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):
- \( \approx 8000 \) permanent (Pr.+researchers) + \( \approx 32000 \) students
- Topics: mathematics, physics, chemistry, biology, medical
The Laboratoire de Chimie Théorique of the Université Pierre et Marie Curie
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- Laboratoire de Chimie théorique:
  - Selectivity & environment
    Complex (bio)organic and (bio)inorganic systems
  - Chemistry & universe
    Interstellar reactions, small molecules...
  - Chemistry & surface
    Reactivity on oxyde surfaces...
  - Methodology
    DFT, QMC, local $\Psi$ method development
  - Concepts & interpretative methods
    ELF, MPD, VB develop.+appli.
  - 26 permanent (prof.+CNRS)
  - ~50 (+students)

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

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    - DFT, QMC, local $\Psi$ method development
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- 26 permanent (prof.+CNRS)
- 52 (permanent+phD+postdocs)
+ students ($\approx$10-20)
• **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

VB dominated the mental map of chemistry
~1940-1960: The MO-VB rivalry

Successes of MO theory vs. VB «failures»
~1960-1980: The downfall

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:

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

*Lewis model, arrow-pushing language, VSEPR, hybridization,...*
Chemists’ «schizophrenia»

- **Concepts and models** based on a localized vision:
  - Localized electron pairs
  - Chemical bond concept

- **Quantitative theory** all-interacting delocalized particles vision:
  - delocalized particles (e\(^{-}\), n\(^{+}\))
  - indistinguishable and all-interacting (no chemical bond)

\[ \hat{H} \Psi = E \Psi \]

Lewis model, arrow-pushing language, VSEPR, hybridization,...
Chemists’ «schizophrenia»

\[ \Delta H_{\text{rxn}} \]

\[ \Delta H^\dagger \]

etc.

\[ \Psi \]

Why ...

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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 chemists’ 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:

• VB wave functions:
  - Electrons occupy localized orbitals (atomics, hybrids,...)
  - A bond = two singlet-coupled electrons in two orbitals
  => bonds are essentially covalent + minor ionics

\[ \Psi = \left| (c_1 h_1 + h_1 c_1)(c_2 h_2 + h_2 c_2)(c_3 h_3 + h_3 c_3)(c_4 h_4 + h_4 c_4) \right| \]
Valence Bond theory

- When more than one Lewis structure is needed:

\[ \Psi(1\leftrightarrow 2) = C_1(\Psi_1) + C_2(\Psi_2) \]

- 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:

\[ \Psi(1\leftrightarrow2) = C_1(\Psi_1) + C_2(\Psi_2) \]

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

\[ \rightarrow \text{structure weights:} \ 73\%, \ 27\% \]
Valence Bond theory

• When more than one Lewis structure is needed:

\[
\Psi(1\leftrightarrow2) = C_1(\Psi_1) + C_2(\Psi_2)
\]

=> structure weights: 73%, 27%

=> resonance energy: \( R.E. = E(\Psi_1) - E(\Psi_{1\leftrightarrow2}) = 37 \text{ kcal/mol} \)

=> 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

\[
C_1 \begin{array}{c}
\text{F} \quad \text{F}
\end{array} + C_2 \begin{array}{c}
\text{F} \quad \text{F}^+
\end{array} + C_2 \begin{array}{c}
\text{F}^+ \quad \text{F}^-
\end{array}
\]
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

  - **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
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Why VB-QMC ?

★ No non-orthogonality problem !

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

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

\[
\begin{align*}
J \times \left( \begin{array}{c}
F\cdots F \\
F^-F^+ \\
F^+F^-
\end{array} \right) \\
\text{Jastrow function} \\
(\text{explicit correlation} : ee, en, een)
\end{align*}
\]

\[
\begin{align*}
\text{VBSCF determinantal part} \\
(\text{static correlation})
\end{align*}
\]

★ 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

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

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

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

and $l_{\text{max}}$ 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:

\[
\Psi_T = \sum_{k=1}^{N_{\text{det}}} c_k \begin{vmatrix}
    e^{J_1(r_i \neq r_1)} \phi_{k_1}(r_1) & \cdots & e^{J_1(r_N \neq r_N)} \phi_{k_1}(r_N) \\
    \vdots & \ddots & \vdots \\
    e^{J_{N_1}(r_i \neq r_1)} \phi_{k_{N_1}}(r_1) & \cdots & e^{J_{N_1}(r_N \neq r_N)} \phi_{k_{N_1}}(r_N)
\end{vmatrix}.
\]

\[
J_k(r_i \neq r_j) = \frac{1}{2} \sum_{j \neq i} \sum_\alpha \left[ s_k(\vec{r}_{ij}) - p_{k\alpha}(\vec{r}_{ia}) - p_{k\alpha}(\vec{r}_{ja}) \right]
\]

\[
+ g_{k\alpha} r_{ia} r_{ja} + g_{k\alpha} (\vec{r}_{ia} + \vec{r}_{ja}) \cdot \vec{r}_{ij},
\]

Different Jastrow for active/inactive...

VB-QMC : benchmarking

De error (kcal/mol)

- VBSCF
- J-VB(DMC)
- J-VB(VMC)
- J-FVCAS(DMC)
- Sans titre 1
- Exact

165 CSFs
24 CSFs

C2 N2 O2 F2


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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
«Pancake bonding»

- DTCNE$_2^{2-}$:

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

Electrostatic complex ?...

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

- DTCNE$_2^{2-}$:

«Pancake bonding»

- Same bonding distance whatever the environment!

⇒ not only electrostatic... also an interfragment bond
"Pancake bonding"

- Other "pancake bonding" systems:

- Same bonding distance whatever the system!

- $d_{C-C} < \text{sum of vdW radii} (3.45\text{Å})$, 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

Right geom: significant bonding force overcome repulsive electrostatics!

$D_e \approx 11$ kcal/mol
Qualitative MO analysis

Left fragment

Right fragment

[TCNE]$^{-}$

Na$^{+}$
Qualitative MO analysis

\[ \text{[TCNE]}^- \quad \pi \quad [\pi-\text{TCNE}_2]^{2-} \quad [\text{TCNE}]^- \]

$\Rightarrow$ a simple 4 centers / 2 electrons bond?
Qualitative MO analysis

Other «pancake bonding» systems: n center / 2e⁻ bonds
Quantitative MO computations

- GVB calculations of the axial conformation:

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

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

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

Let us apply qualitative VB analysis first:

**Effective Hamiltonian**: \( H_{\text{eff}} = (h(1) + h(2) + h(3) + \ldots) \)

**Parameters**: \( \beta, S, \varepsilon \) (same as in the MO framework)

1) Energy of a determinant:

\[
\langle D_i | H | D_i \rangle = -\frac{2n\beta S}{1 - S^2} \quad n = N\# \text{ of neighboring } (\uparrow \uparrow) \text{ pairs}
\]

2) Off diagonal terms:

- Determinants differ by 2 spinorbitals:

\[
\left\langle \begin{pmatrix} a & b \end{pmatrix} | H \left| \begin{pmatrix} b & a \end{pmatrix} \right. \right\rangle = 2\beta_{ab} S_{ab}
\]

- Determinants differ by + than 2 spinorbitals:

\[
\langle D_i | H | D_j \rangle = 0
\]
Qualitative VB

• 2e-bond:

\[ \psi_{VB} = \frac{|ab| + |b\overline{a}|}{\sqrt{2(1+S^2)}} \]

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

• Triplet repulsion:

\[ \psi_{VB} = \frac{|ab| \otimes |b\overline{a}|}{\sqrt{2(1+S^2)}} \]

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

Same as 3e-repulsion:

\[ \psi_{VB} = |a\overline{ab}| \]

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Qualitative VB

- Elementary interactions:

1-e bond (A↑B) = \[ \frac{\beta}{1 + S} \]

2-e bond (A–B) = \[ \frac{2\beta S}{1 + S^2} \]

3-e bond (A: B) = \[ \frac{\beta(1-3S)}{1 - S^2} \]

Triplet / 3-e repulsion (A↓↑ ↑B) = \[ \frac{-2\beta S}{1 - S^2} \]

4-e repulsion (A↑↓ ↓↑B) = \[ \frac{-4\beta S}{1 - S^2} \]

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Qualitative VB analysis

- VB set of structures for DTCNE$_2^{2-}$:
Qualitative VB analysis

- VB set of structures for DTCNE\(_2^{2-}\):

⇒ No structure is bonding by itself, all the bonding comes from the resonance!
Qualitative VB analysis

• What about three-electron bonding ?...

At infinite distance, each fragment displays a $3e^{-} \pi$ bond:

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

\[ \pi^* \pi \]
Qualitative VB analysis

• What is the three-electron bond?...

Examples: $\text{He}_2^+$, $\text{RS} \cdot \cdot \cdot \text{SR'}$, radical intermediates:

VB description:

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

MO description:

$$
\Psi_{MO} = \left| \sigma \bar{\sigma} \sigma^* \right|
$$
Qualitative VB analysis

• What is the three-electron bond?...

Examples: $\text{He}_2^+$, $\text{RS} \cdot \cdot \cdot \text{SR'}$, radical intermediates:

**VB description:**

**MO description:**

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

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

• What is the three-electron bond?...

The most common 3e bonds: the two $\pi$ bonds in $O_2$ ground state:

**VB description:**

**MO description:**
Qualitative VB analysis

- VB set of structures for $\text{DTCNE}_2^{2-}$:

1. 

2. 

3. 

4. 

5. 

6.
Qualitative VB analysis

- $2 \leftrightarrow 3$ and $1 \leftrightarrow 4$: intra-fragment $3e^{-}\pi$ bond (upper fragment):
Qualitative VB analysis

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

![Diagram showing 2↔3 and 1↔4 intra-fragment 3e⁻ \( \pi \) bond]

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

![Diagram showing 1↔3 and 2↔4 intra-fragment 3e⁻ \( \pi \) bond]
Qualitative VB analysis

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

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

⇒ 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:

\[
\Psi_{HF} = |a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u}| = ... = \Psi_{VB}^1 \Psi_{VB}^2 + \Psi_{VB}^3 + \Psi_{VB}^4 \Psi_{VB}^5 \Psi_{VB}^6
\]
Qualitative VB analysis

- «VB reading» of MO determinants:

Development of the 1\textsuperscript{st} excited det. in the VB basis of structures:

\[
\Psi_{1-\text{ext}} = a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} = \cdots = + \Psi_{1}^{VB} + \Psi_{2}^{VB} \bigotimes \Psi_{3}^{VB} \bigotimes \Psi_{4}^{VB} \bigotimes \Psi_{5}^{VB} \bigotimes \Psi_{6}^{VB}
\]
Qualitative VB analysis

• «VB reading» of MO determinants:

Development of the 2\textsuperscript{nd} excited det. in the VB basis of structures:

\[ \Psi_{2-ext} = \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = ... = + \Psi_{VB}^1 + \Psi_{VB}^2 + \Psi_{VB}^3 + \Psi_{VB}^4 + \Psi_{VB}^5 + \Psi_{VB}^6 \]
• «VB reading» of MO determinants:

Development of the 3\textsuperscript{rd} excited det. in the VB basis of structures:

\[
\Psi_{3-\text{ext}} = |b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g}| = \ldots = -\Psi_{VB_1} - \Psi_{VB_2} - \Psi_{VB_3} - \Psi_{VB_4} + \Psi_{VB_5} + \Psi_{VB_6}
\]
Qualitative VB analysis

- «VB reading» of MO determinants:

\[
\begin{align*}
\Psi_{HF} &= \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} \right| = ... = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\
\Psi_{1-ext} &= \left| a_g \bar{a}_g b_{3u} \bar{b}_{3u} b_{1g} \bar{b}_{1g} \right| = ... = +\Psi_1^{VB} + \Psi_2^{VB} - \Psi_3^{VB} - \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB} \\
\Psi_{2-ext} &= \left| a_g \bar{a}_g b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = ... = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} - \Psi_5^{VB} - \Psi_6^{VB} \\
\Psi_{3-ext} &= \left| b_{3u} \bar{b}_{3u} b_{2u} \bar{b}_{2u} b_{1g} \bar{b}_{1g} \right| = ... = +\Psi_1^{VB} + \Psi_2^{VB} + \Psi_3^{VB} + \Psi_4^{VB} + \Psi_5^{VB} + \Psi_6^{VB}
\end{align*}
\]

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

the VB analysis which reveals the 3e-bond nature
• Conclusion of the qualitative VB analysis:

Bonding in DTCNE: two inter-fragment 3e bonds?
Quantitative calculations

- Diethylene dianion system test:

\[
\begin{align*}
\Delta E &= 10.9 \text{ kcal.mol}^{-1} \\
\Delta E^* &= 4.7 \text{ kcal.mol}^{-1}
\end{align*}
\]

CCSD(T)/TZP+cc

\[\text{Na} \quad \text{Na}\]

\[\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}\]

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Quantitative calculations

- Diethylene dianion system test:
  
  \[
  \Delta E = 10.9 \text{ kcal.mol}^{-1}
  \]
  
  \[
  \Delta E^* = 4.7 \text{ kcal.mol}^{-1}
  \]

  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:

\[ \Delta E = 10.9 \text{ kcal.mol}^{-1} \]
\[ \Delta E^* = 4.7 \text{ kcal.mol}^{-1} \]

\[ \Delta E = 7.9 \text{ kcal.mol}^{-1} \]
\[ \Delta E^* = 1.5 \text{ kcal.mol}^{-1} \]
Quantitative calculations

- **DTCNE$_2^{2-}$** dissociation energy:

<table>
<thead>
<tr>
<th>Method</th>
<th>$D_e$ (kal/mol)</th>
<th>$R_e$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)/VTZ+cc</td>
<td>11.6</td>
<td>2.56</td>
</tr>
<tr>
<td>GVB+PT2/VTZ+cc</td>
<td>11.2</td>
<td>2.7</td>
</tr>
<tr>
<td>VBSCF</td>
<td>-24.5</td>
<td></td>
</tr>
<tr>
<td>J-VB(VMC)/VTZ$^*$</td>
<td>5.2(9)</td>
<td></td>
</tr>
<tr>
<td>J-VB(DMC)/VTZ$^*$</td>
<td>9.7(9)</td>
<td></td>
</tr>
</tbody>
</table>

- **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. 20.2%
  2. 20.2%
  3. 16.1%
  4. 16.1%
  5. 10.1%
  6. 10.1%
• DTCNE$_2^{2-}$: computed weights (J-VB):

<table>
<thead>
<tr>
<th></th>
<th>MO Map 1</th>
<th>MO Map 2</th>
<th>MO Map 3</th>
<th>MO Map 4</th>
<th>MO Map 5</th>
<th>MO Map 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20.2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>16.1%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>16.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.1%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.1%</td>
</tr>
</tbody>
</table>

• Interfragment 2e bond?

MO/VB mapping:

Purely covalent $\pi^* - \pi^*$ 2-e bond = $1 + 2 + 3 + 4$ (equal weights)
DTCNE$_2^{2-}$: computed weights (J-VB):

<table>
<thead>
<tr>
<th>Bond</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.2%</td>
</tr>
<tr>
<td>2</td>
<td>20.2%</td>
</tr>
<tr>
<td>3</td>
<td>16.1%</td>
</tr>
<tr>
<td>4</td>
<td>16.1%</td>
</tr>
<tr>
<td>5</td>
<td>10.1%</td>
</tr>
<tr>
<td>6</td>
<td>10.1%</td>
</tr>
</tbody>
</table>

Interfragment 2e bond:

$(\text{covalent} + \varepsilon_{\text{ionic}})\pi-\pi^*2$-e bond = $1 + 2 + 3 + 4 + \varepsilon (5 + 6)$

However, $\varepsilon = 3.6\%$ in a stretched C-C bond:
VB/QMC calculations

- **DTCNE$_2^{2-}$**: computed weights (J-VB):

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

- **Interfragment 2e bond?**

  \((\text{covalent } + \varepsilon \text{ ionic}) \pi - \pi^* 2\text{-e bond} = 1 + 2 + 3 + 4 + \varepsilon (5 + 6)\)

  However, \(\varepsilon = 3.6\%\) in a stretched C-C bond:

  \(\Rightarrow\) The inter-fragment bond cannot be a simple \(\pi - \pi^* 2\text{-e bond}\)
Some tests of credibility:

1) Large equilibrium distances: \(d(\text{S—S}) \approx 2.0 \text{ Å} \); \(d(\text{S : : S}^-) \approx 2.8 \text{ Å}\)

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

3) Importance of dynamical correlation

Characteristics of 3e bonds:

- 3-e \(\pi\) bonds
- 3-e \(\sigma\) bonds
**VB/QMC calculations**

1) Interfragment bond length close to 3e⁻ bonded ethane anion:
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)
3) Contribution of dynamic correlation to bonding:

- In $[\text{F} : \text{F}]^-$, dynamic correlation contributes $\sim 30 \text{ kcal/mol}$ to bonding

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

\[ \Delta E(\text{«reference»}) \approx 11. \text{kcal/mol} \]

\[ 5.2 \text{kcal/mol} \]

\[ 9.7 \text{kcal/mol} \]
VB/QMC calculations

$\Delta E$

$\Rightarrow$ Without str. 5-6, DTCNE becomes repulsive!

J-VB(VMC) 6str.

$2x$

J-VB(VMC) 1$\leftrightarrow$2$\leftrightarrow$3$\leftrightarrow$4

10.6 kcal/mol

5.2 kcal/mol

J-VB(DMC) 6str.

9.7 kcal/mol

dimanche 29 juillet 12
Conclusion

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

Quantum Mechanics

MO QMC

Chemists' vision

VB
Conclusion

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

(Prof. Keating, Dead Poets Society)
Conclusion

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

(Prof. Keating, Dead Poets Society)

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