Part 3. Qualitative Valence Bond

Stop me at any time !

Qualitative VB

- **Basic ingredients :**

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

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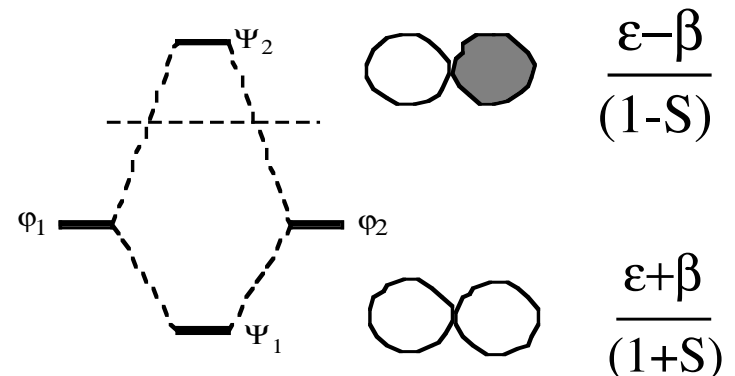
Qualitative VB

- **Basic ingredients :**

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

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

  2) Parametrization : ε, β, S

  Same as in Hückel theory :

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

  $\dfrac{\varepsilon - \beta}{(1-S)}$

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

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

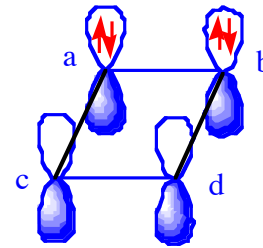 **Overlaps S**

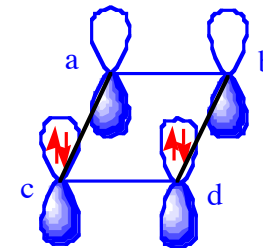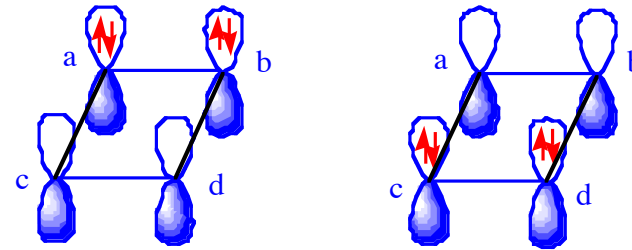# Qualitative VB

- **General calculus rules :**

    1) Rule for calculating determinant overlaps :

    Generate permutations :
    - between identical spins
    - only one side

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

Qualitative VB

- **General calculus rules :**

  1) Rule for calculating determinant overlaps :

  Generate permutations :
  - between identical spins
  - only one side

  $$\frac{1}{\sqrt{4}}\left|a\bar{a}b\bar{b}\right| \qquad \frac{1}{\sqrt{4}}\left|c\bar{c}d\bar{d}\right|$$

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

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

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

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

Qualitative VB

- **General calculus rules :**

  2) Rule for calculating Hamiltonian matrix elements :

  Generate permutations :
  - between identical spins
  - only one side

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

Qualitative VB

- **General calculus rules :**

  2) Rule for calculating Hamiltonian matrix elements :

  Generate permutations :
  - between identical spins
  - only one side

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

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

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

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

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

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

Qualitative VB

- **General calculus rules :**

  2) Rule for calculating Hamiltonian matrix elements :

  Generate permutations :
  - between identical spins
  - only one side

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

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

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

  $$\frac{1}{4}\left\langle (|a\bar{a}b\bar{b}|) \left| \hat{h}_3 \right| (|c\bar{c}d\bar{d}|) \right\rangle = \ldots$$ Rather tedious...

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

Qualitative VB

- **Simplified expressions :**

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

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

$$\begin{cases} \varepsilon_i = h_{ii} - \dfrac{1}{n}\displaystyle\sum_{i=1}^{n} h_{ii} \\[2em] \beta_{ij} = h_{ij} - \dfrac{1}{n}\displaystyle\sum_{i=1}^{n} h_{ii} \end{cases}$$

Qualitative VB

- **Simplified expressions :**

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

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

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

Qualitative VB

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

  2) Approximation :

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

Qualitative VB

- **Elementary interactions energies :**

    1) The QC state :
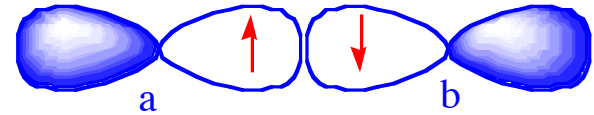
    $$\Psi_{QC} = \left| a\bar{b} \right|$$

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

    Same for all **spin-alternant determinants** (choice of energy reference) :
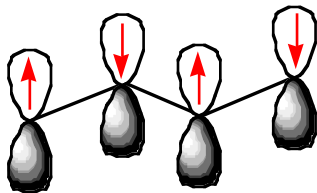
       E=0

Qualitative VB

- **Elementary interactions energies :**
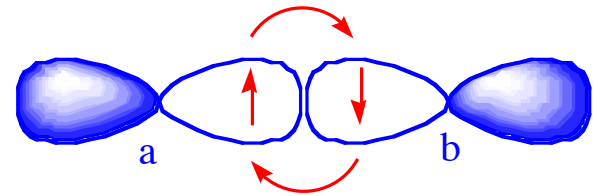
  2) The two electron bond :

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

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

Qualitative VB

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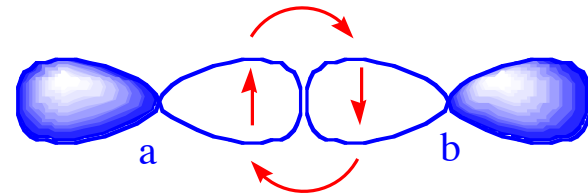
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$$\langle\Psi|\hat{H}^{eff}|\Psi\rangle \Rightarrow \begin{cases} \text{Diagonal terms (two)} : \left\langle\left(\left|a\bar{b}\right|\right)\left|\hat{h}_1 + \hat{h}_2\right|\left(\left|a\bar{b}\right|\right)\right\rangle = \varepsilon_1 + \varepsilon_2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

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

Different in MO-Hückel theory :
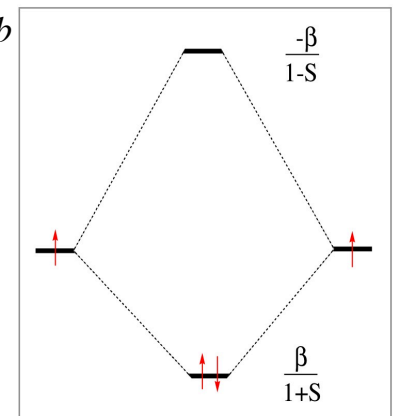
$$D_e = 2\beta/(1+S)$$

Qualitative VB

- **Elementary interactions energies :**

  3) The triplet repulsion :
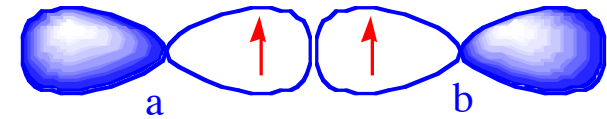
$$\Psi_T = \frac{\left|a\bar{b}\right| - \left|b\bar{a}\right|}{\sqrt{2(1-S^2)}}$$

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

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

Same in MO-Hückel theory :
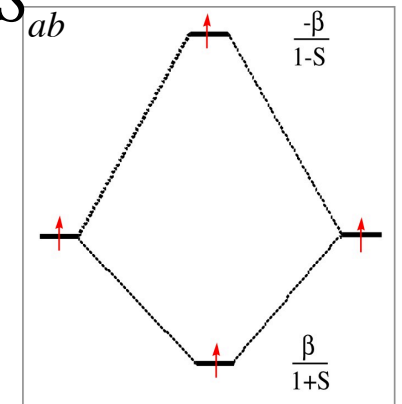
$$E = \frac{\beta}{1+S} + \frac{-\beta}{1-S} = \frac{-2\beta S}{1-S^2}$$

Qualitative VB

- **Elementary interactions energies :**

  3) The triplet repulsion :

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

  MO

  σ_u

  a ——— b

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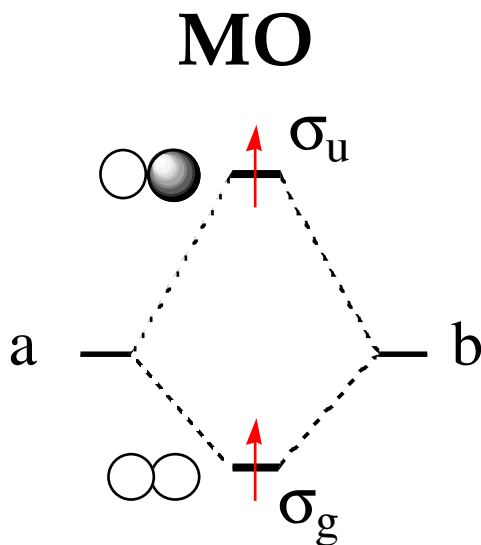
  VB
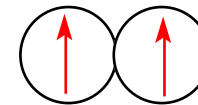
  $\psi_{VB} \propto |ab|$

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

Qualitative VB

- **Elementary interactions energies :**

- Lecture 1 :
$$\Delta E_{ST} \approx 2De$$
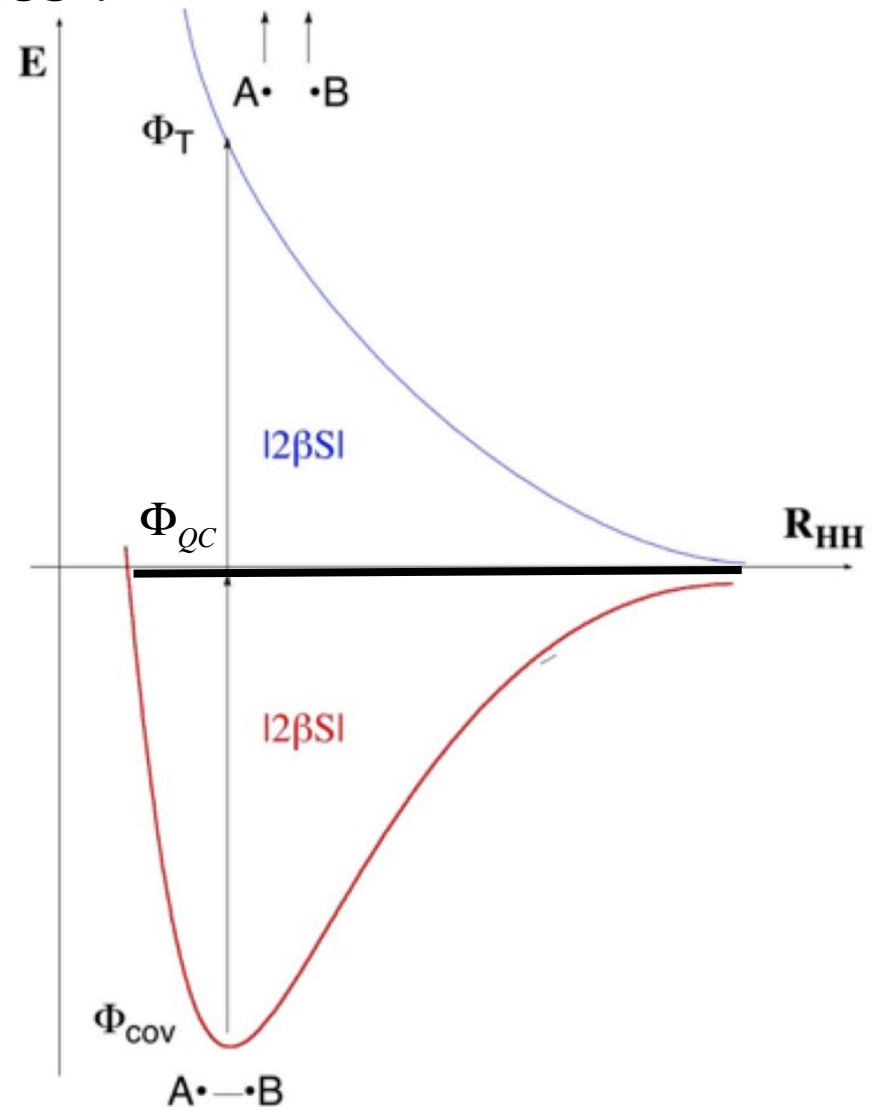
Qualitative VB

- **Elementary interactions energies :**

4) All repulsions :

	VB	MO

- 3e repulsion : **same** as triplet :
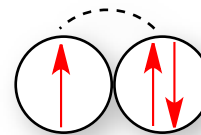
$$\frac{-2\text{ßS}}{1-S^2}$$ **Same**

- 4e repulsion : **two times** triplet :
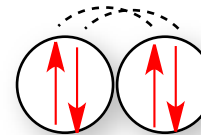
$$\frac{-4\text{ßS}}{1-S^2}$$ **Same**

- NCI : **half time** triplet :

   bond… single electron

$$\frac{-\text{ßS}}{1-S^2}$$ /

   bond… bond

$$\frac{-\text{ßS}}{1-S^2}$$ /
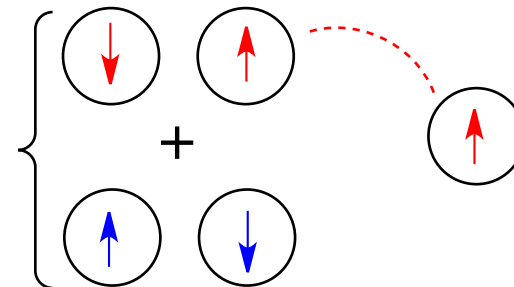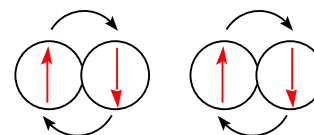
Qualitative VB

- **Elementary interactions energies :**

5) The 3e bond :

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

(methionylglycine)

MO

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

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

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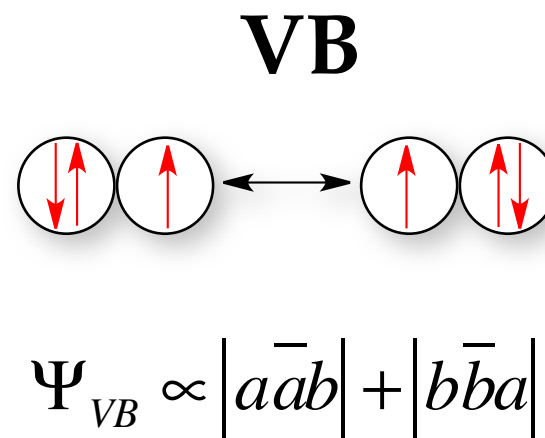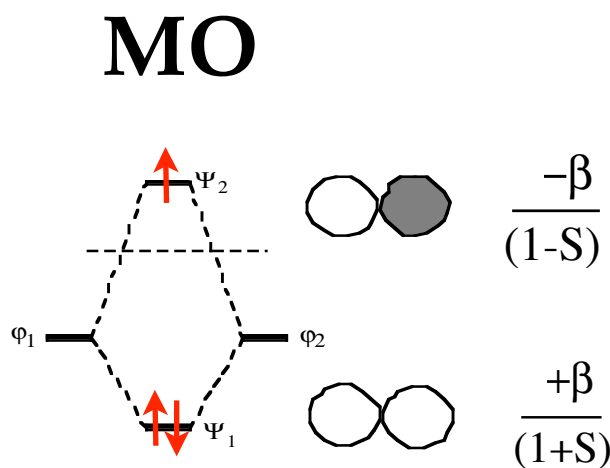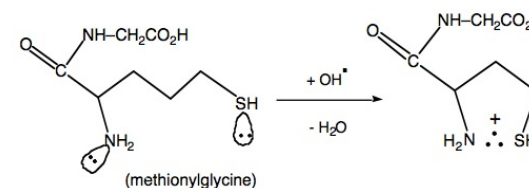
$$\Psi_{VB} \propto \left| a\bar{a}b \right| + \left| b\bar{b}a \right|$$

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

$$\Rightarrow \quad D_e = \frac{\beta(1-3S)}{(1-S^2)} \overset{\beta=k\alpha S}{=} \frac{k\alpha S(1-3S)}{(1-S^2)} \quad \Rightarrow \quad \boxed{S_{opt} \approx 0.17} \quad \text{☞} \quad \textit{Remind for later use !}$$

Qualitative VB
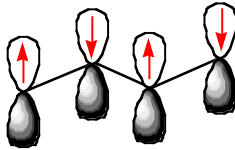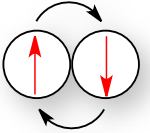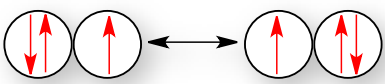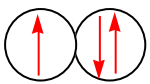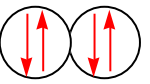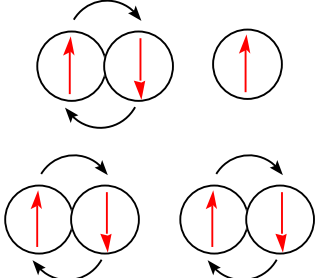
- **Elementary interactions energies :**

Energy of a determinant with *n pairs of interacting e⁻* : $\dfrac{\sigma 2n\beta S}{1+\sigma S^2}$ ☞

σ sign : + if attractive, – if repulsion

Work for all but 3e bond

Qualitative VB

		VB	MO

$$\frac{\sigma 2n\text{ß}S}{1+\sigma S^2}$$

spin-alternated det.   **0**   (VB only)

2-e bond (A–B) = $2\text{ß}S/(1+S^2)$ $2\text{ß}/(1+S)$

3-e bond(A∴B) = $\text{ß}(1-3S)/(1-S^2)$ Same as VB

triplet=3-e repulsion $-2\text{ß}S/(1-S^2)$ Same as VB

4-e repulsion $-4\text{ß}S/(1-S^2)$ Same as VB

bond…single e⁻ and bond...bond $-\text{ß}S/(1-S^2)$ (VB only)

Qualitative VB

➡ **Break : Lewis and Pauling :**

The name is bond...

Valence
The name is Bond, James 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

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

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

MO

VB
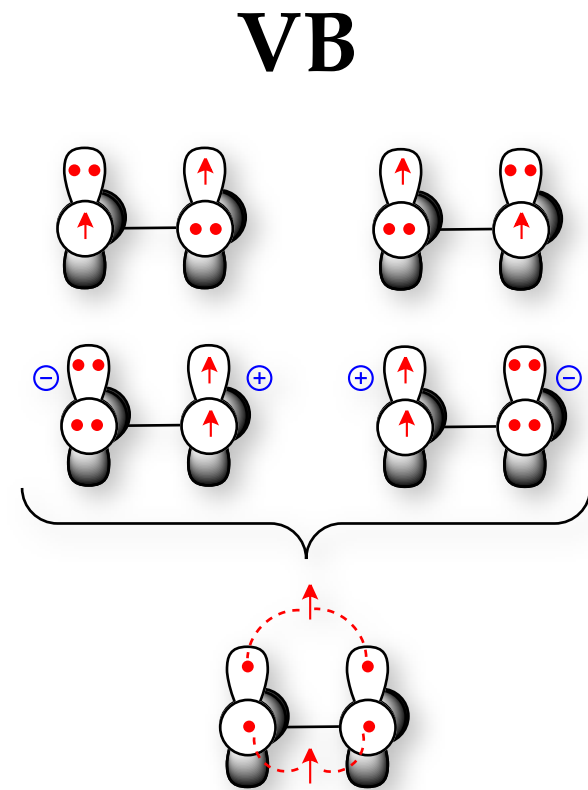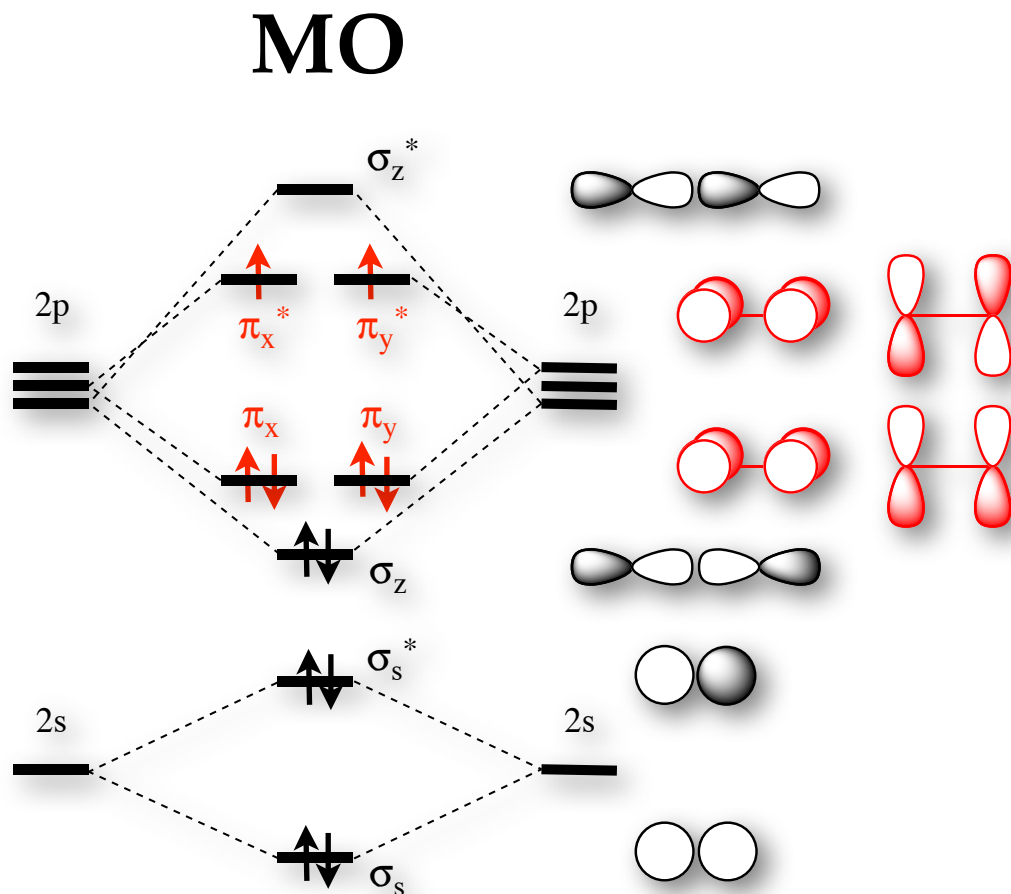
Qualitative VB

➡ **Exercise 4 : ground state of O$_2$:**

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

2) Same question for the closed-shell singlet state, corresponding to the usual Lewis structure used for this molecule.

3) Take the difference, and conclude which state is predicted to be the lowest at the qualitative VB level of theory.

Singlet   **Triplet**
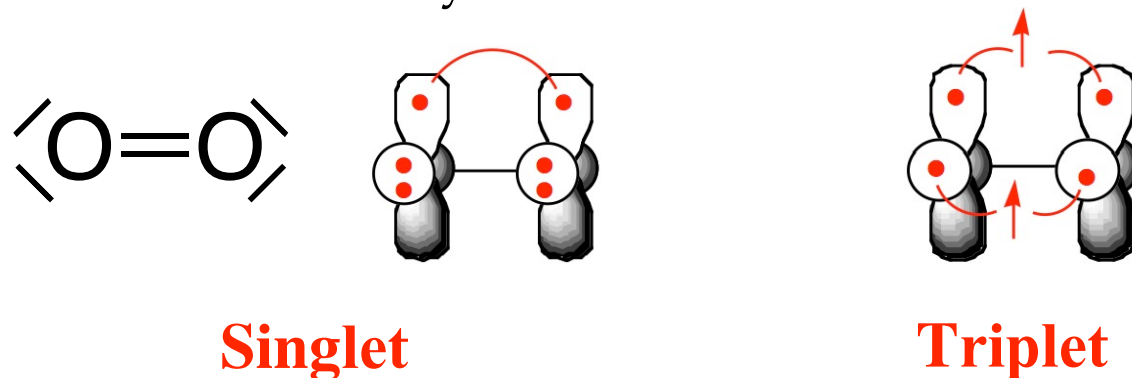
Qualitative VB

➡ **Exercise 4 : ground state of O2 (answer) :**
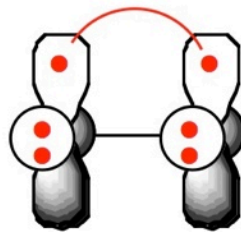
$$E(S) = 2\beta S /(1+S^2) - 4\beta S /(1-S^2)$$
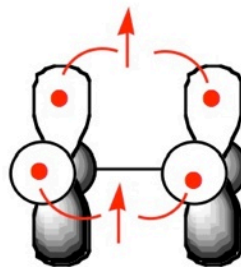
$$E(T) = 2\beta (1 - 3S)/(1-S^2)$$

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

➡ *The triplet state is always the lower*

➡ **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

➡ **Exercise 5 : spin polarization in allyl radical :**

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

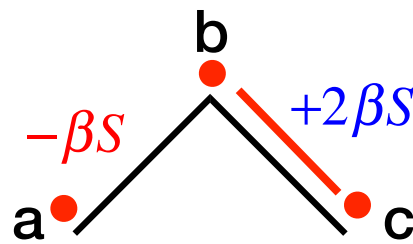$$\psi(II) = \frac{1}{\sqrt{2}}(|ab\bar{c}| + |ac\bar{b}|)$$

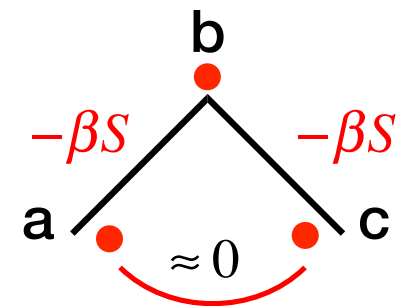$$\psi(III) = \frac{1}{\sqrt{2}}(|ab\bar{c}| + |cb\bar{a}|) = \psi(I) + \psi(II)$$

Qualitative VB

➡ **Exercise 5 : spin polarization in allyl radical :**
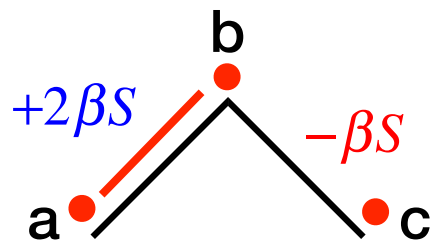
$$\Rightarrow E(I) = +\beta S < 0$$
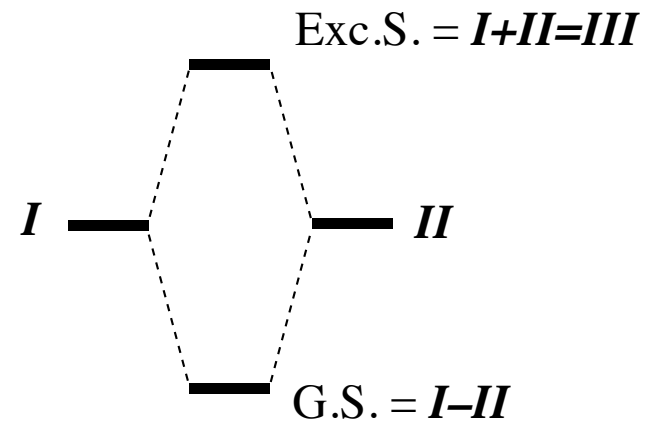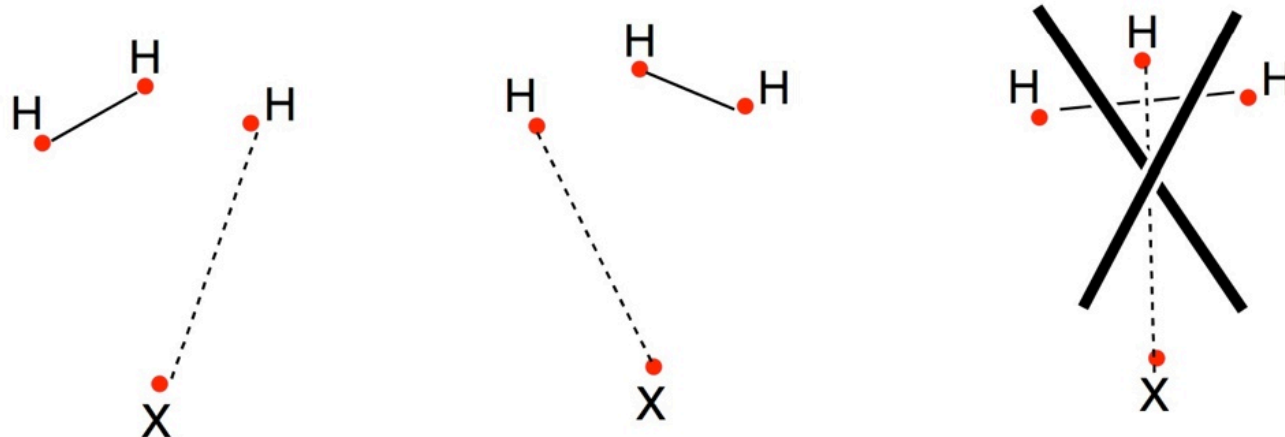
$$\Rightarrow E(II) = +\beta S < 0$$

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

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

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

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

Exc.S. = **I+II=III**

I ——— ——— **II**

G.S. = **I–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 : H_3 radical

➡ **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 :**

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

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

EPR

-0.2   +0.6
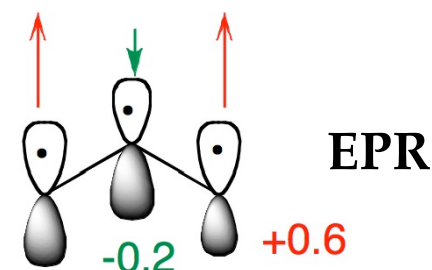
⇒ much closer to experiment than UHF

$|a\bar{b}c|$

$D_b = D_{QC}$

$|\bar{a}bc|$

D_a

$|ab\bar{c}|$

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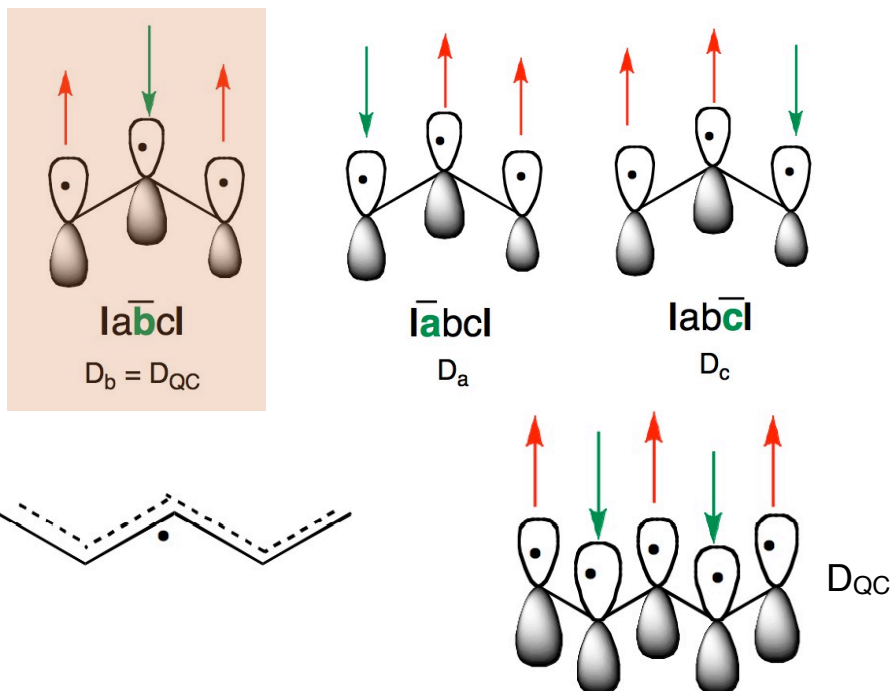
☞ The spin alternant determinant D_{QC}, having the lowest energy, control the spin density pattern

D_{QC}

☞ General rule, works for all polyenes

Qualitative VB

➡ **Break2 : McWeeny :**

Application
Electronic structure of the DTCNE dimer

«Pancake bonding»

- DTCNE$_2{}^{2-}$:
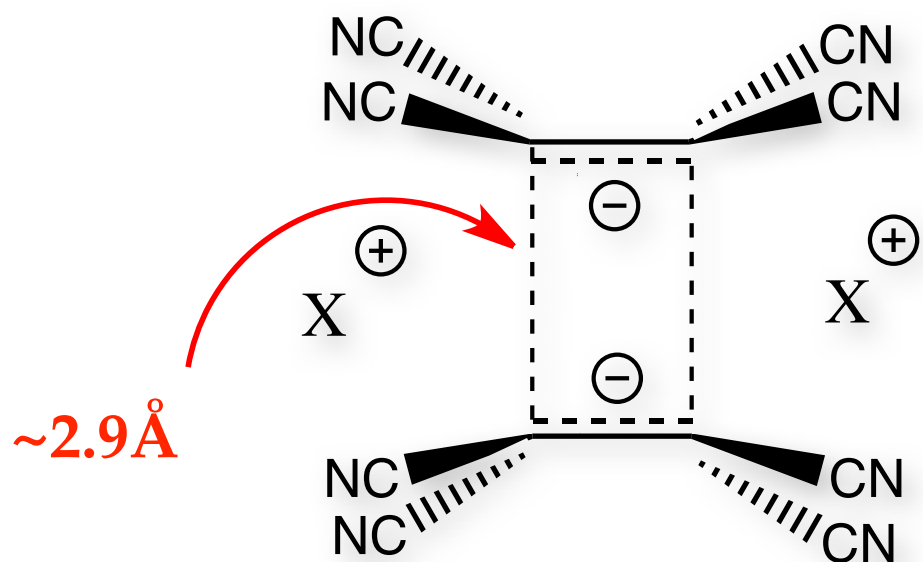
X^+ : Na^+, Cs^+, $[iPr_4N]^+$, $[Cr(C_6Me_3H_3)_2]^+$, ...

~2.9Å

Electrostatic complex ?...

- Strong bonds

- Same bonding distance whatever the size of the cations !

«Pancake bonding»

- DTCNE$_2^{2-}$:

2.9 Å

Stable in the crystal

3.05 Å

Stable in solution
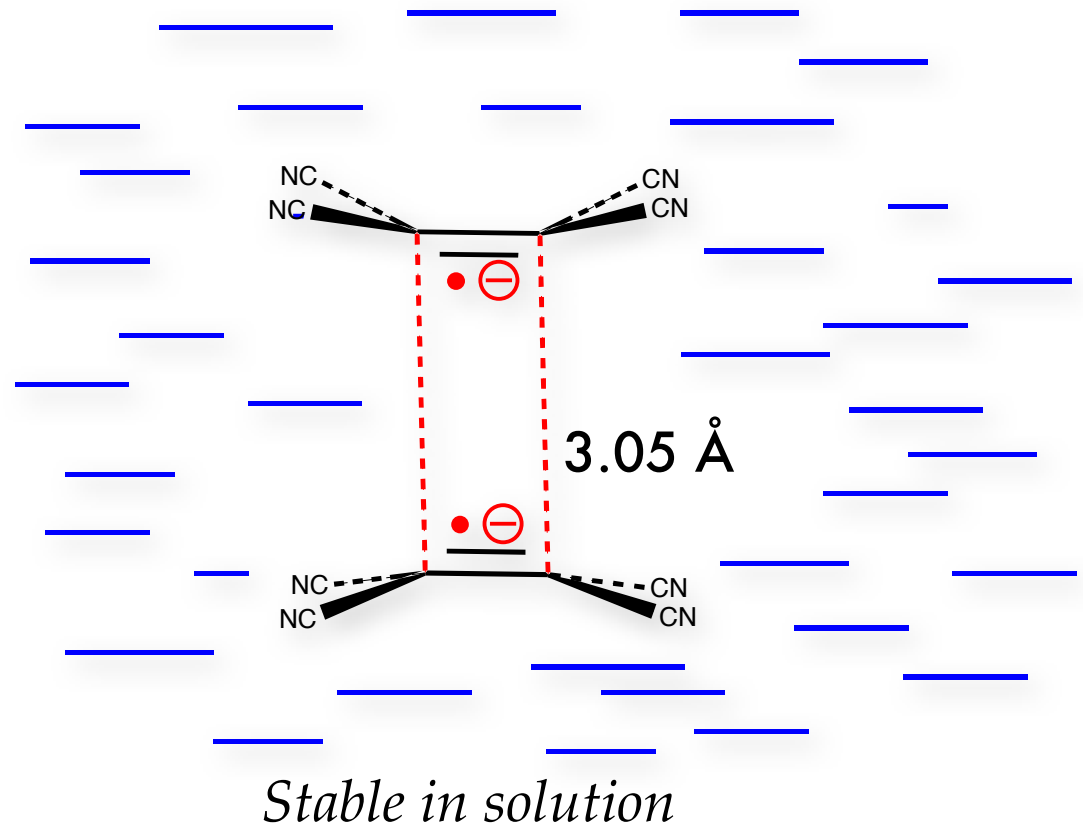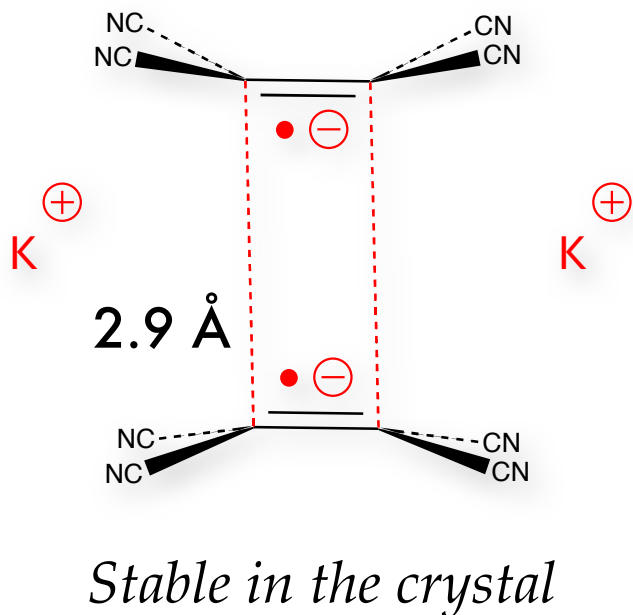
- Same bonding distance whatever the environment !

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

«Pancake bonding»

- Other «pancake bonding» systems :

[TCNP]$_2$

[TCNQ]$_2$

2.9±0.05

[DDQ]$_2$

[CA]$_2$
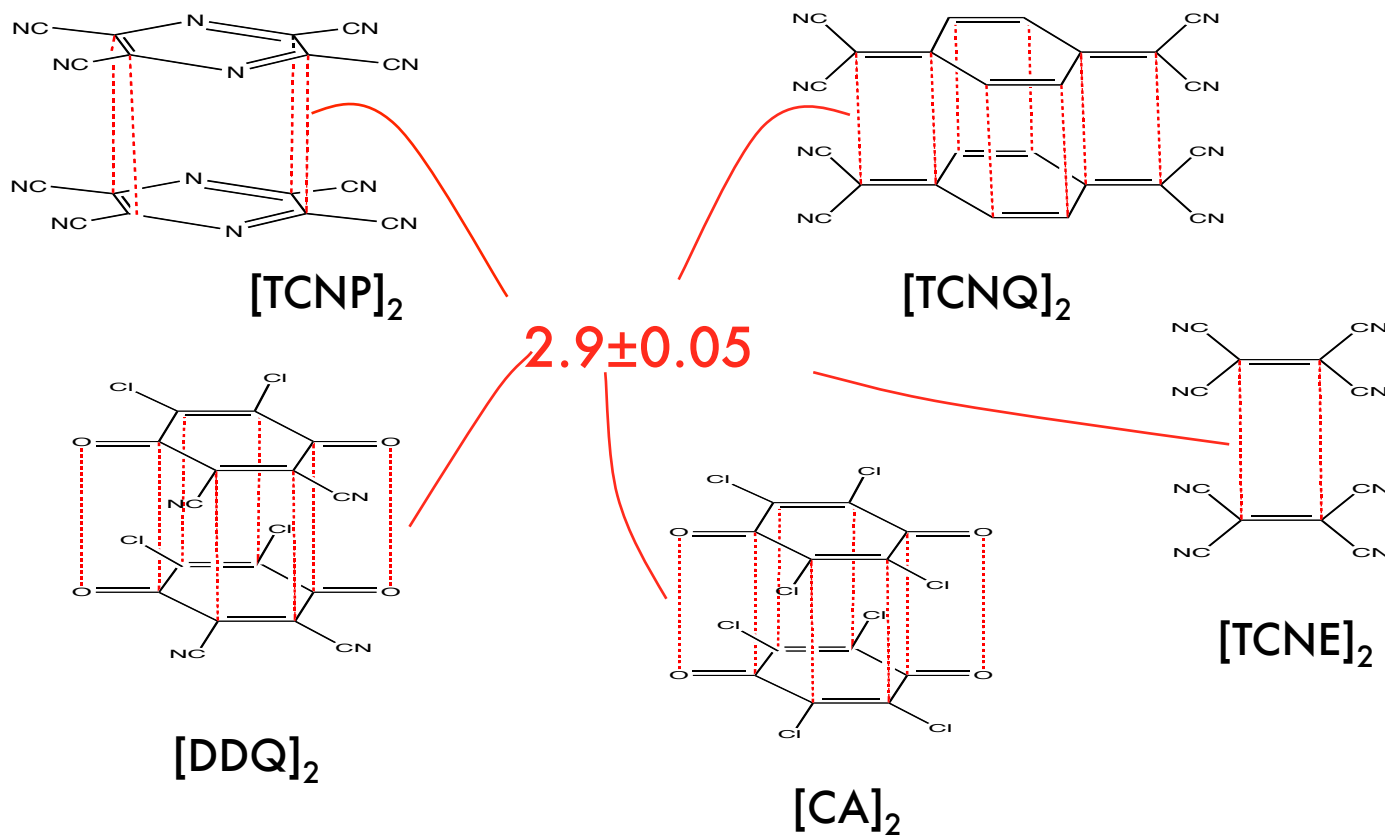
[TCNE]$_2$

- Same bonding distance whatever the system !

- d_{C---C} < sum of vdW radii (3.45Å) , but much longer than C-C 2e bonds (1.54Å)

«Pancake bonding»

- What kind of bonding in DTCNE$_2^{2-}$?
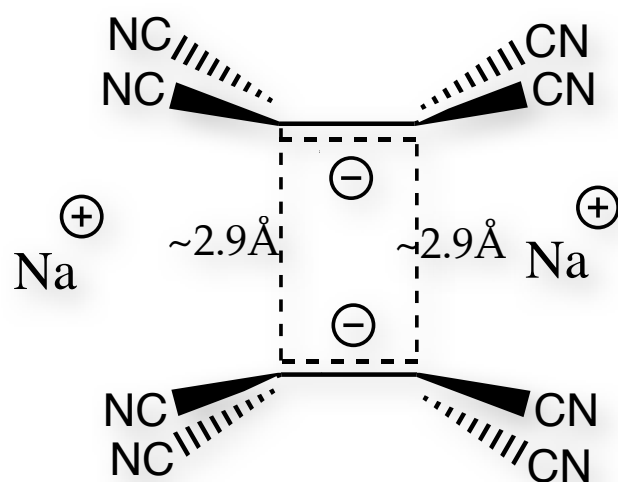
$D_e \approx 80.\ kcal/mol$
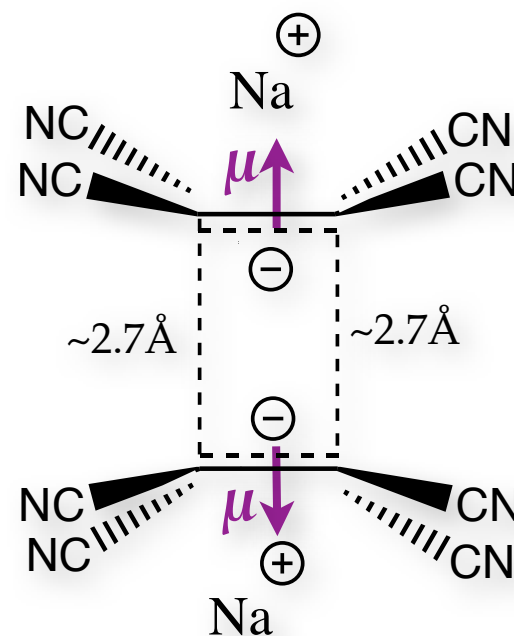
$D_e \approx 11.\ kcal/mol$

Right geom : significant bonding force overcome repulsive electrostatics !

Qualitative MO analysis

π*   overlap   π*

4-e repulsion

π   π

Na⁺   [TCNE]⁻   [TCNE]⁻   Na⁺

Left fragment   **Right fragment**
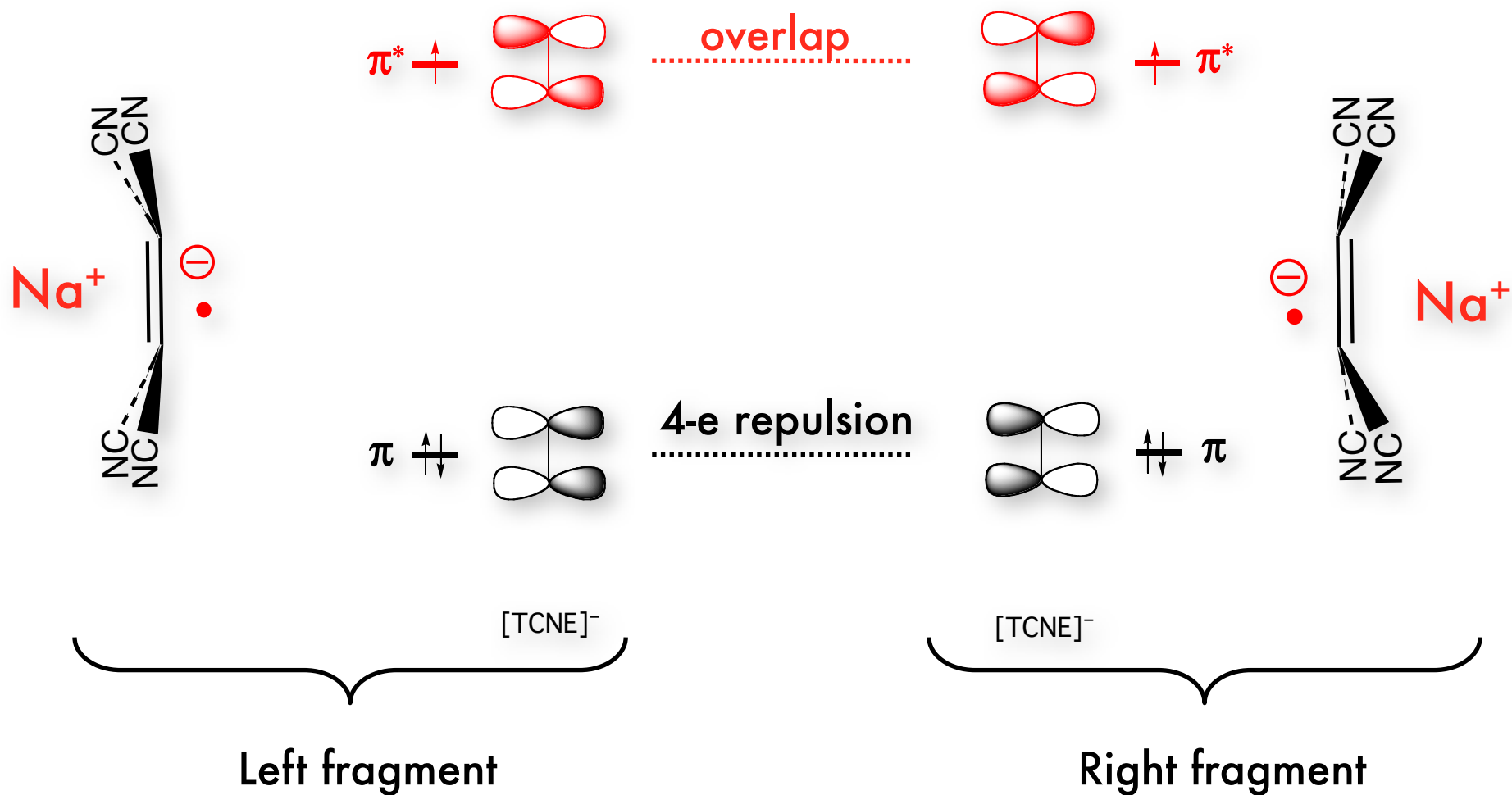
Qualitative MO analysis
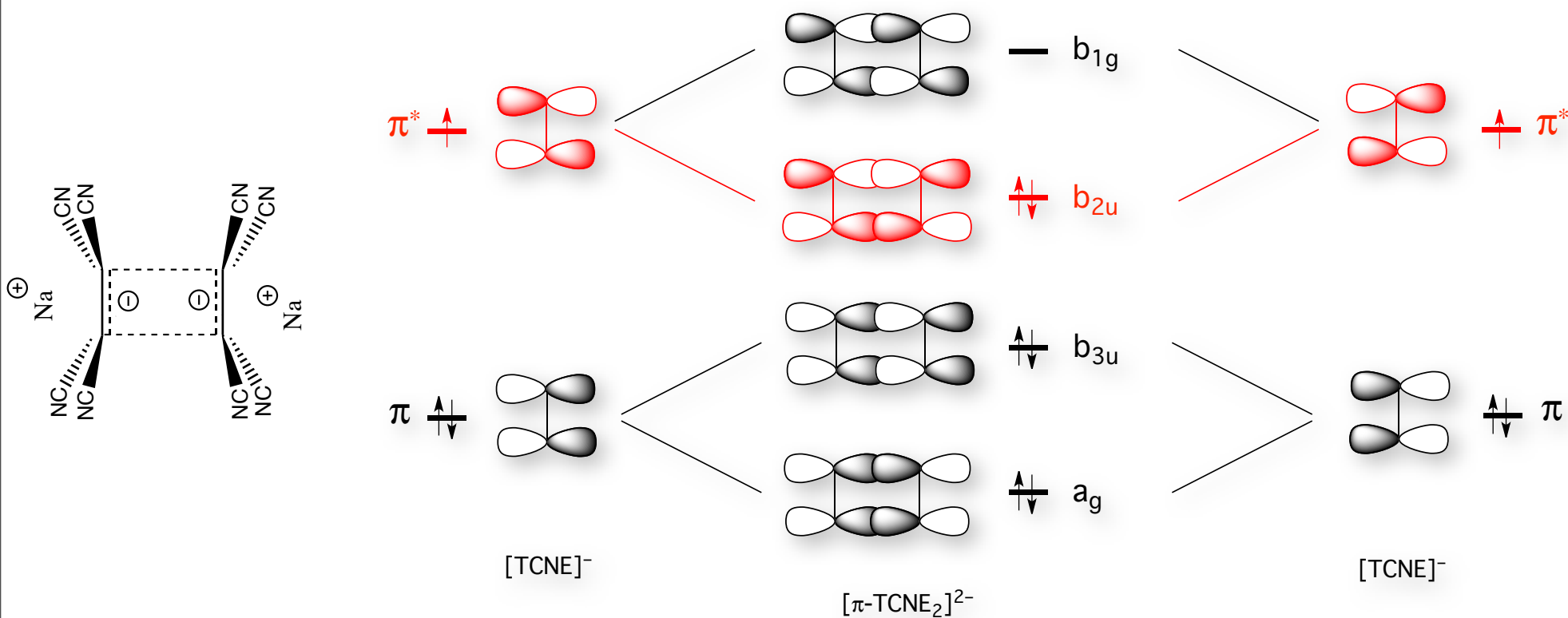
$\Longrightarrow$ a simple **4 centers / 2 electrons bond ?**

Qualitative MO analysis

π^* b$_{1g}$

π^*

b_{2u}

π^*

π b$_{3u}$

a$_g$

π

[TCNE]$^-$

[π-TCNE$_2$]$^{2-}$

[TCNE]$^-$
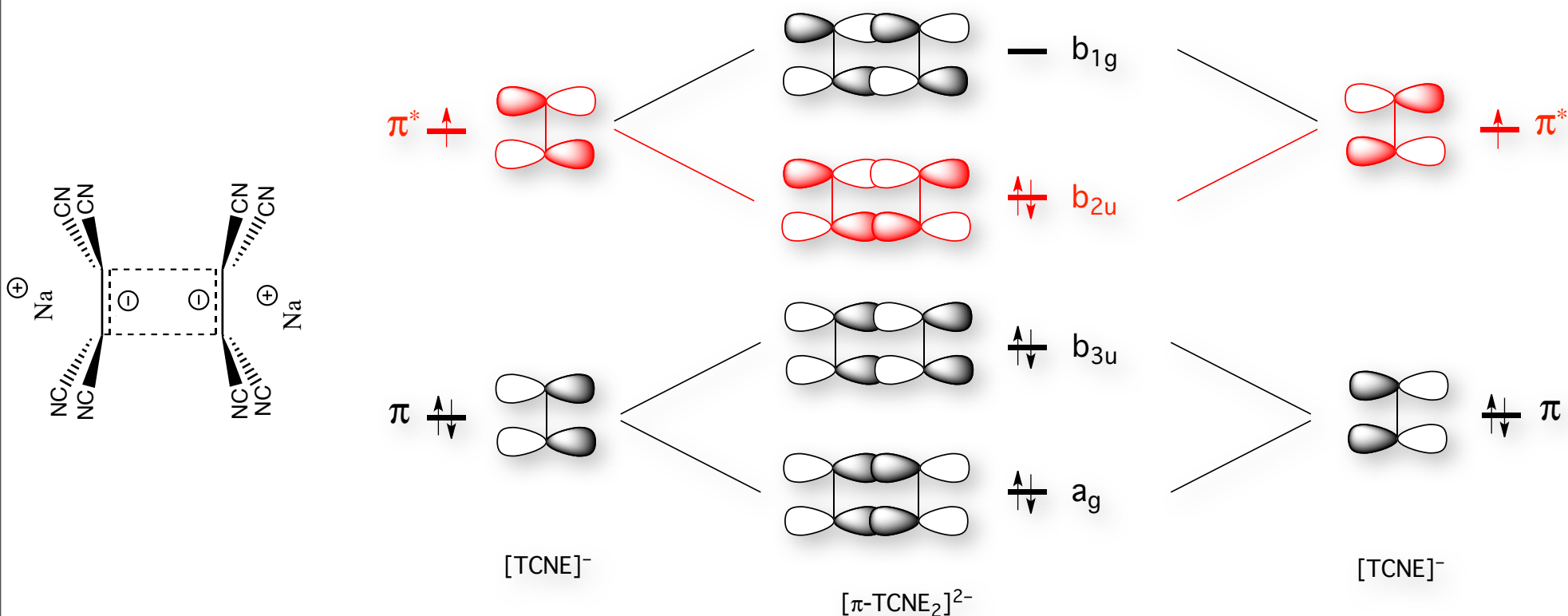
Other «pancake bonding»
systems : **n center / 2e$^-$ bonds**
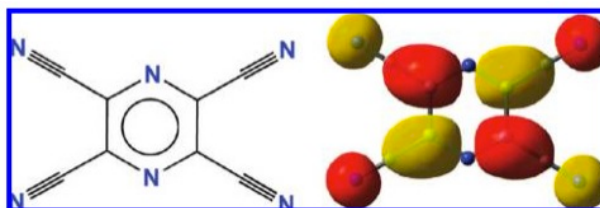
8c/2e$^-$

12c/2e$^-$
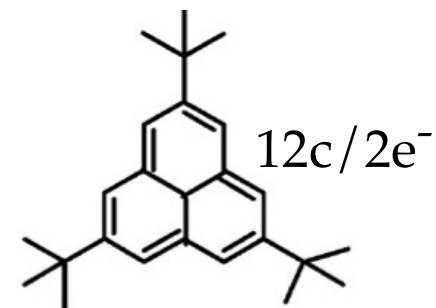
Quantitative MO computations

- GVB calculations of the axial conformation :

M. Head-Gordon et al., *PCCP* **2004**, *6*, 2008
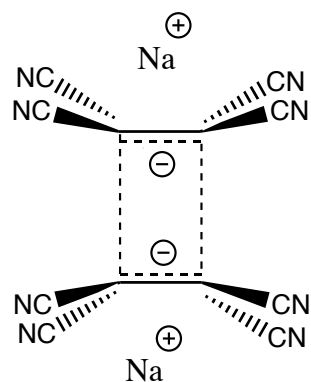
Contribution of
dynamic correlation
to bonding:
> 23 kcal/mol !

BSSE-corrected
2x2CASSCF+MP2
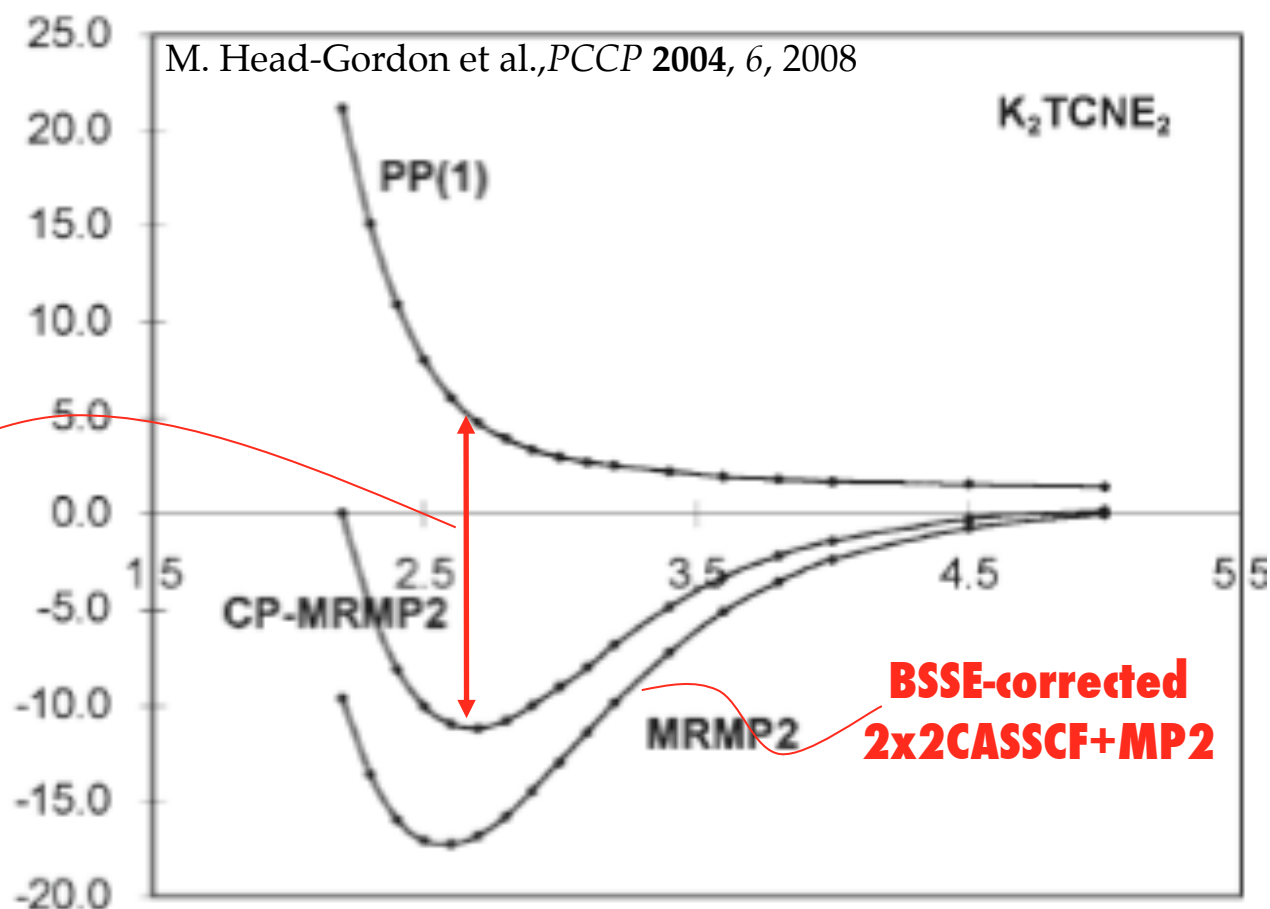
- 2x2 CASSCF describes well 2e bonds (particularly stretched...) : not the case here !

- Contribution of dynamical correlation energy huge !

Situation

- What kind of bonding in $DTCNE_2^{2-}$?
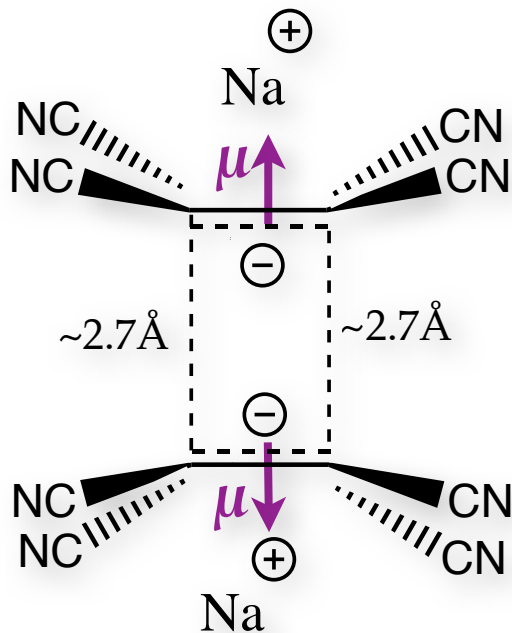
- Same bonding distance whatever the counter-ion, the environment, the system...

- 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...

$D_e \approx 11.\ kcal/mol$

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

Qualitative VB analysis

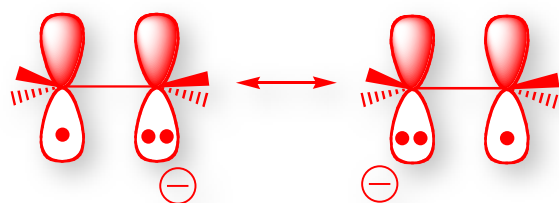- VB set of structures for $DTCNE_2^{2-}$:
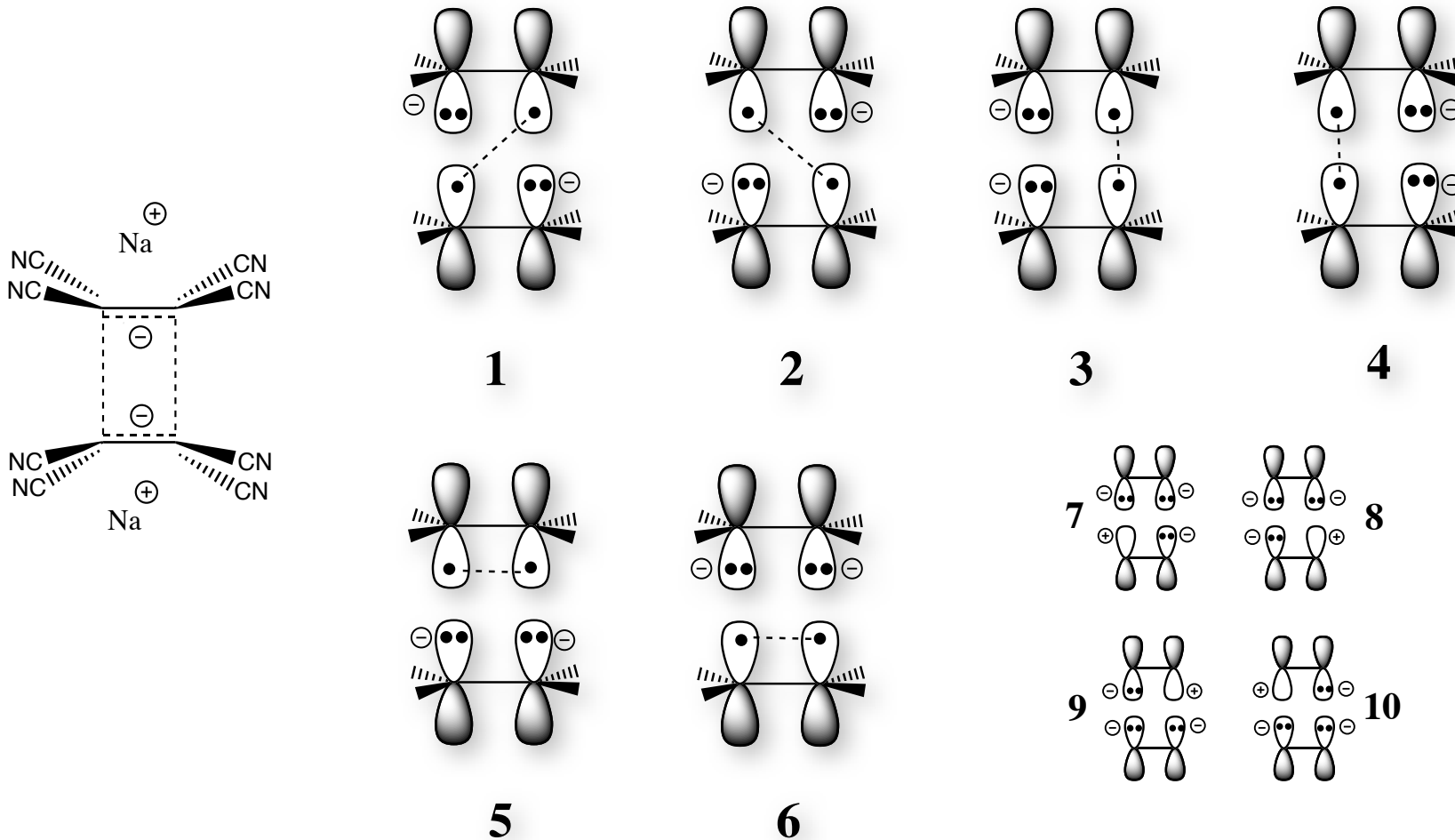
Qualitative VB analysis

- VB set of structures for $DTCNE_2^{2-}$:
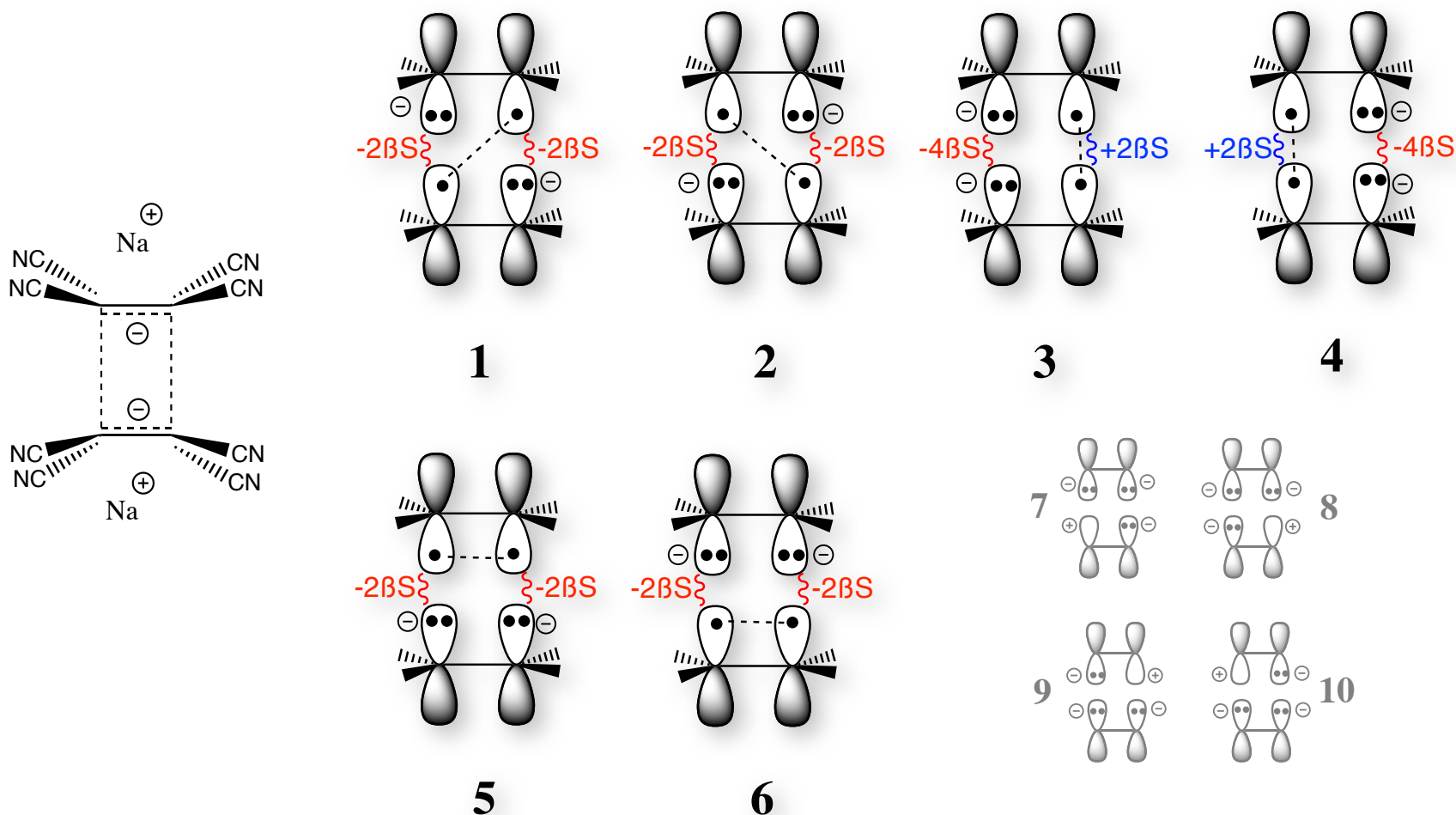
$\Rightarrow$ No structure is bonding by itself, **all the bonding comes from the resonance !**
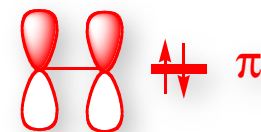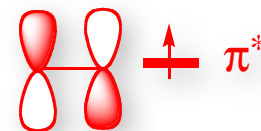
Qualitative VB analysis

- What about three-electron bonding ?...

At infinite distance, each fragment displays a **3e⁻ π bond** :
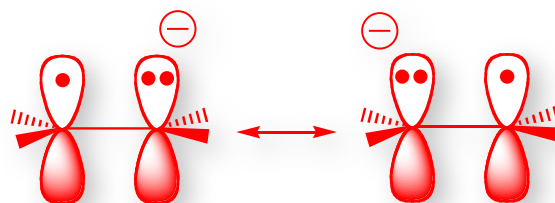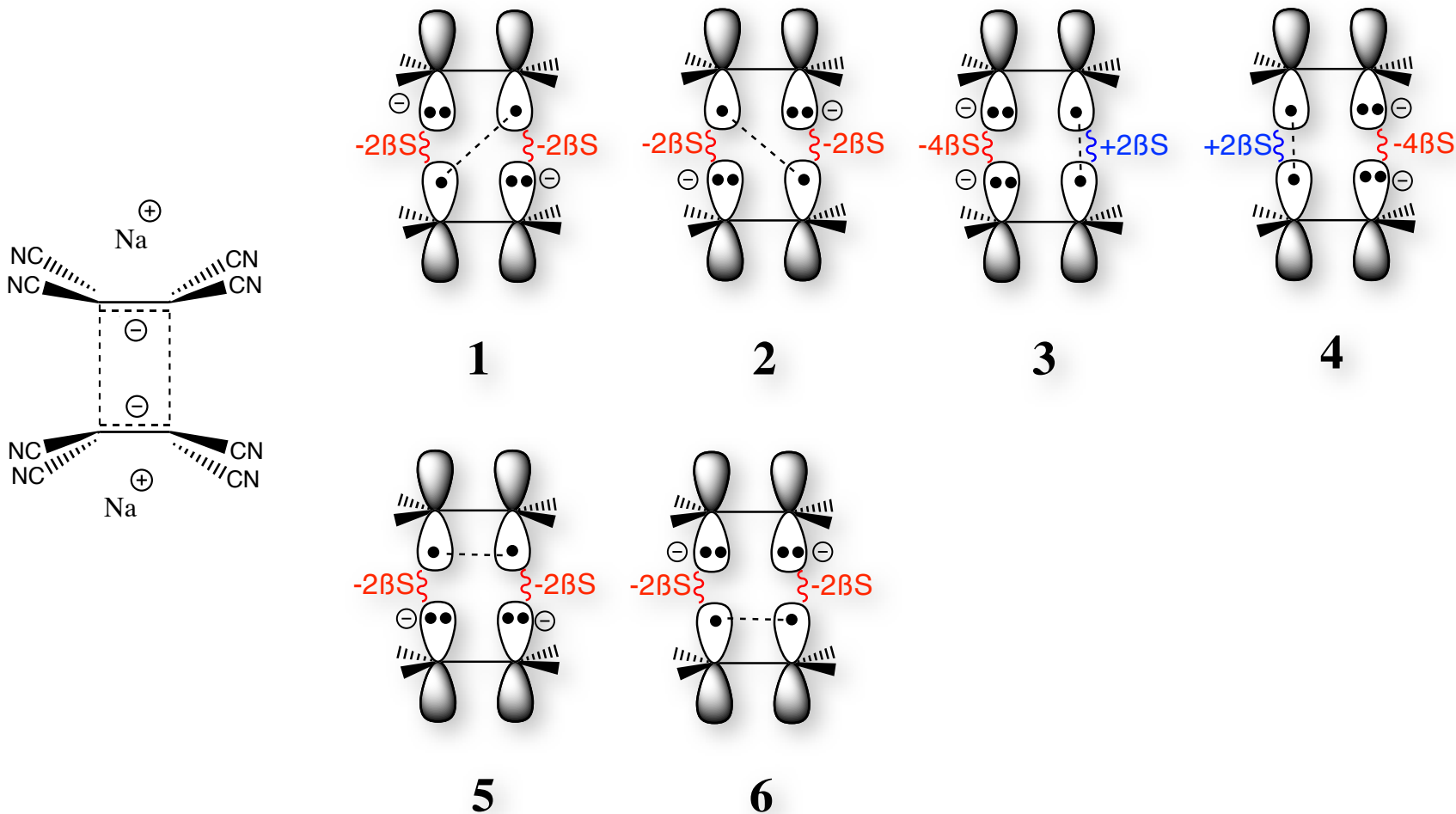
Left-right exchange of the negative charge, equivalent to:

∞

Qualitative VB analysis

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

Qualitative VB analysis

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

2   **3**   **1**   **4**

Qualitative VB analysis

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

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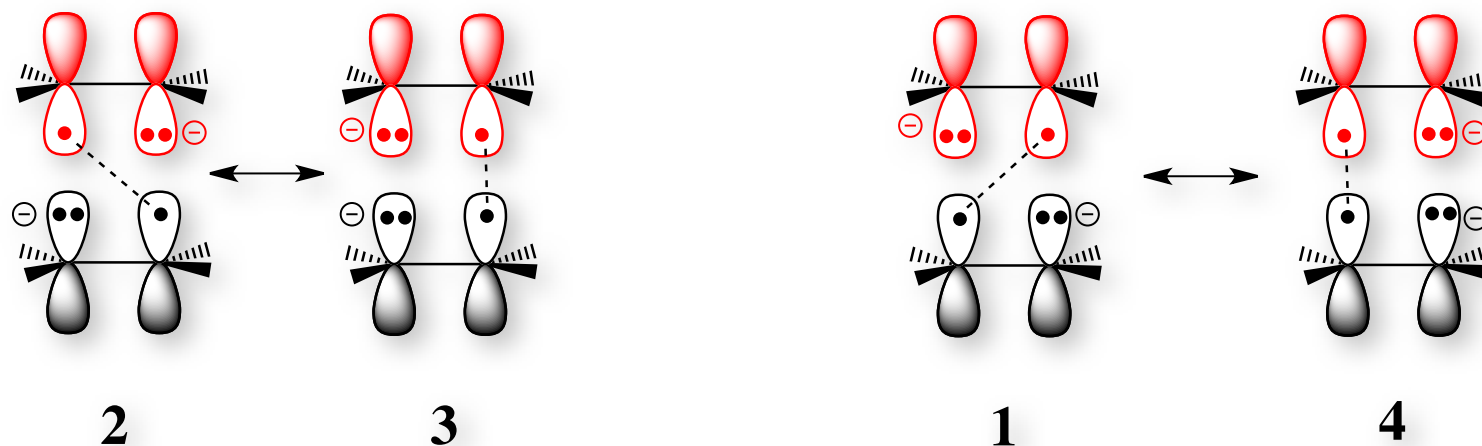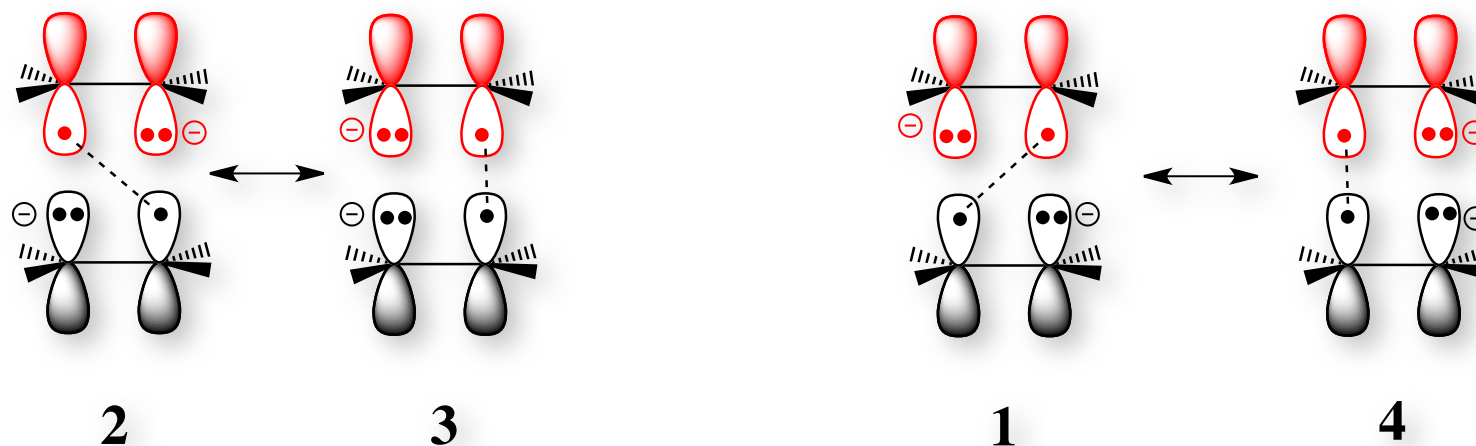
- 1↔3 and 2↔4 : **intra-fragment 3e⁻ π bond** (lower fragment) :

1   **3**   **2**   **4**
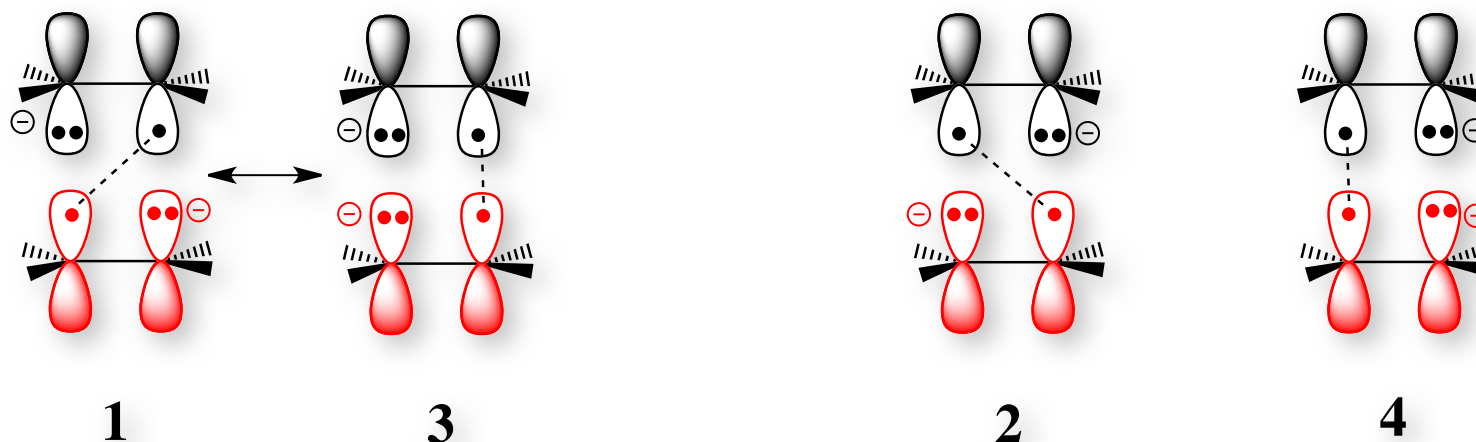
Qualitative VB analysis

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

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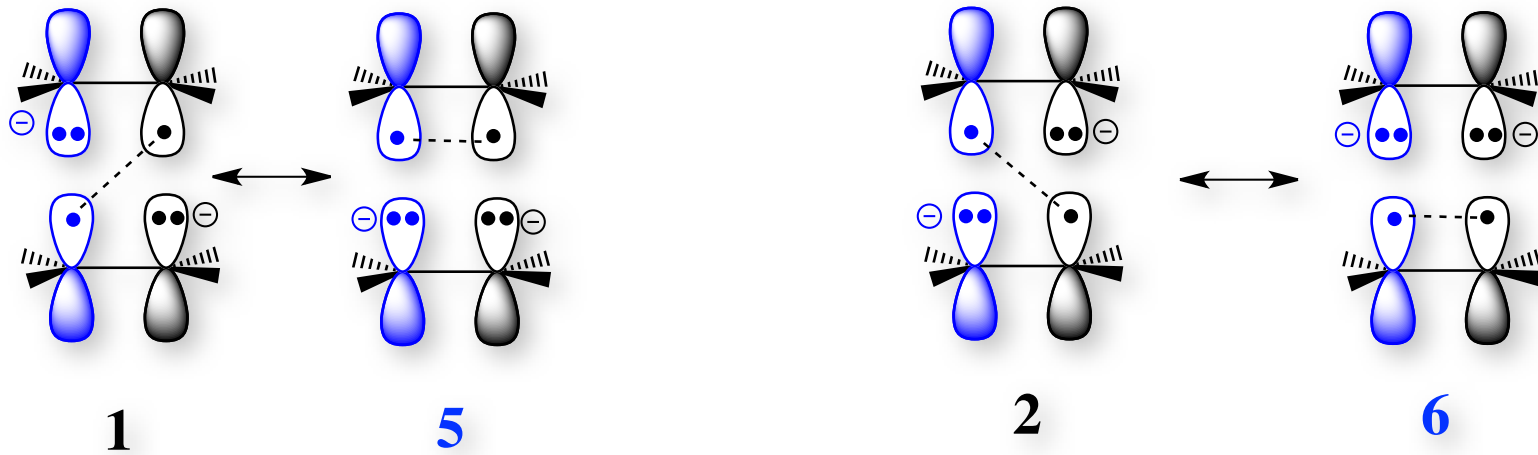
- 2↔5 and 1↔6 : **inter-fragment 3e⁻ π bond** (right-hand side) :

1   **6**   **2**   **5**

Qualitative VB analysis

Intra-fragment 3-e π bond   Inter-fragment 3-e σ bond
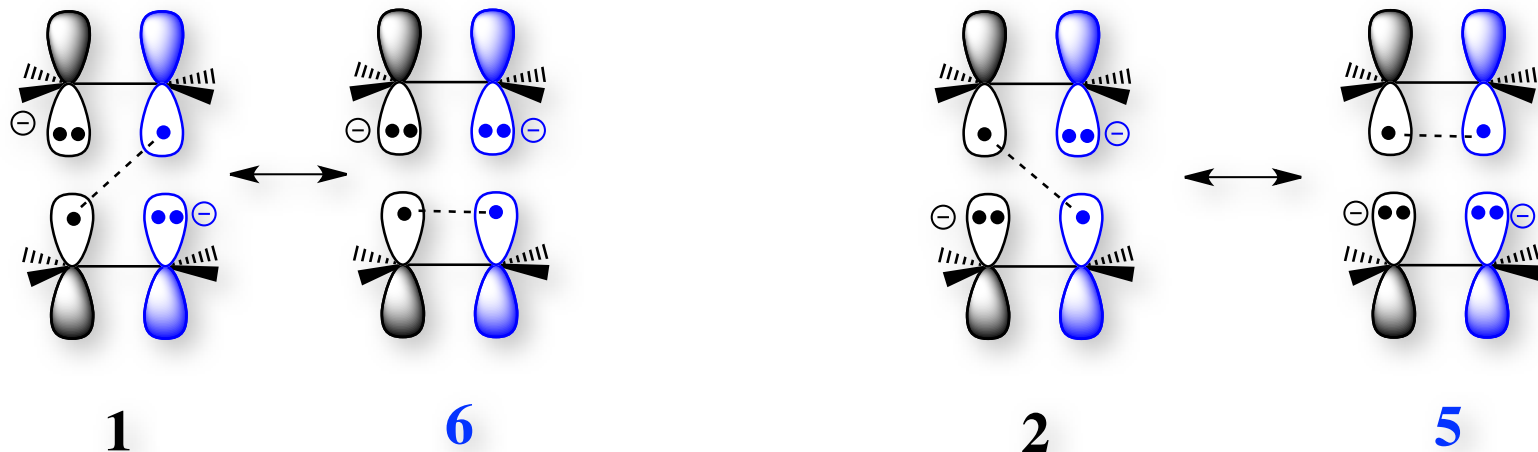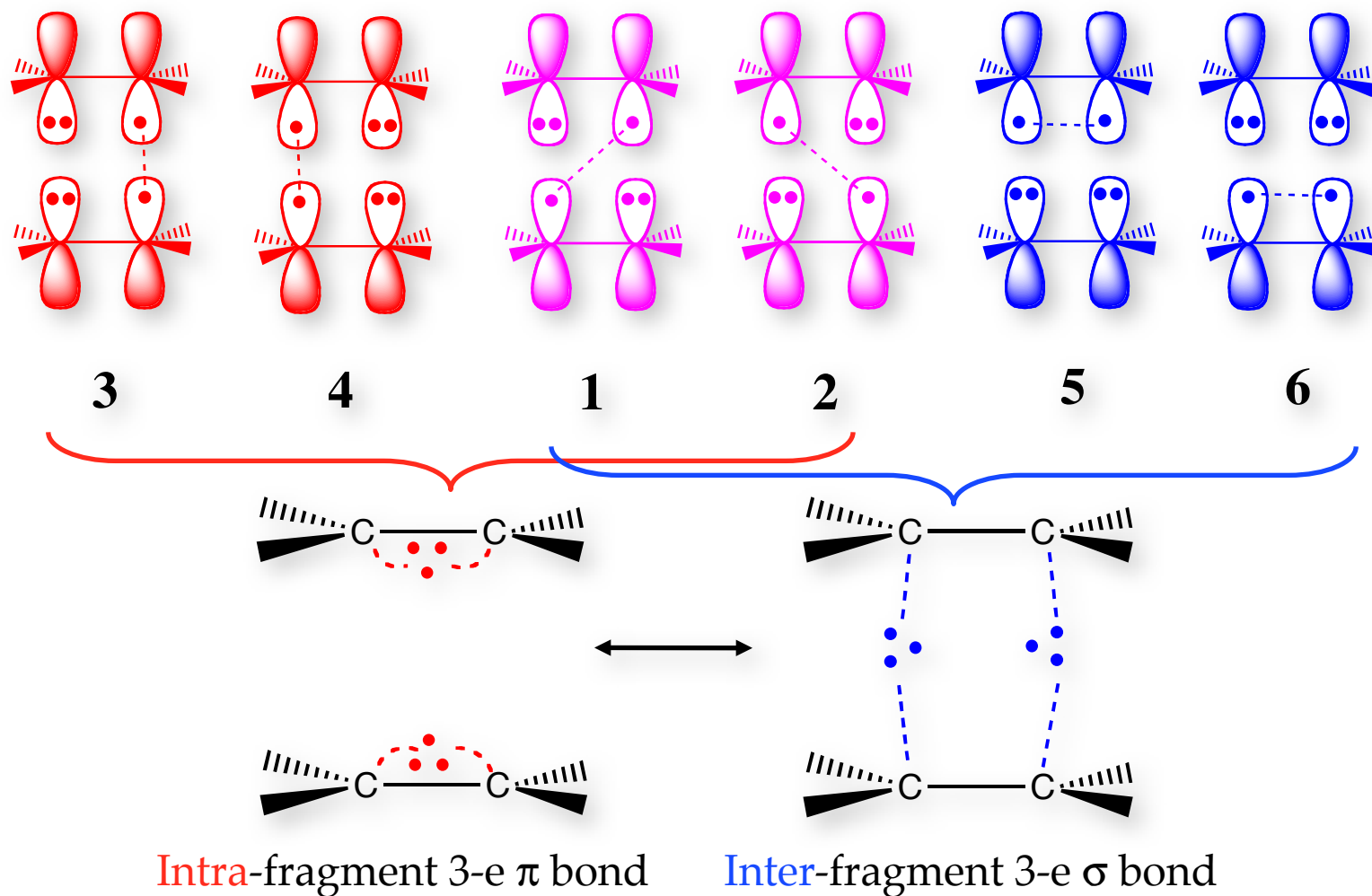
⇒ bonding in DTCNE : two inter-fragment 3e bonds ?

Ab initio VB calculations

- Some tests of credibility :

3-e π bonds ⟷ 3-e σ bonds
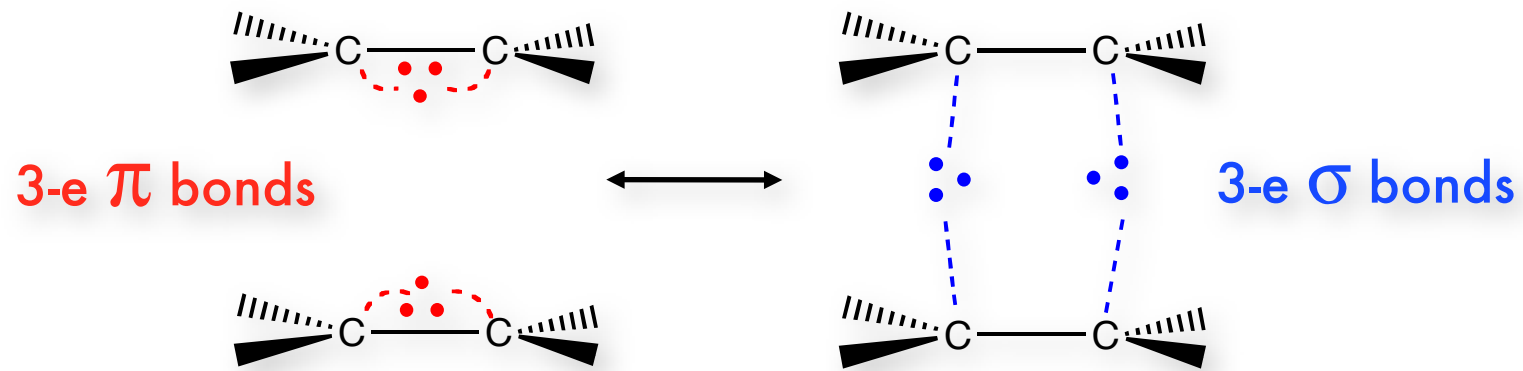
Characteristics of 3e bonds :

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

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

3) Importance of dynamical correlation

Ab initio VB calculations

3-e π bonds   ⟷   3-e σ bonds
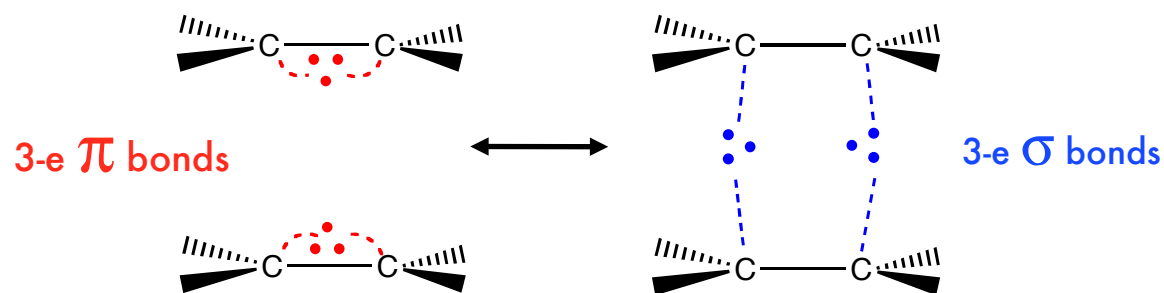
1) Interfragment bond length close to 3e⁻ bonded ethane anion :

2.65Å

~2.6Å   ~2.6Å
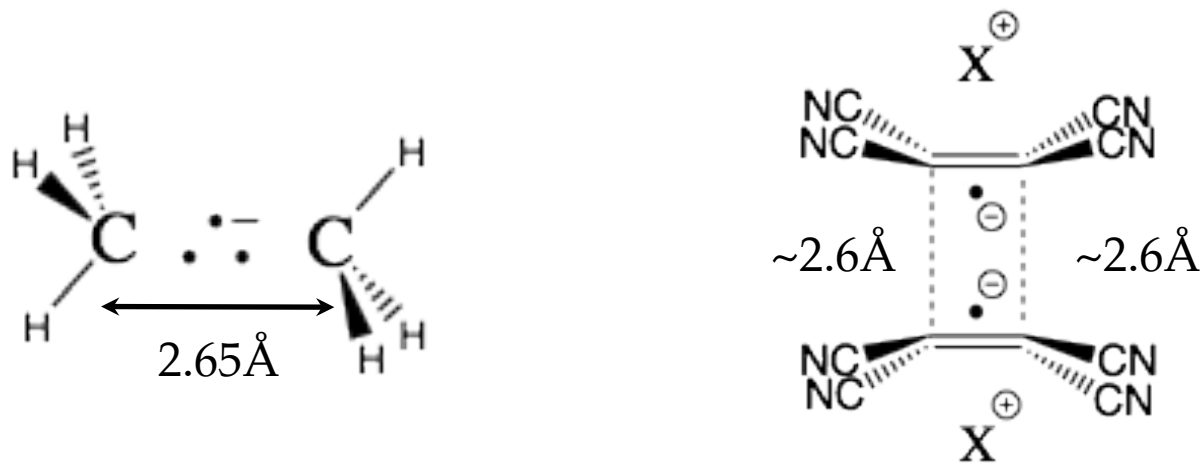
Ab initio VB calculations
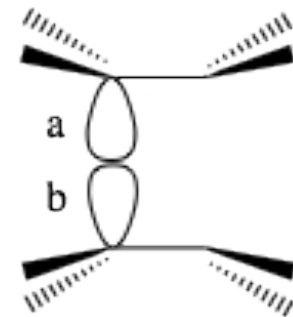

3-e π bonds   3-e σ bonds
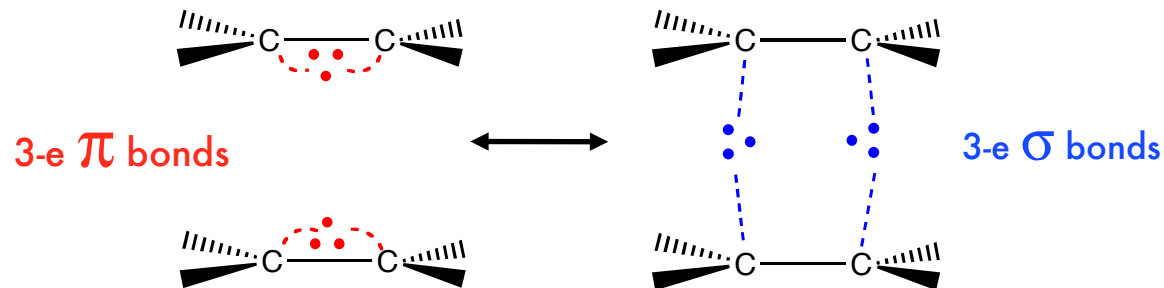
2) Interfragment orbital overlaps close to optimal 3e⁻ bond value :
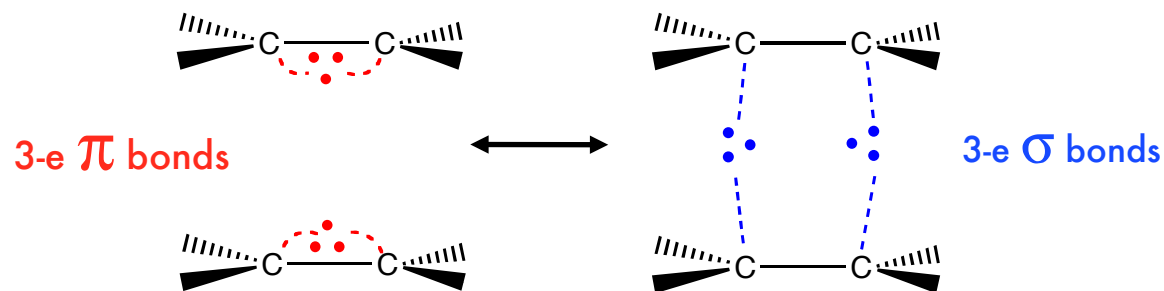
$$S_{opt} \approx 0.17$$

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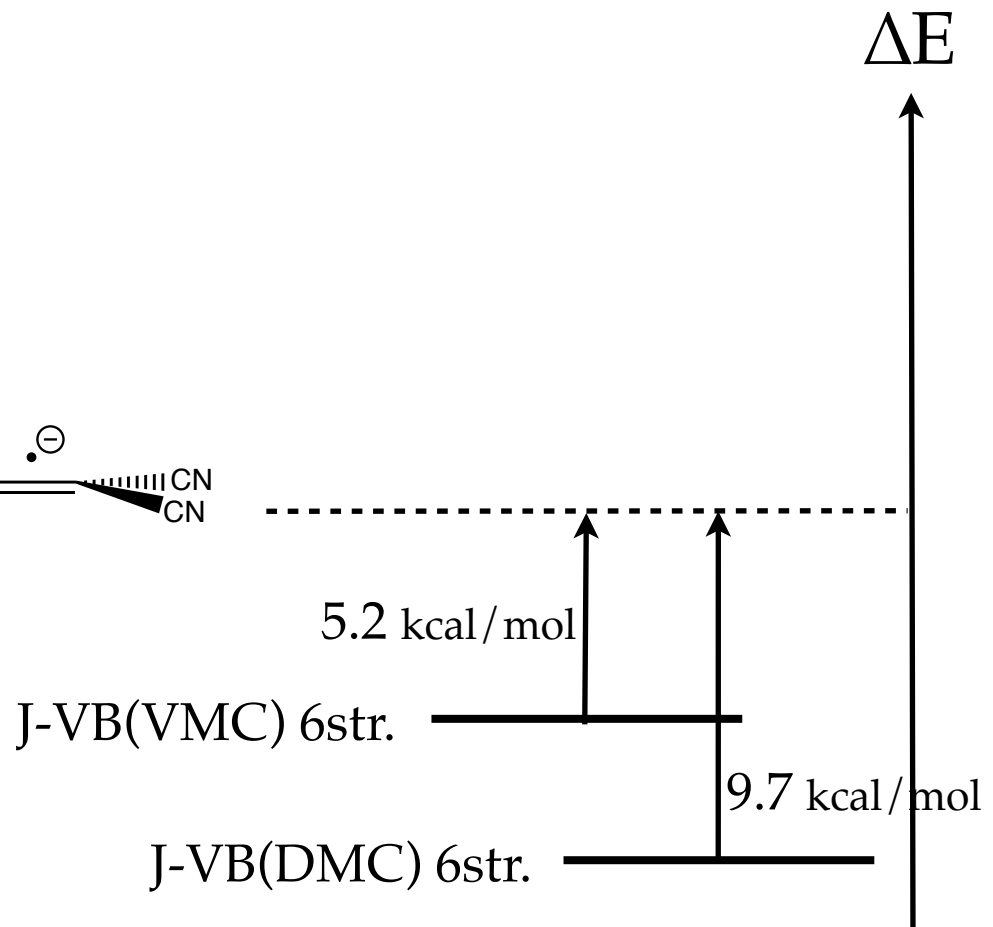as well as Extended Hückel theory)

$$S_{ab} = 0.15$$

(computed)

a

b

Ab initio VB calculations

3-e π bonds   3-e σ bonds

3) Contribution of dynamic correlation to bonding:

- In $[F \therefore F]^-$, dynamic correlation contributes ~ 30 kcal/mol to bonding

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

Ab initio VB calculations

$1 \leftrightarrow 2 \leftrightarrow 3 \leftrightarrow 4$ $1 \leftrightarrow 2 \leftrightarrow$ **5** $\leftrightarrow$ **6**

ΔE

2x

5.2 kcal/mol

J-VB(VMC) 6str.

9.7 kcal/mol

J-VB(DMC) 6str.
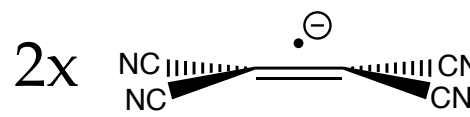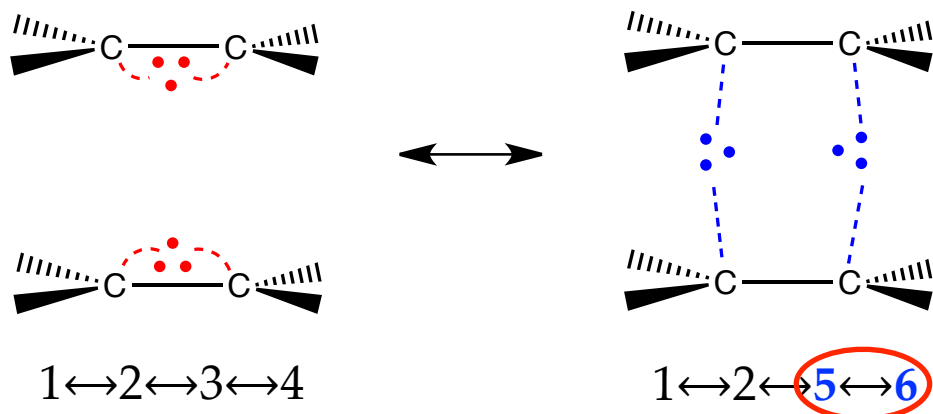
ΔE(«reference») ≈ 11. kcal/mol

Ab initio VB calculations

1↔2↔3↔4

1↔2↔**5**↔**6**

ΔE

J-VB(VMC)
1↔2↔3↔4

10.6 kcal/mol

2x

5.2 kcal/mol

J-VB(VMC) 6str.

9.7 kcal/mol

J-VB(DMC) 6str.
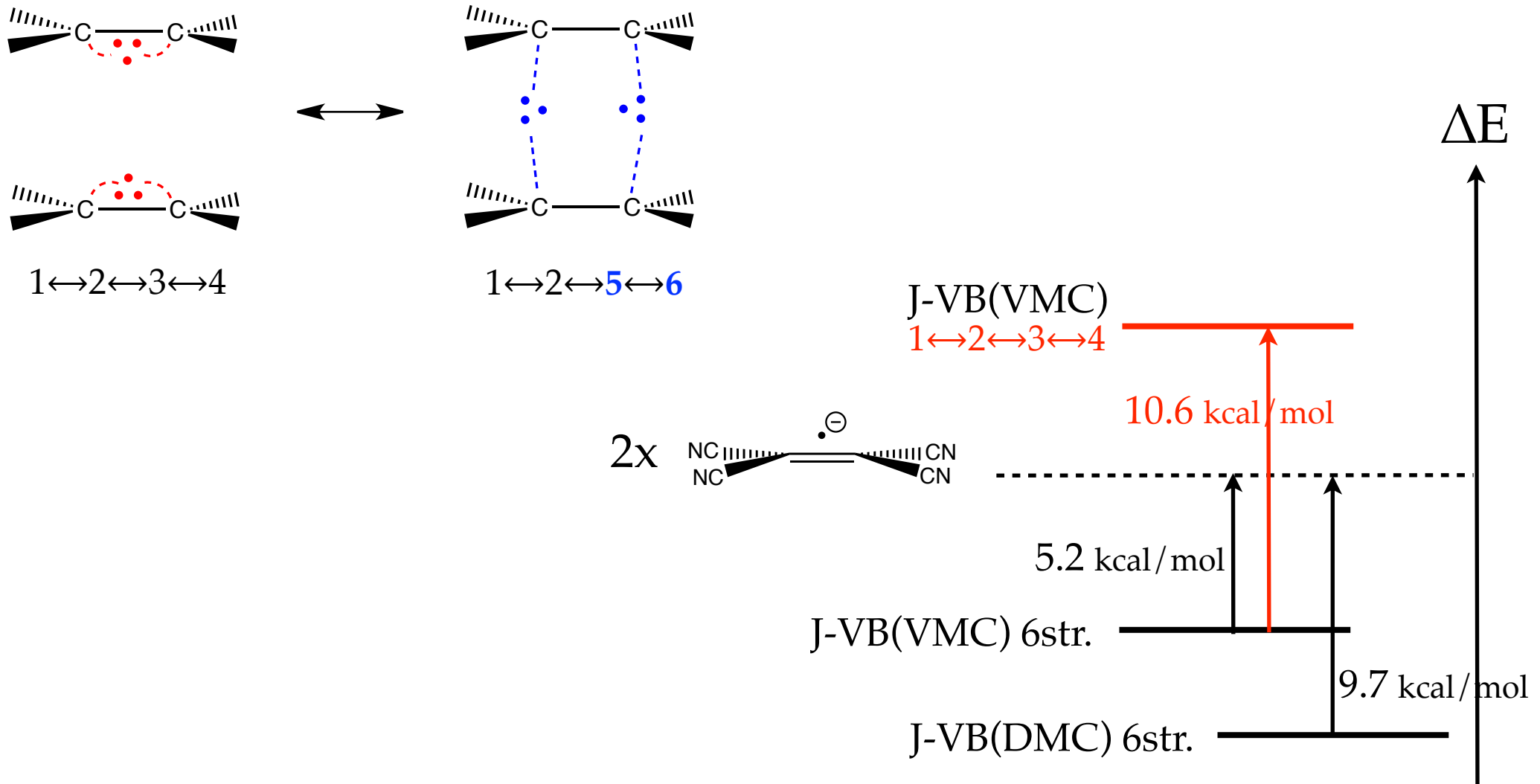
⟹ Without str. 5-6, DTCNE becomes repulsive !

Conclusion

- About $[TCNE]_2^{2-}$:
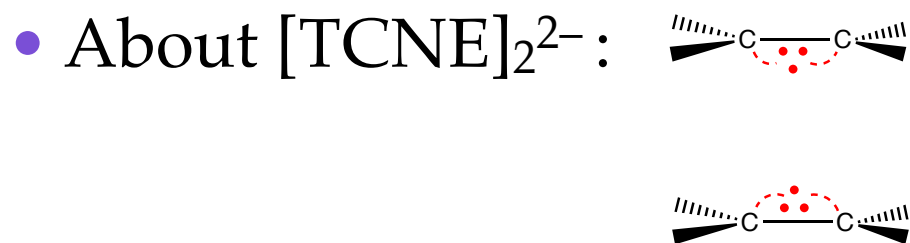
- Even when electrostatic interaction is repulsive (axial conformation), the two fragment anions are directly bonded by **a pair of 3-e bonds**

- 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.

B Braida,* K Hendrickx, D Domin, J. P. Dinnocenzo, and P. C. Hiberty* JCTC 2013, 9, 2276−2285