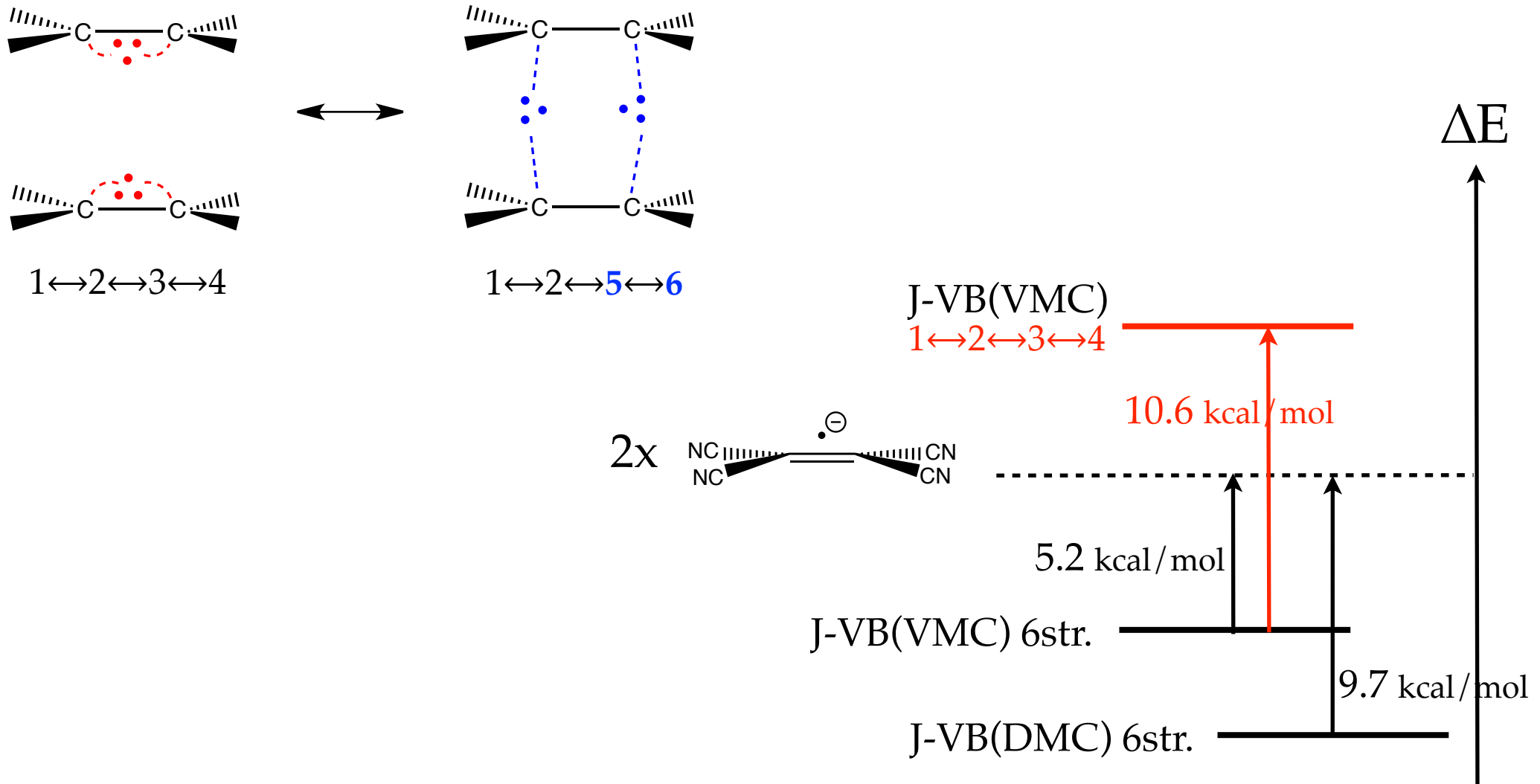
3) Contribution of dynamic correlation to bonding:

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

Ab initio VB calculations

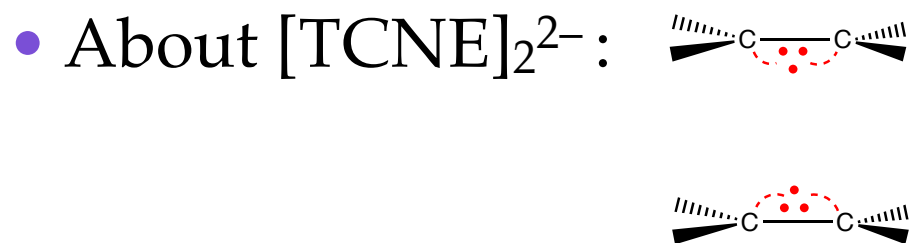


Ab initio VB calculations



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

Conclusion



- 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.