Benoît BRAÏDA

QMC in Apuan Alps July 2012

A Valence Bond /Quantum Monte Carlo study of « pancake » bonding

Laboratoire de Chimie Théorique

Université Pierre et Marie Curie - Paris6

The Laboratoire de Chimie Théorique of the Université Pierre et Marie Curie

- Université Pierre et Marie Curie (Paris) :

- ≈8000 permanent (Pr.+researchers) + ≈32000 students
- Topics : mathematics, physics, chemistry, biology, medecine

The Laboratoire de Chimie Théorique of the Université Pierre et Marie Curie

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- Laboratoire de Chimie théorique :

Methodology

DFT, QMC, local Ψ method development

Selectivity & environment

Complex (bio)organic and (bio)inorganic systems

Concepts & interpretative methods

ELF, MPD, VB develop.+appli.

- 26 permanent (prof.+CNRS)
- ~50 (+students)

Chemistry & universe

Interstellar reactions, small molecules...

Chemistry & surface

Reactivity on oxyde surfaces...

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- 26 permanent (prof.+CNRS)
- 52 (permanent+phD+postdocs)
+ students (≈10-20)

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Outline

- **Valence Bond theory :**
  - Motivation and basic concepts
  - Mixed Valence Bond / Quantum Monte Carlo methods
- **Application on «pancake bonding» in $DTCNE_2^{2-}$:**
  - MO analysis and MO-based calculations
  - Qualitative VB analysis
  - Quantitative VB calculations

- Birth and origins:

1916

G.N. Lewis

1928-34

L. Pauling

VB: a quantum dressing of Lewis model

- ~1930-1950s: Rise and glory

L. Pauling

VB dominated the mental map of chemistry

- ~1940-1960: The MO-VB rivalry

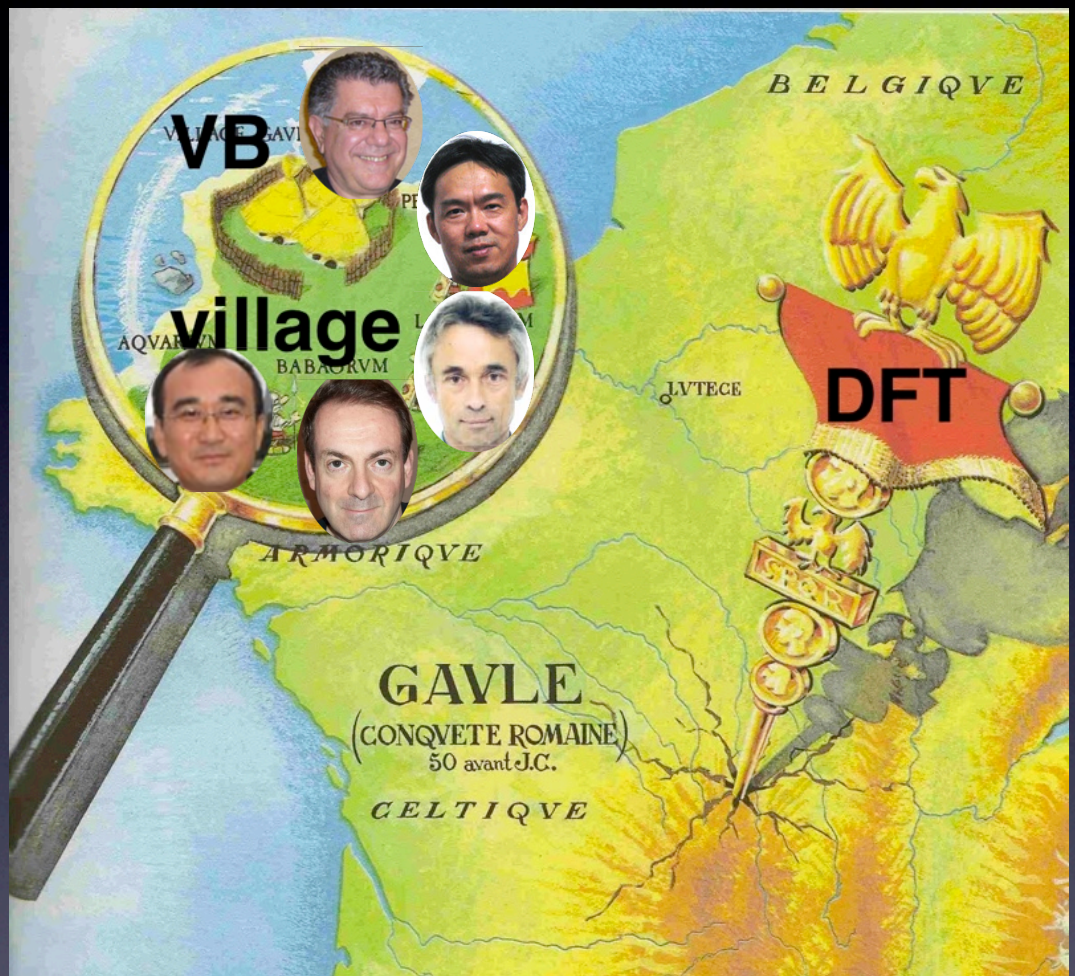
Successes of MO theory vs. VB «failures»

- ~1960-1980: The downfall

Sir John A. Pople

MO programs are developed, VB had nothing

- ~1980-2010: small but active community



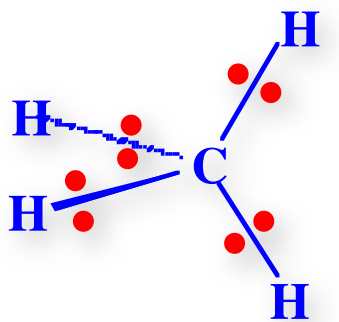
New models, methods, programs, applications

- 2012-...: awakening of the sleeping beauty?

All elements for a Valence Bond revival are ready

Chemists' «schizophrenia»

- **Concepts and models** based on a localized vision :



Lewis model, arrow-pushing language, VSEPR, hybridization,...

- **Localized** electron pairs
- **Chemical bond** concept

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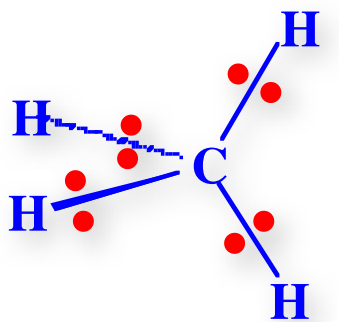
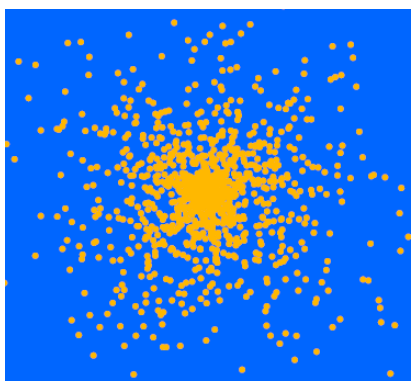


Lewis model, arrow-pushing language, VSEPR, hybridization,...

- **Localized** electron pairs
- **Chemical bond** concept

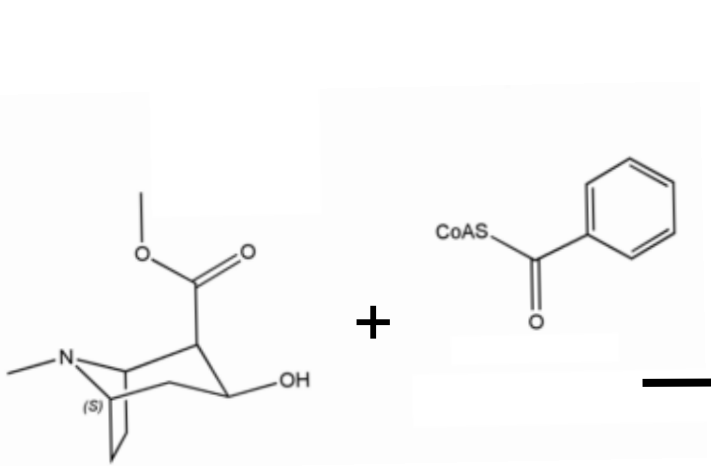
- **Quantitative theory** all-interacting delocalized particles vision :

$$\hat{H}\Psi = E\Psi$$



- **delocalized** particles (e^-, n^+)
- **indistinguishable** and all-interacting (no chemical bond)

Chemists' «schizophrenia»



+

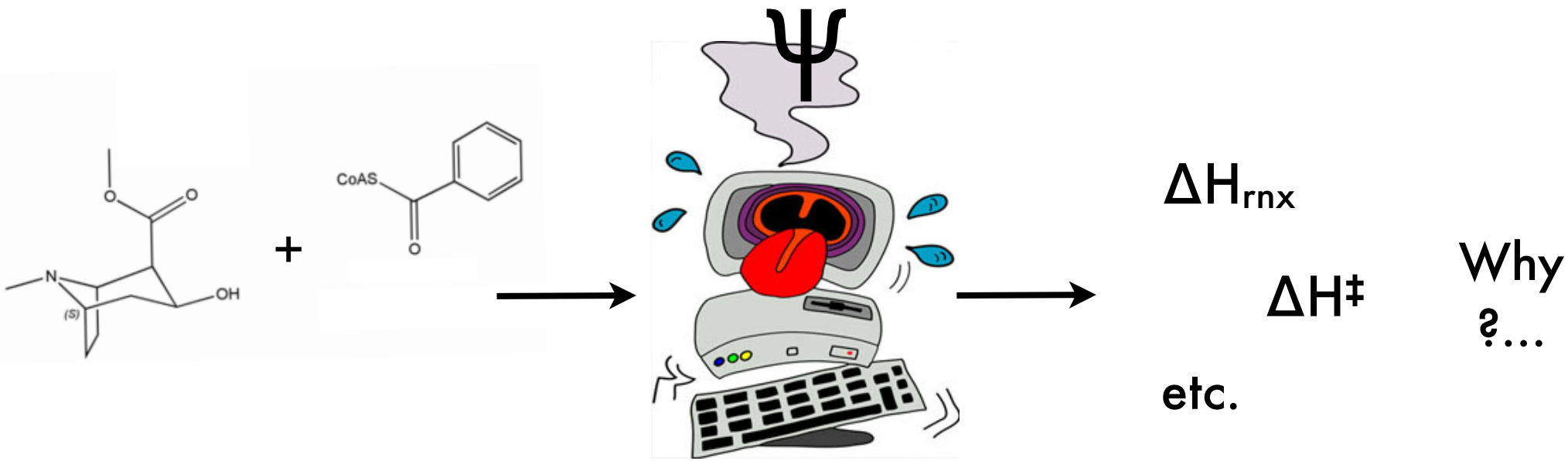
ΔH_{rnx}

$\Delta H^{\ddagger}$

etc.

Why ?...

Chemists' «schizophrenia»



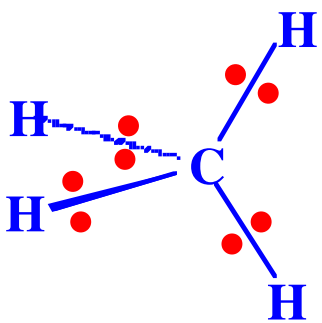
«I know that the computer has understood, but I would like to understand too» (Eugene Wigner)

=> how to build a bridge between quantum mechanics and chimists' vision ?

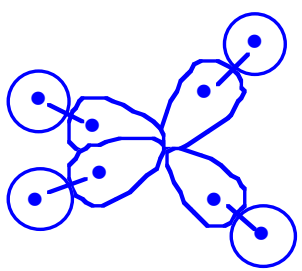
Valence Bond theory

- Quantum dressing of Lewis' picture :

Lewis :



VB :



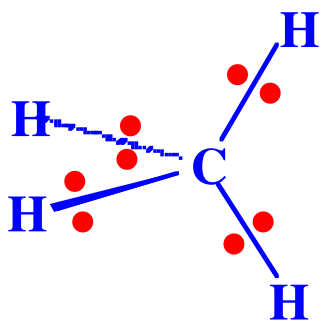
- VB wave functions :
  - Electrons occupy **localized** orbitals (atomics, hybrids,...)
  - A **bond** = two singlet-coupled electrons in two orbitals

=> bonds are essentially **covalent**
+ minor ionics

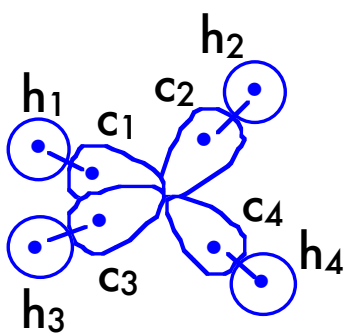
Valence Bond theory

- Quantum dressing of Lewis' picture :

Lewis :



VB :



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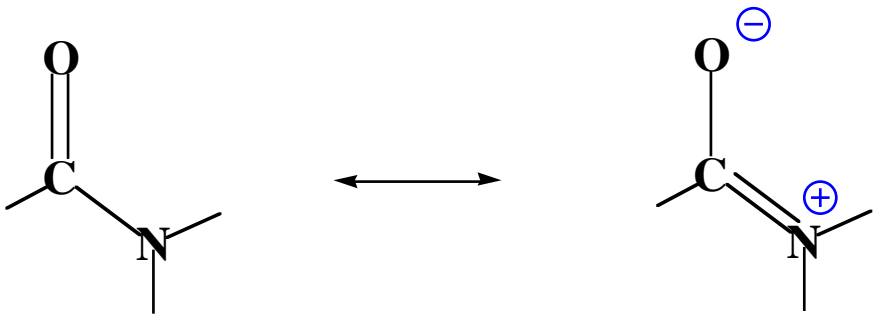
$$\Psi = \left| (c_1\overline{h_1} + h_1\overline{c_1})(c_2\overline{h_2} + h_2\overline{c_2})(c_3\overline{h_3} + h_3\overline{c_3})(c_4\overline{h_4} + h_4\overline{c_4}) \right|$$

Valence Bond theory

- When more than one Lewis structure is needed :



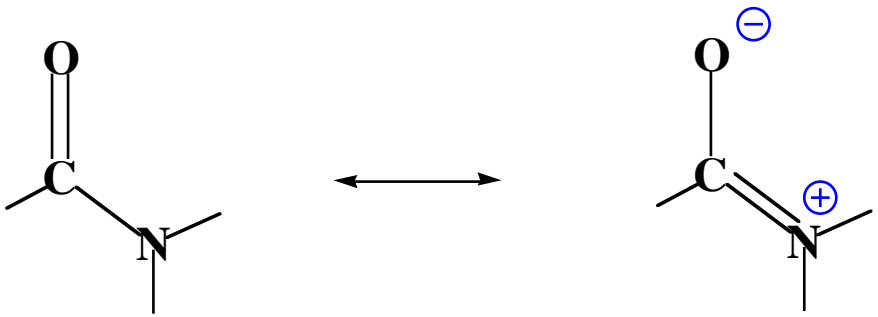
1 **2**

$$\Psi(\mathbf{1}\leftrightarrow\mathbf{2}) = C_1(\Psi_1) + C_2(\Psi_2)$$

- VB wave function : two **resonating** components, each one corresponding to one of the **2 structures**

Valence Bond theory

- When more than one Lewis structure is needed :



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$$\Psi(\mathbf{1}\leftrightarrow\mathbf{2}) = C_1(\Psi_1) + C_2(\Psi_2)$$

=> structure weights : 73% , 27%

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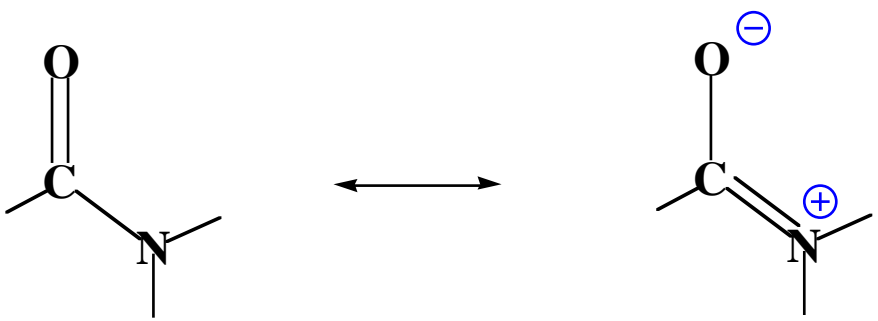
Valence Bond theory

- When more than one Lewis structure is needed :



1 **2**

- VB wave function : two **resonating** components, each one corresponding to one of the **2 structures**

$$\Psi(\mathbf{1}\leftrightarrow\mathbf{2}) = C_1(\Psi_1) + C_2(\Psi_2)$$

=> structure weights : 73% , 27%

=> resonance energy : $R.E. = E(\Psi_1) - E(\Psi_{1\leftrightarrow 2}) =$ 37 kcal/mol

=> rotation barrier due to resonance :

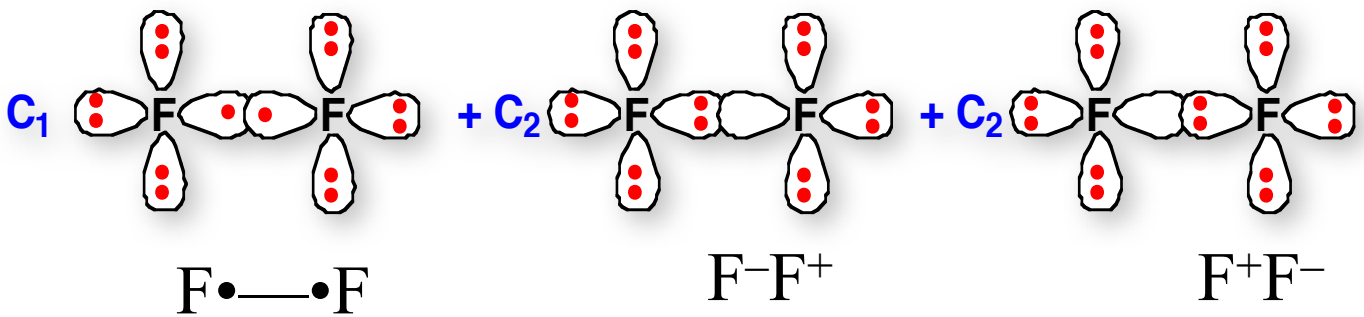
Lauvergnat+Hiberty, JACS 1997, 119, 9478.

Ab initio VB methods

- Some *ab initio* Valence Bond methods :

- VBSCF includes **static correlation** **:** all configurations of electrons into orbitals included, coefs+orbitals optimized, but :

a **common set of orbitals** is optimized => compromise between ≠ configuration



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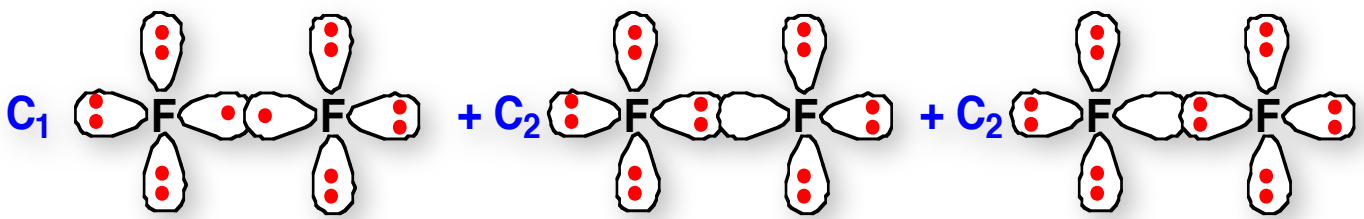
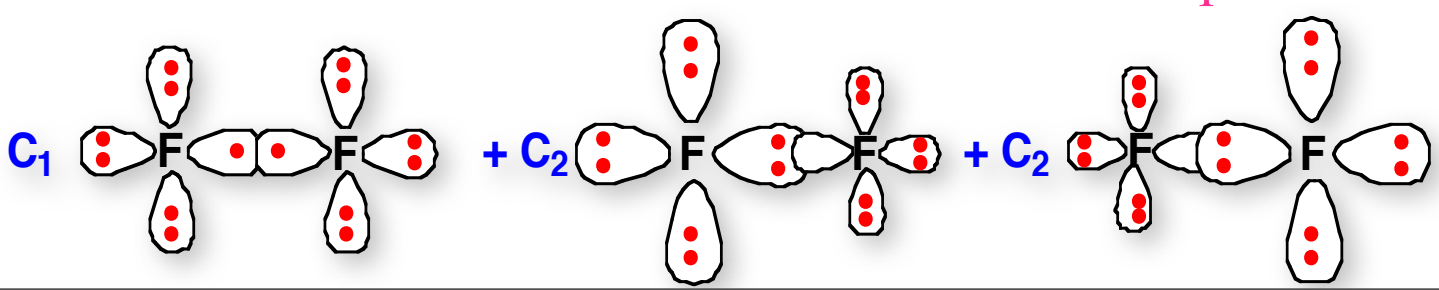


F•—•F F^-F^+ F^+F^-

- BOVB (Breathing Orbitals Valence Bond) includes dynamical correlation :

the coefficients and orbitals are optimized, and furthermore…

different orbitals for different VB structures : orbitals adapted to each config.



Why VB-QMC ?

★ Interest : interpretative capabilities :

- deep insight into the electronic structure
- use the basic language of chemists (Lewis structures,...)

★ Challenges : system size strongly limited :

- **Non-orthogonality !**
- Algorithms scaling (~N^4-5)
- Accuracy (inclusion of static & dynamic correlation)

=> interesting way : VB / QMC mariage

$$
\begin{aligned}
&\left\langle \Psi^{ij}_{x_1 y_1} \middle| \hat{H}_0 \middle| \Psi^{ij}_{x_2 y_2} \right\rangle = \left(E^{(0)}_{inact} - \varepsilon_i - \varepsilon_j \right) \left\langle \Psi^{ij}_{x_1 y_1} \middle| \Psi^{ij}_{x_2 y_2} \right\rangle \\
&+ \left\{ \left(4 s_{x_2 x_1} s_{y_2 y_1} - 2 s_{y_2 x_1} s_{x_2 y_1} \right) E^{(0)}_{act} \right. \\
&+ 4 f_{x_2 x_1} s_{y_2 y_1} + 4 f_{y_2 y_1} s_{x_2 x_1} - 2 f_{x_2 y_1} s_{y_2 x_1} - 2 f_{y_2 x_1} s_{x_2 y_1} \\
&+ \left[\left(f_{tx_1} s_{x_2 y_1} s_{y_2 u} + f_{ty_1} s_{y_2 x_1} s_{x_2 u} - 2 f_{tx_1} s_{y_2 y_1} s_{x_2 u} - 2 f_{ty_1} s_{x_2 x_1} s_{y_2 u} \right) \right. \\
&+ \left(f_{tx_2} s_{y_2 x_1} s_{y_1 u} + f_{ty_2} s_{x_2 y_1} s_{x_1 u} - 2 f_{tx_2} s_{y_2 y_1} s_{x_1 u} - 2 f_{ty_2} s_{x_2 x_1} s_{y_1 u} \right) \\
&+ \left. \left(f_{y_2 x_1} s_{y_1 u} s_{x_2 t} + f_{x_2 y_1} s_{x_1 u} s_{y_2 t} - 2 f_{x_2 x_1} s_{y_1 u} s_{y_2 t} - 2 f_{y_2 y_1} s_{x_1 u} s_{x_2 t} \right) \right] D^{tu} \\
&+ \left[f_{tu} \left(s_{y_2 x_1} s_{x_2 v} s_{y_1 w} + s_{x_2 y_1} s_{y_2 v} s_{x_1 w} - 2 s_{y_2 y_1} s_{x_2 v} s_{x_1 w} - 2 s_{x_2 x_1} s_{y_2 v} s_{y_1 w} \right) \right. \\
&+ \left. \left(f_{tx_1} s_{x_2 u} s_{y_1 v} s_{y_2 w} + f_{ty_1} s_{y_2 u} s_{x_1 v} s_{x_2 w} + f_{tx_2} s_{y_2 v} s_{x_1 u} s_{y_1 w} + f_{ty_2} s_{x_2 v} s_{y_1 u} s_{x_1 w} \right) \right] \Pi^{tv,uw} \\
&+ \left. f_{tu} s_{y_2 v_1} s_{x_2 w_1} s_{y_1 v_2} s_{x_1 w_2} \Gamma^{t v_1 w_1, u v_2 w_2} \right\} \\
&+ \delta^{ij} \left\{ \left(4 s_{x_2 y_1} s_{y_2 x_1} - 2 s_{x_2 x_1} s_{y_2 y_1} \right) E^{(0)}_{act} \right. \\
&+ 4 f_{x_2 y_1} s_{y_2 x_1} + 4 f_{y_2 x_1} s_{x_2 y_1} - 2 s_{x_2 x_1} f_{y_2 y_1} - 2 f_{x_2 x_1} s_{y_2 y_1} \\
&+ \left[\left(f_{tx_2} s_{y_2 y_1} s_{x_1 u} + f_{ty_2} s_{x_2 x_1} s_{y_1 u} - 2 f_{ty_2} s_{x_2 y_1} s_{x_1 u} - 2 f_{tx_2} s_{y_2 x_1} s_{y_1 u} \right) \right. \\
&+ \left(f_{ty_1} s_{x_2 x_1} s_{y_2 u} + f_{tx_1} s_{y_2 y_1} s_{x_2 u} - 2 f_{ty_1} s_{y_2 x_1} s_{x_2 u} - 2 f_{tx_1} s_{x_2 y_1} s_{y_2 u} \right) \\
&+ \left. \left(f_{y_2 y_1} s_{x_1 u} s_{x_2 t} + f_{x_2 x_1} s_{y_1 u} s_{y_2 t} - 2 f_{x_2 y_1} s_{x_1 u} s_{y_2 t} - 2 f_{y_2 x_1} s_{y_1 u} s_{x_2 t} \right) \right] D^{tu} \\
&\left[+ f_{tu} \left(s_{y_2 y_1} s_{x_2 v} s_{x_1 w} + s_{x_2 x_1} s_{y_2 v} s_{y_1 w} - 2 s_{x_2 y_1} s_{y_2 v} s_{x_1 w} - 2 s_{y_2 x_1} s_{x_2 v} s_{y_1 w} \right) \right. \\
&+ \left. \left(f_{ty_1} s_{x_2 u} s_{x_1 v} s_{y_2 w} + f_{tx_1} s_{y_2 u} s_{y_1 v} s_{x_2 w} + f_{tx_2} s_{y_1 u} s_{y_2 v} s_{x_1 w} + f_{ty_2} s_{x_1 u} s_{x_2 v} s_{y_1 w} \right) \right] \Pi^{tv,uw} \\
&+ \left. \left. f_{tu} s_{y_2 v_1} s_{x_2 w_1} s_{x_1 v_2} s_{y_1 w_2} \Gamma^{t v_1 w_1, u v_2 w_2} \right\} \right.
\end{aligned}
$$

Why VB-QMC ?

★ **No non-orthogonality problem !** $e_l(w_i) = \left(\frac{\hat{H}\psi_T}{\psi_T} \right)(w_i)$; $p = |\psi_T|^2$

★ Efficient parallel algorithm ; and scaling : N_e^3 but with a HUGE prefactor !

★ New form of correlated VB wave-function : **Jastrow-VBSCF**

$$J \times \left(C_1 \; F\bullet\!\!-\!\!\bullet F \; + C_2 \; F^-F^+ \; + C_2 \; F^+F^- \right)$$

Jastrow function
(explicit correlation : ee, en, een)

VBSCF determinantal part
(static correlation)

★ Moderate size basis sets are sufficient (converged at TZP level)

★ **We keep all the insight of a real Valence Bond wave function (VMC)** : weights, separate structures calculations...

The Jastrow function

★ Padé expansion :

The Jastrow factor J is written as

$$J = J_{en} J_{ee} J_{een} = \exp(f_{en} + f_{ee} + f_{een})$$

where

$$f_{en}(R_{i\alpha}) = \sum_{i=1}^{N_{\text{elec}}} \sum_{\alpha=1}^{N_{\text{nuc}}} \left[\left(\frac{a_1 R_{i\alpha}}{1 + a_2 R_{i\alpha}} + \sum_{p=2}^{N_{\text{ord}}} a_{p+1} R_{i\alpha}^p \right) - \left(\frac{a_1 R_c}{1 + a_2 R_c} + \sum_{p=2}^{N_{\text{ord}}} a_{p+1} R_c^p \right) \right]$$

$$f_{ee}(R_{ij}) = \sum_{i=2}^{N_{\text{elec}}} \sum_{j=1}^{i-1} \left[\left(\frac{b_1 R_{ij}}{1 + b_2 R_{ij}} + \sum_{p=2}^{N_{\text{ord}}} b_{p+1} R_{ij}^p \right) - \left(\frac{b_1 R_c}{1 + b_2 R_c} + \sum_{p=2}^{N_{\text{ord}}} b_{p+1} R_c^p \right) \right]$$

$$f_{een}(R_{i\alpha}, R_{j\alpha}, R_{ij}) = \sum_{i=2}^{N_{\text{elec}}} \sum_{j=1}^{i-1} \sum_{\alpha=1}^{N_{\text{nuc}}} \sum_{p=2}^{N_{\text{ord}}} \sum_{k=p-1}^{0} \sum_{l=l_{\max}}^{0} c_n R_{ij}^k (R_{i\alpha}^l + R_{j\alpha}^l)(R_{i\alpha} R_{j\alpha})^m, \quad \text{where } m = \frac{p-k-l}{2}$$

and $l_{\max}$ is $p-k$ if $k \neq 0$ and $p-k-2$ if $k = 0$. Only terms for which $m = \frac{p-k-l}{2}$ is an integer are included.

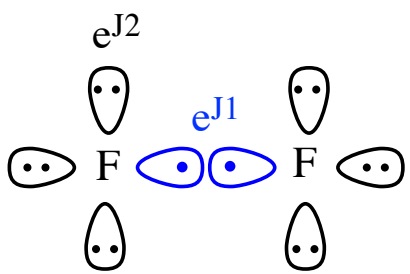
The Jastrow function

★ Multi-Jastrow approach :

$$\Psi_T = \sum_{k=1}^{N_{\text{det}}} c_k \begin{vmatrix} e^{J_{k_1^\uparrow}(\mathbf{r}_1|\mathbf{r}_i\neq\mathbf{r}_1)}\phi_{k_1^\uparrow}(\mathbf{r}_1) & \dots & e^{J_{k_1^\uparrow}(\mathbf{r}_{N_\uparrow}|\mathbf{r}_i\neq\mathbf{r}_{N_\uparrow})}\phi_{k_1^\uparrow}(\mathbf{r}_{N_\uparrow}) \\ \vdots & \vdots & \vdots \\ e^{J_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_1|\mathbf{r}_i\neq\mathbf{r}_1)}\phi_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_1) & \dots & e^{J_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_{N_\uparrow}|\mathbf{r}_i\neq\mathbf{r}_{N_\uparrow})}\phi_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_{N_\uparrow}) \end{vmatrix} \begin{vmatrix} e^{J_{k_1^\downarrow}(\mathbf{r}_{N_\uparrow+1}|\mathbf{r}_i\neq\mathbf{r}_{N_\uparrow+1})}\phi_{k_1^\downarrow}(\mathbf{r}_{N_\uparrow+1}) & \dots & e^{J_{k_1^\downarrow}(\mathbf{r}_N|\mathbf{r}_i\neq\mathbf{r}_N)}\phi_{k_1^\downarrow}(\mathbf{r}_N) \\ \vdots & \vdots & \vdots \\ e^{J_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_{N_\uparrow+1}|\mathbf{r}_i\neq\mathbf{r}_{N_\uparrow+1})}\phi_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_{N_\uparrow+1}) & \dots & e^{J_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_N|\mathbf{r}_i\neq\mathbf{r}_N)}\phi_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_N) \end{vmatrix}.$$

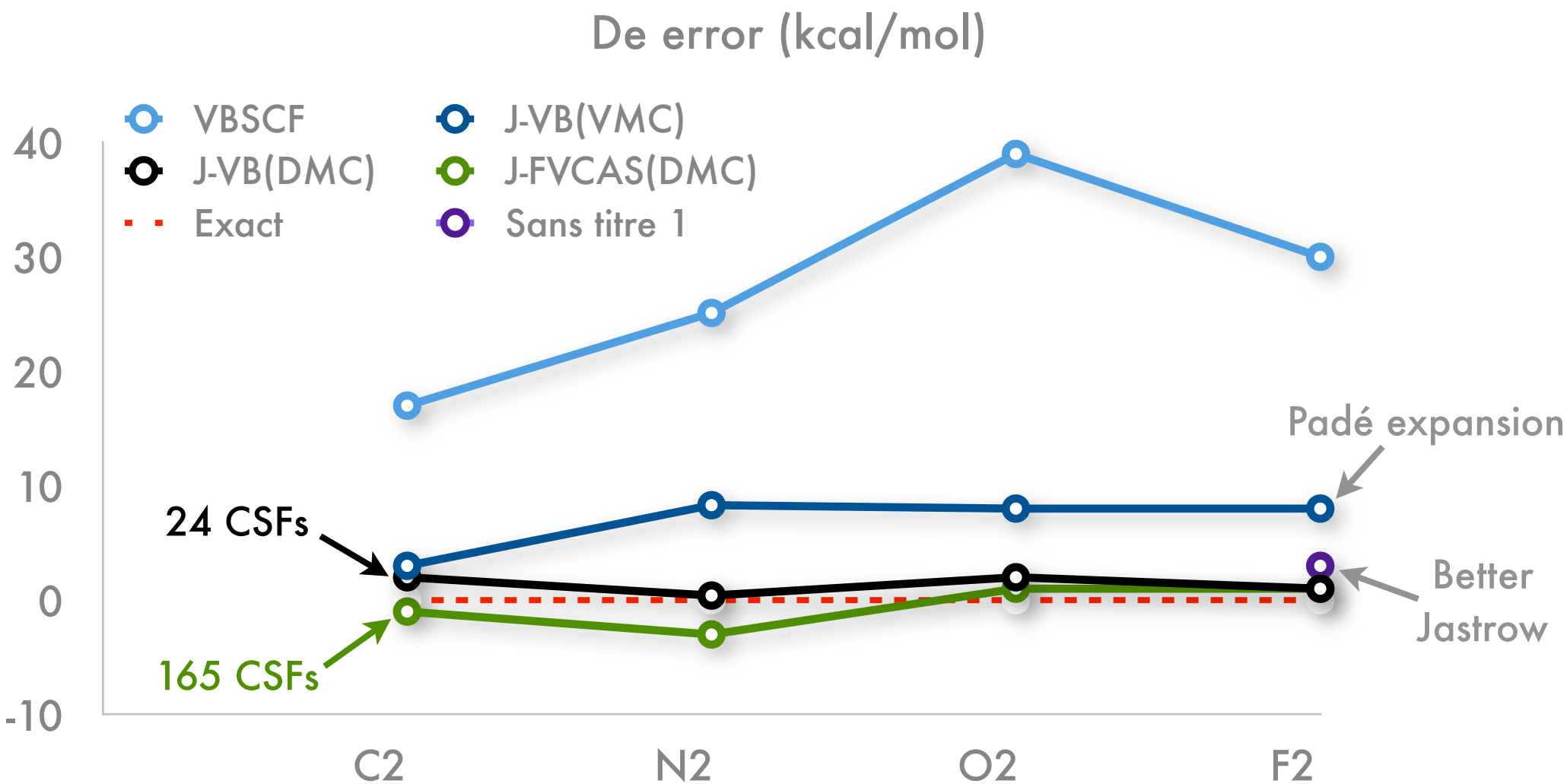
$$J_k(\mathbf{r}_i|\mathbf{r}_j\neq\mathbf{r}_i) = \frac{1}{2}\sum_{j\neq i}\sum_{\alpha}[s_k(\tilde{r}_{ij}) - p_{k\alpha}(\tilde{r}_{i\alpha}) - p_{k\alpha}(\tilde{r}_{j\alpha}) + g_{k\alpha}^{(1)}\tilde{r}_{i\alpha}^2\tilde{r}_{j\alpha}^2 + g_{k\alpha}^{(2)}(\tilde{r}_{i\alpha}^2+\tilde{r}_{j\alpha}^2)\tilde{r}_{ij}^2],$$

Different Jastrow for active/inactive...



* T. Bouabça, B. Braïda, and M. Caffarel, *J. Chem. Phys.* **2010,** 133, 044111

VB-QMC : benchmarking



* B. Braïda, J. Toulouse, M. Caffarel & C. J. Umrigar, J. Phys. Chem., **2011**, 134, 084108

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- **Application on «pancake bonding» in $DTCNE_2^{2-}$:**
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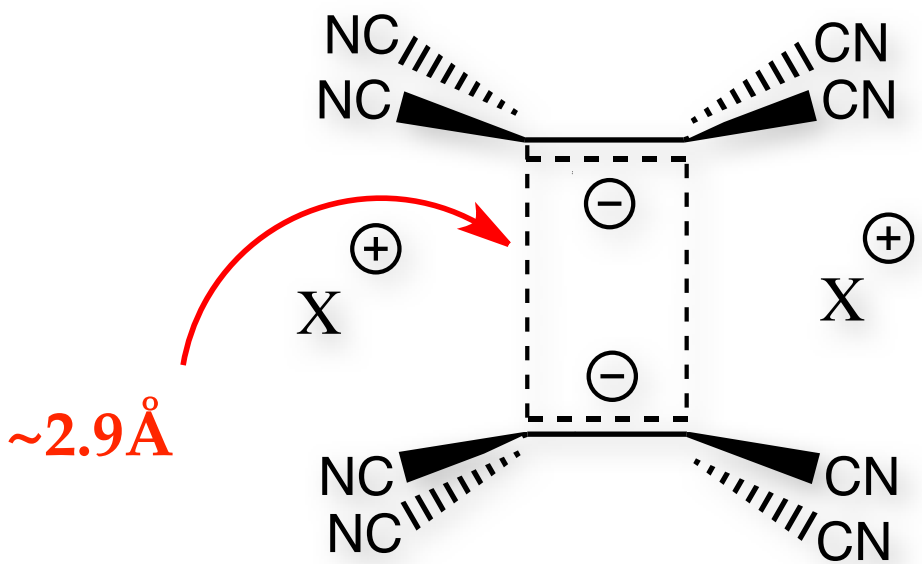
«Pancake bonding»

- $DTCNE_2^{2-}$:



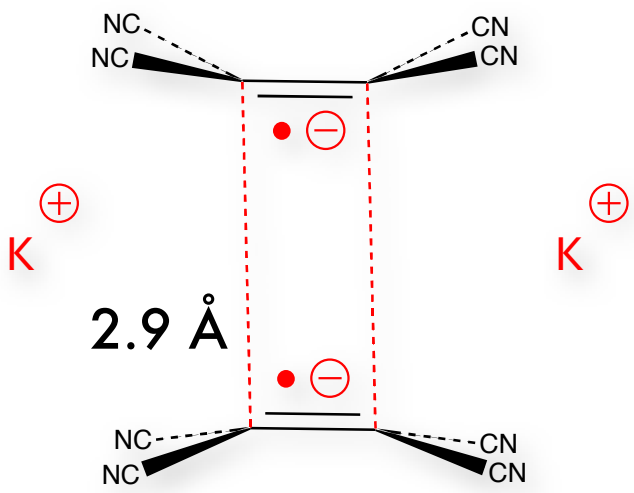
X^+ : Na^+, Cs^+, $[iPr_4N]^+$, $[Cr(C_6Me_3H_3)_2]^+$, ...

Electrostatic complex ?...

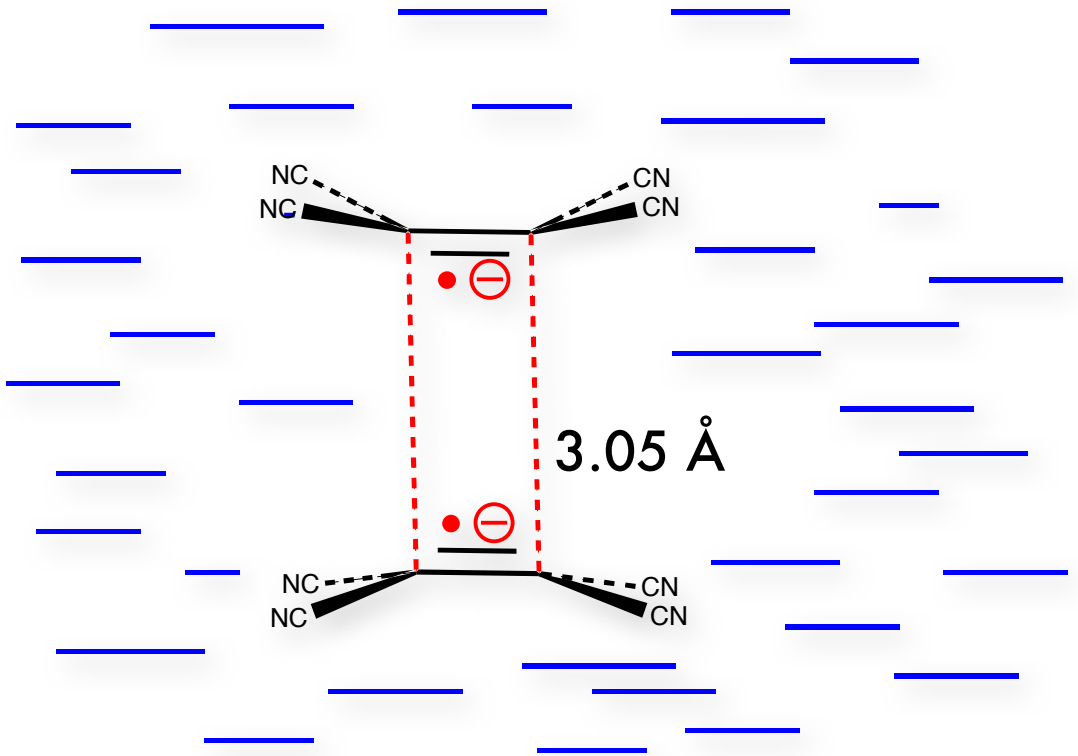
- Strong bonds
- Same bonding distance whatever the size of the cations !

«Pancake bonding»

- $DTCNE_2^{2-}$:



Stable in the crystal



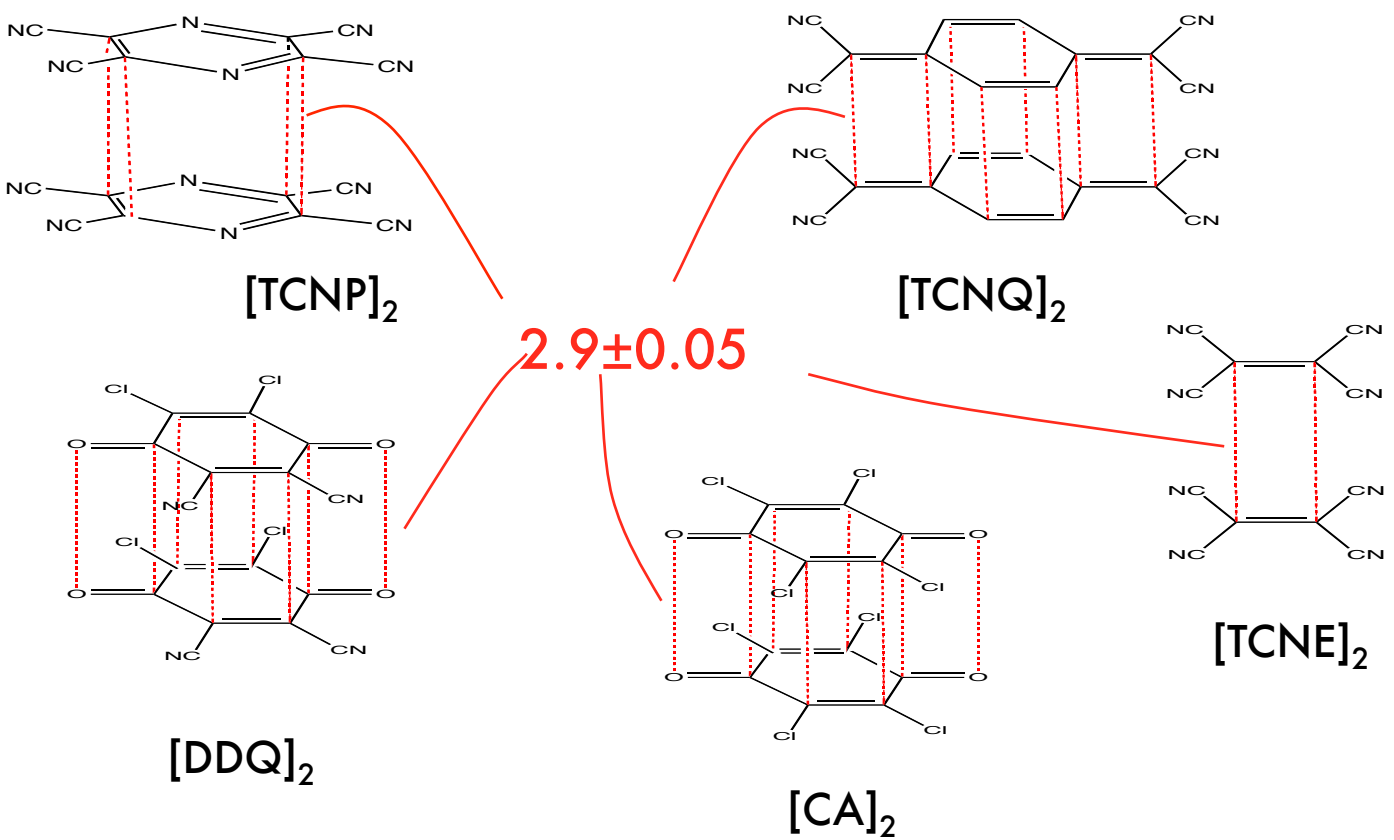
Stable in solution

- Same bonding distance whatever the environment !

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

«Pancake bonding»

- Other «pancake bonding» systems :

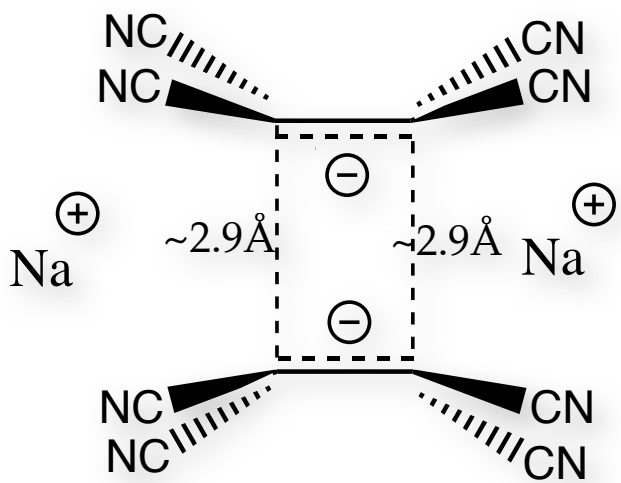


- Same bonding distance whatever the system !

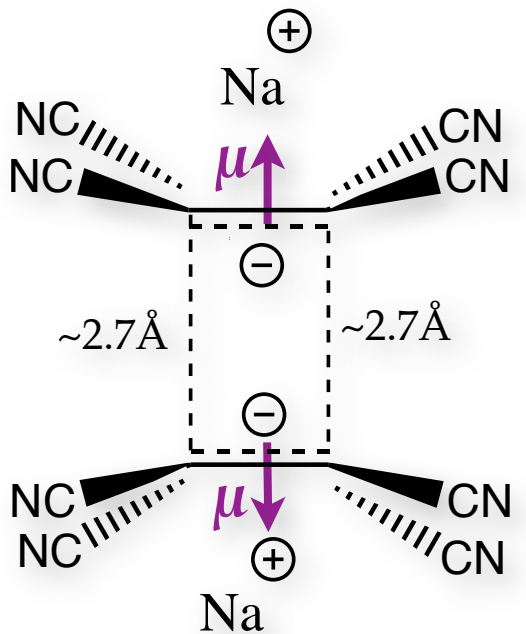
- $d_{C\text{---}C}$ < sum of vdW radii (3.45Å) , but much longer than C-C 2e bonds (1.54Å)

«Pancake bonding»

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



$D_e \approx 80.\ kcal/mol$

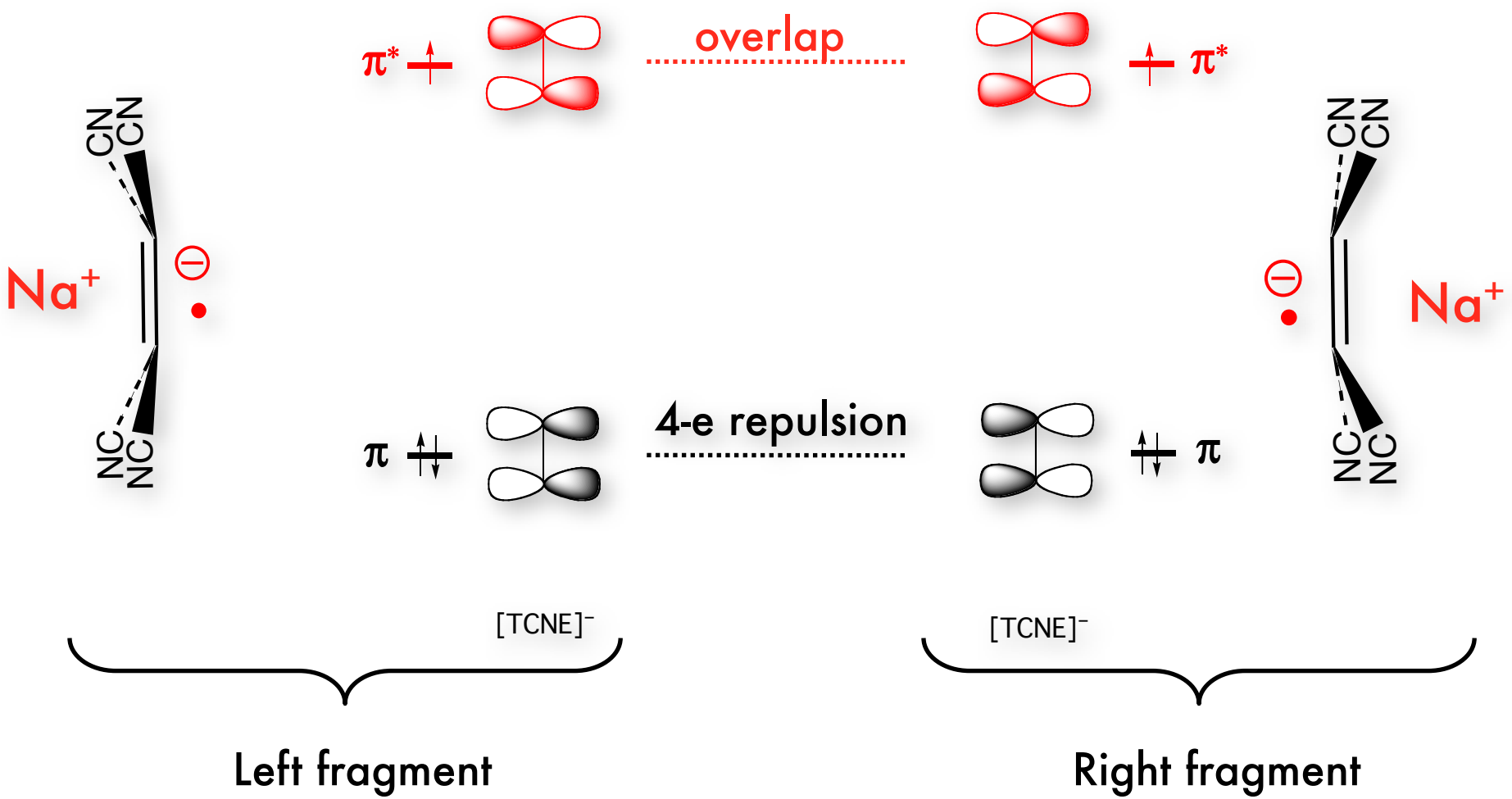


!

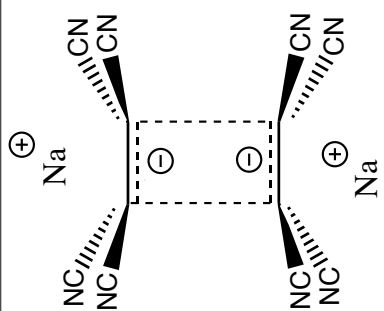
$D_e \approx 11.\ kcal/mol$

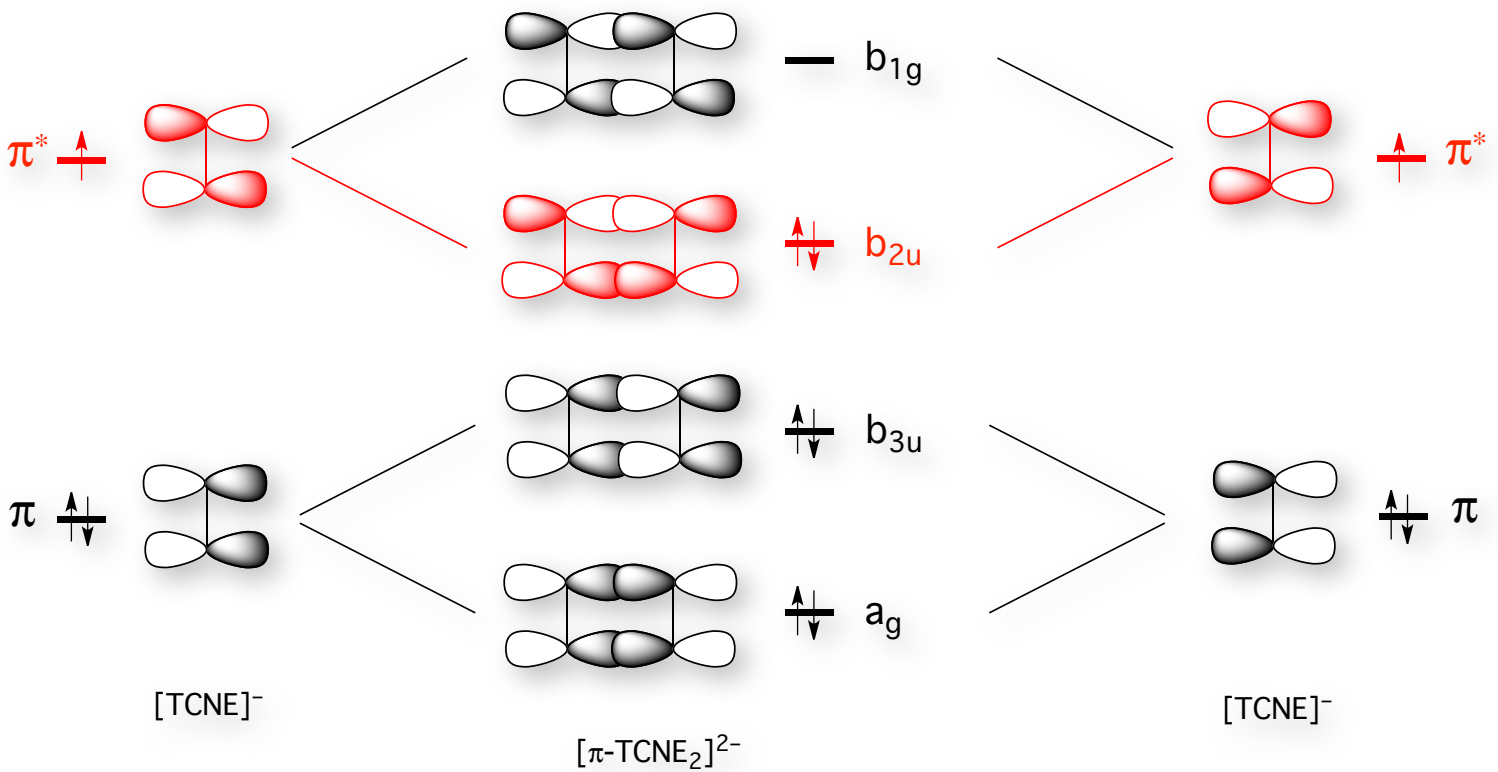
Right geom : significant bonding force overcome repulsive electrostatics !

Qualitative MO analysis



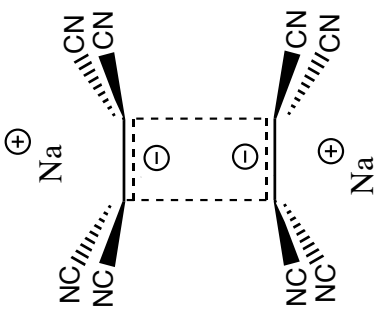
Qualitative MO analysis

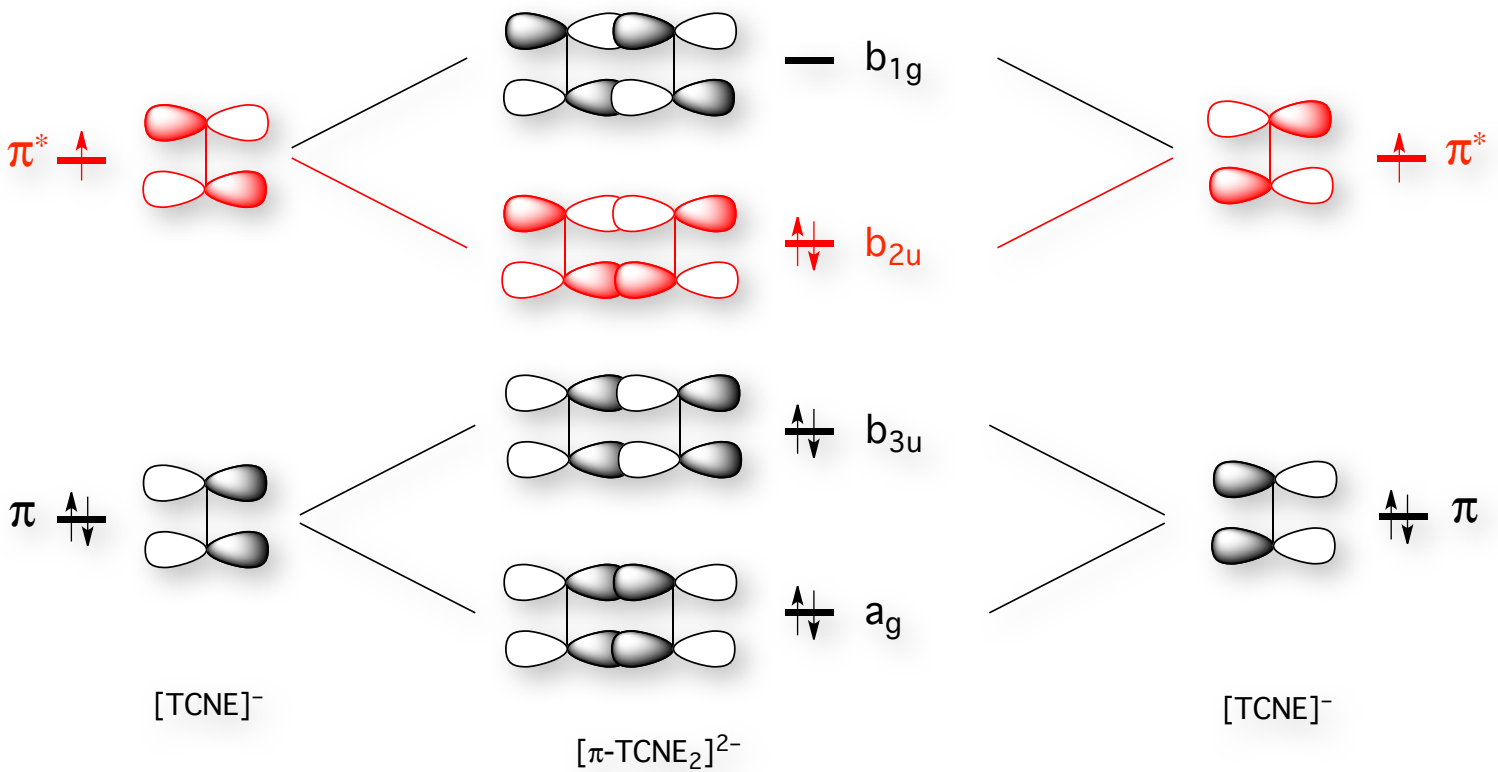




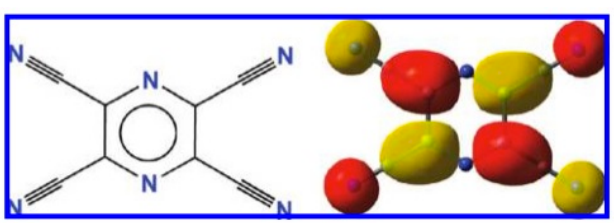
⟹ a simple **4 centers / 2 electrons bond ?**

Qualitative MO analysis

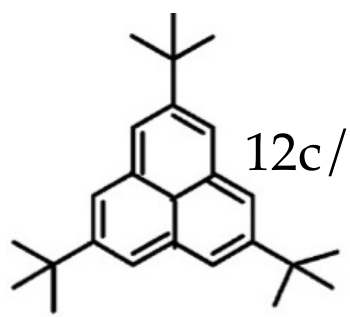




Other «pancake bonding» systems : **n center / 2e⁻ bonds**



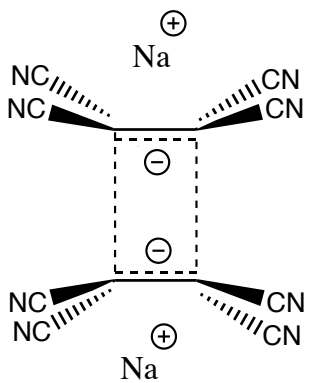
8c/2e⁻



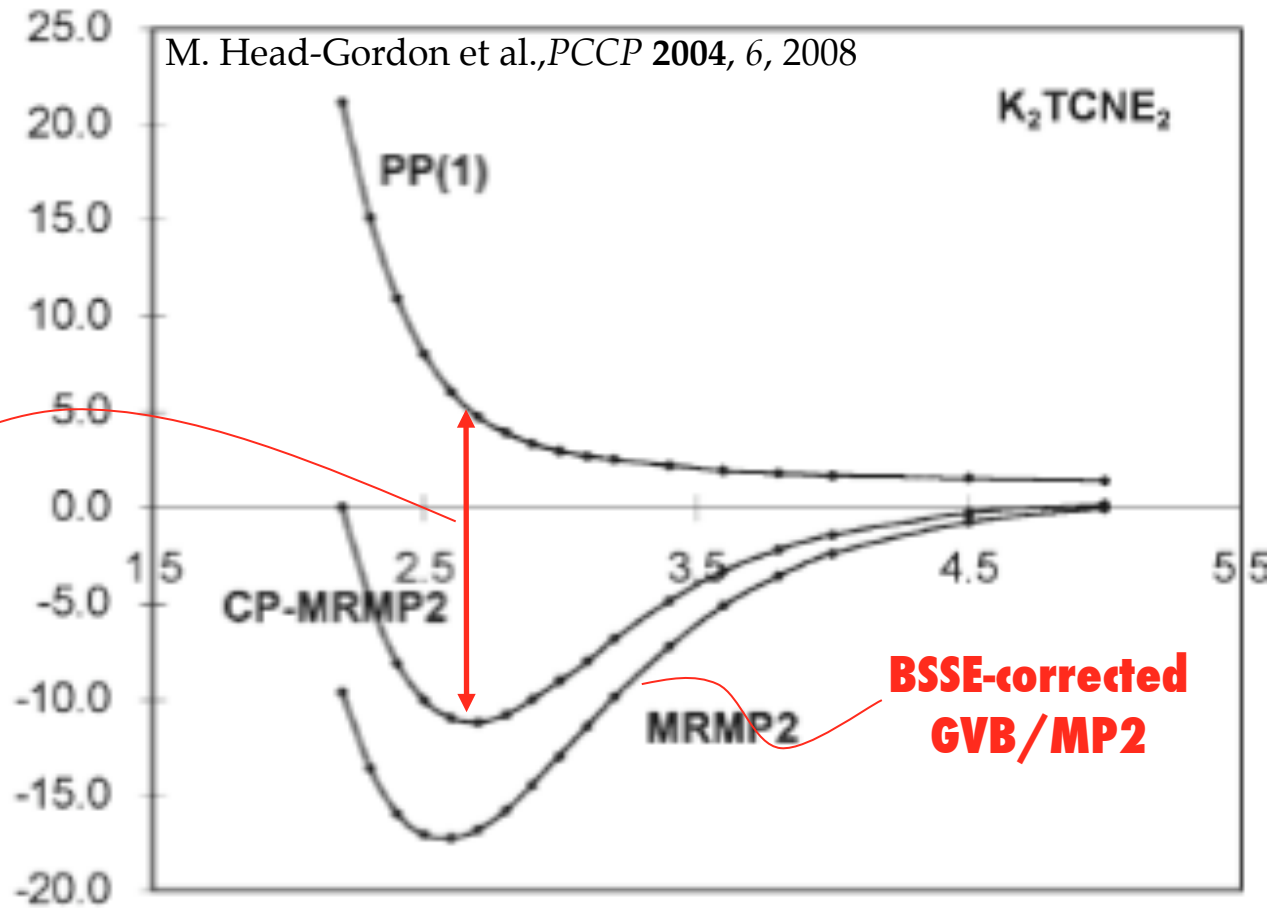
12c/2e⁻

Quantitative MO computations

- GVB calculations of the axial conformation :



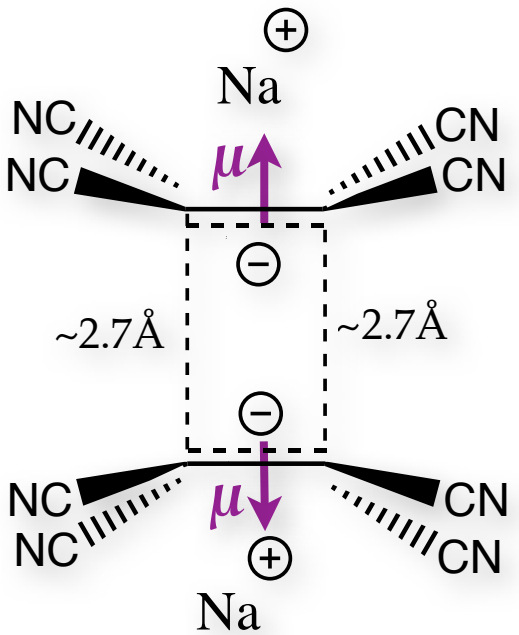
Contribution of dynamic correlation to bonding: > 23 kcal/mol !



- GVB-PP 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* !

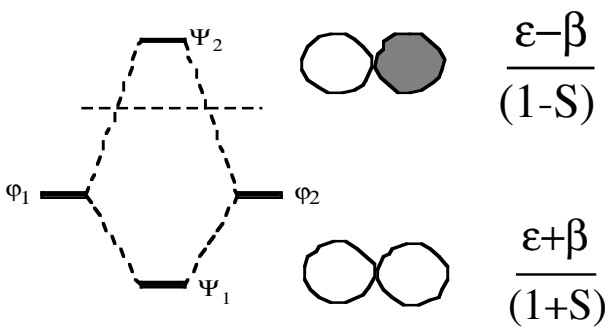
$\Longrightarrow$ **try a different perspective... with VB theory !**

Qualitative VB

- Let us apply qualitative VB analysis first :

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

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



1) Energy of a determinant :

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

n **= N# of neighboring (↑↑) pairs**

2) Off diagonal terms :

- Determinants differ by 2 spinorbitals:

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

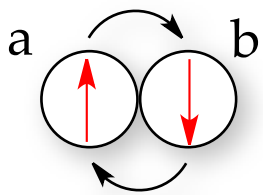
- Determinants differ by + than 2 spinorbitals :

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

Qualitative VB

- **2e-bond :**

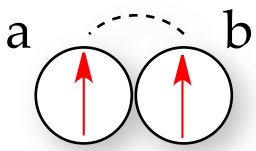
$$\psi_{VB} = \frac{|a\bar{b}| + |b\bar{a}|}{\sqrt{2(1+S^2)}}$$



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

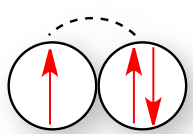
- **Triplet repulsion :**

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



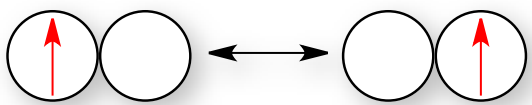
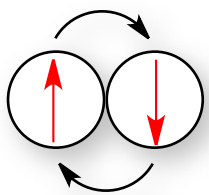
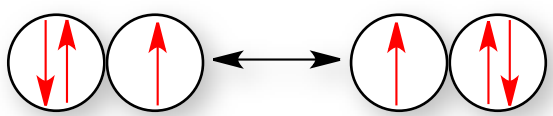
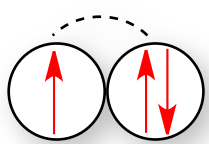
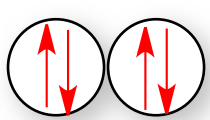
$$\Rightarrow \quad E = \langle \psi_{VB} | H | \psi_{VB} \rangle = \frac{-2\beta S}{(1-S^2)}$$

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



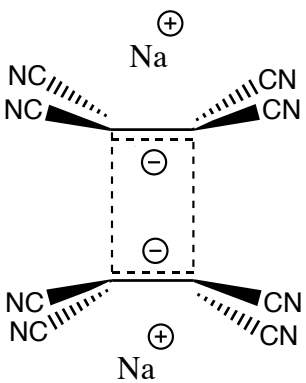
Qualitative VB

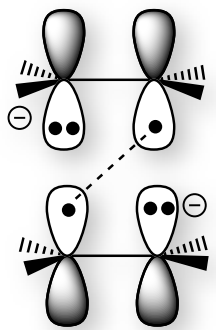
- Elementary interactions :

		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) =		$\frac{-4ßS}{1-S^2}$	$\frac{-4ßS}{1-S^2}$

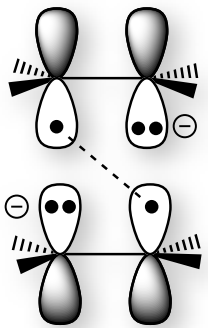
Qualitative VB analysis

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





1



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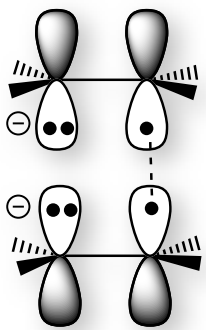

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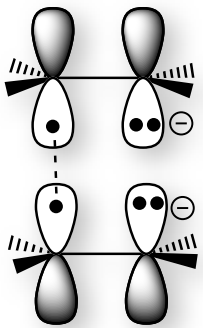
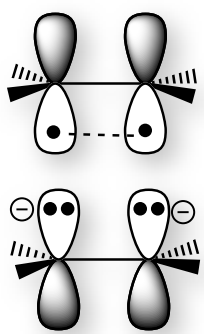


4



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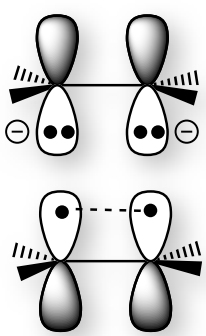

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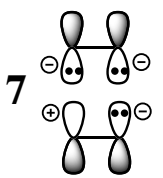

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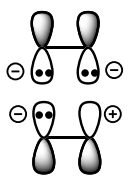

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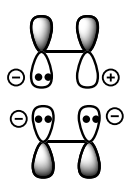
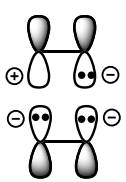


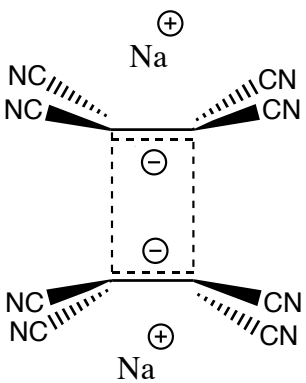
9

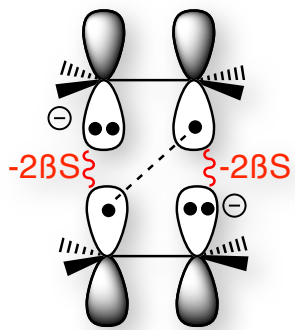


10

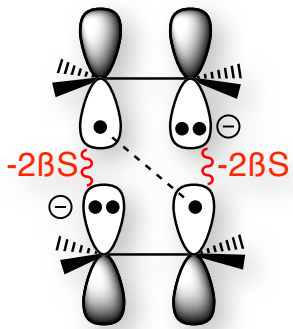
Qualitative VB analysis

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

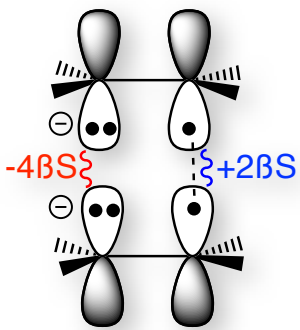




1



2



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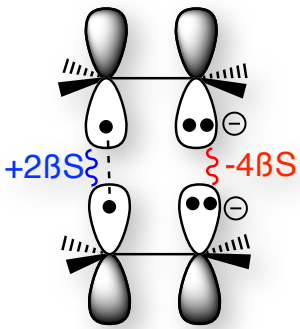

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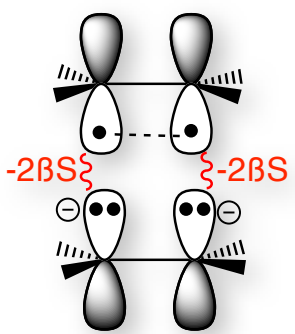

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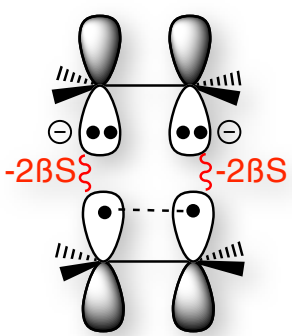

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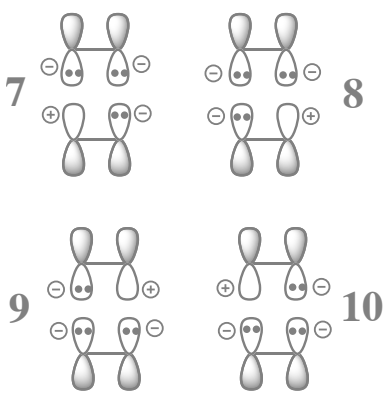
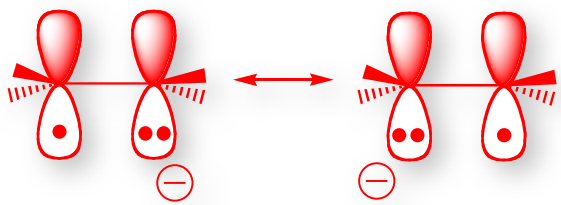


⟹ No structure is bonding by itself, **all the bonding comes from the resonance !**

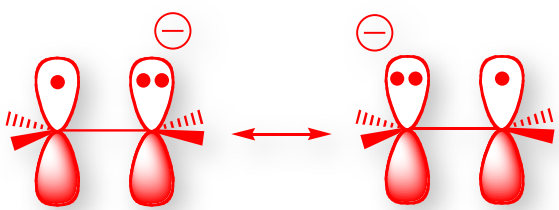
Qualitative VB analysis

- What about three-electron bonding ?...

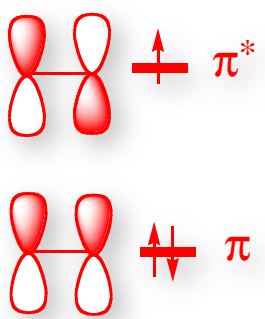


At infinite distance, each fragment displays a **3e⁻ π bond** :

∞



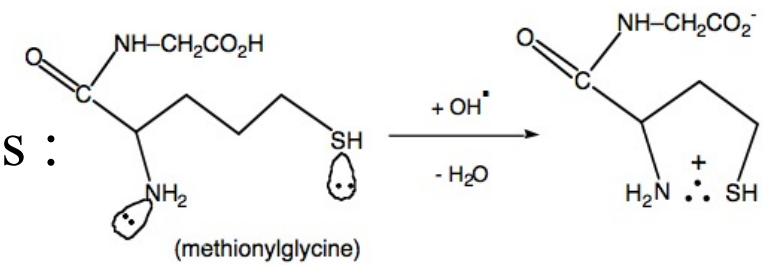
Left-right exchange of the negative charge, equivalent to:



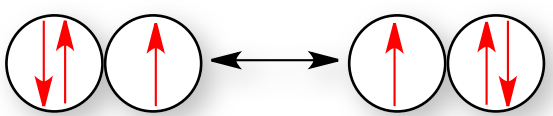
Qualitative VB analysis

- What is the three-electron bond ?...

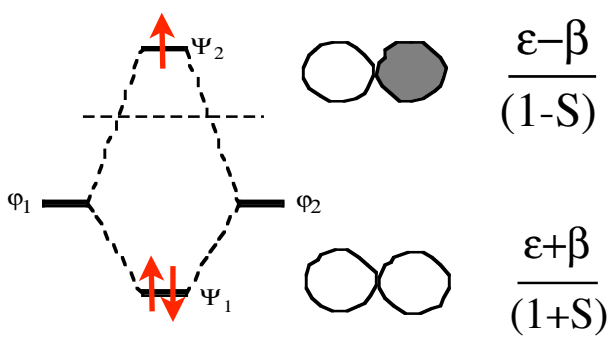
Examples : He_2^+, $RS^{\ominus}\therefore SR'$, radical intermediates :



VB description :



MO description :



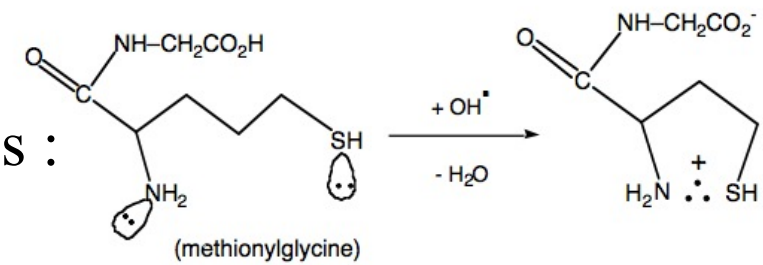
$$\Psi_{VB} = |a\bar{a}b| + |b\bar{b}a|$$

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

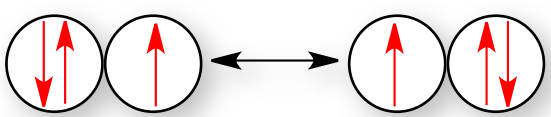
Qualitative VB analysis

- What is the three-electron bond ?...

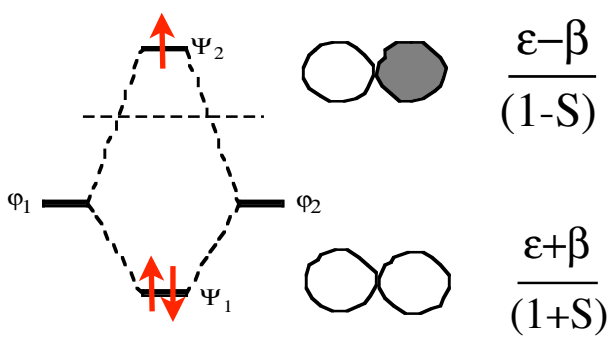
Examples : He_2^+, RS $\overset{\ominus}{\therefore}$ SR', radical intermediates :



VB description :



MO description :



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

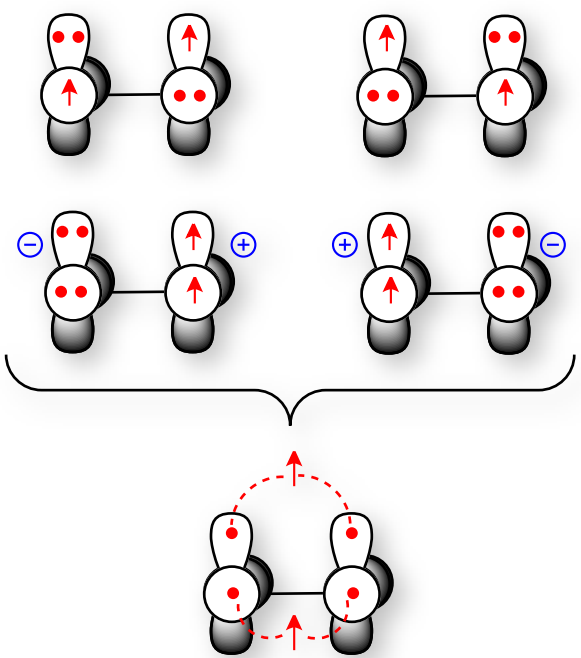
$$\Rightarrow \quad D_e = \frac{\beta(1-3S)}{(1-S^2)} \quad \Rightarrow \quad S_{opt} \approx 0.17$$

Qualitative VB analysis

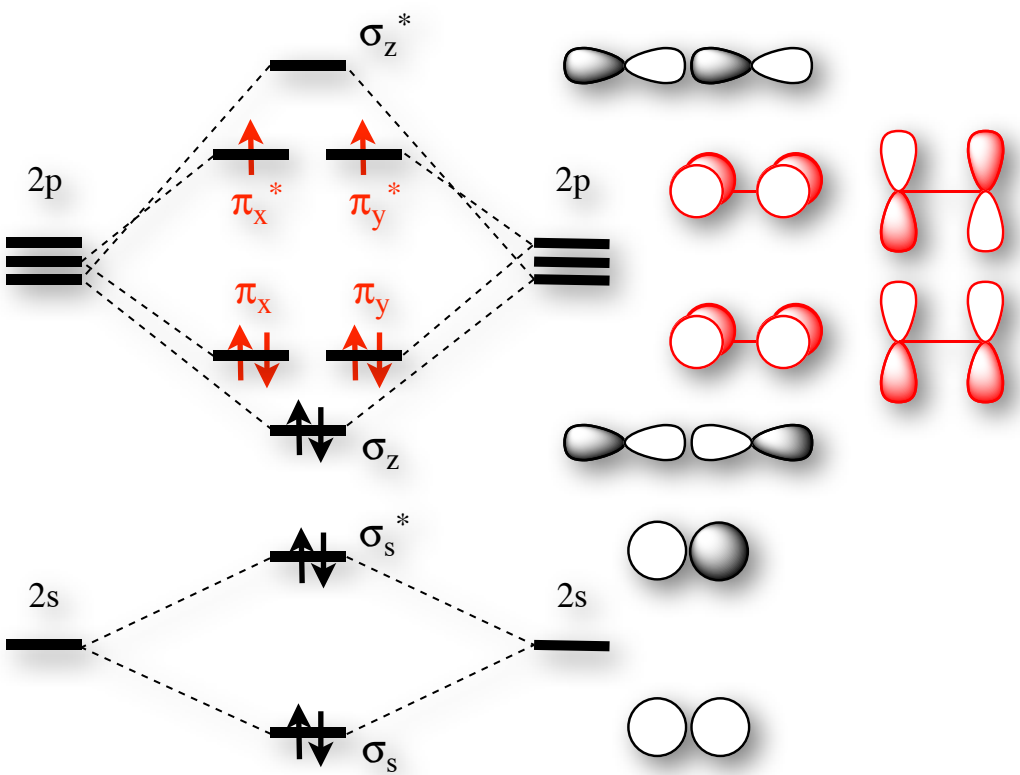
- What is the three-electron bond ?...

The most common 3e bonds : the two π bonds in O_2 ground state :

VB description :

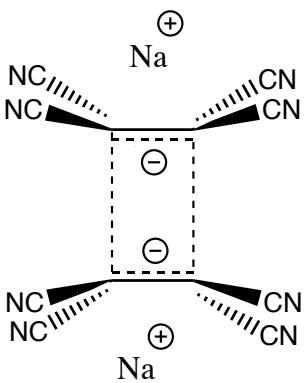


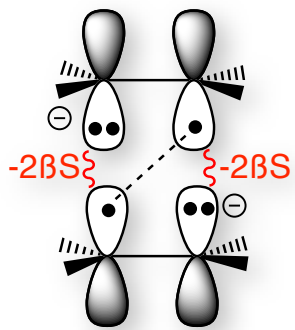
MO description :



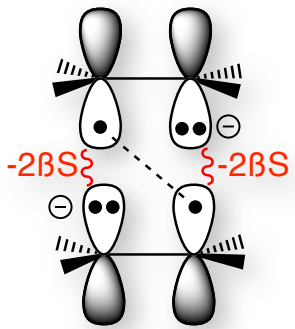
Qualitative VB analysis

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

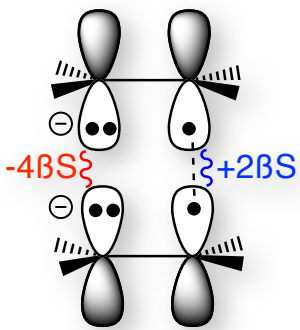




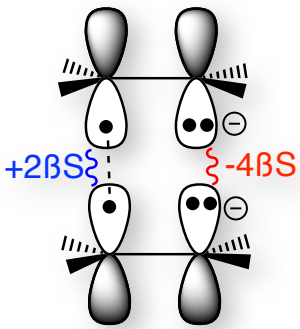
1



2



3



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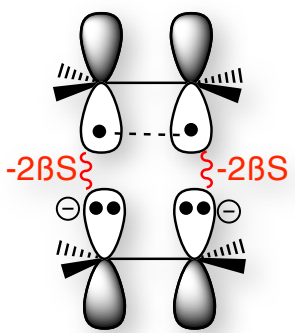

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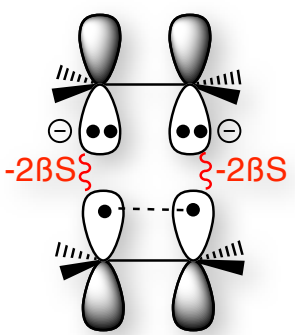
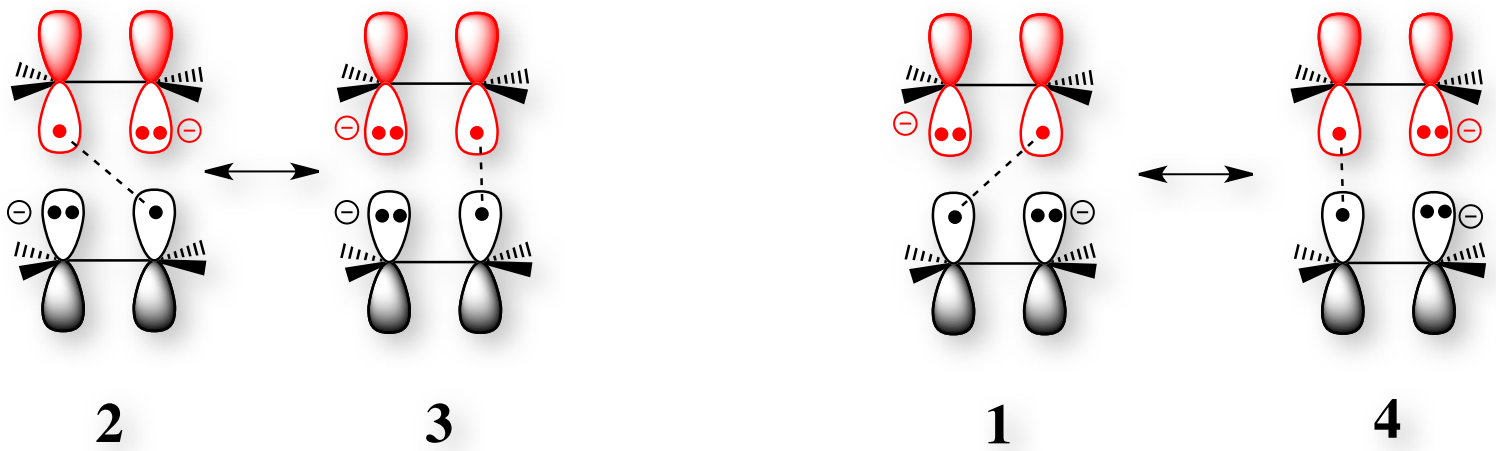


6

Qualitative VB analysis

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



Qualitative VB analysis

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

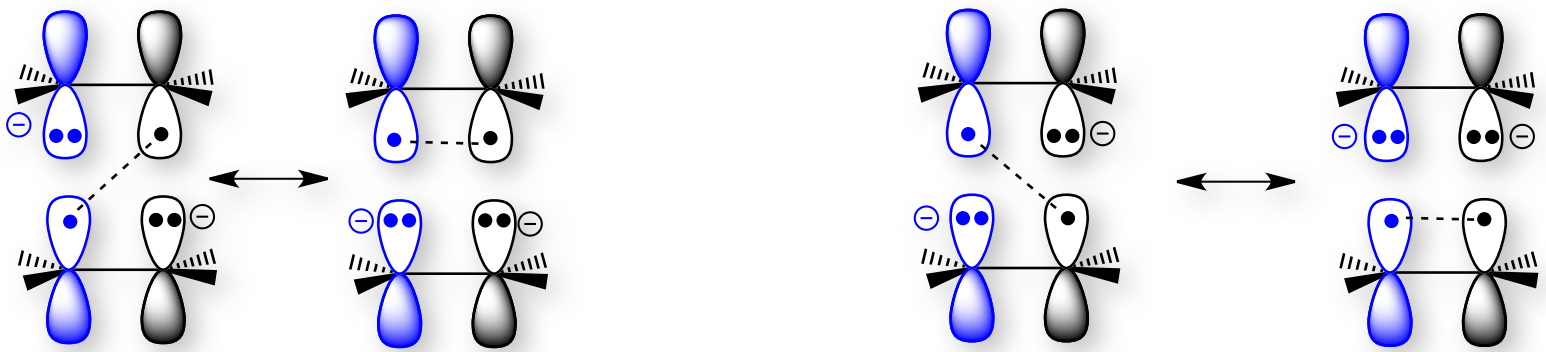
2 **3** **1** **4**

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

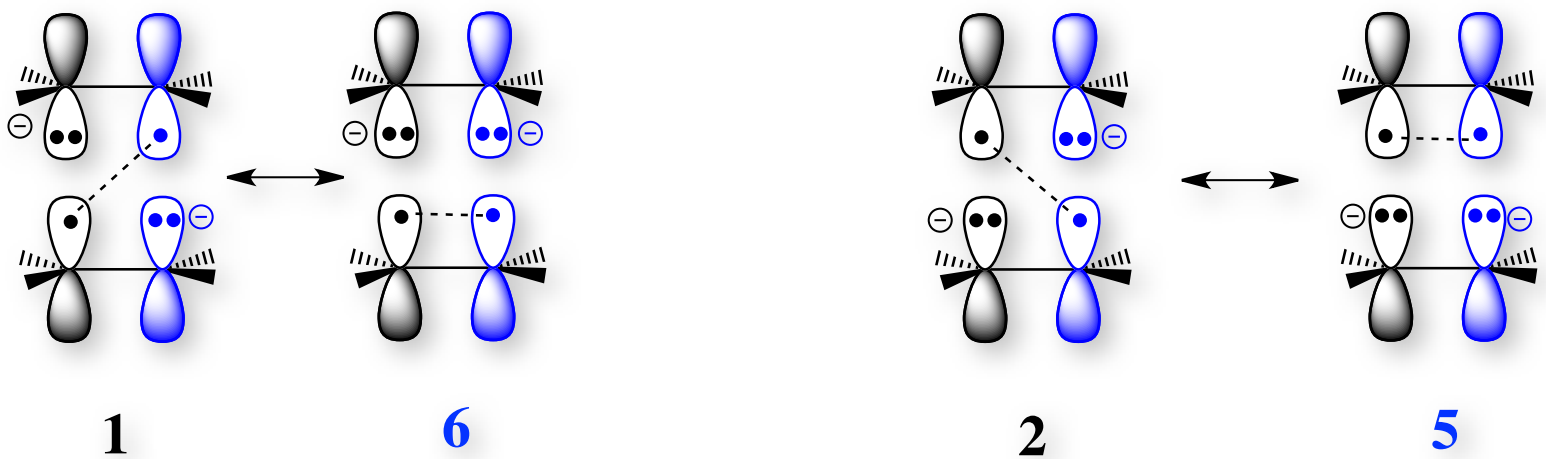
1 **3** **2** **4**

Qualitative VB analysis

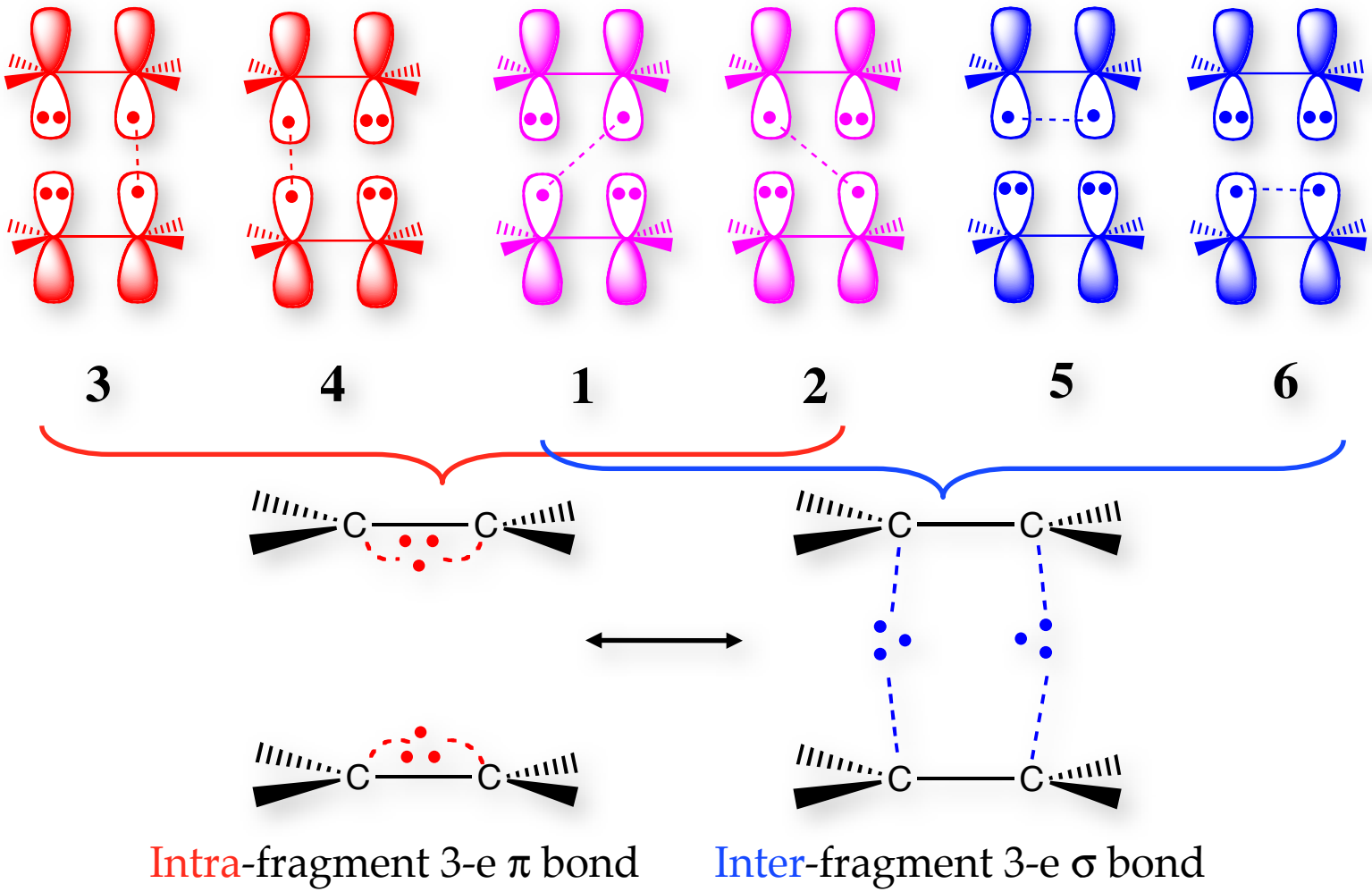
- 1↔5 and 2↔6 : **inter-fragment 3e⁻ π bond** (left-hand side) :



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



Qualitative VB analysis



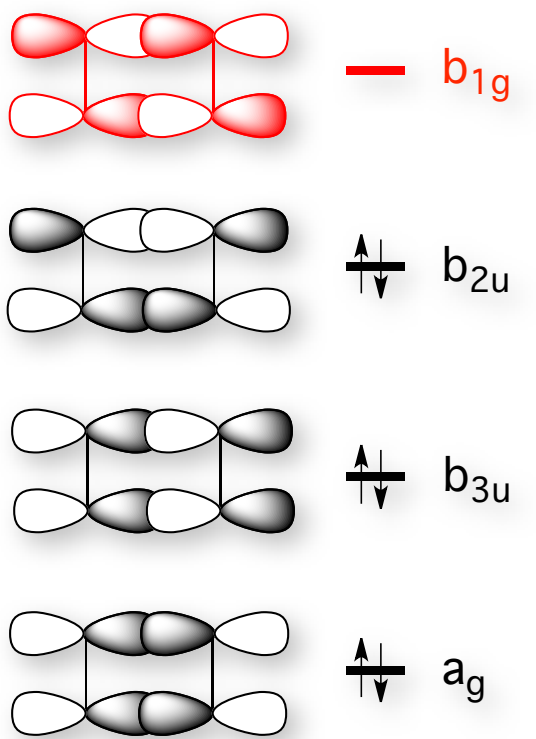
Intra-fragment 3-e π bond Inter-fragment 3-e σ bond

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

Qualitative VB analysis

- «VB reading» of MO determinants :

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

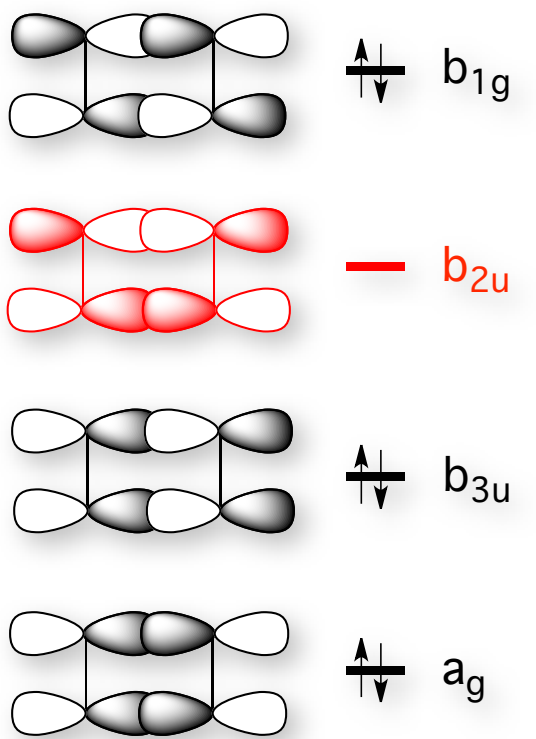


$$\Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = -\Psi_1^{VB} - \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB}$$

Qualitative VB analysis

- «VB reading» of MO determinants :

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

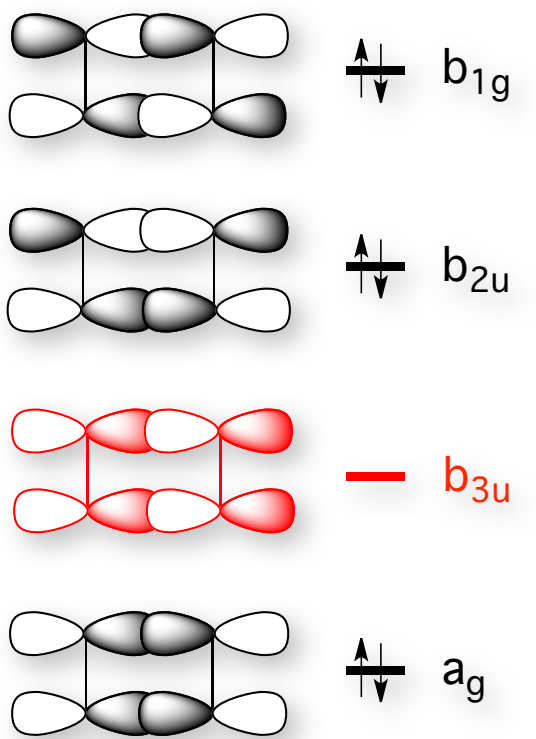


$$\Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} \ominus \Psi_3^{VB} \ominus \Psi_4^{VB} \ominus \Psi_5^{VB} \ominus \Psi_6^{VB}$$

Qualitative VB analysis

- «VB reading» of MO determinants :

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

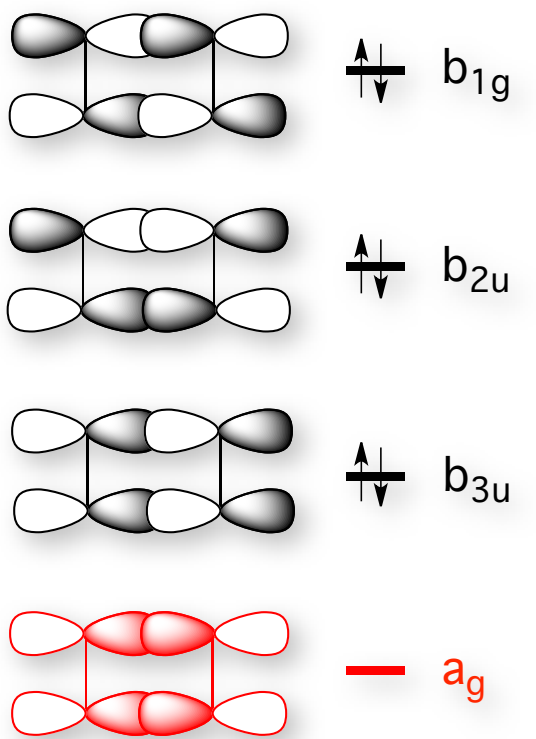


$$\Psi_{2-ext} = \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB}$$

Qualitative VB analysis

- «VB reading» of MO determinants :

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

- «VB reading» of MO determinants :

CAS(4,4) ⇔ 6 VB structures mixing :

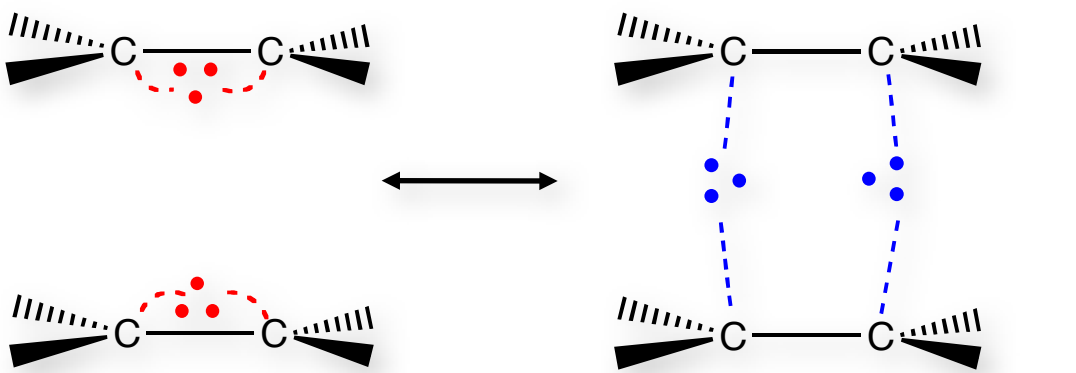
$$\begin{cases} \Psi_{HF} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = \ldots = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\ \Psi_{1-ext} = \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = \ldots = +\Psi_1^{VB}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

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

the VB analysis which reveals the 3e-bond nature

Qualitative VB analysis

- Conclusion of the qualitative VB analysis :



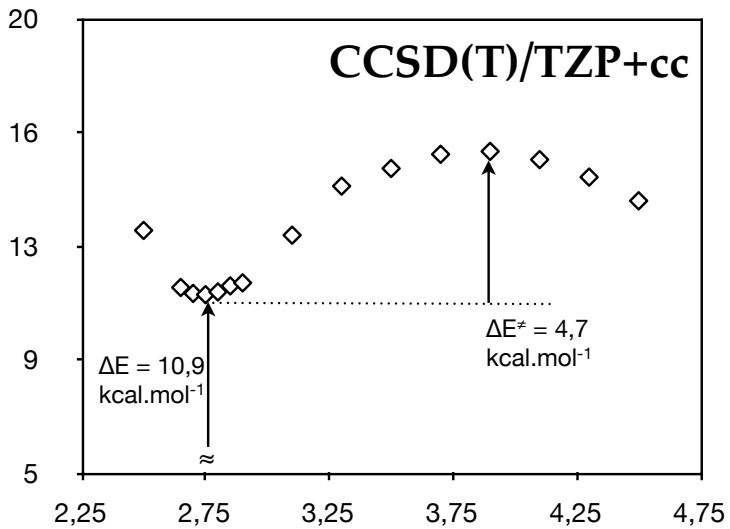
Intra-fragment 3-e π bond Inter-fragment 3-e σ bond

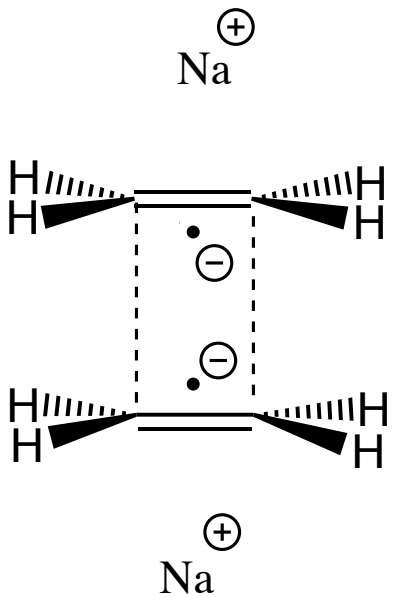
Bonding in DTCNE :

two inter-fragment 3e bonds ?...

Quantitative calculations

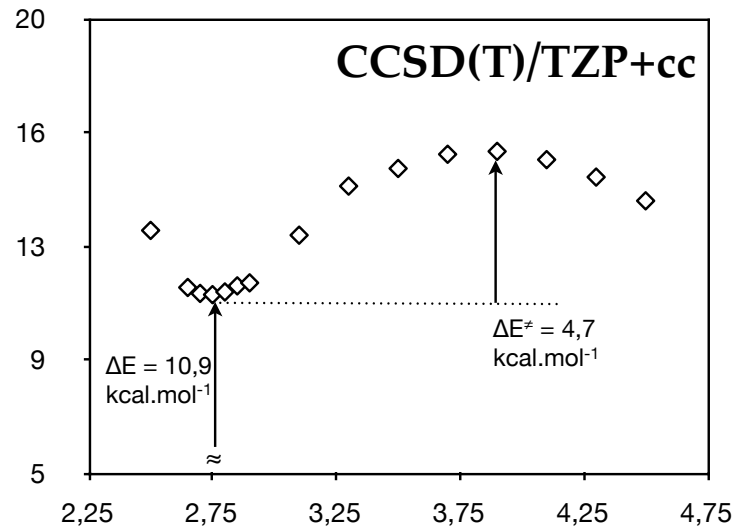
- Diethylene dianion system test :

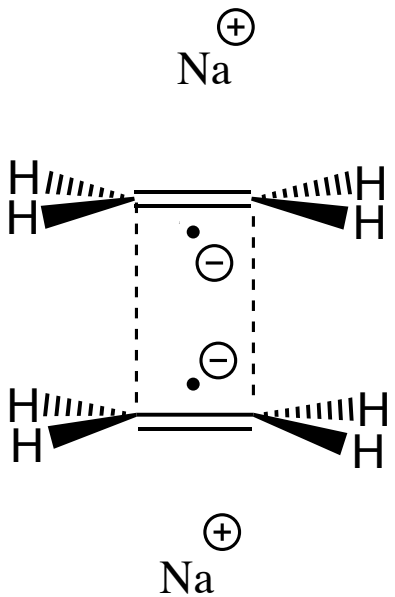


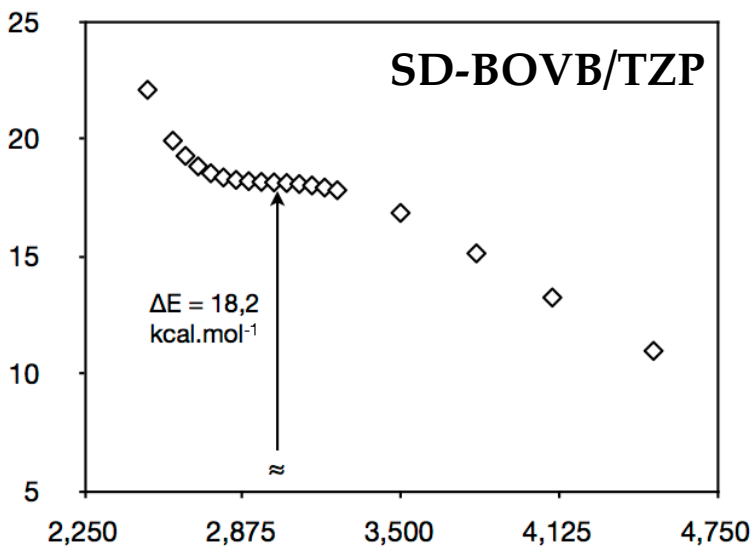


Quantitative calculations

- Diethylene dianion system test :





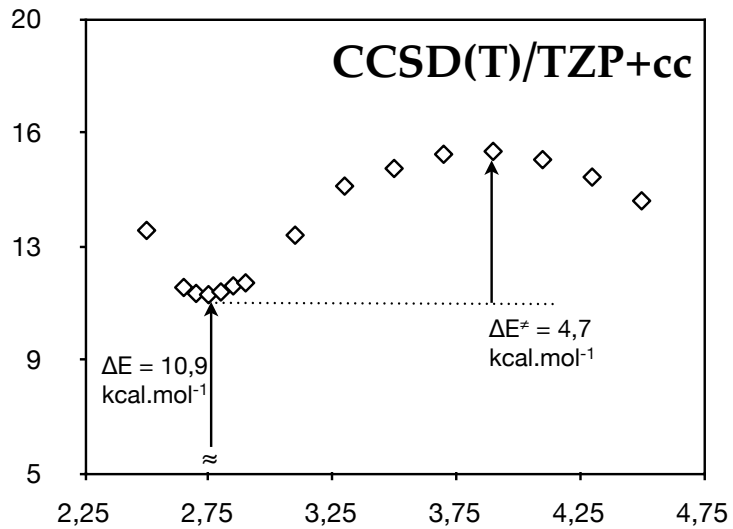


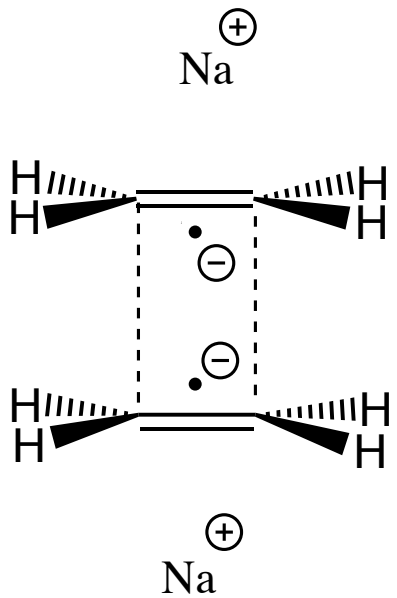
SD-BOVB disappointing :

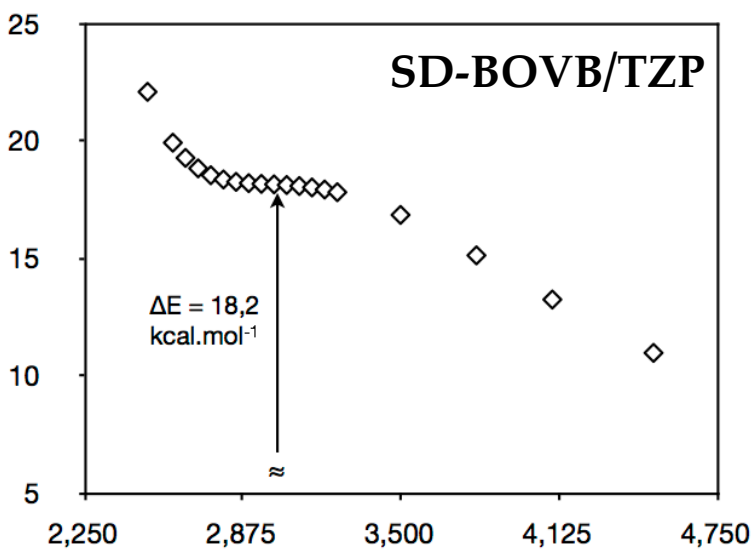
- Not accurate enough (fails to find a minimum) ;
- Too long : ~20 hours to converge (4 heavy atoms, 26 electrons)

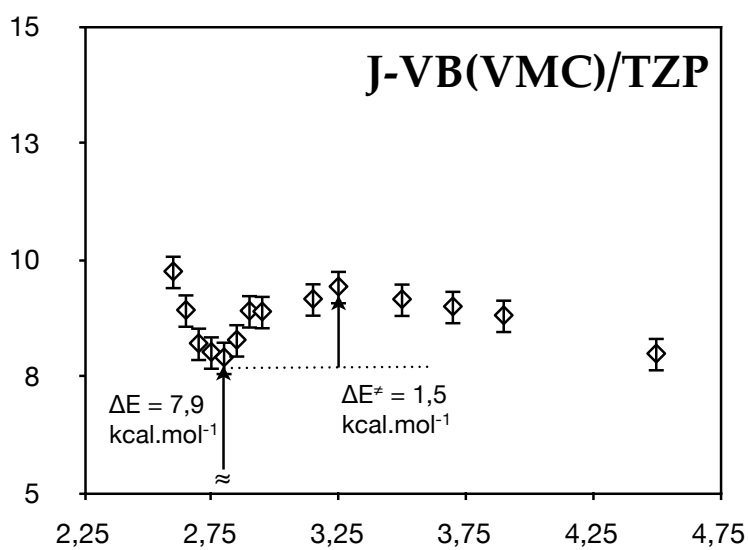
Quantitative calculations

- Diethylene dianion system test :



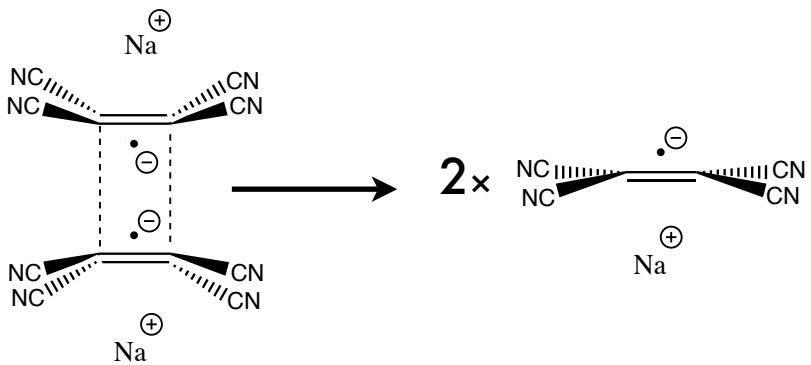






Quantitative calculations

- $DTCNE_2^{2-}$ dissociation energy :



	De (kal/mol)	Re (Å)
CCSD(T)/VTZ+cc	**11.6**	**2.56**
GVB+PT2/VTZ+cc	**11.2**	**2.7**
VBSCF	**-24.5**	
J-VB(VMC)/VTZ★	**5.2(9)**	
J-VB(DMC)/VTZ★	**9.7(9)**	

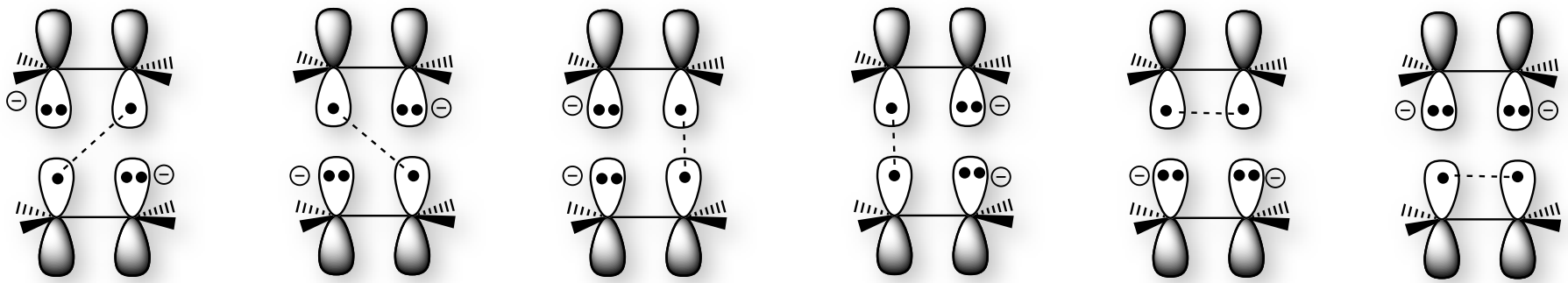
←No dynamic correlation

- VB/QMC quantitatively reliable (even when dynamical correlation is strong)
- VB/QMC can treat large systems (22 heavy atom / 90 electrons here)

★ *CHAMP program by C. J. UMRIGAR, C. FILIPPI and J. TOULOUSE*

VB/QMC calculations

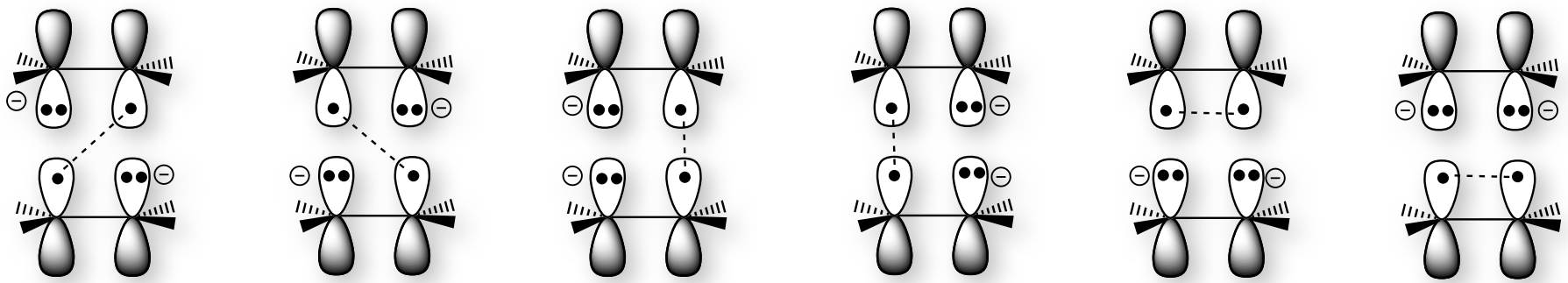
- $DTCNE_2^{2-}$: computed weights (J-VB) :



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

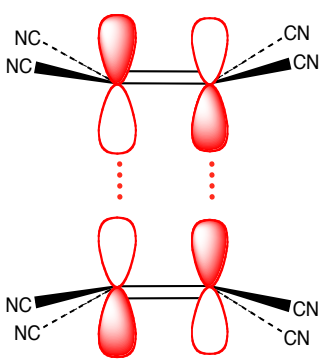
VB/QMC calculations

- $DTCNE_2^{2-}$: 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 ?

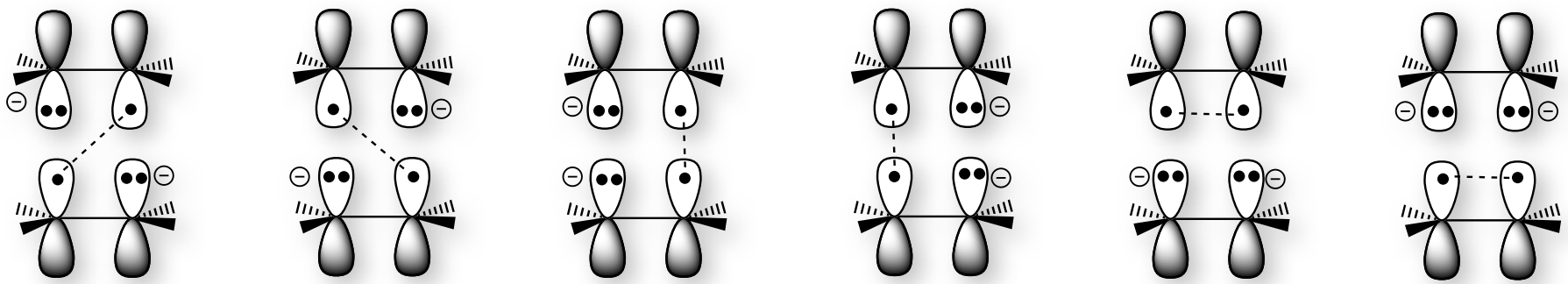


MO/VB maping :

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

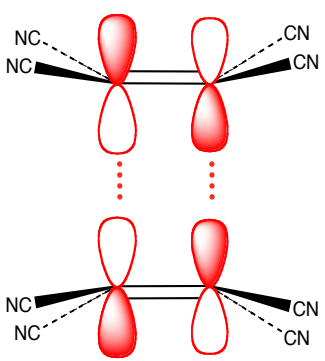
VB/QMC calculations

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



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

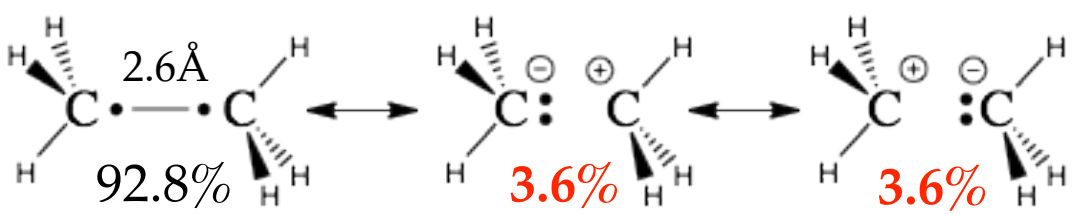
- Interfragment 2e bond ?



(covalent + ε ionic) π-π* 2-e bond =

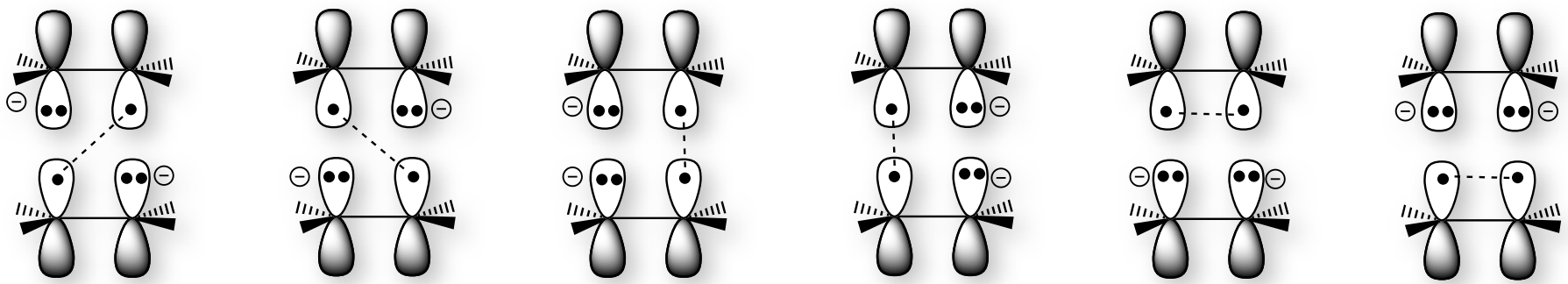
1 + **2** + **3** + **4** + ε (**5** + **6**)

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



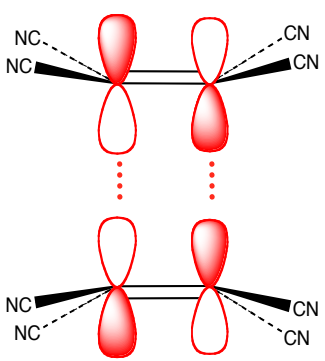
VB/QMC calculations

- $DTCNE_2^{2-}$: 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 =

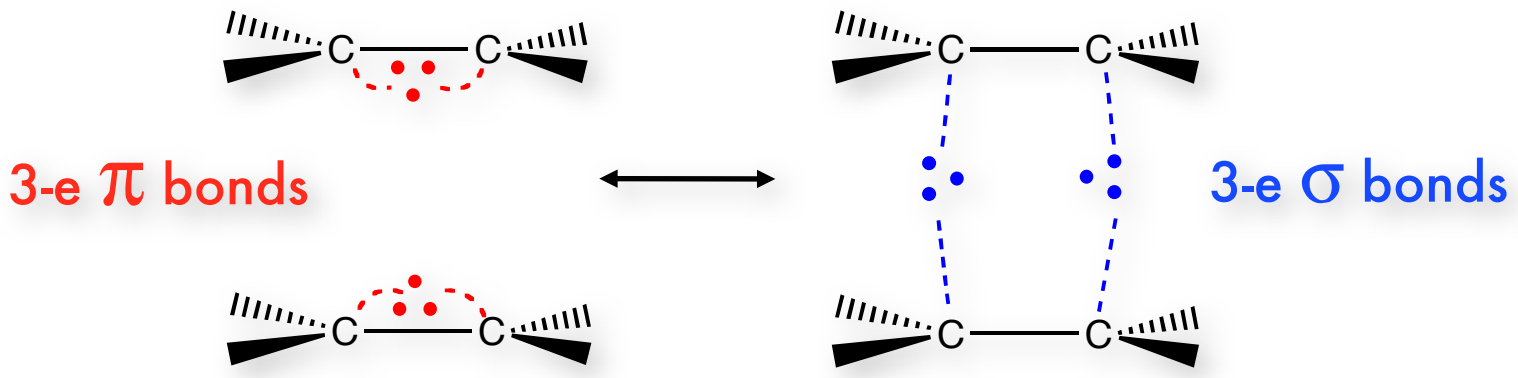
1 + **2** + **3** + **4** + **ε** (**5** + **6**)

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

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

VB/QMC calculations

- Some tests of credibility :



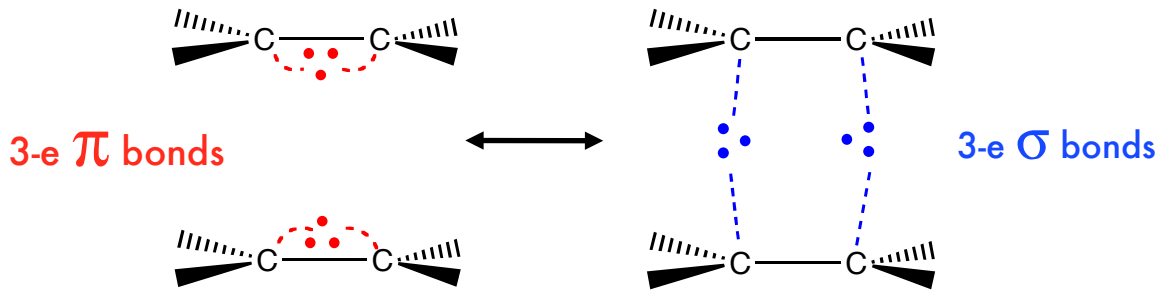
Characteristics of 3e bonds :

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

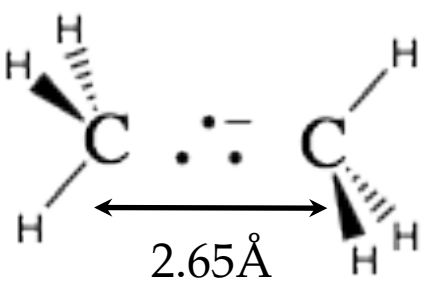
2) Small overlap ($S_{opt} \approx 0.17$)

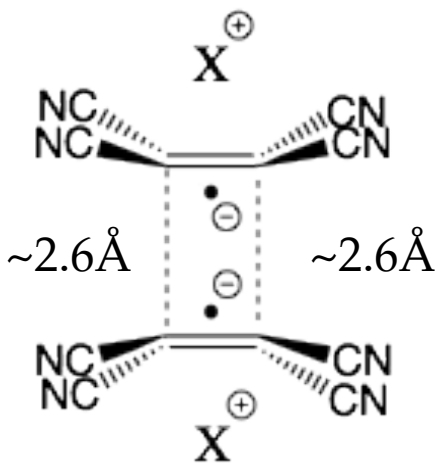
3) Importance of dynamical correlation

VB/QMC calculations

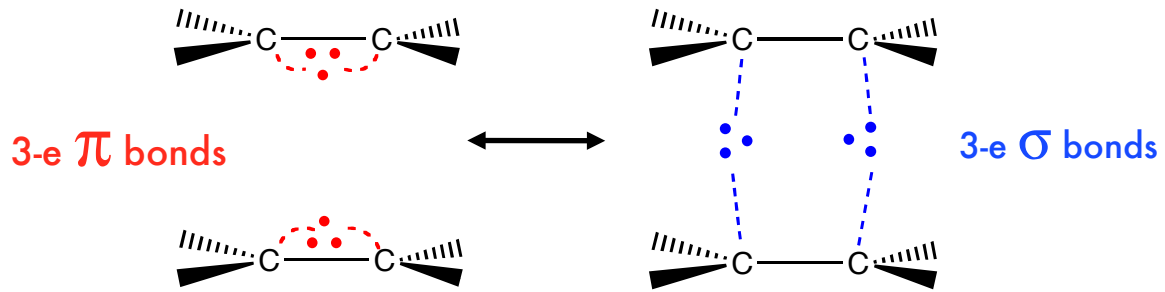


1) Interfragment bond length close to $3e^-$ bonded ethane anion :





VB/QMC calculations



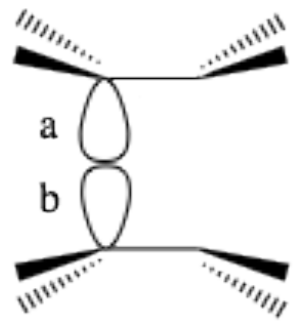
2) Interfragment orbital overlaps close to optimal 3e- bond value :

$S_{opt} \approx 0.17$

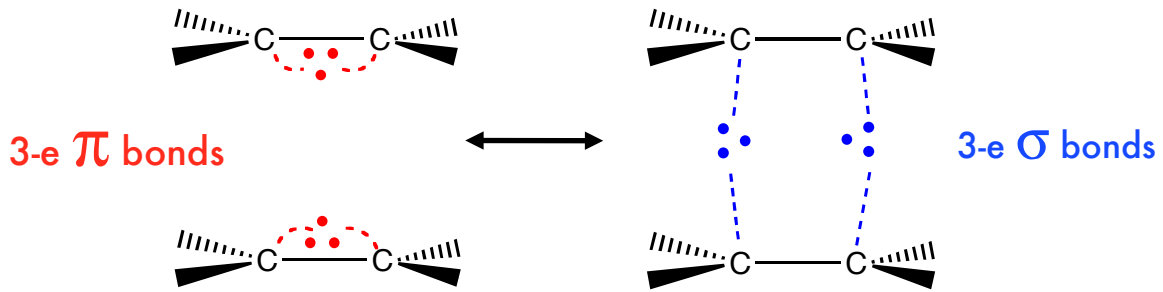
for any 3-e bond
(demonstrated in
qualitative VB theory
as well as Extended Hückel theory)

$S_{ab} = 0.15$

(computed)



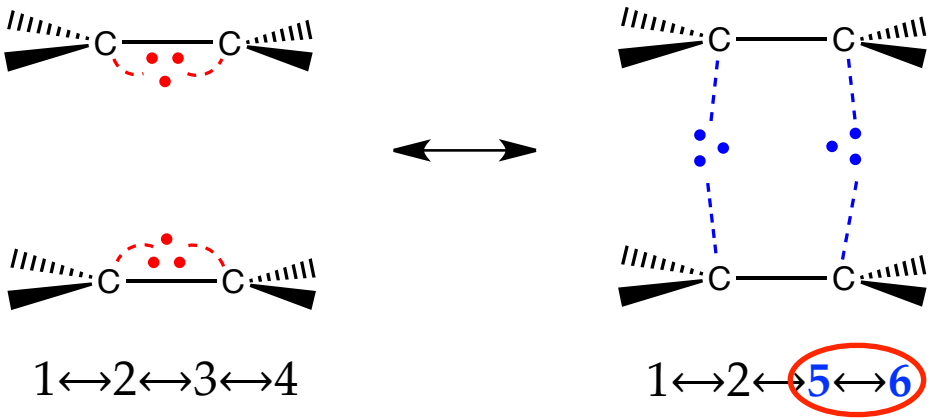
VB/QMC calculations

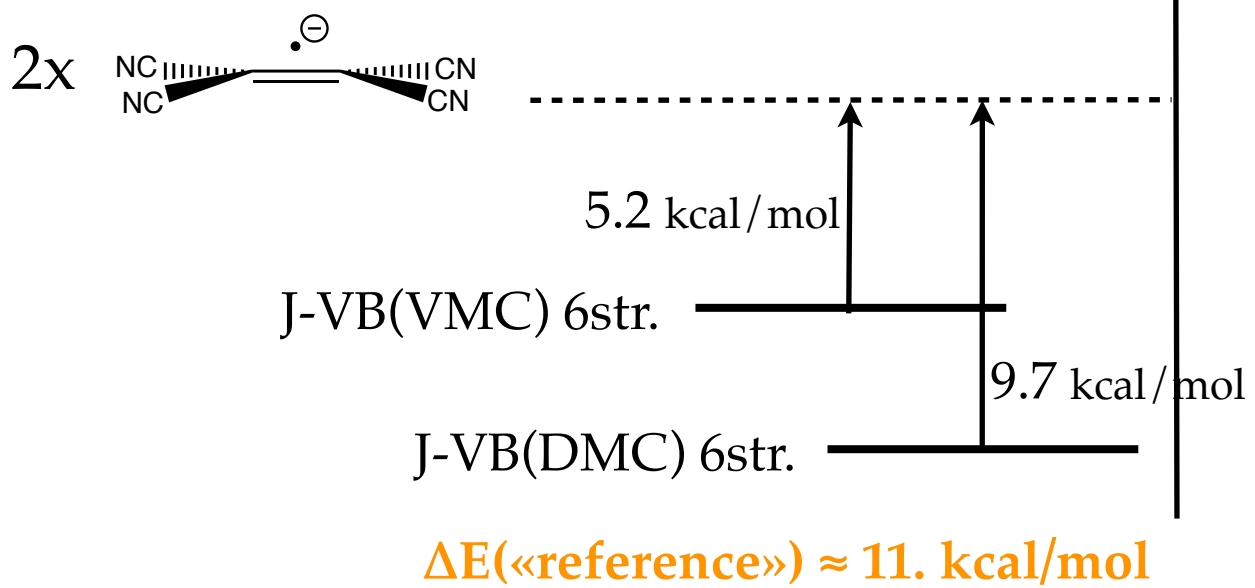


3) Contribution of dynamic correlation to bonding:

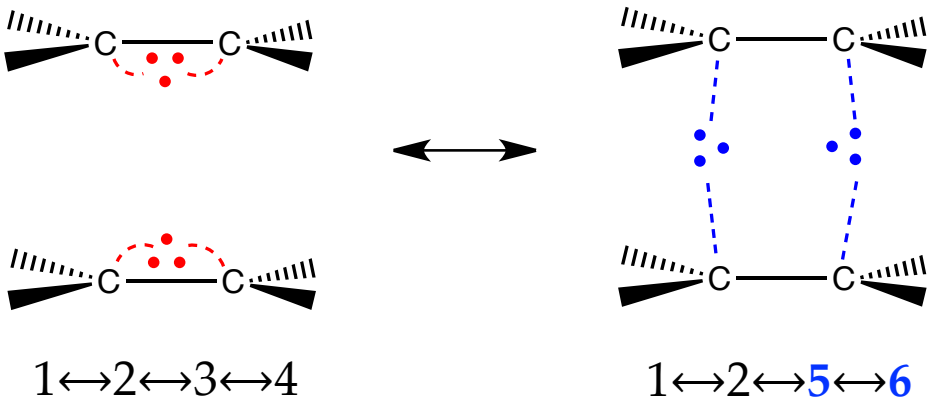
- In $[F\therefore F]^-$, dynamic correlation contributes ~ 30 kcal/mol to bonding
- In $[TCNE]_2^{2-}$, dynamic correlation contributes > 30 kcal/mol to bonding

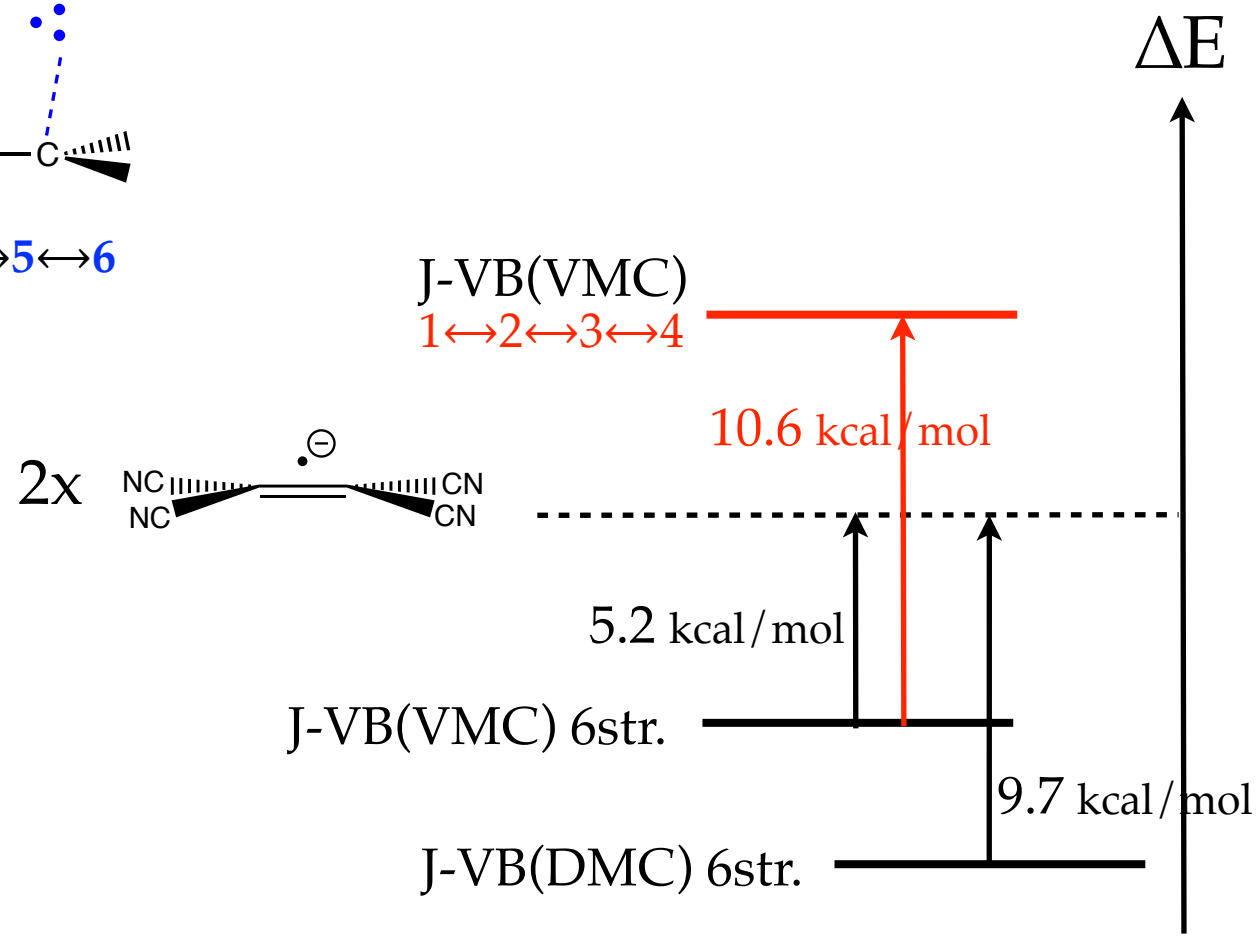
VB/QMC calculations





VB/QMC calculations

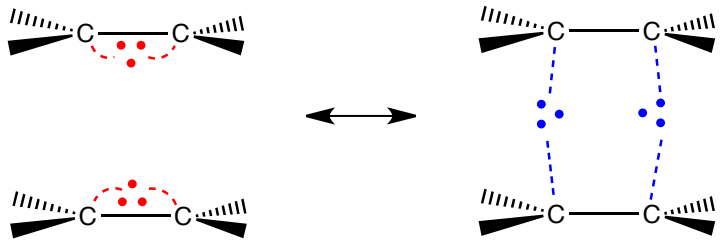




⟹ Without str. 5-6, DTCNE becomes repulsive !

Conclusion

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



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

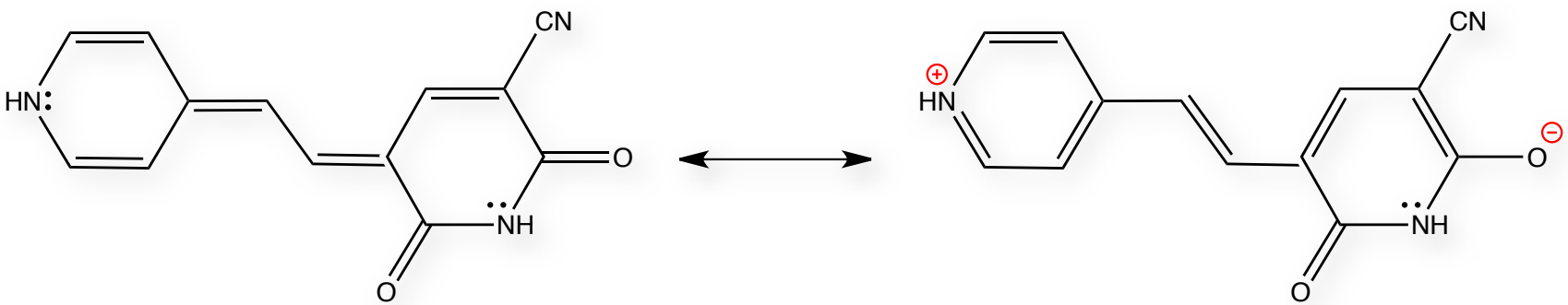
- Even when electrostatic interaction is repulsive (axial conformation), the two fragment anions are directly bonded by **a pair of 3-e bonds**

- This simple picture explains at once :

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

Conclusion

- About VB-QMC :



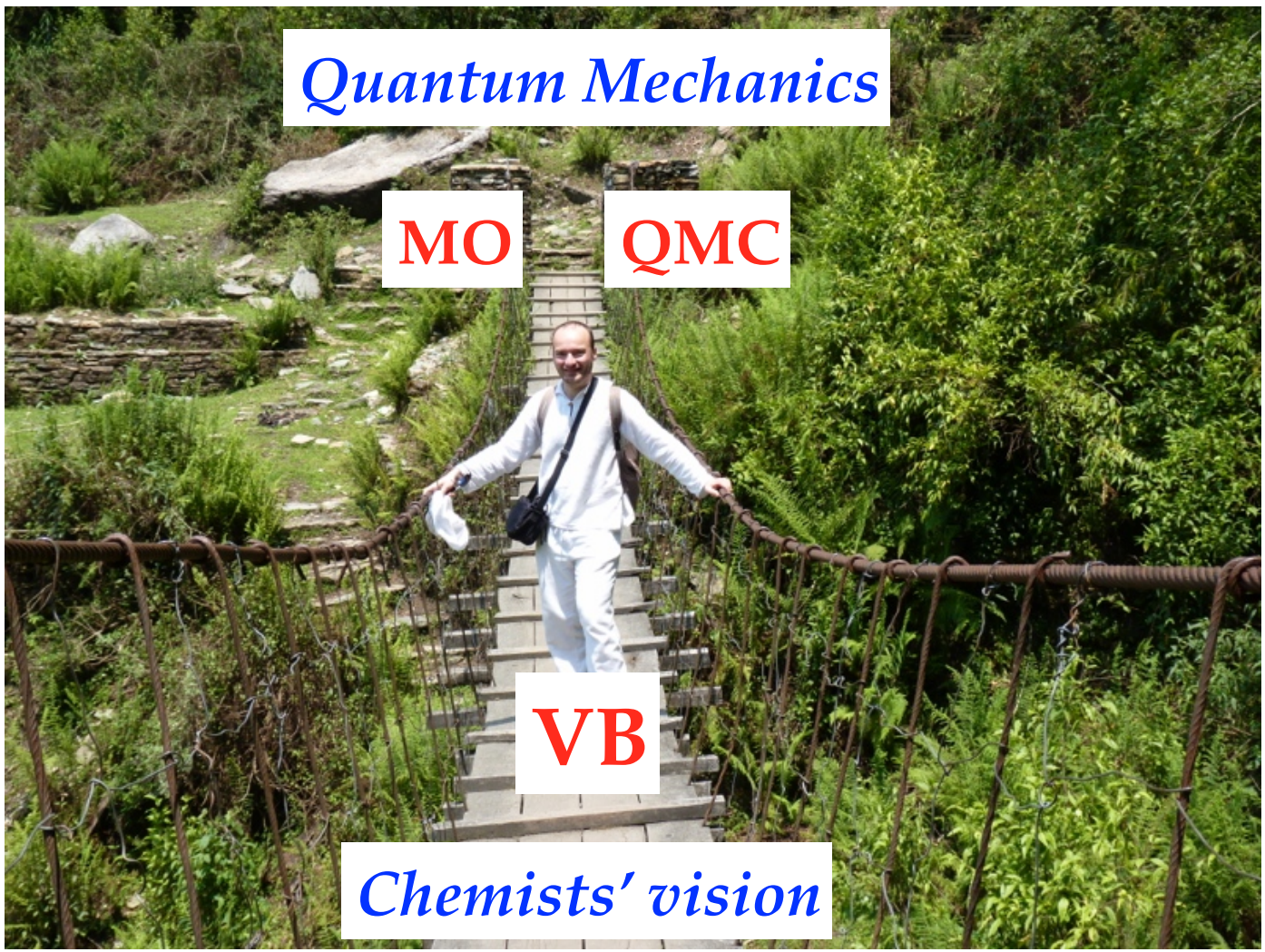
  - up to : ~30 heavy atoms
  - up to : ~100 valence electrons
  - accuracy matching CASPT2 or CCSD(T) on large basis sets

It does more than answering Coulson's request:

Give me insight* and *numbers ! (Coulson)

Conclusion

But all this is finally about building bridges...



Conclusion

... and to look at things from different perspectives !

Conclusion

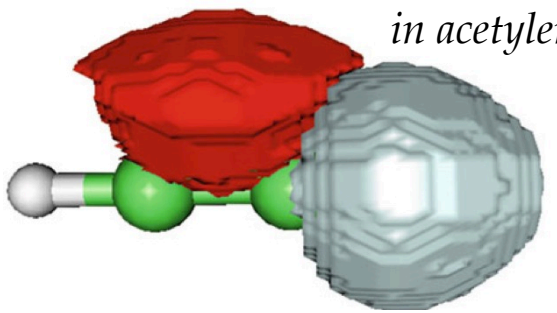
... and to look at things from different perspectives !

Thanks :
Philippe HIBERTY (Orsay)
Kévin HENDRICKS

Opening post-doc positions !

- 1) Maximum Probability Domains :

Banana C-C bonds and C-H bonds in acetylene



- With : A. SAVIN
- Col. : Oviedo (Pendas), Napoli (Causa), Gent (Bultinck), Aachen (Lüchow)

➡ Optimisation algorithms (with CERMIS and lab. J. J. Lions), implementation of new ideas (multi-domains opt., softness,...)

- 2) VB-QMC :

- With : P. HIBERTY, J. TOULOUSE
- Col. : Jerusalem (Shaik), Xiamen (Wu), Cornell (Umrigar), Aachen (Lüchow)

➡ New Jastrows, excited states, w.f. optimization, applications