Part 3. Qualitative Valence Bond

Qualitative VB

- **Basic ingredients :**

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

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

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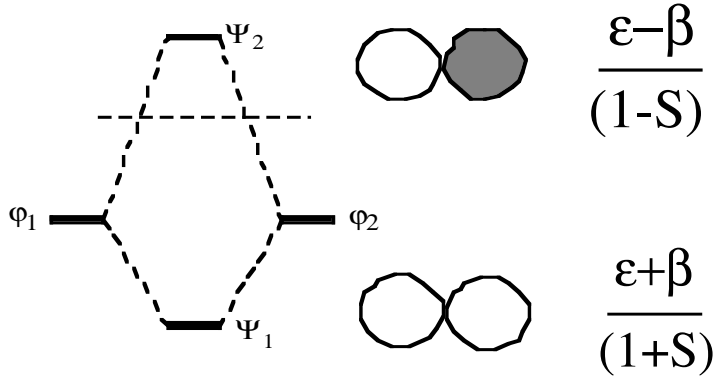
2) Parametrization : ε, β, **S**

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

Same as in Hückel theory :



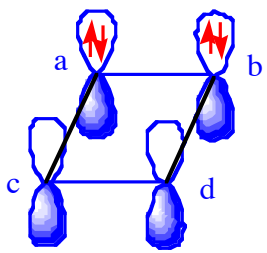
Qualitative VB

- **General calculus rules :**

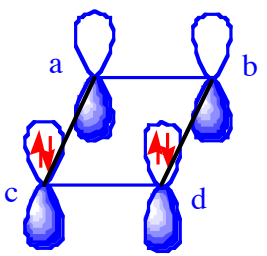
  1) Rule for calculating determinant overlaps :

Generate permutations :

- between identical spins
- only one side



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



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

Qualitative VB

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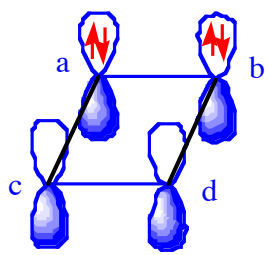

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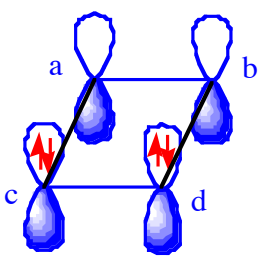

$|c\bar{c}d\bar{d}|$

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

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

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

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

Qualitative VB

- **General calculus rules :**

  2) Rule for calculating Hamiltonian matrix elements :

  Generate permutations :

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

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

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

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

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

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

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Then repeat :

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

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

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

Quite tedious !

Qualitative VB

- **Simplified expressions :**

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

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

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Example :

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

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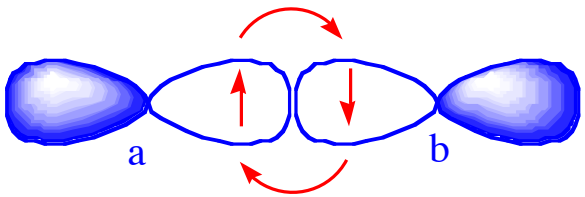
2) Approximations :

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

Qualitative VB

- **Elementary interactions energies :**



1) The two electron bond :

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

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

Qualitative VB

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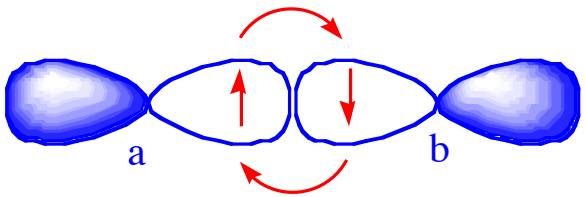

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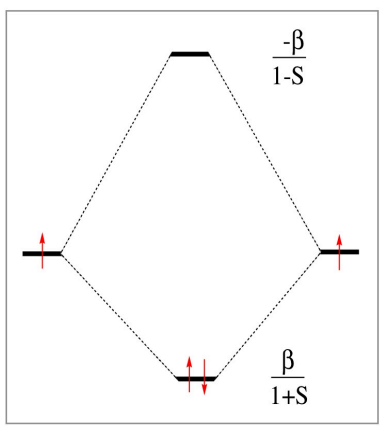
$$\Rightarrow E(2e) = \frac{+2\beta S}{1+S^2} = D_e(2e)$$

Different in MO-Hückel theory :

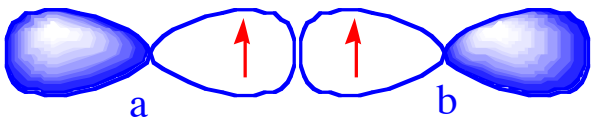


$D_e = 2\beta/(1+S)$

Qualitative VB

- **Elementary interactions energies :**

2) The triplet (2e) repulsion :

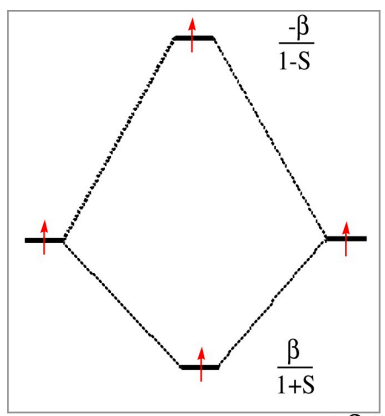


$$\Psi_T = \frac{|a\bar{b}| - |b\bar{a}|}{\sqrt{2(1-S^2)}}$$

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

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

Same in MO-Hückel theory :



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

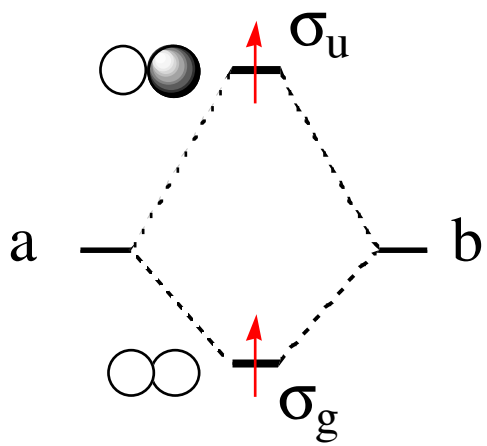
Qualitative VB

- **Elementary interactions energies :**

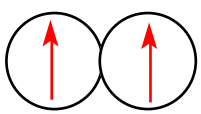
2) The triplet (2e) repulsion :

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

MO



VB



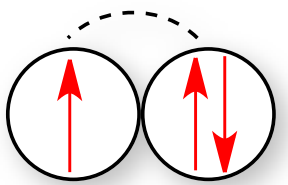
$$\psi_{VB} \propto |ab|$$

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

Qualitative VB

- **Elementary interactions energies :**

3) The 3e repulsion :



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

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

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

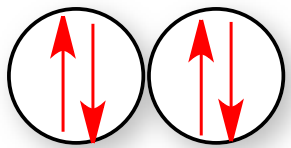
$$\Rightarrow E(3e_{rep}) = \frac{-2\beta S}{1-S^2}$$

Same as triplet

Qualitative VB

- **Elementary interactions energies :**

4) The 4e repulsion :



➡ **Exercise 3 :**

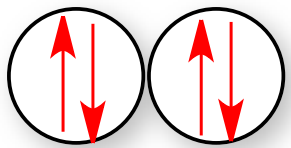
1) Calculate the energy expression of the 4e repulsion at the qualitative VB level.

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

Qualitative VB

- **Elementary interactions energies :**

4) The 4e repulsion :



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

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

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

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

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

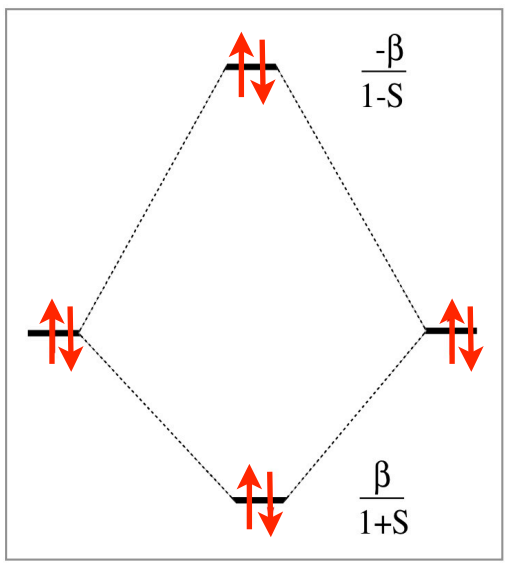
Double as triplet and 3e repulsion

Qualitative VB

- **Elementary interactions energies :**

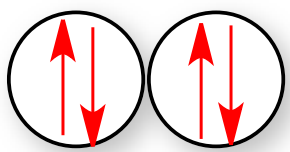
4) The 4e repulsion :

MO



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

VB



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

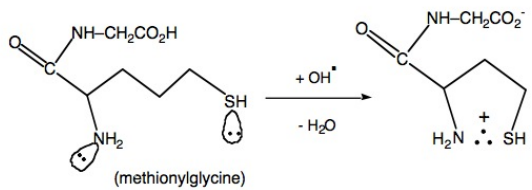
$$E(4e_{rep}) = \frac{-4\beta S}{1-S^2}$$

Qualitative VB

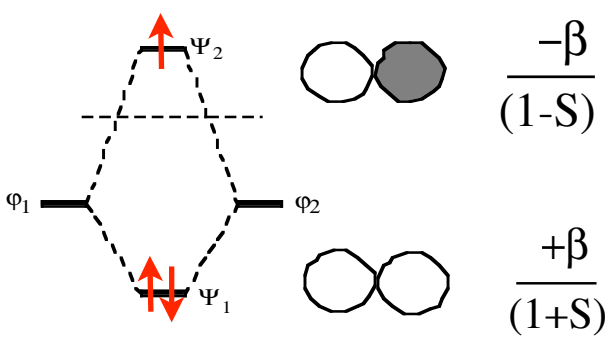
- **Elementary interactions energies :**

5) The 3e bond :

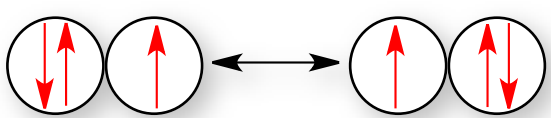
Examples : He_2^+, $RS^{\ominus}\therefore SR'$,
radical intermediates :



MO



VB



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

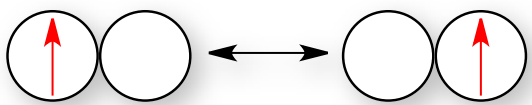
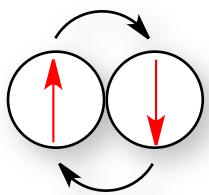
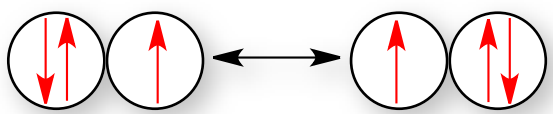
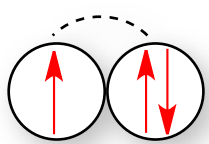
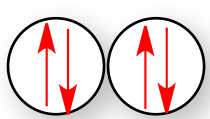
$$\Psi_{MO} \propto |\sigma\bar{\sigma}\sigma^*| = |(a+b)\overline{(a+b)}(a-b)^*| = \ldots = -|a\bar{a}b| - |b\bar{b}a| \propto \Psi_{VB}$$

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

Remind for later use !

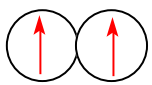
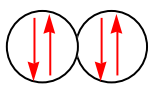
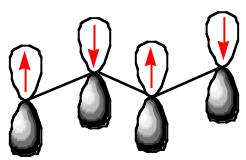
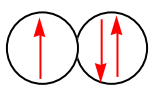
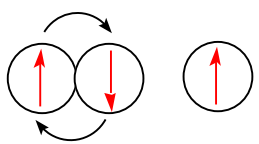
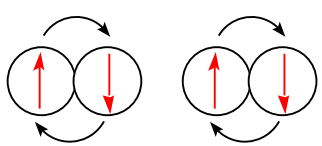
Qualitative VB

- **Elementary interactions energies :**

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

Qualitative VB

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

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

Qualitative VB

- **Elementary interactions energies :**

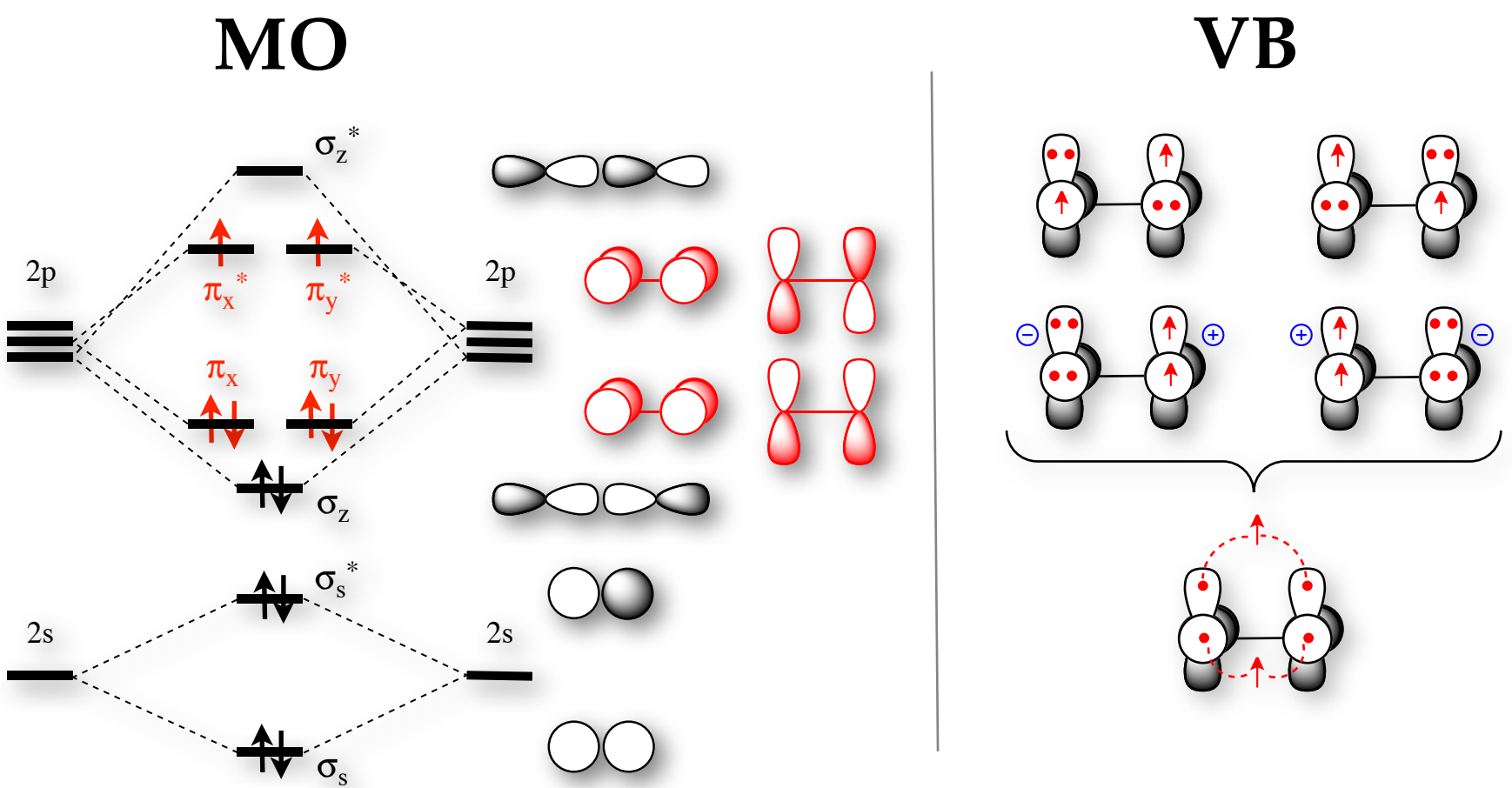
Energy of a determinant with *n pairs of interacting* e^- : $\sigma 2n\beta S$ ☞

σ sign : + if attractive, – if repulsion

Qualitative VB

- **Illustration : ground state of O_2 :**

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



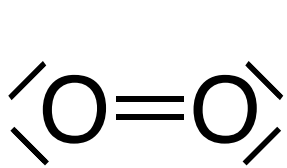
Qualitative VB

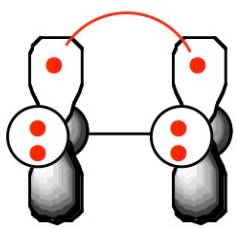
➡ **Exercise 4 : ground state of O_2 :**

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

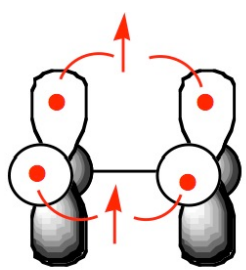
2) Same question for the closed-shell singlet state, corresponding to the usual Lewis structure used for this molecule.

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





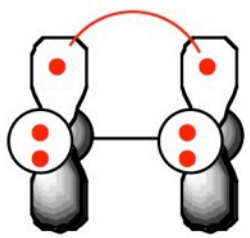
Singlet



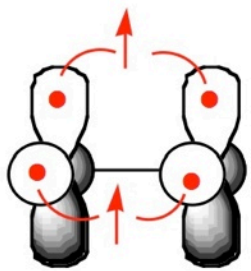
Triplet

Qualitative VB

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



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



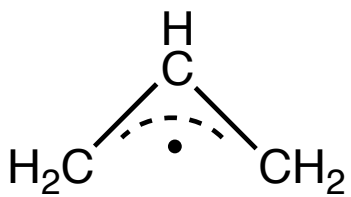
$$E(T) = 2\beta\,(1 - 3S)/(1-S^2)$$

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

➡ *The triplet state is always the lower*

Qualitative VB

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



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

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

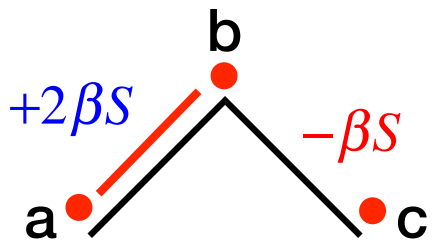
2) Show that the third structure can be expressed as a linear combination of the first two structures, and thus that only two of the three covalent structures form a complete basis of non-redundant structures (Rumer basis).

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

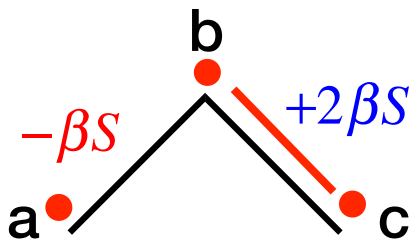
Continuation of the exercise : https://wiki.lct.jussieu.fr/workshop/index.php/VBTutorial2

Qualitative VB

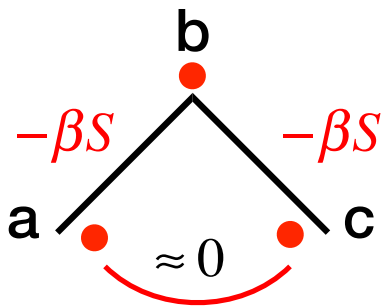
➡ **Exercise 5 : spin polarization in allyl radical :**



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



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

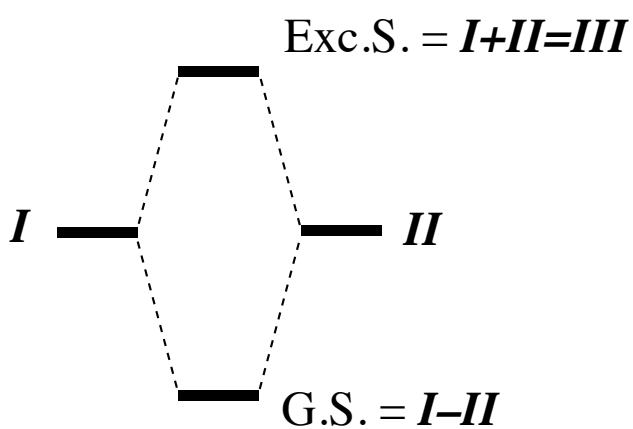


$\Rightarrow E(III) = -2\beta S$

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

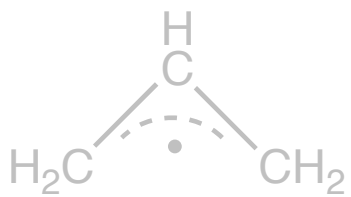
$$\psi(II) = \frac{1}{\sqrt{2}}(|ab\bar{c}| + |ac\bar{b}|)$$

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



Qualitative VB

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



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

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

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

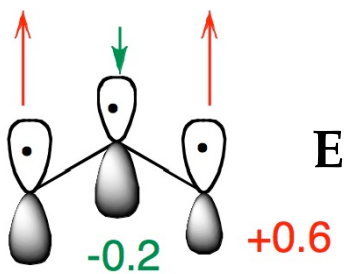
3) EPR measurements show that the spin density on the central atom is +0.2, whereas a value of -1. is predicted at the RHF level. Express the HL w.f. corresponding to the ground state, and calculate the predicted spin density.

Qualitative VB

➡ Exercise 5 : spin polarization in allyl radical :

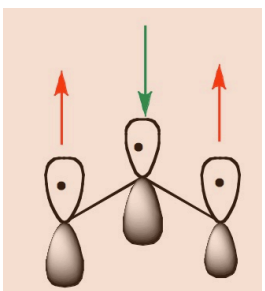
$$\psi_{GS} = \frac{1}{\sqrt{6}}(2|a\bar{b}c| + |b\bar{a}c| + |a\bar{c}b|)$$

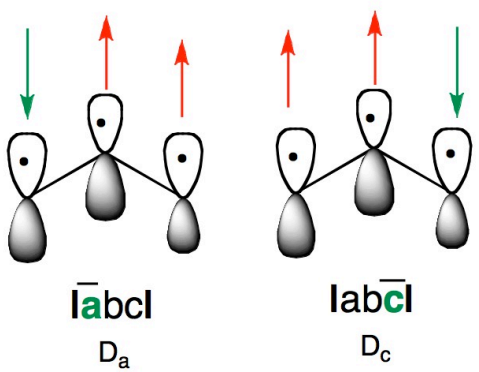
Spin density on center b : $\rho_b = \underbrace{c_2^2 + c_3^2}_{\text{alpha spin on b}} - \underbrace{c_1^2}_{\text{beta spin on b}} = -0.33$



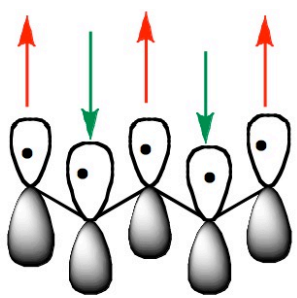
EPR

$\Rightarrow$ much closer to experiment than RHF (and also UHF)





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

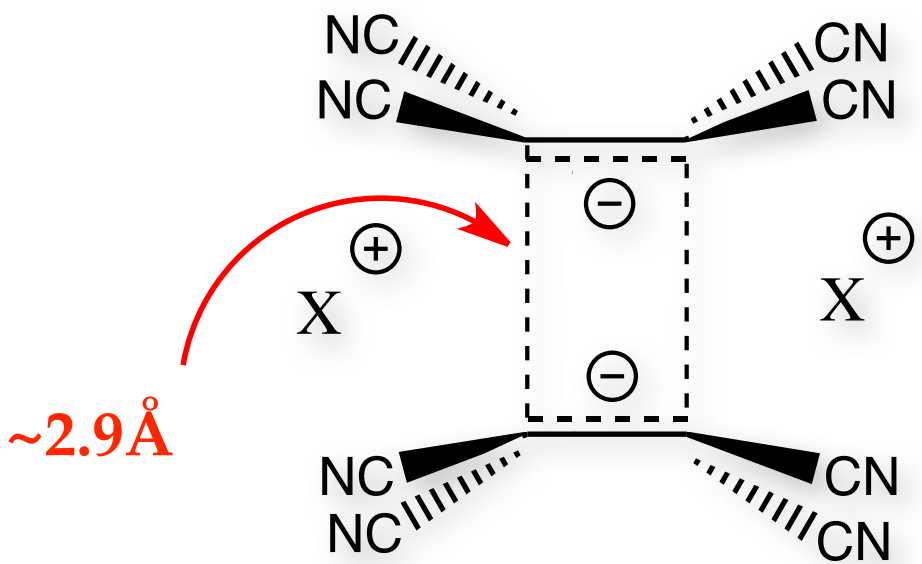


☞ General rule, works for all polyenes

Application
Electronic structure of the DTCNE dimer

«Pancake bonding»

- $DTCNE_2^{2-}$:



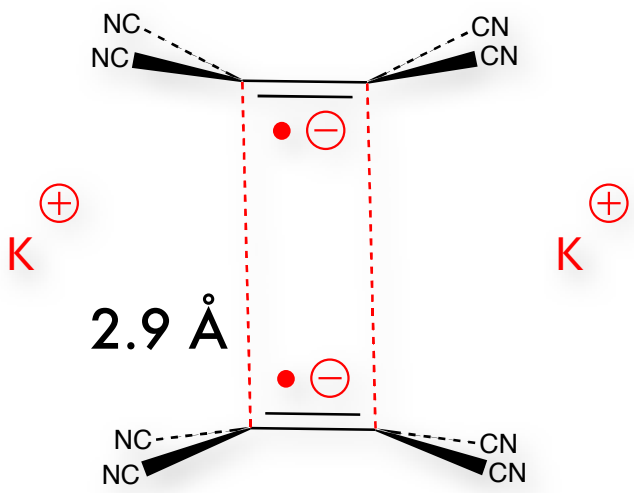
X^+ : Na^+, Cs^+, $[iPr_4N]^+$, $[Cr(C_6Me_3H_3)_2]^+$, ...

Electrostatic complex ?...

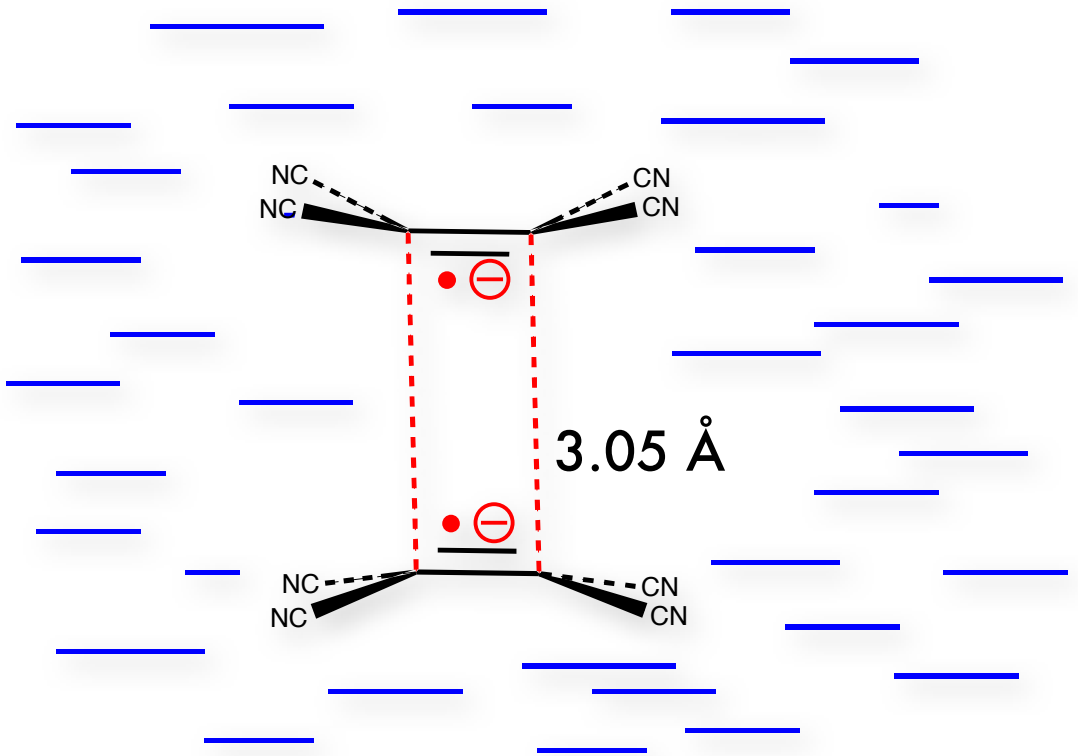
- Strong bonds
- Same bonding distance whatever the size of the cations !

«Pancake bonding»

- $DTCNE_2^{2-}$:



Stable in the crystal



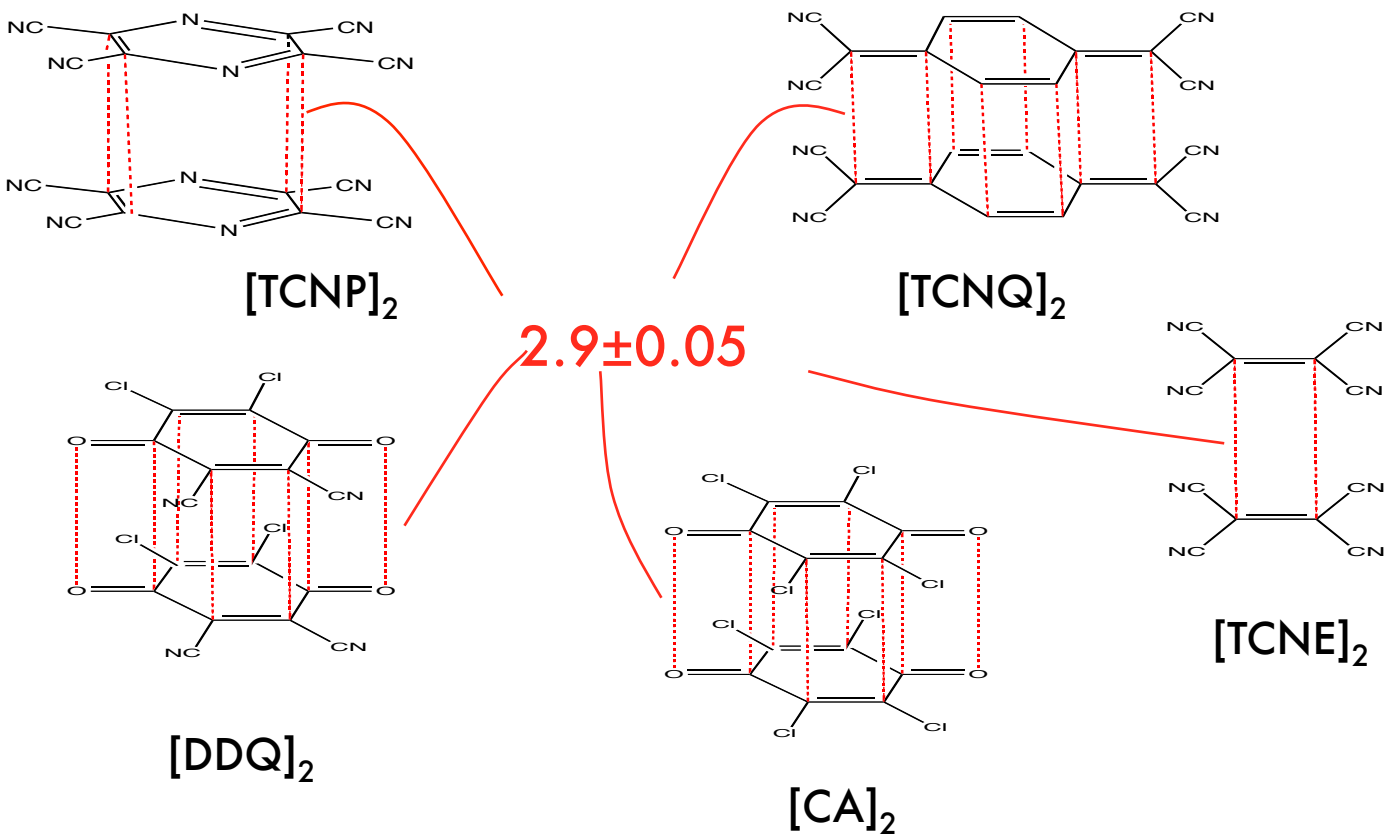
Stable in solution

- Same bonding distance whatever the environment !

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

«Pancake bonding»

- Other «pancake bonding» systems :

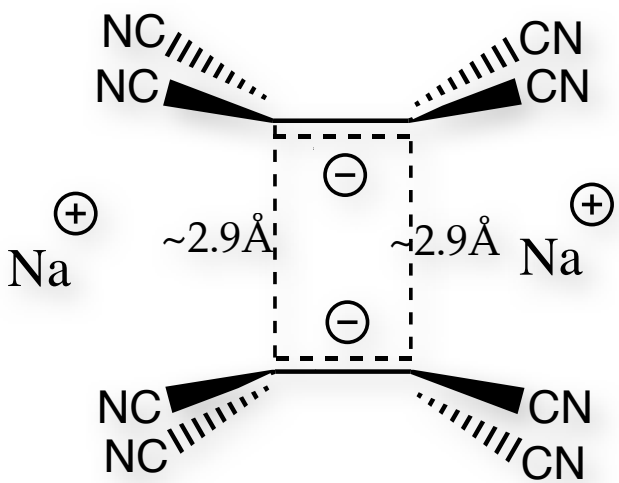


- Same bonding distance whatever the system !

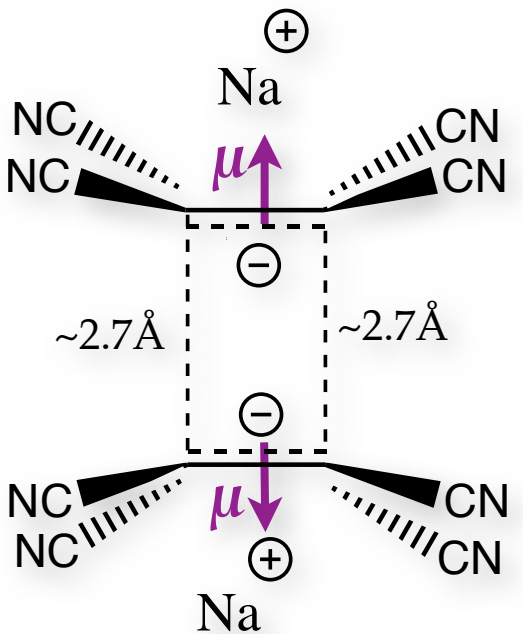
- $d_{C\text{---}C}$ < sum of vdW radii (3.45Å) , but much longer than C-C 2e bonds (1.54Å)

«Pancake bonding»

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



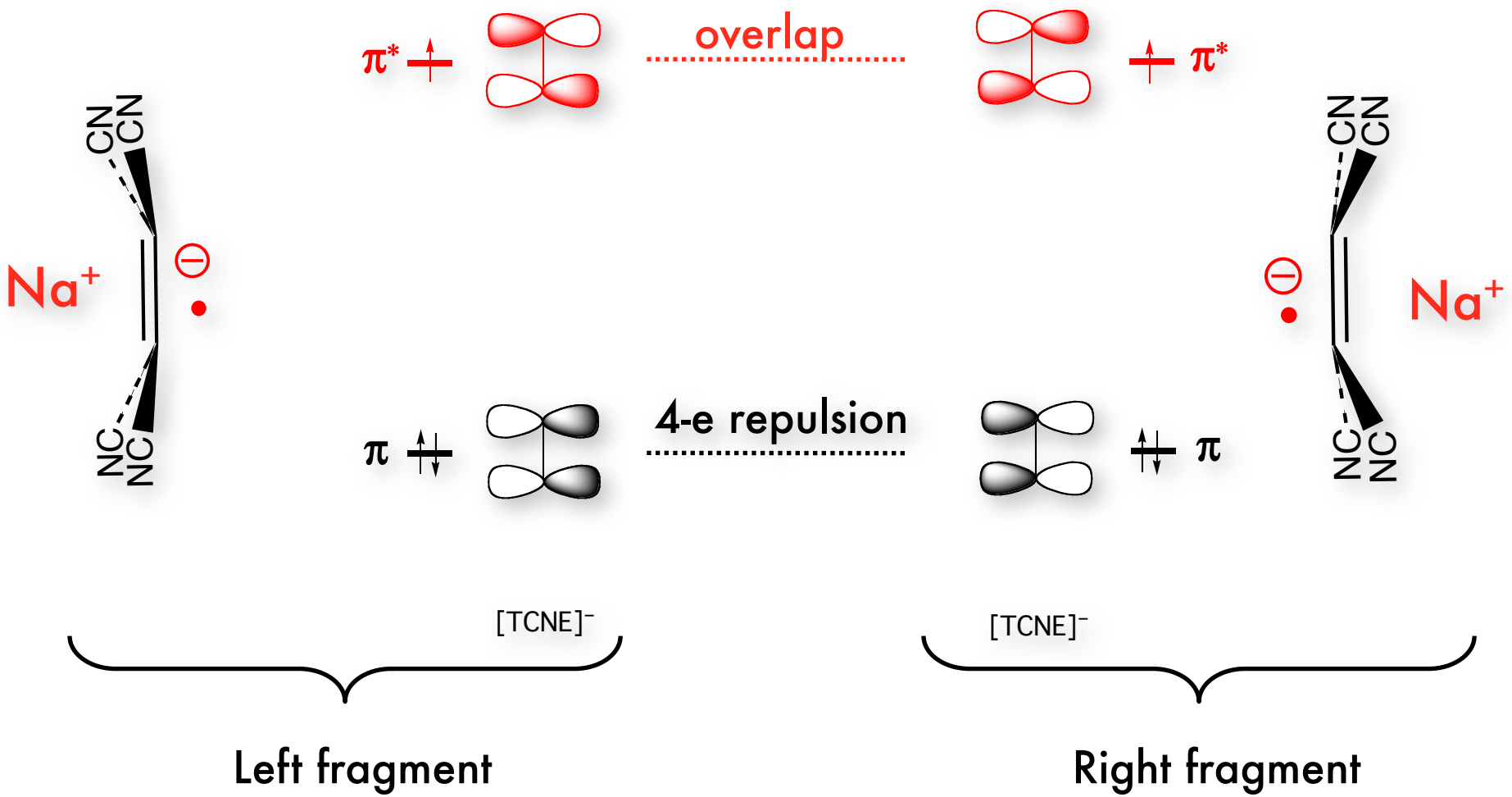
$D_e \approx 80.\ kcal/mol$



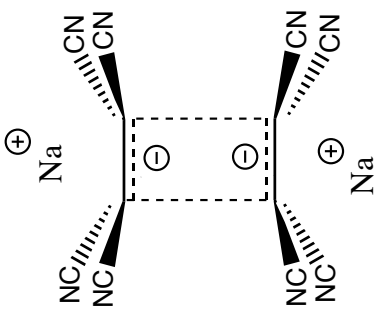
$D_e \approx 11.\ kcal/mol$!

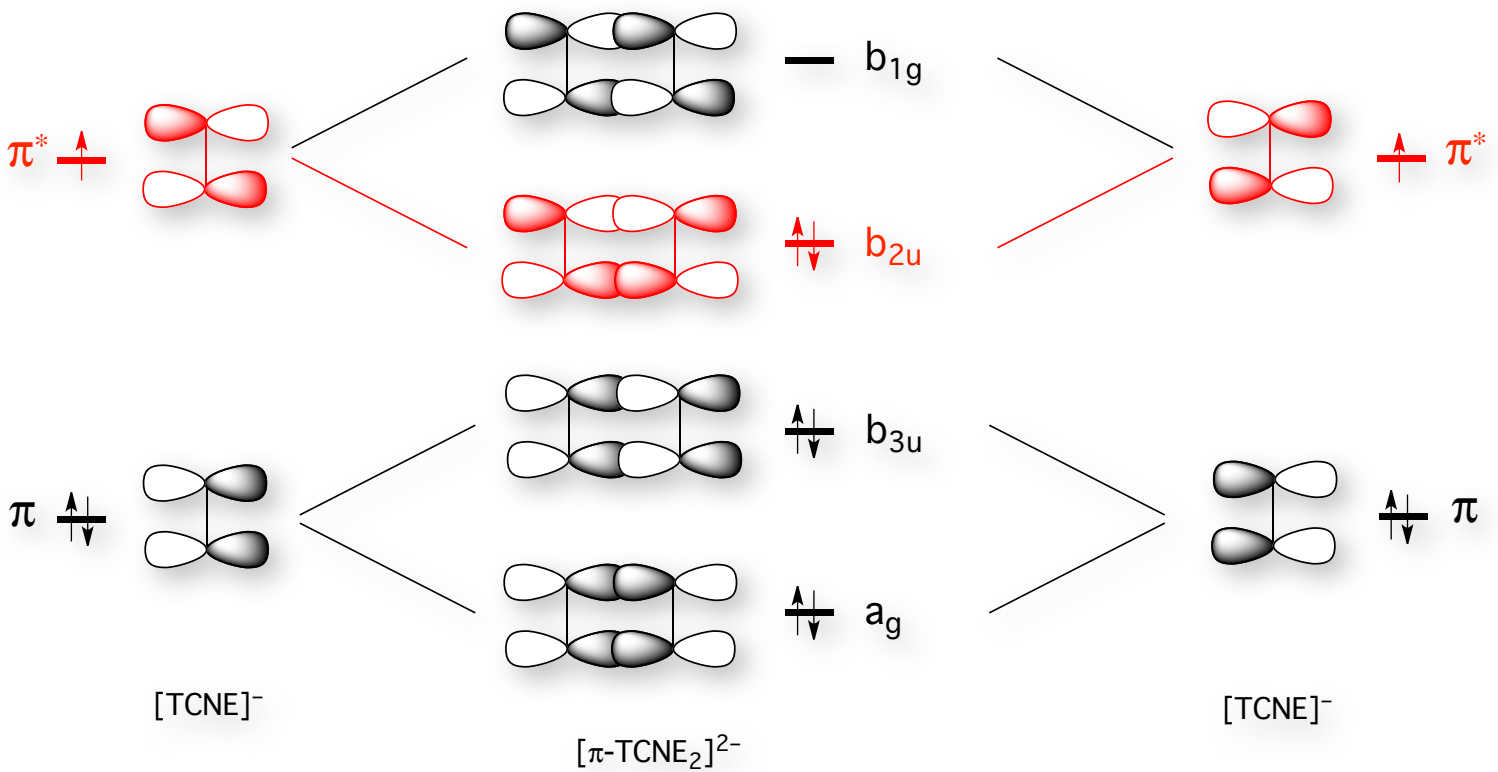
Right geom : significant bonding force overcome repulsive electrostatics !

Qualitative MO analysis



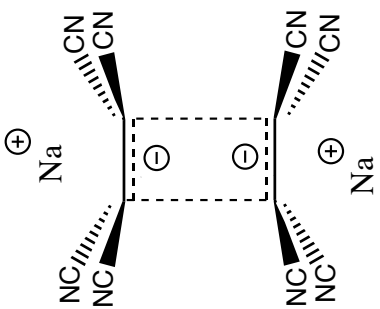
Qualitative MO analysis

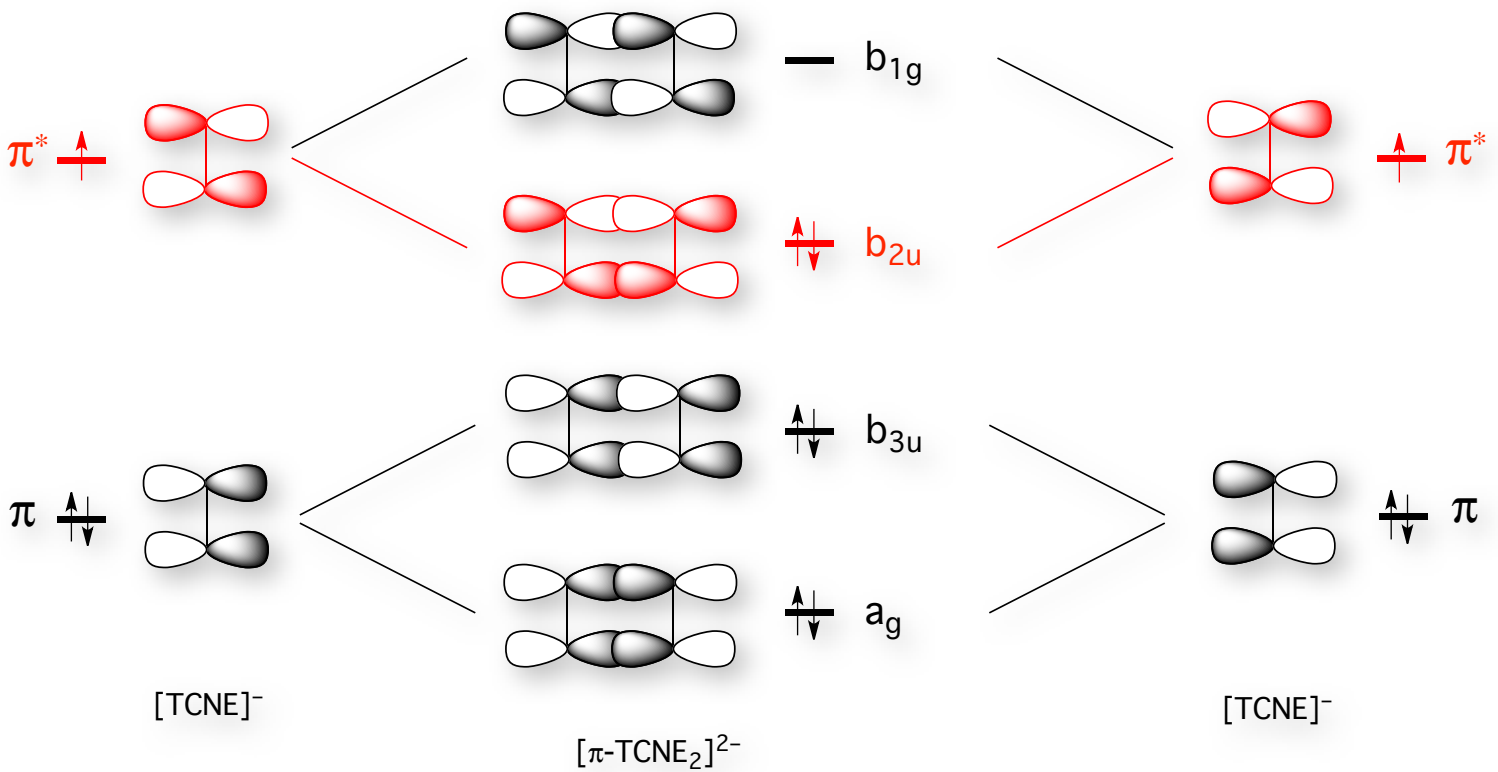




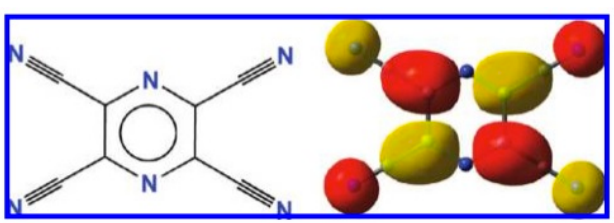
⟹ a simple **4 centers / 2 electrons bond ?**

Qualitative MO analysis

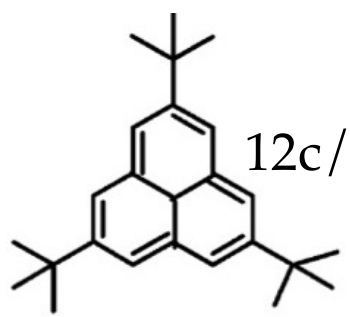




Other «pancake bonding» systems : **n center / 2e⁻ bonds**



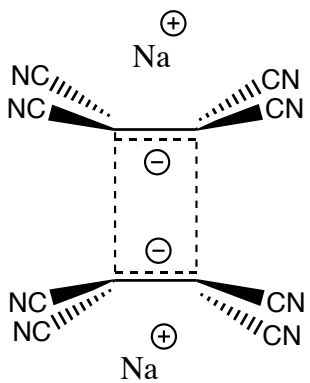
8c/2e⁻



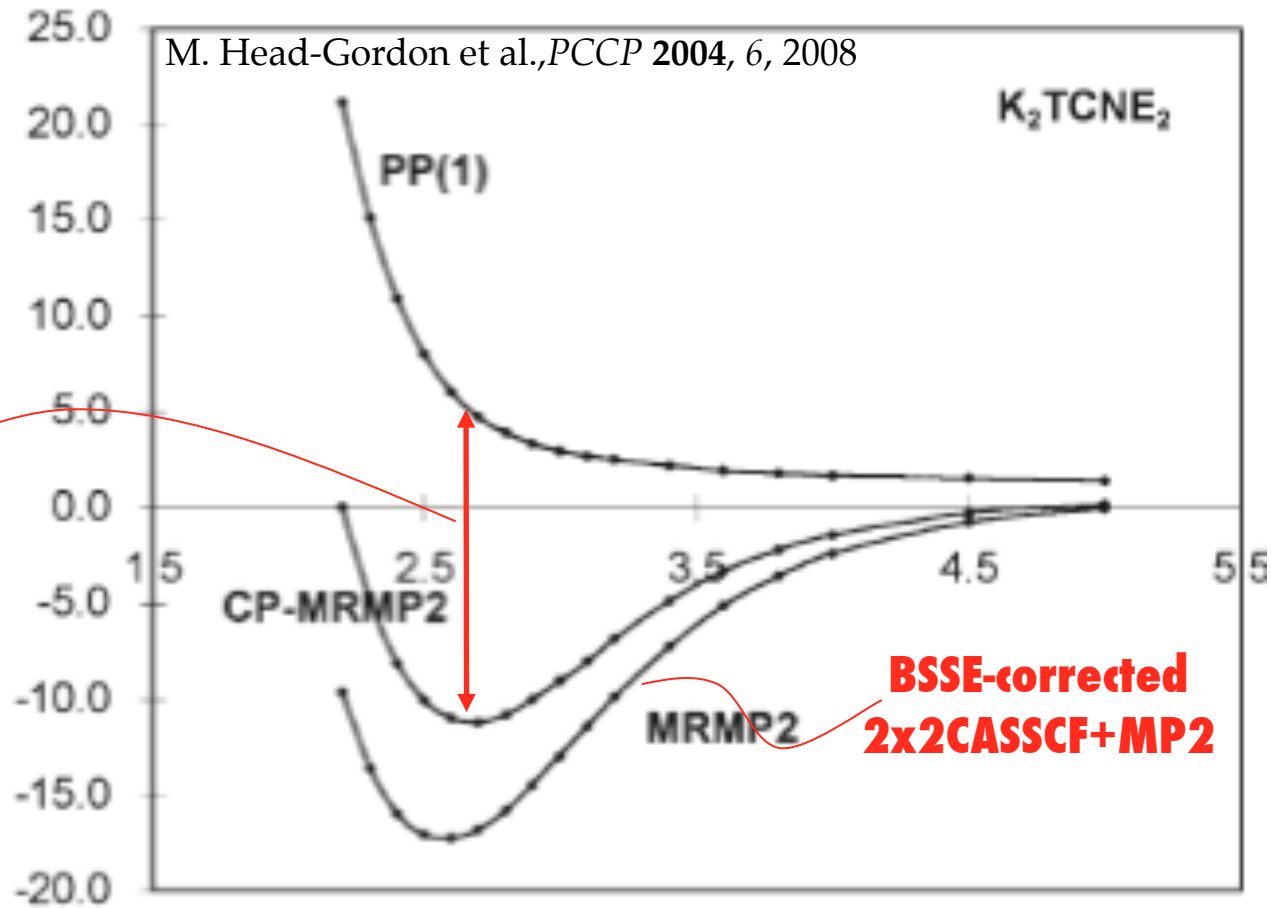
12c/2e⁻

Quantitative MO computations

- GVB calculations of the axial conformation :



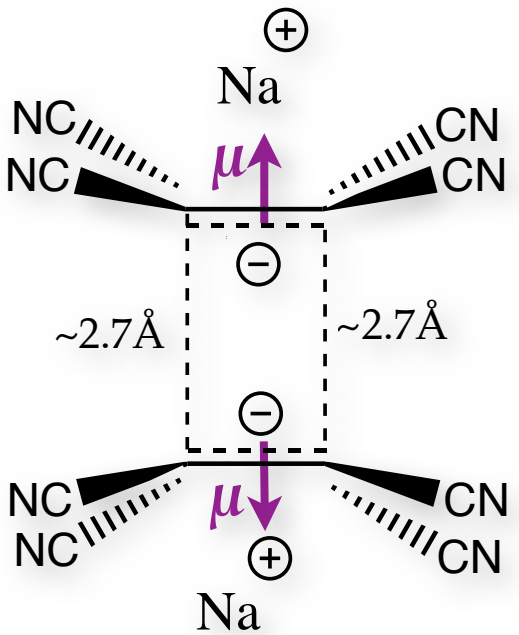
Contribution of dynamic correlation to bonding: > 23 kcal/mol !



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

Situation

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



$D_e \approx 11.$ *kcal/mol* !

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

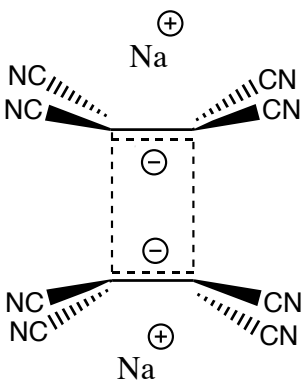
- MO analysis propose a 4c/2e bond, but GVB-PP fails to account for any bonding...

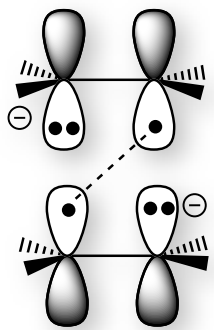
- Distance too short, bond energy too strong to be dispersion...

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

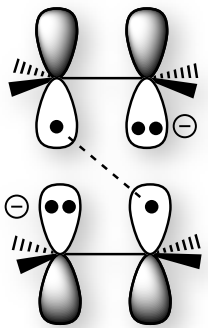
Qualitative VB analysis

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





1



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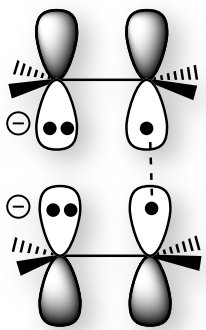

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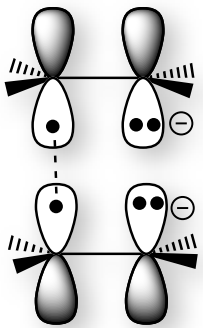

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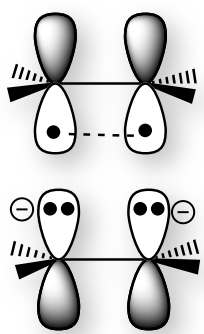

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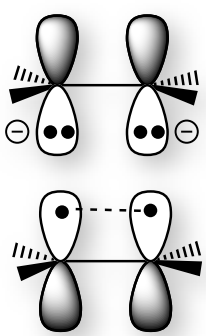

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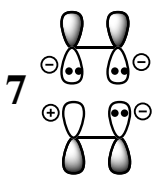

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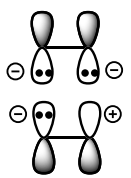
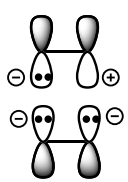


8



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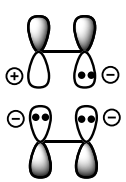
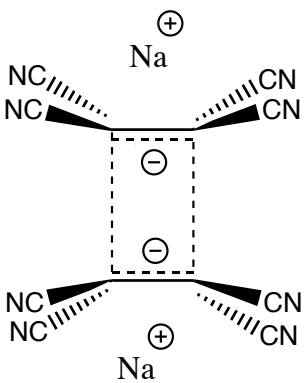
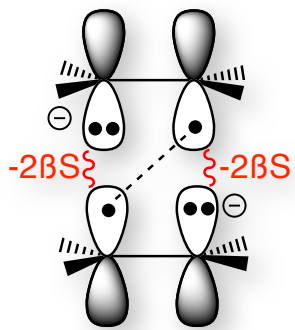


10

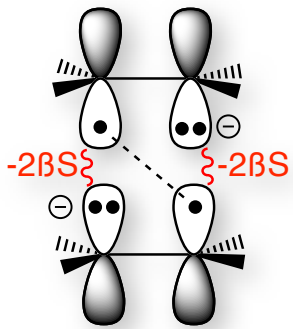
Qualitative VB analysis

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

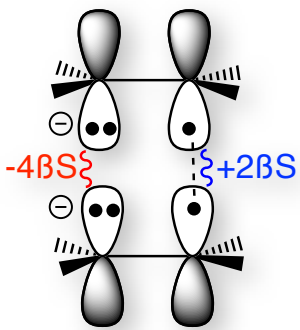




1



2



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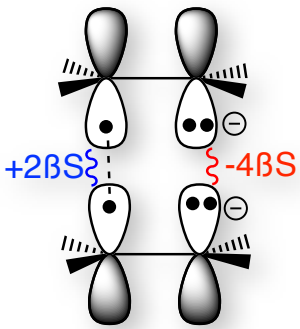

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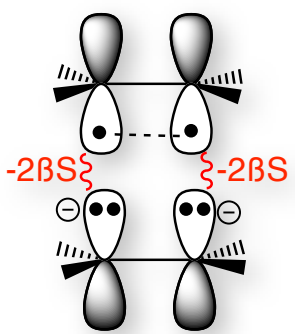

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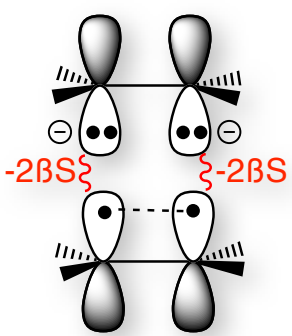

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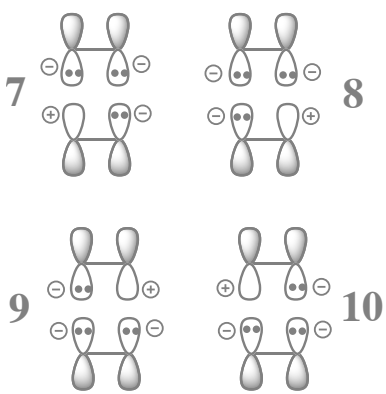
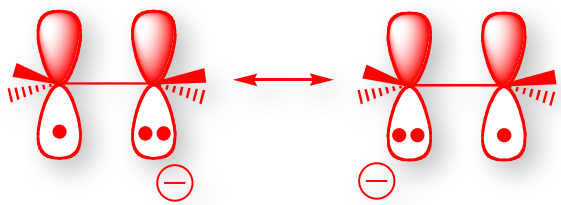


⟹ No structure is bonding by itself, **all the bonding comes from the resonance !**

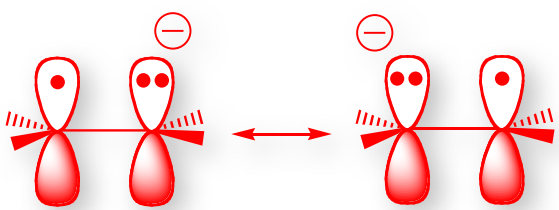
Qualitative VB analysis

- What about three-electron bonding ?...

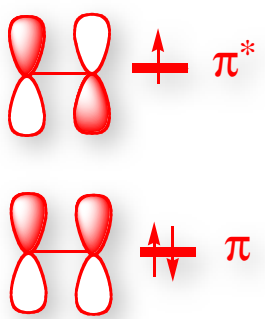


At infinite distance, each fragment displays a **3e⁻ π bond** :

∞

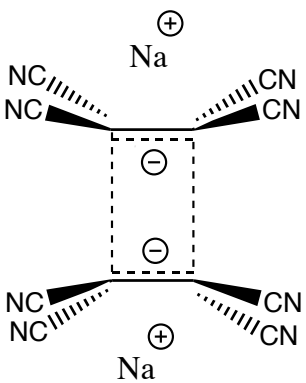


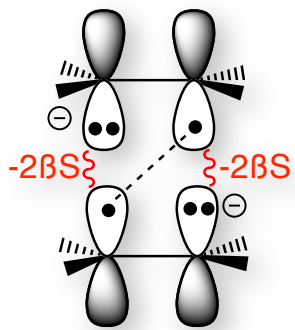
Left-right exchange of the negative charge, equivalent to:



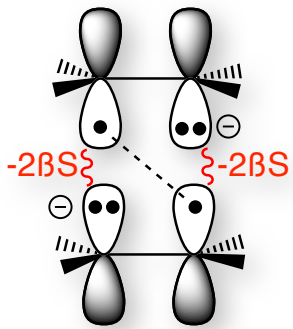
Qualitative VB analysis

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

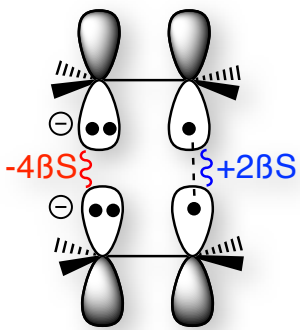




1



2



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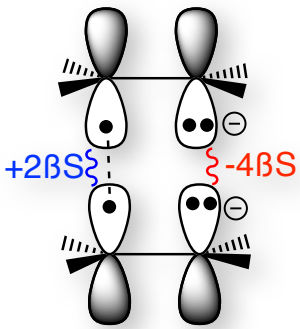

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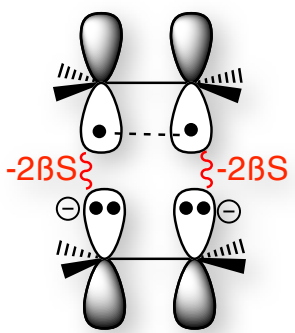

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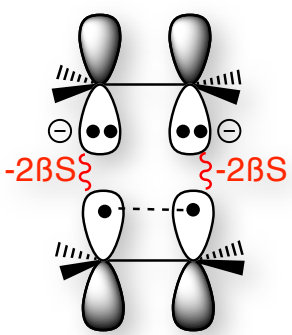
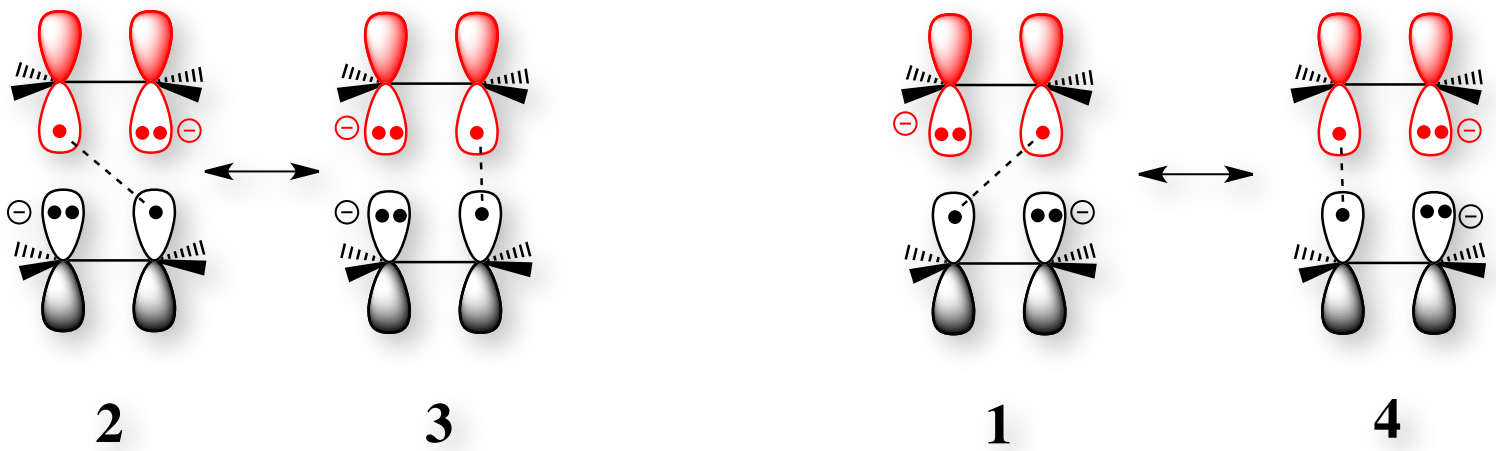


6

Qualitative VB analysis

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



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

Qualitative VB analysis

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

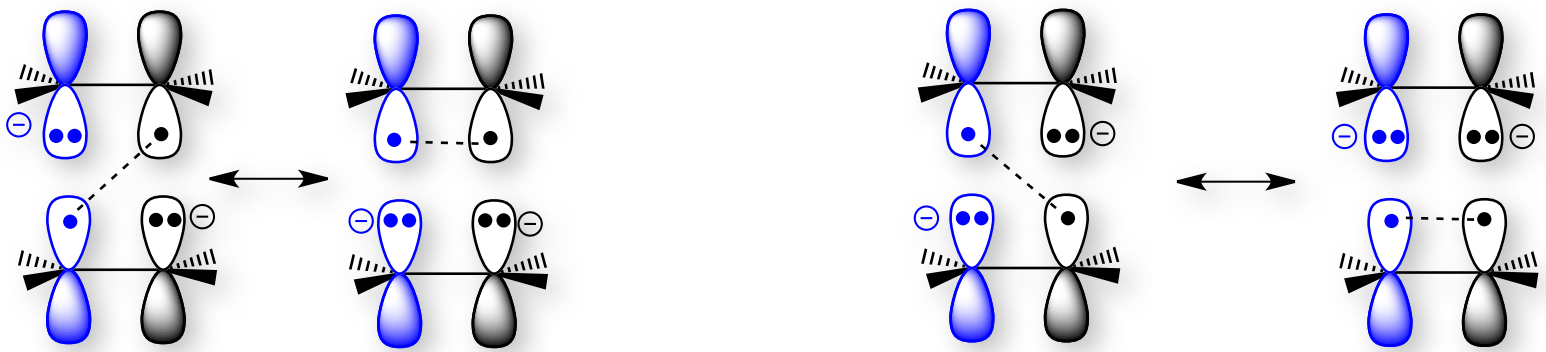
2 **3** **1** **4**

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

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

Qualitative VB analysis

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

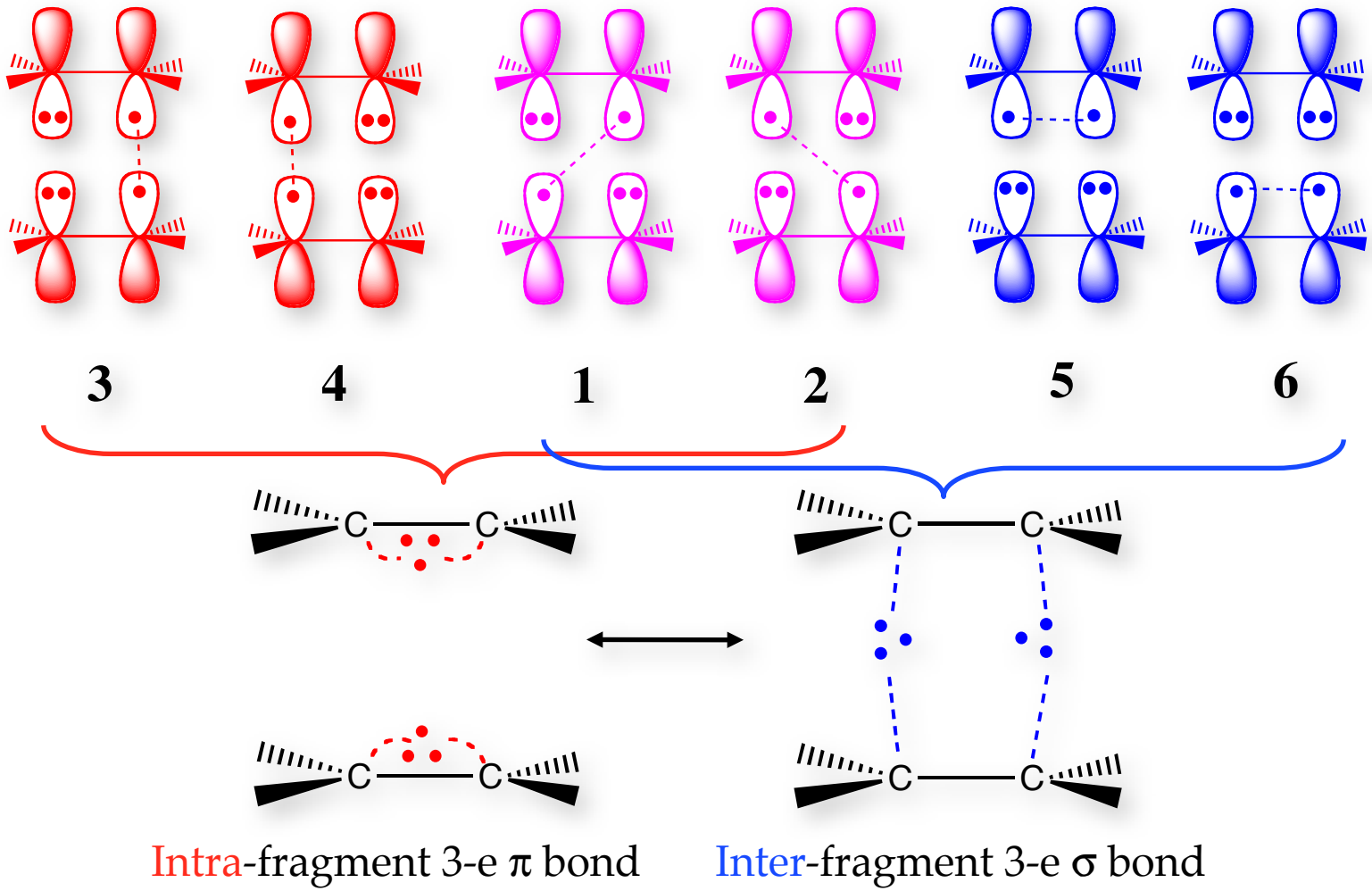


1 **5** **2** **6**

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

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

Qualitative VB analysis



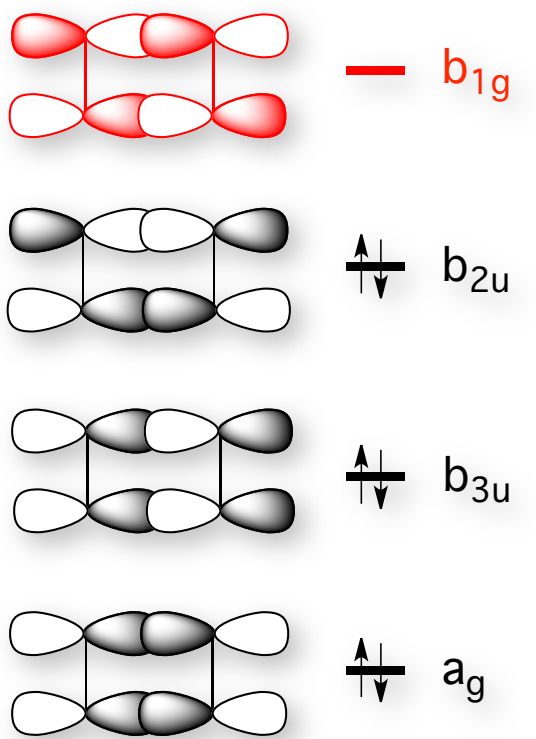
Intra-fragment 3-e π bond Inter-fragment 3-e σ bond

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

Qualitative VB analysis

- MO/VB mapping :

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

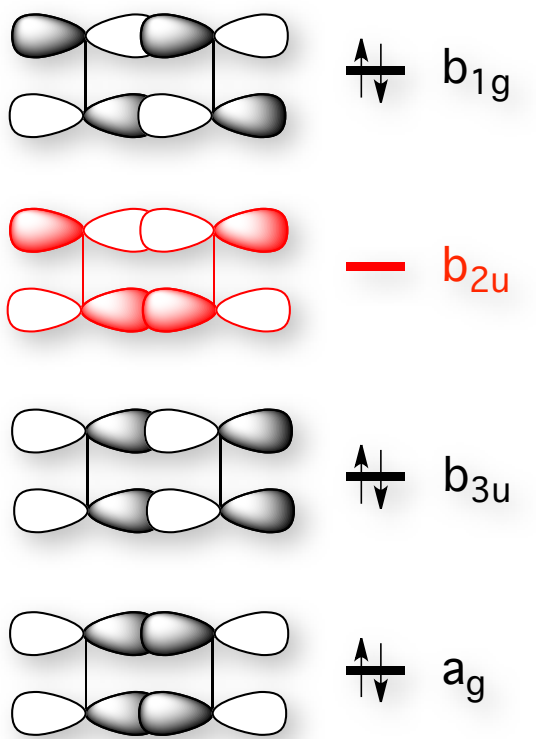


$$\Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = -\Psi_1^{VB} - \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB}$$

Qualitative VB analysis

- MO/VB mapping :

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

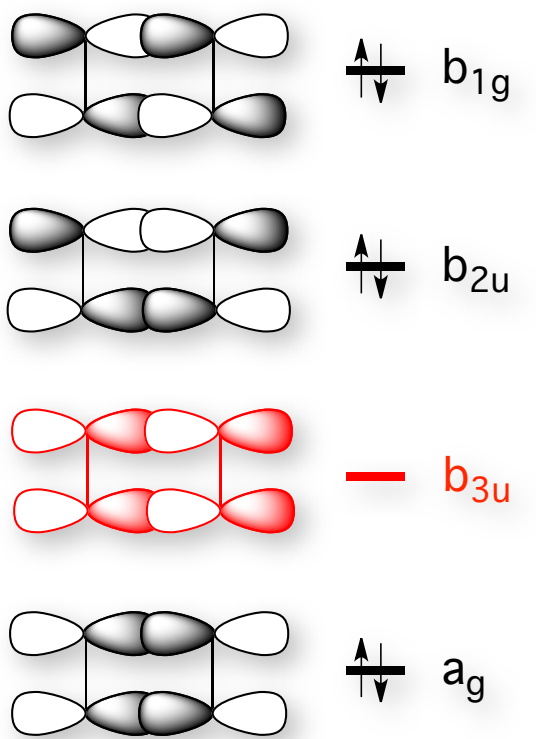


$$\Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} \ominus \Psi_3^{VB} \ominus \Psi_4^{VB} \ominus \Psi_5^{VB} \ominus \Psi_6^{VB}$$

Qualitative VB analysis

- MO/VB mapping :

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

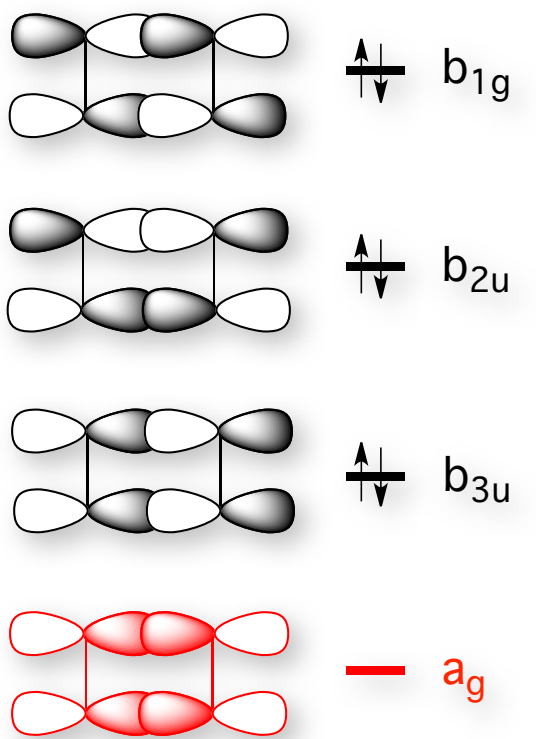


$$\Psi_{2-ext} = \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB}$$

Qualitative VB analysis

- MO/VB mapping :

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



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

Qualitative VB analysis

- MO/VB mapping :

CAS(4,4) $\Leftrightarrow$ 6 VB structures mixing :

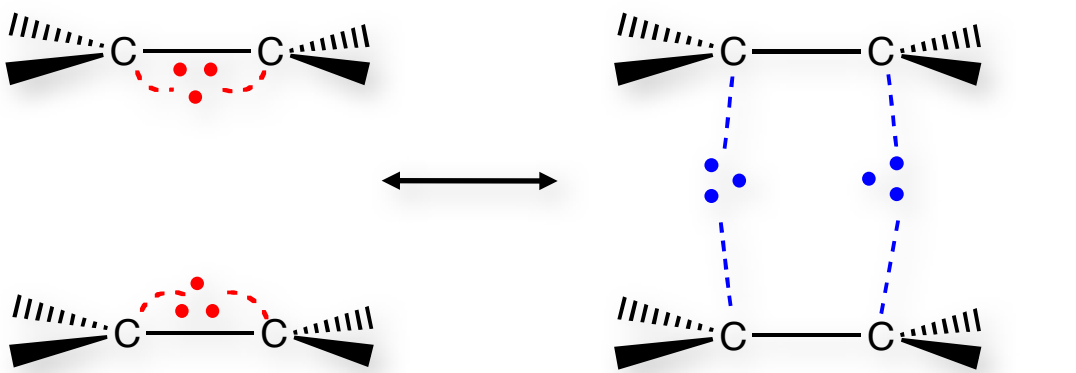
$$\begin{cases} \Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\ \Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB}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

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

the VB analysis which reveals the 3e-bond nature

Qualitative VB analysis

- Conclusion of the qualitative VB analysis :



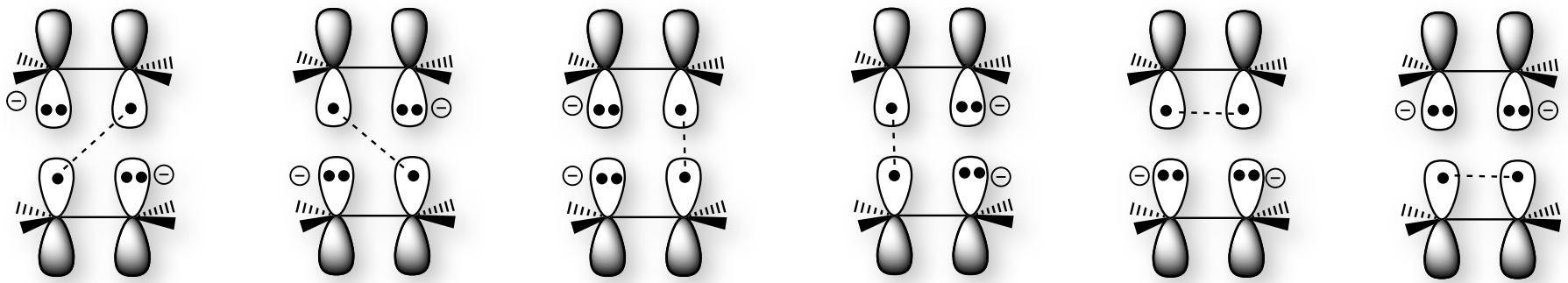
Intra-fragment 3-e π bond Inter-fragment 3-e σ bond

Bonding in DTCNE :

two inter-fragment 3e bonds ?...

Ab initio VB calculations

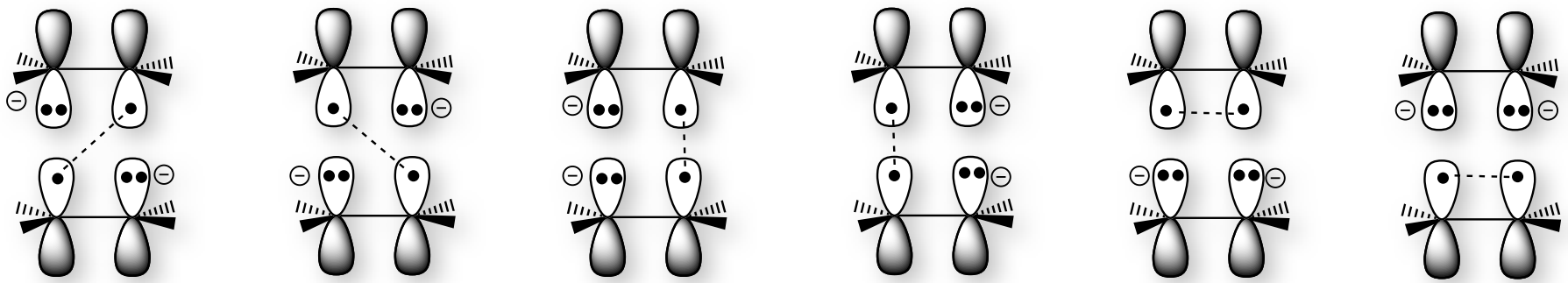
- $DTCNE_2^{2-}$: computed weights (J-VB) :



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

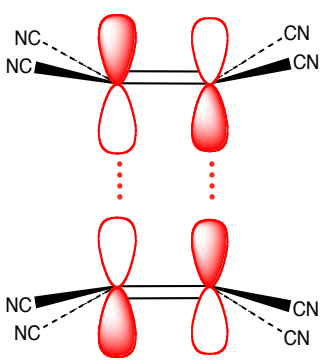
Ab initio VB calculations

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



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

- Interfragment 2e bond ?

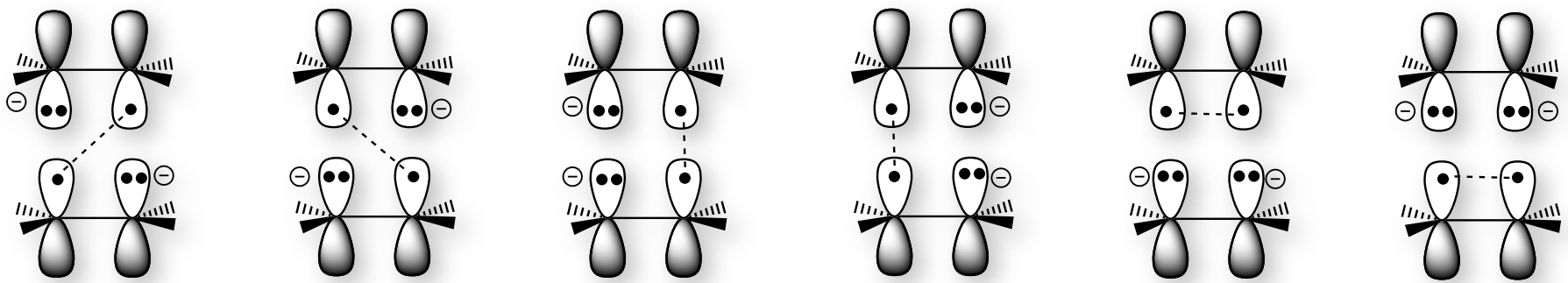


MO/VB maping :

Purely covalent π*-π* 2-e bond =
1 + **2** + **3** + **4** (equal weights)

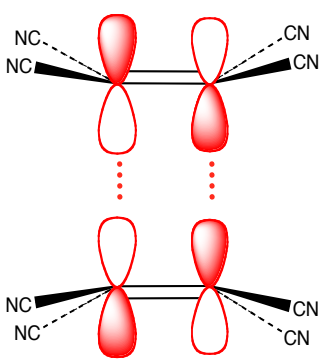
Ab initio VB calculations

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



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

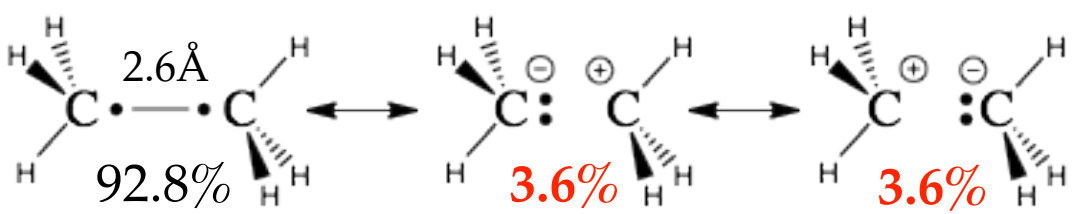
- Interfragment 2e bond ?



(covalent + Ɛ ionic) π-π* 2-e bond =

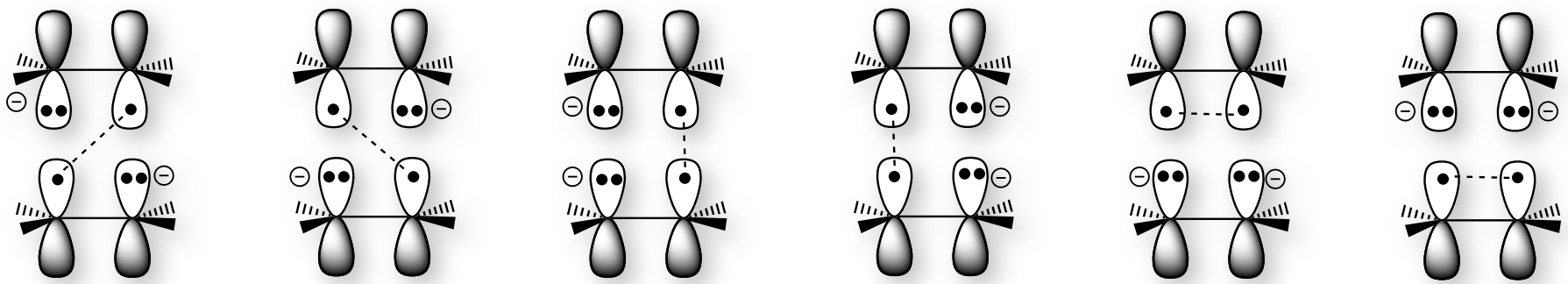
1 + **2** + **3** + **4** + Ɛ (**5** + **6**)

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



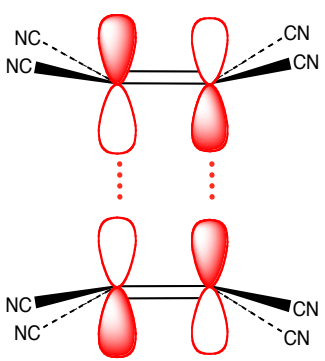
Ab initio VB calculations

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



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

- Interfragment 2e bond ?



(covalent + ε ionic) π-π* 2-e bond =

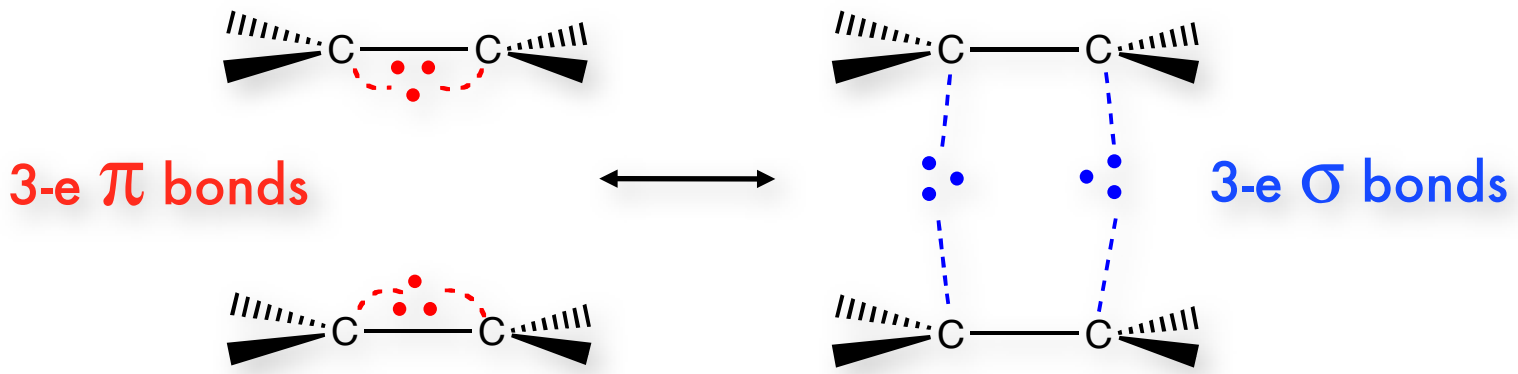
1 + **2** + **3** + **4** + ε (**5** + **6**)

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

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

Ab initio VB calculations

- Some tests of credibility :



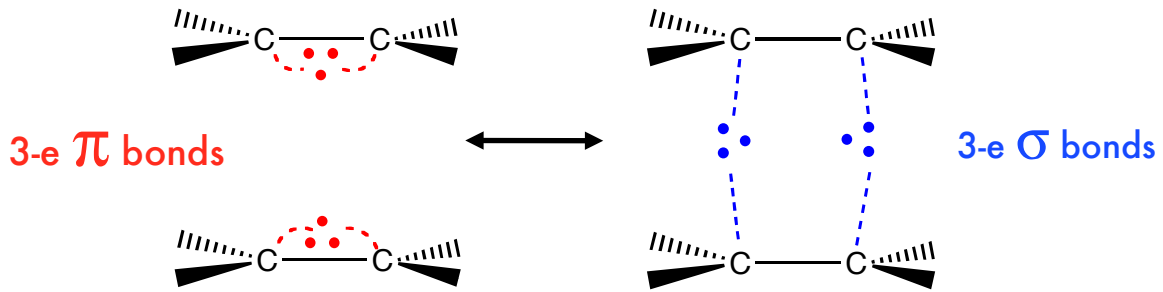
Characteristics of 3e bonds :

1) Large equilibrium distances : d(S—S) ≈ 2.0 Å ; d(S ∴S^-) ≈ 2.8 Å

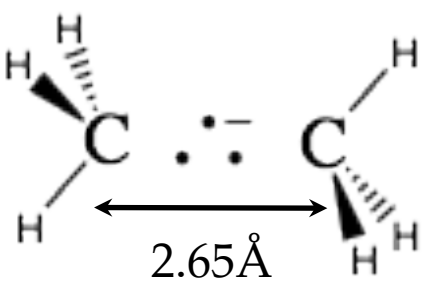
2) Small overlap ($S_{opt} \approx 0.17$)

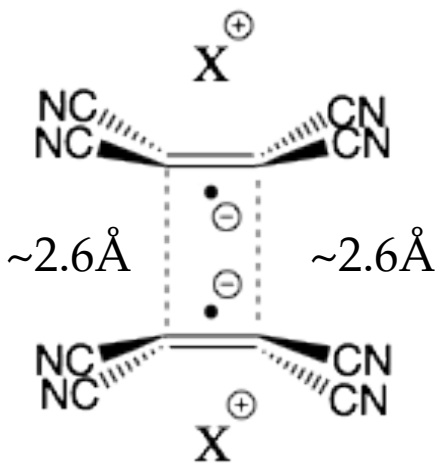
3) Importance of dynamical correlation

Ab initio VB calculations

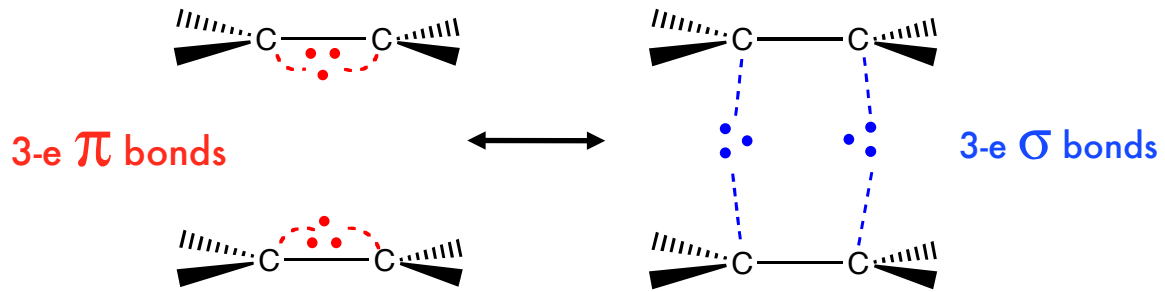


1) Interfragment bond length close to $3e^-$ bonded ethane anion :





Ab initio VB calculations



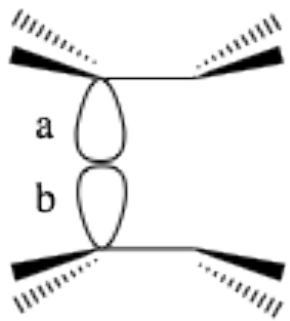
2) Interfragment orbital overlaps close to optimal 3e- bond value :

$S_{opt} \approx 0.17$

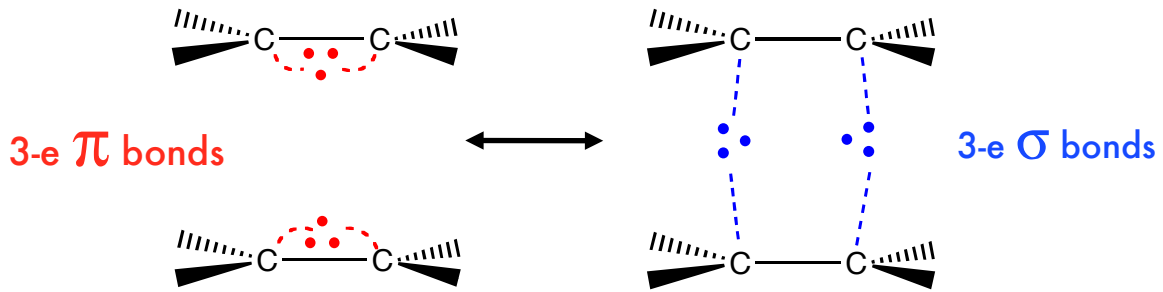
for any 3-e bond
(demonstrated in
qualitative VB theory
as well as Extended Hückel theory)

$S_{ab} = 0.15$

(computed)



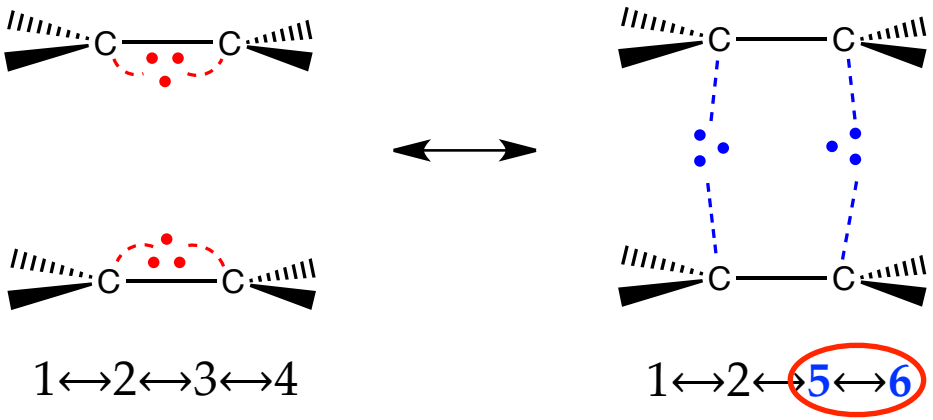
Ab initio VB calculations

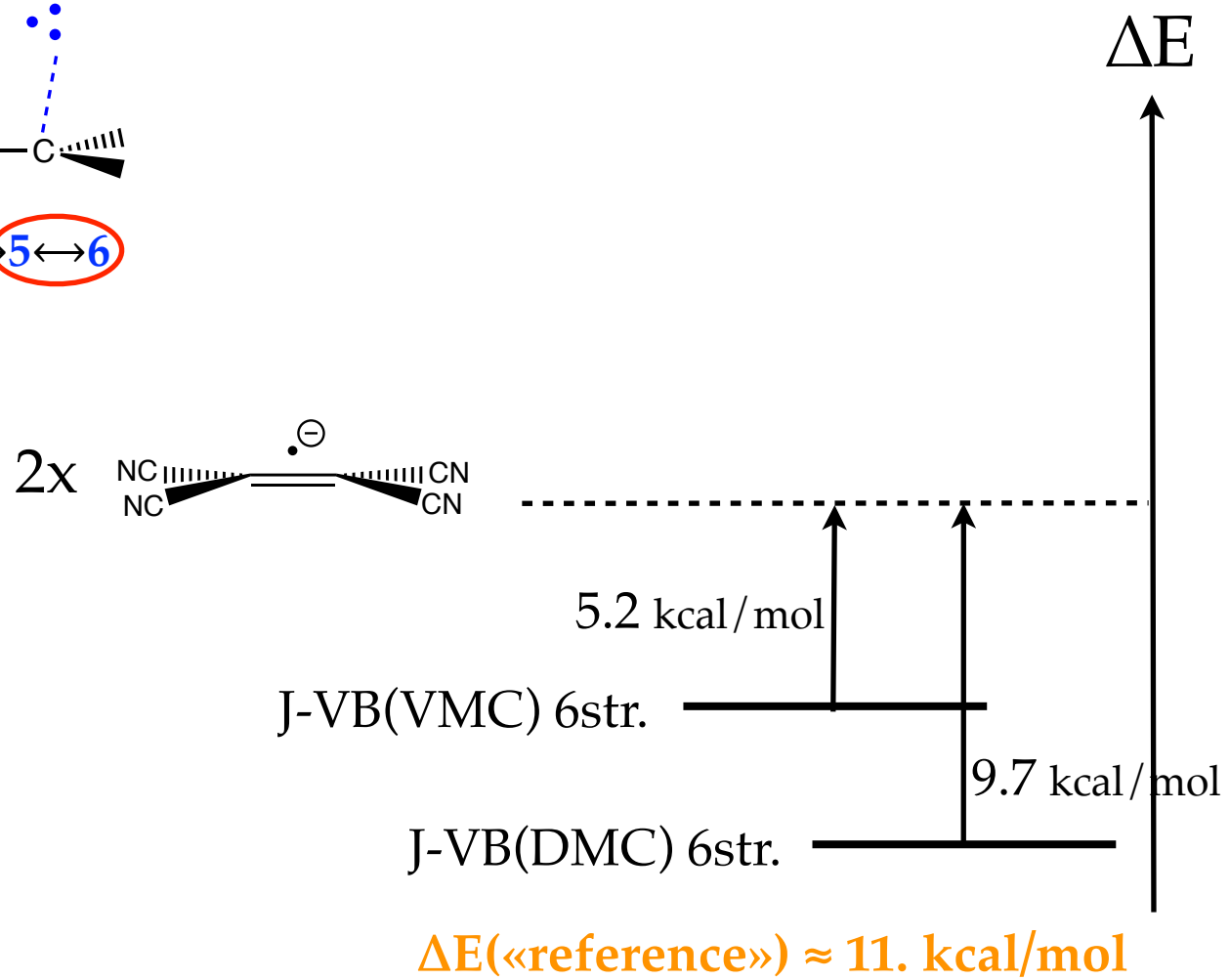


3) Contribution of dynamic correlation to bonding:

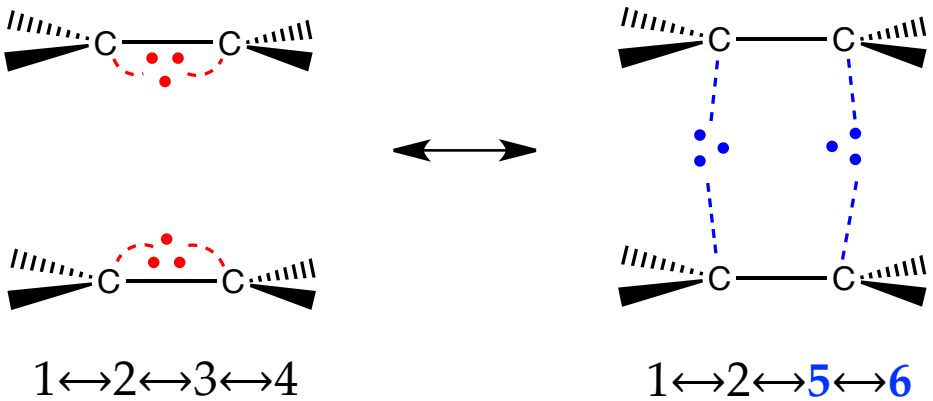
- In $[F \therefore F]^-$, dynamic correlation contributes ~ 30 kcal/mol to bonding
- In $[TCNE]_2^{2-}$, dynamic correlation contributes > 30 kcal/mol to bonding

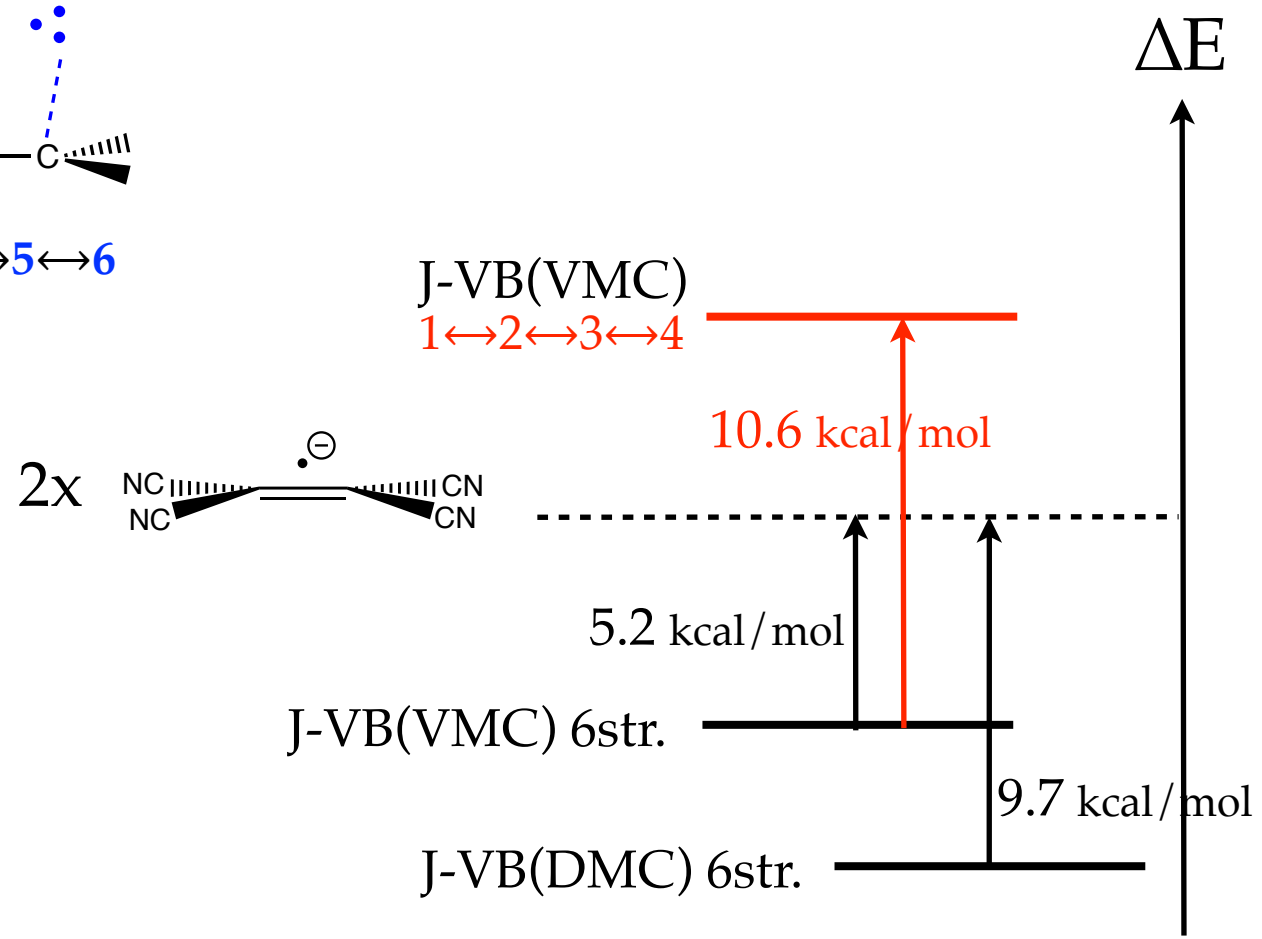
Ab initio VB calculations





Ab initio VB calculations

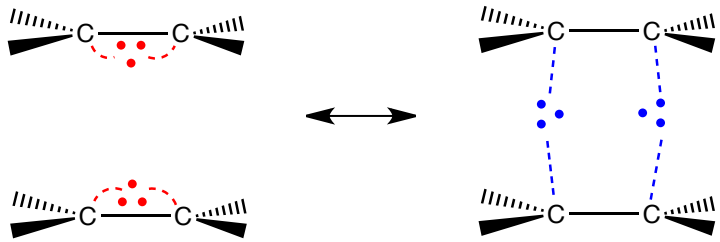




⟹ Without str. 5-6, DTCNE becomes repulsive !

Conclusion

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



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

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

- This simple picture explains at once :

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

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