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Is qualitative VB theory useful for current chemical problems ?

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Purpose

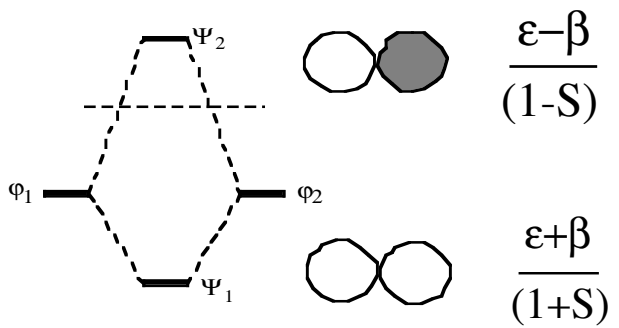
Models (VB theory here) can bring useful insight on non-trivial system

- Basics of qualitative VB theory
- MO & VB analysis of «pancake bonding» DTCNE
- Verification by correlated VB calculations

Qualitative VB

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

Parameters: β, **S**, ε (same as in the MO framework)



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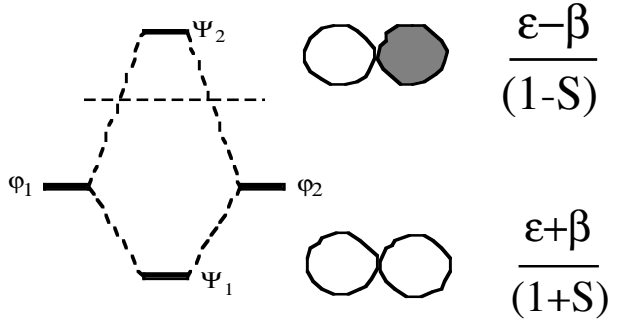

1) Energy of a determinant :

$$\langle D_i | H | D_i \rangle = \frac{-2n\beta S}{1 - S^2}$$

n **= N# of neighboring (↑↑) pairs**

Qualitative VB

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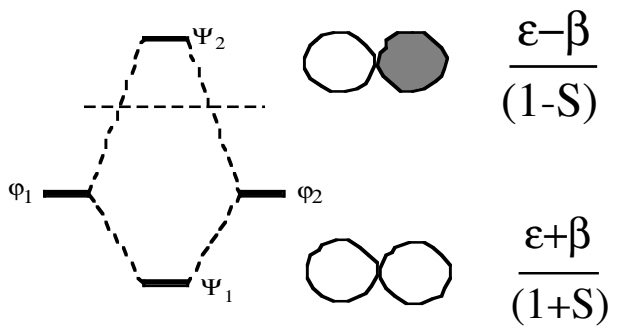


1) Energy of a determinant :

$$\langle D_i | H | D_i \rangle = \frac{-2n\text{ß}S}{1 - S^2}$$

n **= N# of neighboring (↑↑) pairs**

2) Off diagonal terms :

- Determinants differ by 2 spinorbitals:

$$\langle (|a\bar{b}|) | H | (|b\bar{a}|) \rangle = 2\beta_{ab} S_{ab}$$

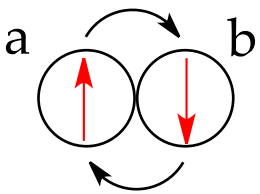
- Determinants differ by + than 2 spinorbitals :

$$\langle D_i | H | D_j \rangle = 0$$

Qualitative VB

- **2e-bond :**

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



$$\Rightarrow \quad E = \langle \psi_{VB} | H | \psi_{VB} \rangle = \ldots = \frac{2\beta S}{(1+S^2)} = D_e(2e-bond)$$

Qualitative VB

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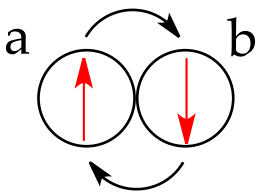
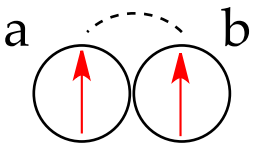


$$\Rightarrow \quad E = \langle \psi_{VB} | H | \psi_{VB} \rangle = \ldots = \frac{2\beta S}{(1+S^2)} = D_e(2e-bond)$$

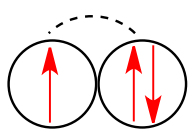
- **Triplet repulsion :**

$$\psi_{VB} = \frac{|a\bar{b}| \ominus |b\bar{a}|}{\sqrt{2(1+S^2)}}$$



$$\Rightarrow \quad E = \langle \psi_{VB} | H | \psi_{VB} \rangle = \frac{\ominus 2\beta S}{(1 \ominus S^2)}$$

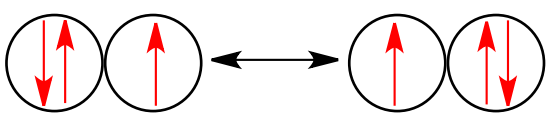
Same as 3e-repulsion : $\psi_{VB} = |a\bar{a}b|$



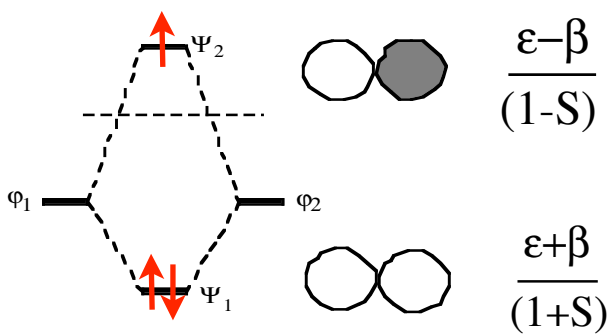
Qualitative VB

- **3-e bond :** Examples : the He_2^+ dimer cation , RS $\overset{\ominus}{\therefore}$ SR' , π bonds in O_2 G.S

VB description :



MO description :



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

$$\Psi_{MO} = |\sigma\bar{\sigma}\sigma^*|$$

Qualitative VB

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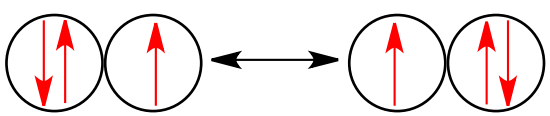
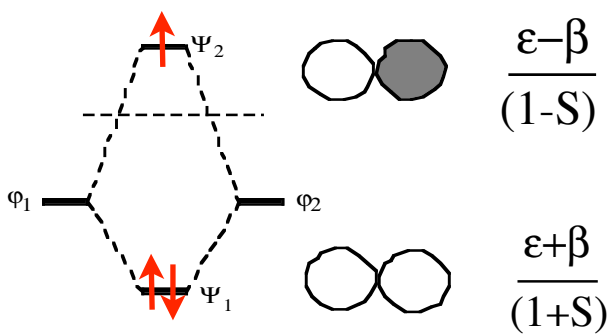
VB description :



MO description :

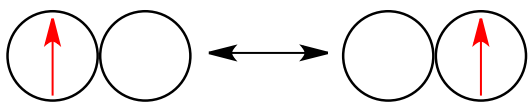
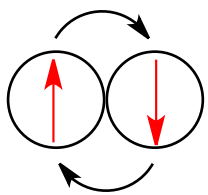
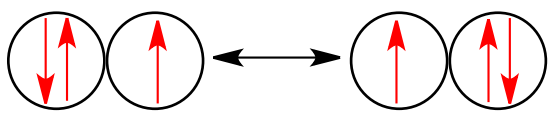
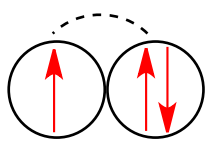
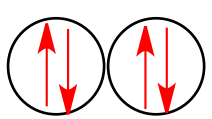


$$\Psi_{MO} = \left|\sigma\bar{\sigma}\sigma^*\right| = \left|(a+b)\overline{(a+b)}(a-b)^*\right| = \ldots = -\left|a\bar{a}b\right| - \left|b\bar{b}a\right| = -\Psi_{VB}$$

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

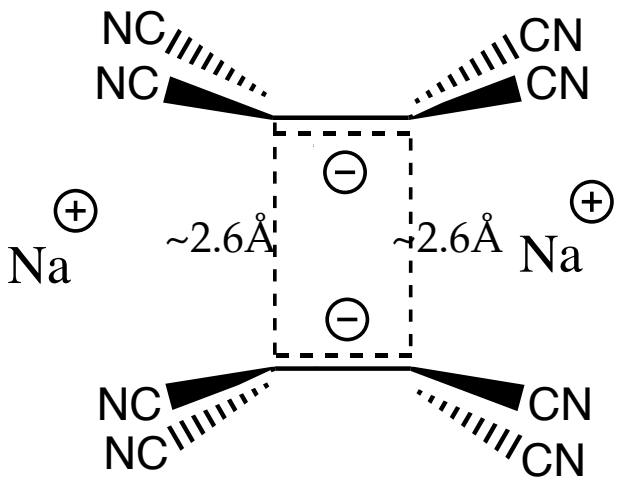
Qualitative VB

- Elementary interactions :

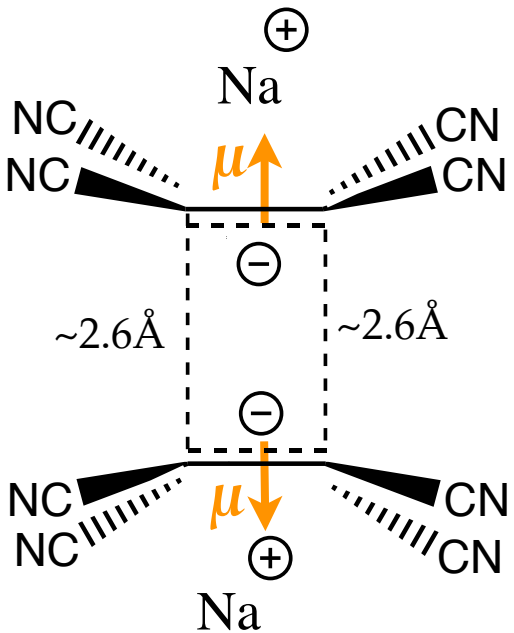
		VB	MO
1-e bond (A↑B) =		$\frac{ß}{1+S}$	$\frac{ß}{1+S}$
2-e bond (A–B) =		$\frac{2ßS}{1+S^2}$	$\frac{2ß}{1+S}$
3-e bond(A∴B) =		$\frac{ß(1-3S)}{1-S^2}$	$\frac{ß(1-3S)}{1-S^2}$
Triplet / 3-e repulsion (A↓↑ ↑B) =		$\frac{-2ßS}{1-S^2}$	$\frac{-2ßS}{1-S^2}$
4-e repulsion (A↑↓ ↓↑B) =		$\frac{-4ßS}{1-S^2}$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

«Pancake bonding»

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



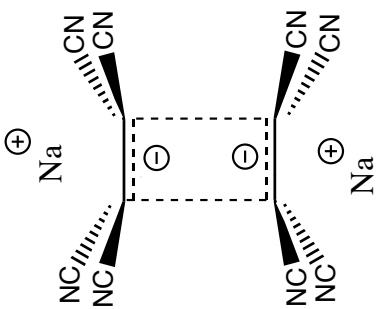
$D_e \approx 80.\ kcal/mol$

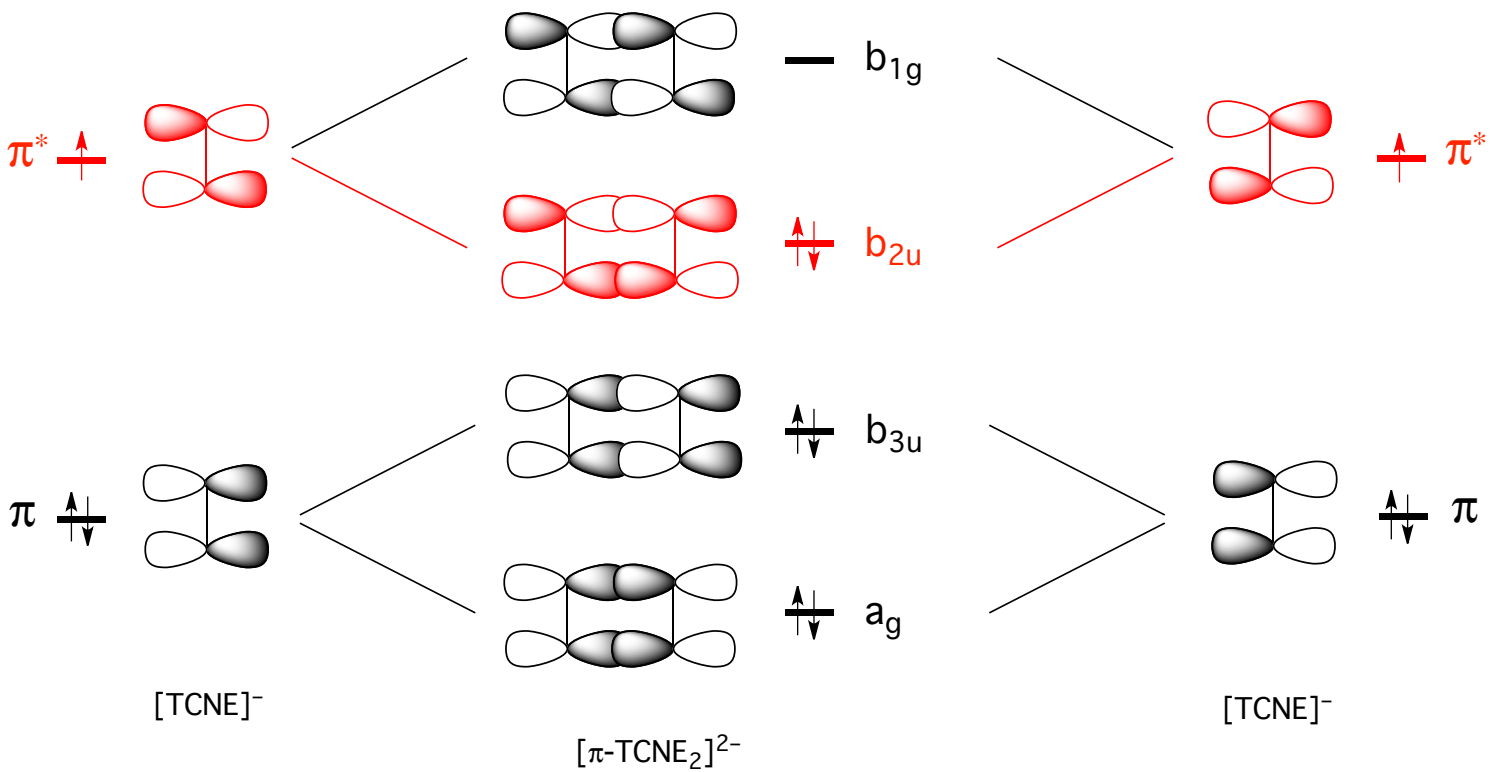


$D_e \approx 11.\ kcal/mol$!

- Right geom : significant bonding force overcome repulsive electrostatics...
- $d_{C\text{---}C}$ < sum of vdW radii (3.4Å) , but much longer than C-C 2e bonds

«First sight» MO analysis





=> a **4c/2e⁻ bond ?**

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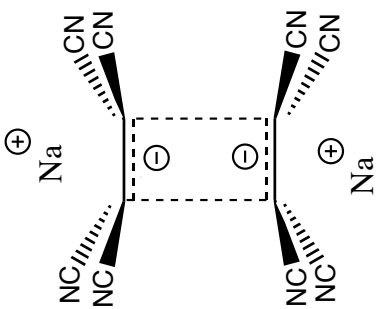

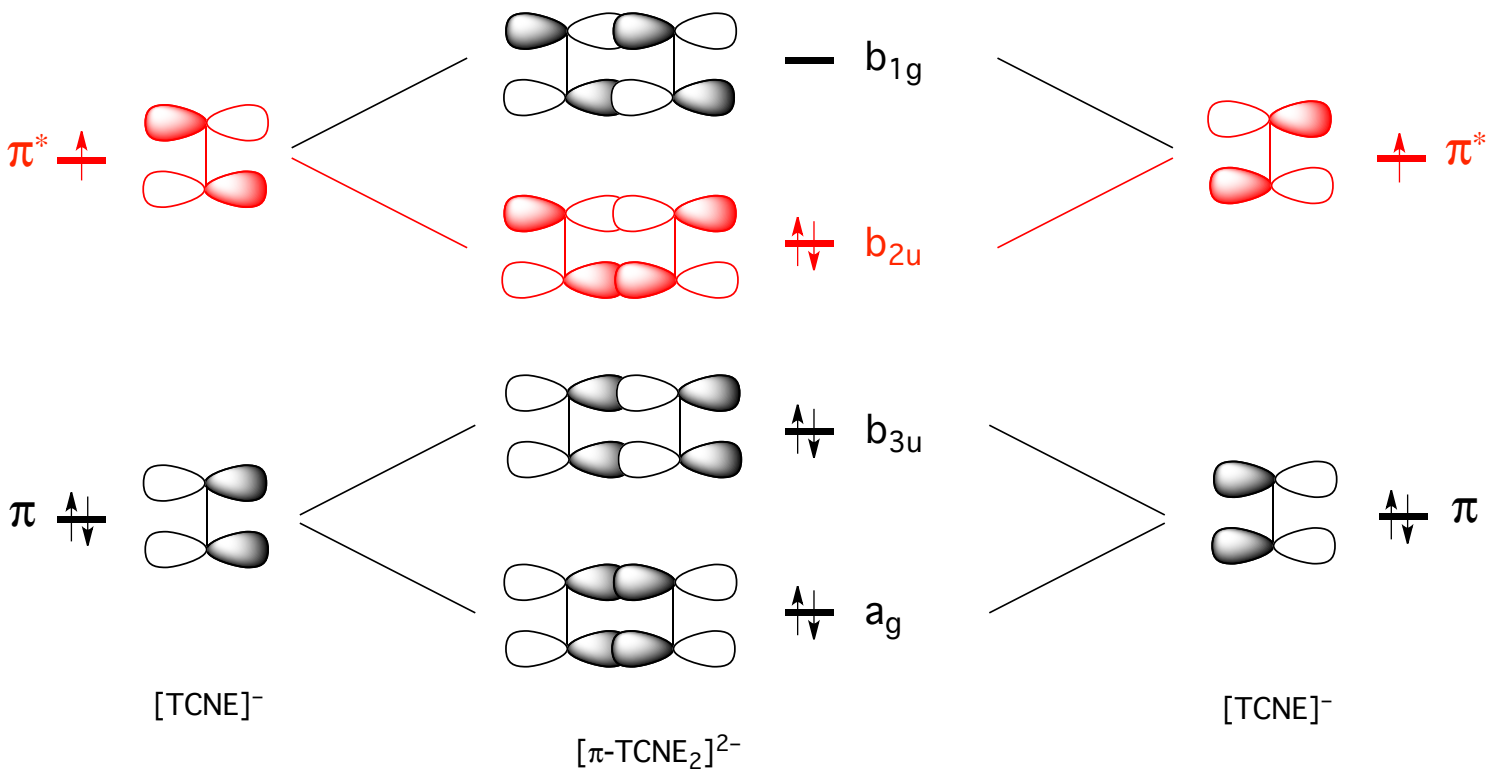

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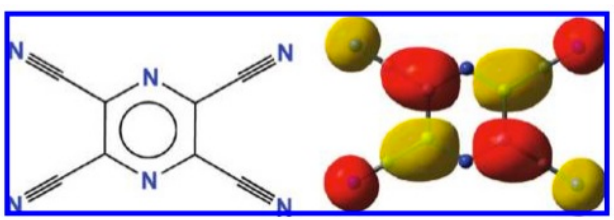
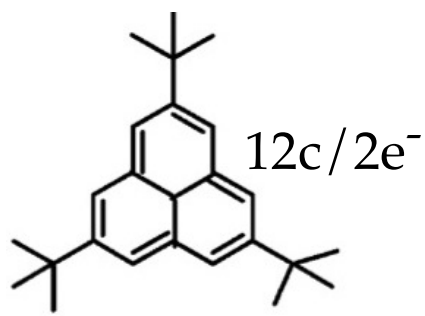


8c/2e⁻

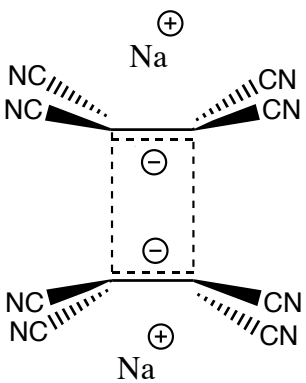


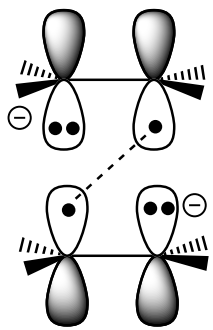
12c/2e⁻

Others «pancacke bondings» : **nc/2e⁻ bond**

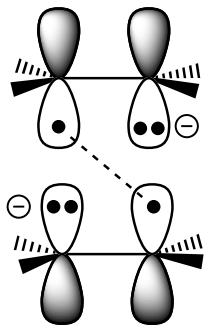
VB analysis

- VB set of structures :





1



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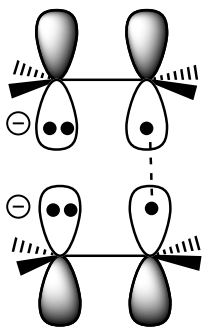

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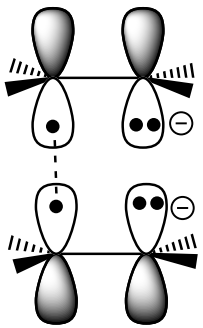

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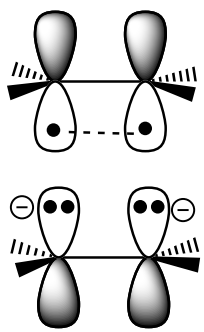

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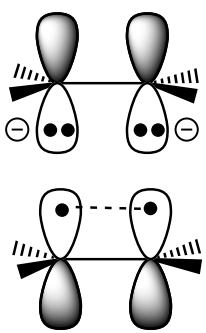

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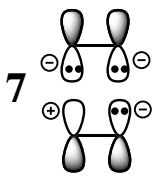

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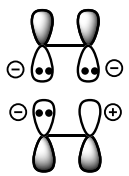

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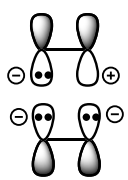

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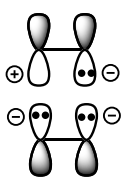

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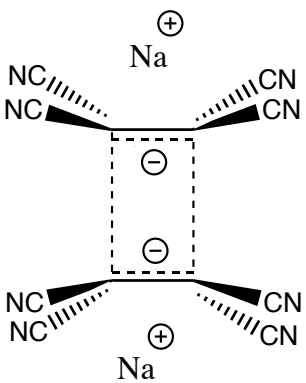
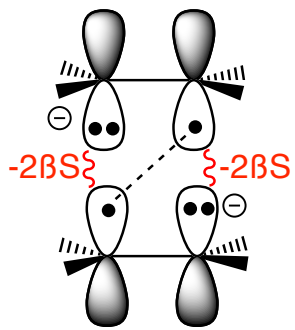
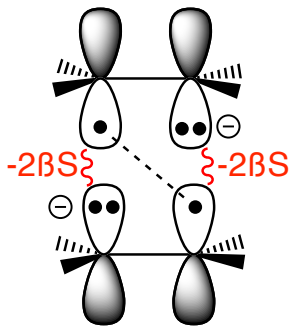
VB analysis

- VB set of structures :





1



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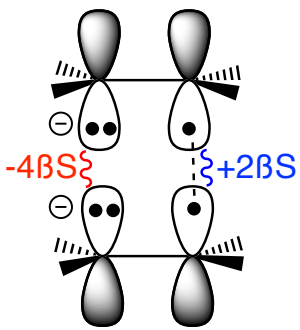

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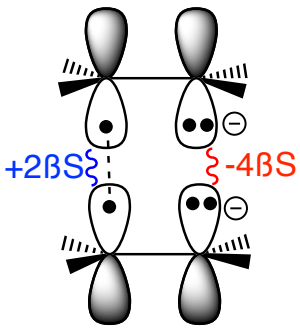

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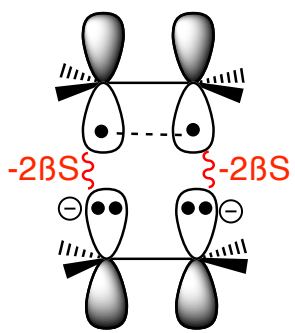

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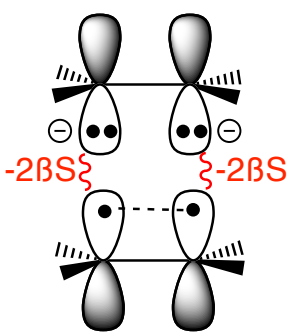

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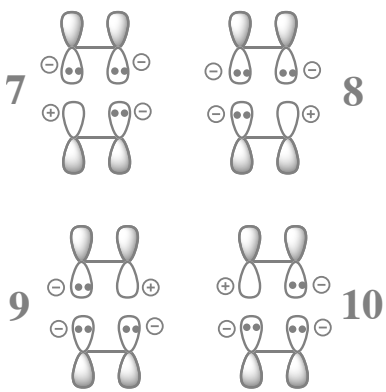
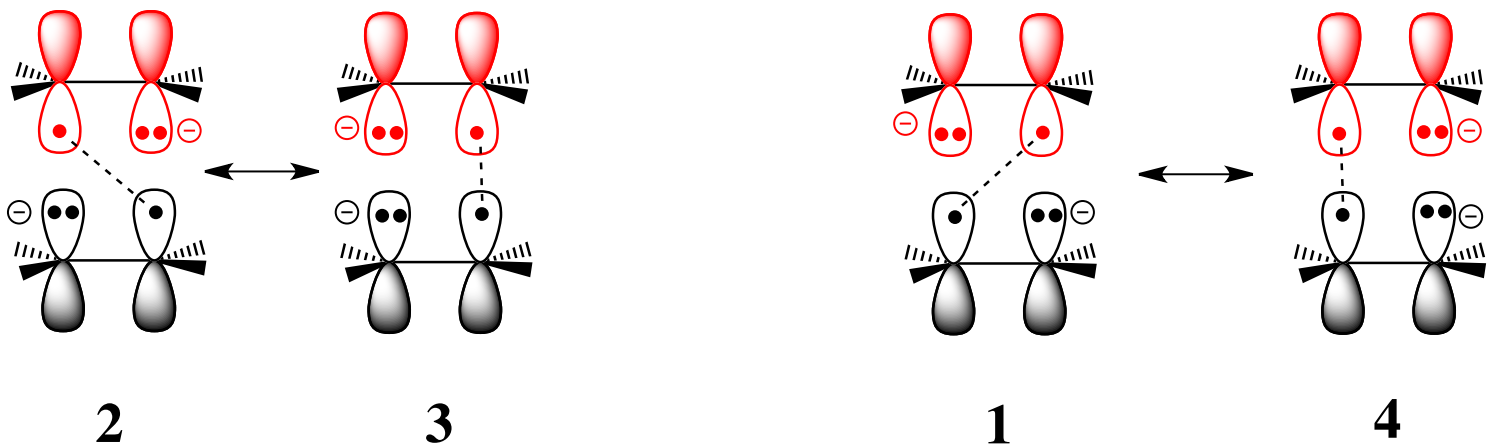


=> No structure is bonding by itself, **all the bonding comes from the resonance**

VB analysis

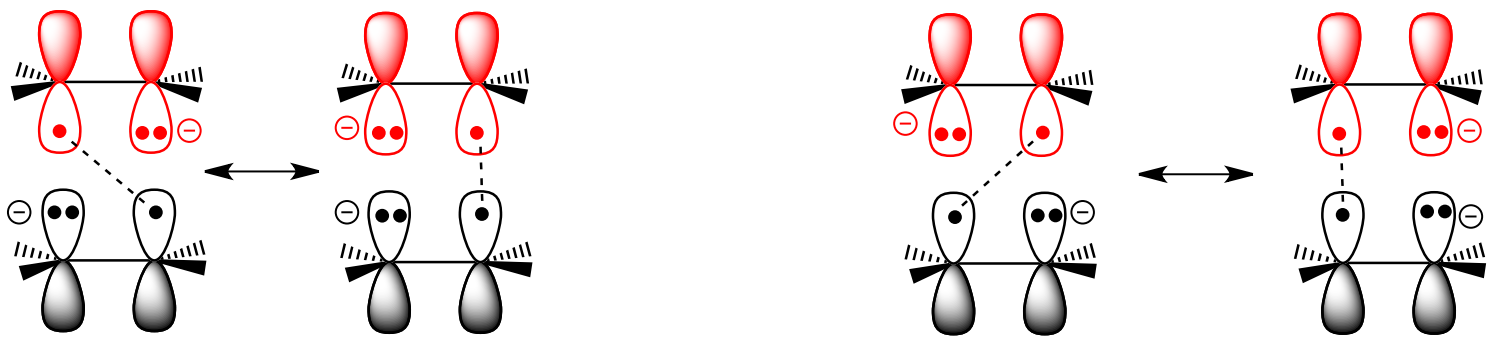
- 2↔3 and 1↔4 : **intra-fragment 3e$^-$ π bond** (upper fragment) :



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

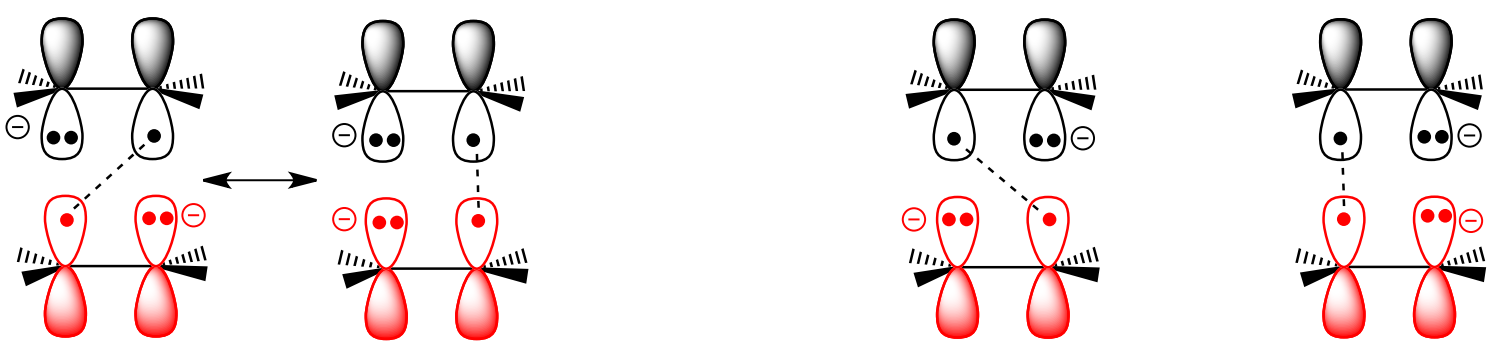
VB analysis

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



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

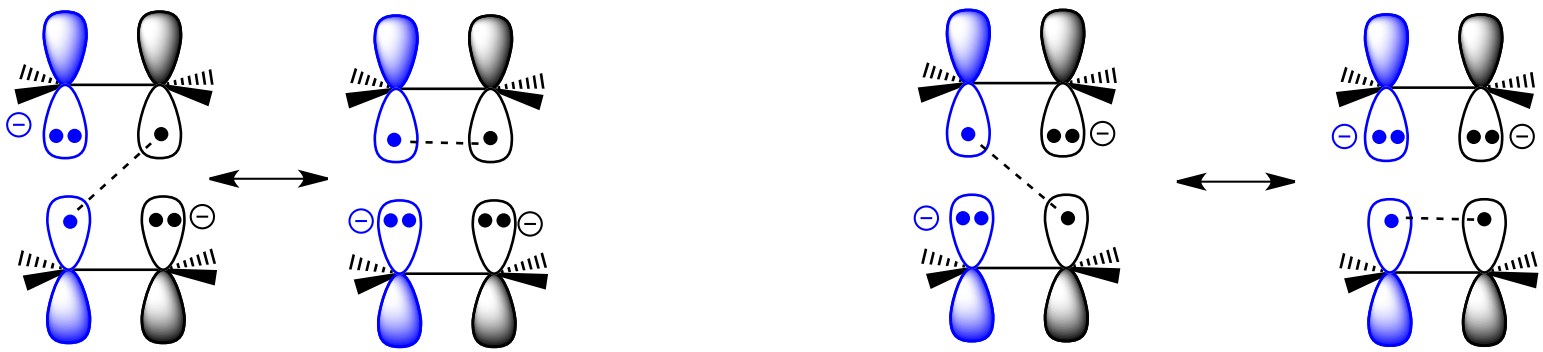
- 1↔3 and 2↔4 : **intra-fragment 3e⁻ π bond** (lower fragment) :



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

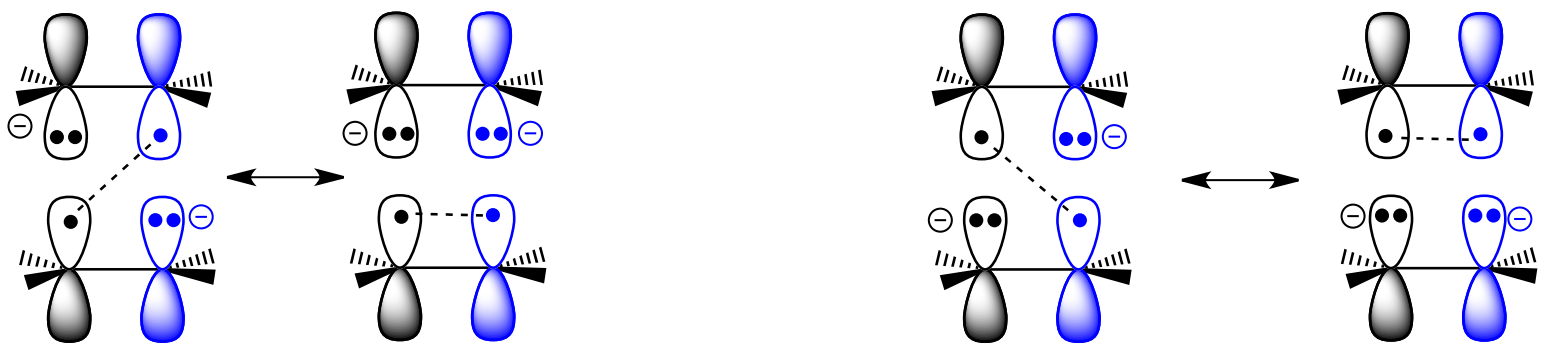
VB analysis

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



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

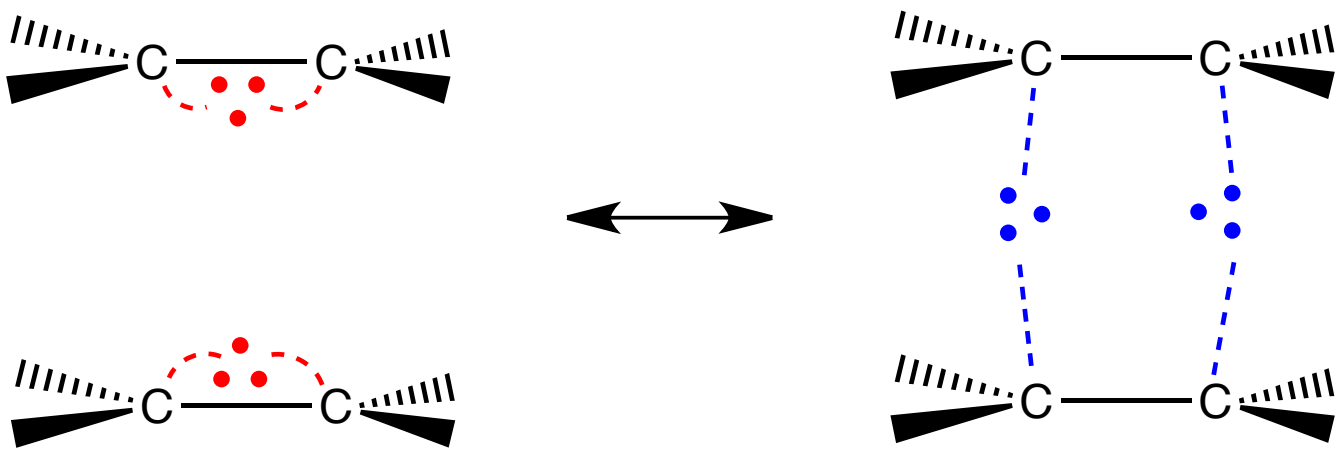
- 2↔5 and 1↔6 : **inter-fragment 3e⁻ π bond** (right-hand side) :



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

VB analysis

- Conclusion of the qualitative VB analysis :



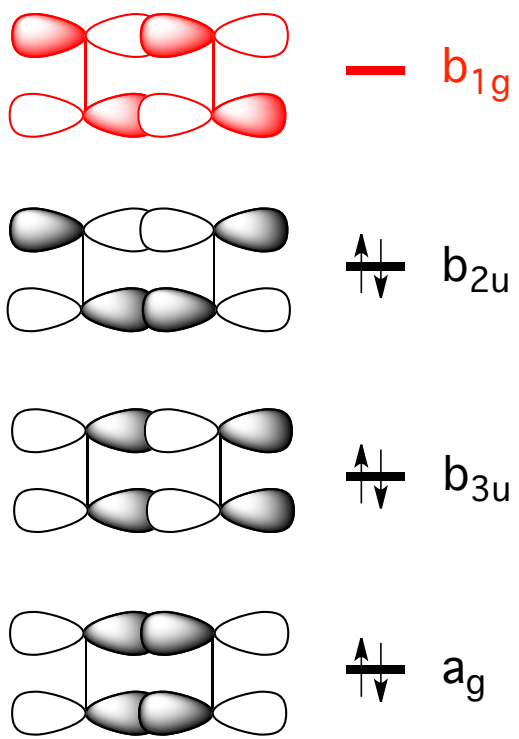
1↔2↔3↔4

1↔2↔**5**↔**6**

=> bonding in DTCNE : two inter-frag. 3e bonds !

MO/VB mapping

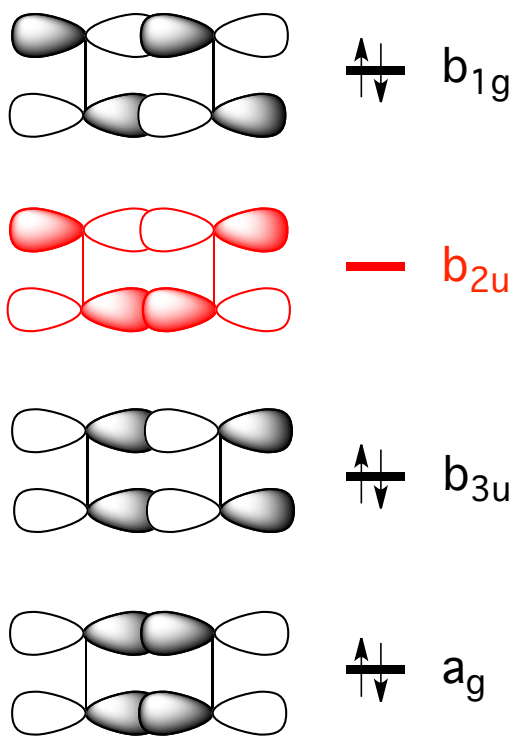
- HF determinant - development in VB basis of structures :



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

MO/VB mapping

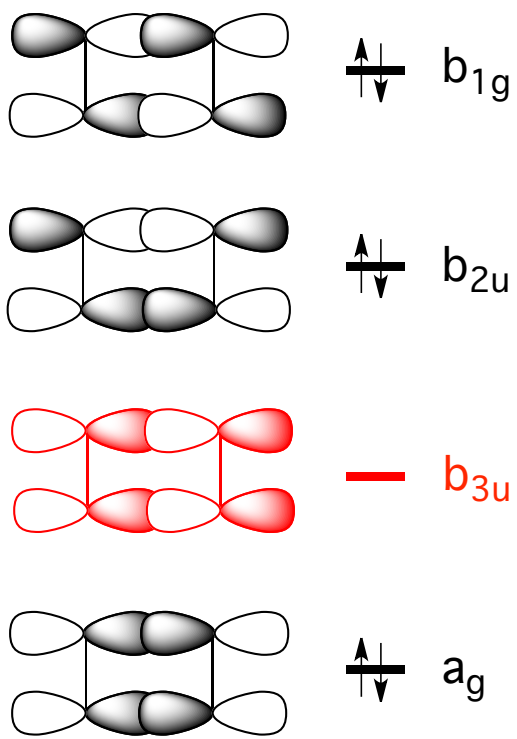
- 1st excited det. - development in VB basis of structures :



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

MO/VB mapping

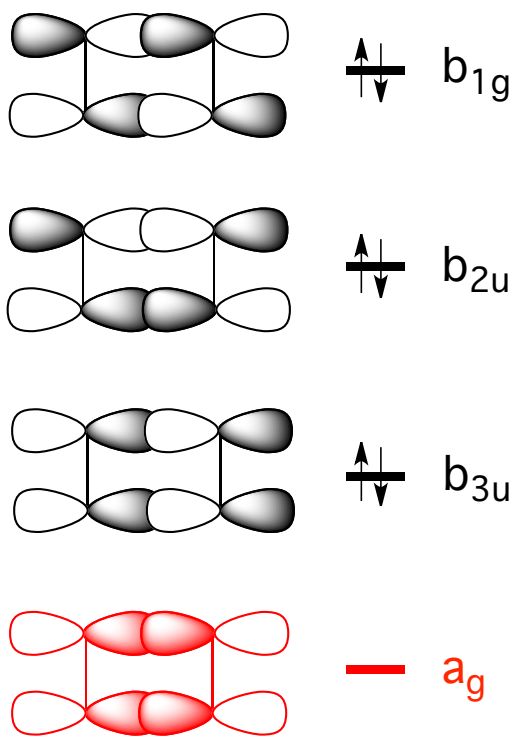
- 2nd excited det. - development in VB basis of structures :



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

MO/VB mapping

- 3rd excited det. - development in VB basis of structures :



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

MO/VB mapping

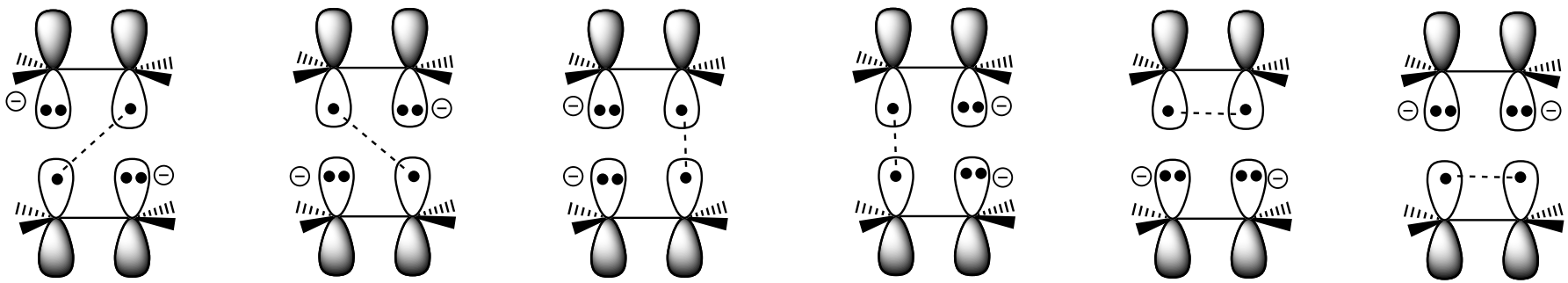
- CAS(4,4) ⇔ 6 VB structures mixing :

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

- MO (4x4) description = VB description
- VB analysis reveals the 3e-bond nature

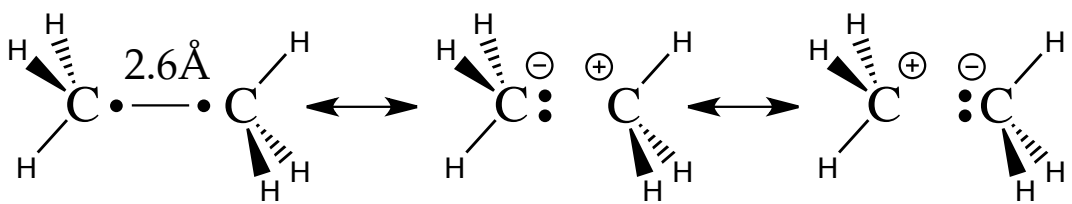
Quantitative VB (1)

- DTCNE computed weights :



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

- Stretched ethane :

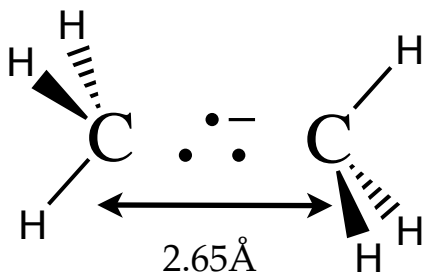


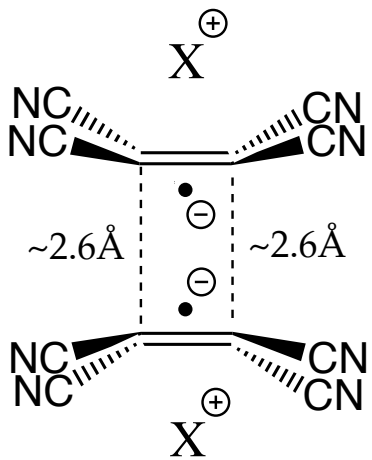
92.8% 3.6% 3.6%

⇒ Str. 5-6 weights are not compatible with a 2c2e bond

Quantitative VB (2)

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

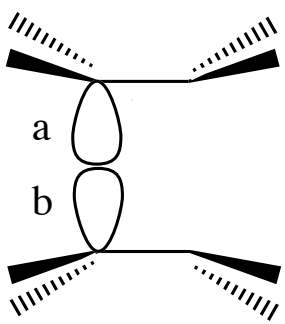




2) DTCNE active orb. overlaps close to optimal $3e^-$ bond value :

$S_{ab} = 0.15$

(computed)

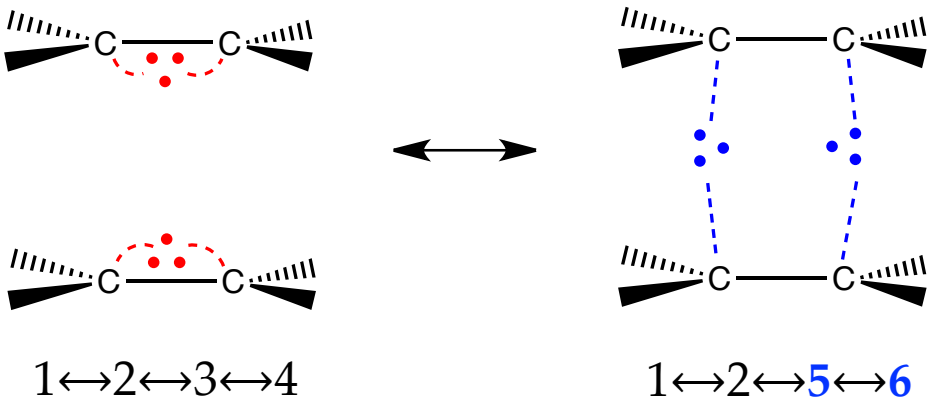


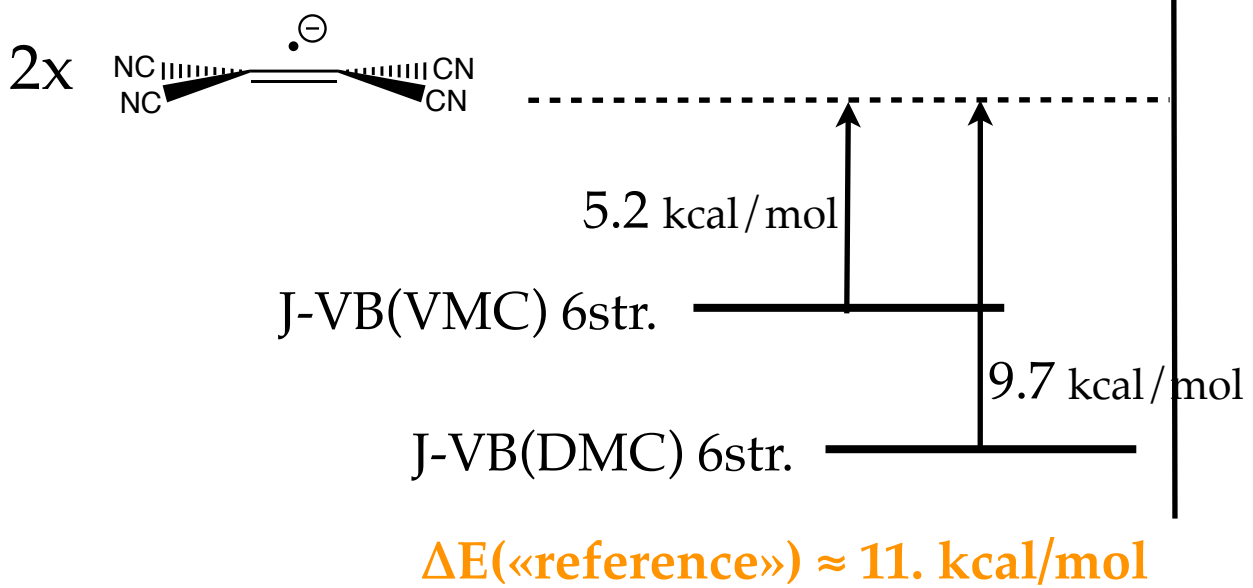
$S_{opt} \approx 0.17$

(from qualitative VB and Hückel)

3) Dynamical Correlation Energy important for DTCNE

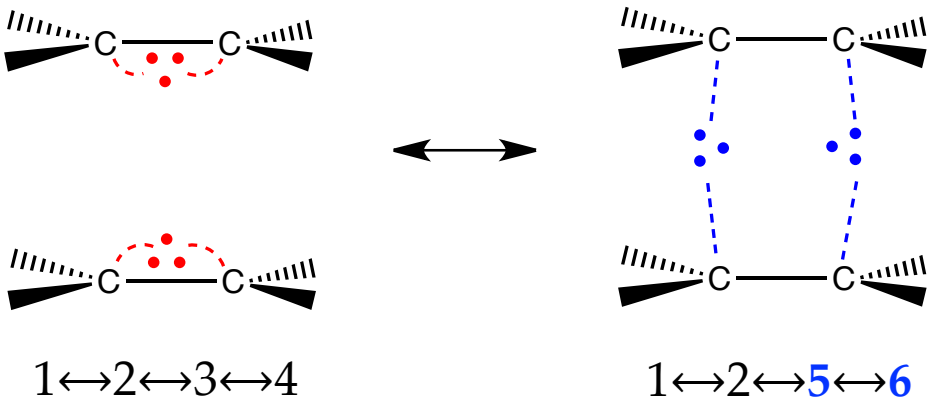
Quantitative proof (3)

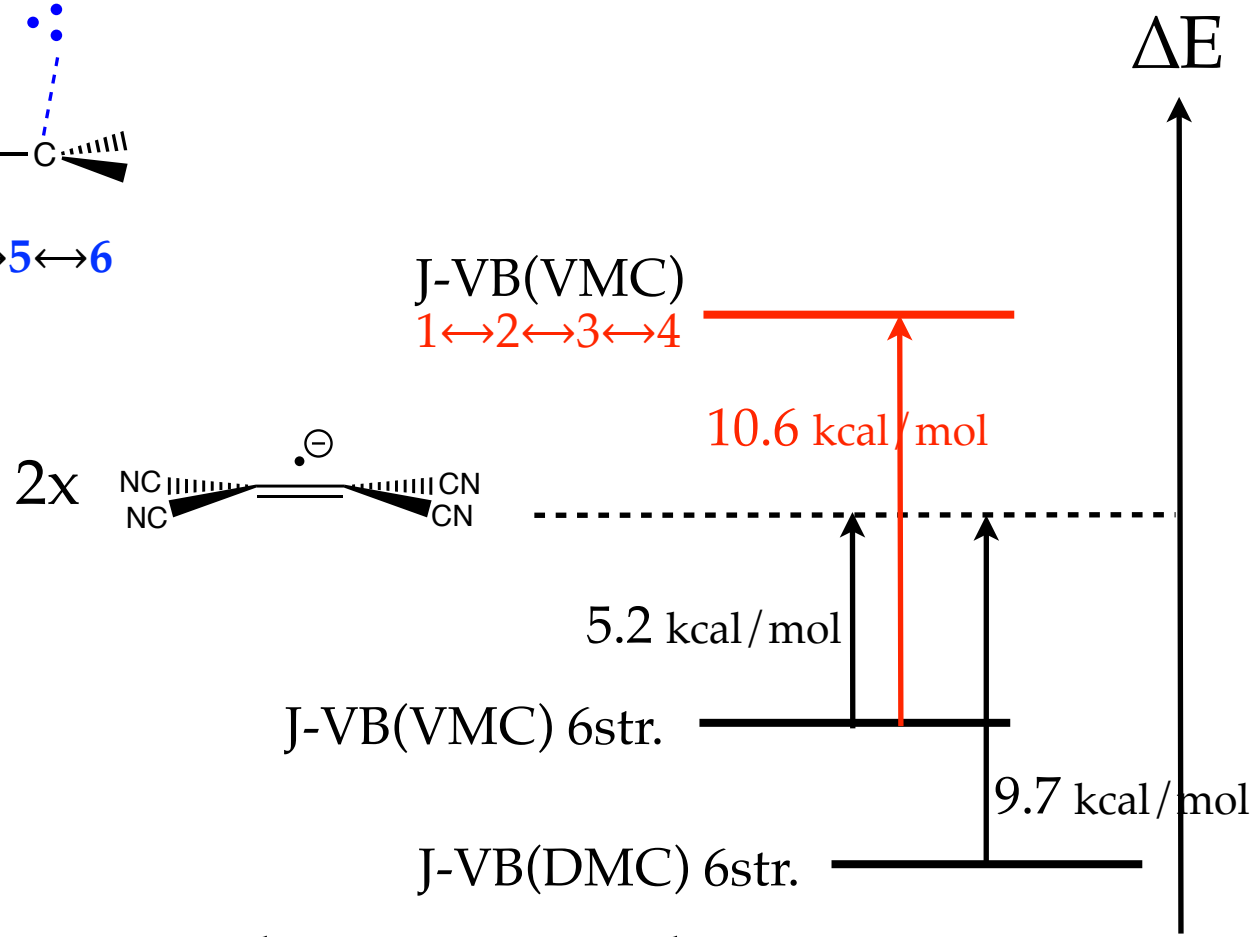




ΔE(«reference») ≈ 11. kcal/mol

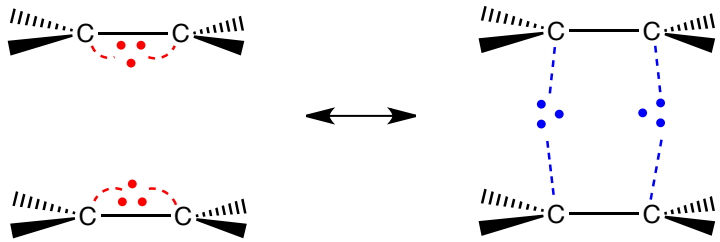
Quantitative proof (3)





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

Conclusion



- Qualitative VB analysis reveals the 3e-bonding nature in DTCNE multicenter «pancake» bonding system
- Confirmed by correlated VB calculations
- Models still important nowadays to «**understand**» :

«I know that the computer has understood,

but I would like to understand too !» (E. Wigner)

Conclusion


- VB allows to see things from a different perspective
(Prof. Keating, Dead Poets Society)
- Combining different models can lead to deeper understanding

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Thanks to :
Philippe HIBERTY, Kévin HENDRICKS

VB workshop in Paris !

Paris, July 2012

- plenary lectures on Valence Bond theory, methods, and related models,
- short talks given by participants on a topic relevant to VB theory,
- space dedicated to free discussions,
- "hands-on" lab : basic initiation to the XMVB and BLW programs (limited to 30 participants)

The name is Bond, Valence Bond !

XMVB

An Ab Initio Non-orthogonal Valence Bond Program

➟ http://wiki.lct.jussieu.fr/workshop

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