An overview of modern ab initio Valence bond methods
An overview of modern ab initio Valence bond methods

\[ \Psi_{VB} \text{ is a multistructure wave function} \]

\[ \Psi_{VB} = \sum_{i} C_i \Phi_i \]

where each \( \Phi_i \) is a VB structure

Example: the \( \pi \) system of benzene

6 electrons, 6 centers

15 possible VB structures (not linearly independent)

Which ones to choose?
An overview of modern ab initio Valence bond methods

\[ \Psi_{VB} = \sum_i C_i \Phi_i \]

where each \( \Psi_i \) is a VB structure

**Exemple: the \( \pi \) system of benzene**

6 electrons, 6 centers

15 possible VB structures (not linearly independent)

Which ones to choose:
- Rumer’s Rules \(^1\)
- Weyl tableaux \(^2\)
- Young tableaux and operators \(^1,3\)

---

\(^1\) : Pauncz book
\(^3\) : McWeeny
An overview of modern ab initio Valence bond methods

Rumer’s rule for a covalent $n$-electron/$n$-orbital system:
1) Put the orbitals around an imaginary circle (doesn’t need to have the shape of the molecule)
2) Generate all possible VB structures not displaying crossing bonds

- Complete and non-redundant set of VB structures
- VB structures are chemically meaningful

- Redundant
- Chemically meaningless
Rumer’s rule for covalent $n$-center/$n$-electron systems

1,3-Butadiene:
Put the orbitals around an imaginary circle, *even if the molecule is not a ring*

\[ 1 + 2 \]

**Major VB structure**
**Explains the barrier to rotation**
Rumer’s rule for covalent $n$-center/$n$-electron systems

1,3-Butadiene:
Other possible (but stupid!) choice:

- Complete and non-redundant set of VB structures
- Chemically meaningless !!
Example benzene:

1) Choose a distribution of charges
2) Apply Rumer’s rules on the rest of the system
3) Choose another distribution of charges…

... and so on…
Rumer’s rule for $m$-center/$n$-electron covalent structures

Example cycopentadienyl anion, $m>n$

1) Choose a center for the lone pair
2) Apply Rumer’s rules on the rest of the system

3) Choose another center for the lone pair…

And so on…

Application on ozone: see tutorials
Rumer’s rule for radicals \((m-e/m-c, m \text{ odd})\)

Exemple : \([H---H---H]\cdot\)

1) Add a fictitious center with one electron
2) Treat the system as a singlet

Same number of structures as in the \((m+1)-e/(m+1)-c\) system

Application on allyl radical: see tutorials
**Rumer’s rule for triplets**

1) Insert the atoms + a fictitious center in the circle
2) Link the fictitious center to two atoms
3) Link the other atoms 2 by 2, applying the non-crossing rule

**Exemple : butadiene**

\[ \Phi_1 + \Phi_2 + \Phi_3 = -\Phi_1 - \Phi_2 + \Phi_3 \]

Complete basis set

Redundant structure
Number of covalent structures for $N$-e/$N$-c systems

Weyl’s formula:

$$f_s^N = \frac{(2S + 1)N!}{(\frac{1}{2}N + S + 1)!(\frac{1}{2}N - S)!}.$$ 

<table>
<thead>
<tr>
<th>$N$</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>…</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_s^N$</td>
<td>2</td>
<td>5</td>
<td>14</td>
<td>42</td>
<td>121</td>
<td>…</td>
</tr>
</tbody>
</table>
Number of covalent+ionic structures for $N$-e/$m$-c systems

Weyl’s formula: 

$$g_{S}^{N,m} = \frac{2S+1}{m+1} \left( \frac{m+1}{N/2 + S+1} \right) \left( \frac{m+1}{N/2 - S} \right)$$

<table>
<thead>
<tr>
<th>$N=m$</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>14</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{S}^{N}$</td>
<td>20</td>
<td>175</td>
<td>1764</td>
<td>2.76×10^6</td>
<td>2.07×10^{14}</td>
</tr>
</tbody>
</table>

**Solution:** treating an **active space** at the VB level (**the bonds that form/break**), and **the rest** as MOs (**« spectator orbitals »**).

Example:

$S_{N}2$ Transition state:
a 4-e/3-orbital VB system

only 6 VB structures
Orbitals in VB structures: localized or semi-localized?

The **localized** orbital option

Active orbitals are strictly localized on a single atom

- An active orbital **must not be delocalized on a center to which it is bonded**
- Covalent and ionic structures must be explicitly generated
The semi-localized orbital option: Coulson-Fischer orbitals

\[ \Psi_{GVB} = | \Phi_a \bar{\Phi}_b | + | \Phi_b \bar{\Phi}_a | \]

\[ \Phi_a = \varphi_a + \varepsilon \varphi_b \]
\[ \Phi_b = \varphi_b + \varepsilon \varphi_a \]

Used in:
- Generalized Valence Bond (GVB, W. A. Goddard)
- Spin-Coupled valence Bond (J. Gerratt, D. L. Cooper, VB Lecture V)
The Generalized Valence Bond Method (GVB)

\[ H_a \quad \cdots \quad H_b \]
\[ \varphi_a \quad \varphi_b \]

\[ \Psi_{GVB} = | \Phi_a \Phi_b | + | \Phi_b \Phi_a | \]

\[ \Phi_a = \varphi_a + \varepsilon \varphi_b \]
\[ \Phi_b = \varphi_b + \varepsilon \varphi_a \]

\[ \Psi_{GVB} = (1+\varepsilon^2)(|\varphi_a \Phi_b | + |\varphi_b \Phi_a |) + 2\varepsilon (|\varphi_a \Phi_a | + |\varphi_b \Phi_b |) \]

\[ H \bullet - \bullet H \]
\[ H^- H^+ + H^+ H^- \]

\[ \Psi_{GVB} \text{ is formally covalent, but physically covalent-ionic optimized} \]
The Generalized Valence Bond Method (GVB)

\[ \Psi_{\text{GVB}} = \Phi_a \Phi_b \Phi_b \Phi_a \]

« GVB pair »
Overlapping distorted AOs

Ionic structures are implicitly included => they must not be explicitly introduced in the GVB wave function

Generalization:

\[ \Psi_{\text{GVB}} = (\phi_1 a \bar{\phi}_1 b + \phi_1 b \bar{\phi}_1 a)(\phi_2 a \bar{\phi}_2 b + \phi_2 b \bar{\phi}_2 a)(\ldots) \]

Four GVB pairs

GVB: - Perfect-pairing (only one spin-coupling)
- Orthogonality of GVB pairs
Spin-coupled VB: no restrictions
Hartree-Fock, GVB, CASSCF … and static correlation energy

« Is it time to retire the hybrid atomic orbitals? »

Significant experimental evidence and theoretical advances indicate that hybrid atomic orbitals do not exist and do not appropriately describe molecular bonding...

Best possible single-configuration wave function

SCF

80%

GVB

20%

CASSCF (1764 conf)
localized or semi-localized orbitals…

To what extent do we (semi-)delocalize the orbitals?

1) On 2 centers only: bond-distorted orbitals (BDOs)

Example: BDOs for a Kekulé structure of benzene

\[ \Psi_{BDOs}^{VB} \propto (\Phi_1 \Phi_2 + \Phi_2 \Phi_1)(\Phi_3 \Phi_4 + \Phi_4 \Phi_3)(\Phi_5 \Phi_6 + \Phi_6 \Phi_5) \]

describes a Kekulé structure « stricto sensu »,
with 3 fully localized π bonds
localized or semi-localized orbitals…
To what extent do we (semi-)delocalize the orbitals?

2) Fully allowed to delocalize: overlap-enhanced orbitals (OEOs)
   (Option used in GVB or SCVB methods)

Example: GVB or SCVB description of benzene with two Kekulé structures

\[ \Psi^{GVB} \propto \left( \Phi_1 \Phi_2 + \Phi_2 \Phi_1 \right) \left( \Phi_3 \Phi_4 + \Phi_4 \Phi_3 \right) \left( \Phi_5 \Phi_6 + \Phi_6 \Phi_5 \right) \]

\[ + \left( \Phi_2 \Phi_3 + \Phi_3 \Phi_2 \right) \left( \Phi_4 \Phi_5 + \Phi_5 \Phi_4 \right) \left( \Phi_6 \Phi_1 + \Phi_1 \Phi_6 \right) \]

Orbitals are delocalized on 3 centers
The relationship to \( \begin{array}{ccc} 6 & 1 & 2 \\ 5 & 4 & 3 \end{array} \) and \( \begin{array}{ccc} 6 & 1 & 2 \\ 5 & 4 & 3 \end{array} \) is less obvious
How does one calculate VB wave functions with localized orbitals?

\[ \Psi_{VB} = \sum_i C_i \Phi_i \]  
where each \( \Phi_i \) is a VB structure

The VBSCF method (Balint-Kurti & van Lenthe)
Example: the \( \text{F}_2 \) molecule

\[ \begin{align*}
\text{F} \cdots \text{F} + \text{C}_1 \begin{array}{c}
\text{F} \vdots \\
\text{F}
\end{array} + \text{C}_2 \begin{array}{c}
\text{F} \vdots \\
\text{F}^+
\end{array} + \text{C}_2 \begin{array}{c}
\text{F} \vdots \\
\text{F}^-
\end{array}
\end{align*} \]

Coefficients \( C_i \) and orbitals optimized simultaneously (like MCSCF)

\textit{All} orbitals are optimized (active as well as spectator ones)

GVB, SCVB \sim \text{equivalent to VBSCF}
Accuracy of the various methods

Test case: the dissociation of $F_2$  

\[ F-F \xrightarrow{\Delta E} F\cdot + F\cdot \]

Calculation of $\Delta E$ for $F-F=1.43\text{Å}$, 6-31G(d) basis:

- Hartree-Fock: $-37$ kcal/mol (repulsive!)
  
  Reason: too much ionic

- Full configuration interaction (6-31G(d) basis)  $30-33$ kcal/mol

- GVB, VBSCF, CASSCF  
  
  Only $\sim 15$kcal/mol

  Reason: we miss dynamic correlation.

What does this physically mean?
What is missing in GVB and VBSCF?

GVB/VBSCF: a closer examination

The coefficients and orbitals are optimized, but...
- The same set of AOs is used for all VB structures:
  optimized for a mean neutral situation

A better wave function:
The « Breathing-Orbital » VB method (BOVB)

• Provides optimized covalent-ionic coefficients (like GVB)

- Orbitals for F•—•F will be the same as VBSCF
- Orbitals for ionic structures will be much improved

• Different orbitals for different VB structures

• One expects

- A better description of ionic structures
- A better bonding energy
Test case: the dissociation of $\text{F}_2$

$$
\text{F–F} \quad \xrightarrow{\Delta E} \quad \text{F}^\bullet + \text{F}^\bullet
$$

Calculation of $\Delta E$ for F–F=1.43Å, 6-31G(d) basis:

<table>
<thead>
<tr>
<th>Iteration</th>
<th>De(kcal)</th>
<th>F•–•F</th>
<th>F+F– ↔ F−F+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical VB</td>
<td>~4.6</td>
<td>0.813</td>
<td>0.187</td>
</tr>
<tr>
<td>GVB,VBSCF</td>
<td>~15</td>
<td>0.768</td>
<td>0.232</td>
</tr>
<tr>
<td>BOVB 1</td>
<td>24.6</td>
<td>0.731</td>
<td>0.269</td>
</tr>
<tr>
<td>2</td>
<td>27.9</td>
<td>0.712</td>
<td>0.288</td>
</tr>
<tr>
<td>3</td>
<td>28.4</td>
<td>0.709</td>
<td>0.291</td>
</tr>
<tr>
<td>4</td>
<td>28.5</td>
<td>0.710</td>
<td>0.290</td>
</tr>
<tr>
<td>5</td>
<td>28.6</td>
<td>0.707</td>
<td>0.293</td>
</tr>
<tr>
<td>Full CI</td>
<td>30-33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The «Breathing-Orbital» VB method (BOVB)

Different orbitals for different VB structures: How different are the orbitals?

The $\pi$ lone pairs of $F_2$ in BOVB:

Small difference in shape, significant effect in energy
Improvements of the BOVB method

• Improvement of the ionic VB structures
  - basic level:

- improved level (« split-level » or S)

The « active » orbital is split. This brings radial electron correlation
• Improvement of the interactions between spectator orbitals

- Spectator orbitals can be:
  - local atomic orbitals
  - bonding and antibonding combinations

Slightly better (« Delocalized » level or D)
The various levels of the BOVB method

- **Basic: L-BOVB**
  - All orbitals are **localized**, ionics are closed-shell
  
- **SL-BOVB**
  - All orbitals are **localized**, but active orbitals in ionics are **split**

- **SD-BOVB**
  - Active orbitals are **split** in ionics
  - Spectator orbitals are **delocalized** in all structures

- **D-BOVB**
  - Spectator orbitals are **delocalized** in all structures
Electron correlation in BOVB

- **Non-dynamic correlation (VBSCF, CASSCF, GVB)**
  - Non dynamic correlation gives the correct ionic/covalent ratio

- **Dynamic correlation**
  - All the rest. This is what is missing in VBSCF-CASSCF-GVB.
  - BOVB brings *that part of dynamic correlation that varies* in the reaction
What is an accurate description of two-electron bonding?

- **Spin exchange between two atomic orbitals**
  - Electrons are on different atoms and they exchange their positions

- **Charge fluctuation**
  - Sometimes both electrons are on the same atom.
  - There is some charge fluctuation. All orbitals instantaneously rearrange in size and shape to follow the charge fluctuation (orbitals « breathe »).

  *This is differential dynamic correlation*
Delocalizing also the *active orbitals* in BOVB?

No! Never! No way! By no means!

- Delocalizing the active orbitals in a formally covalent function is *one way* of taking care of ionic structures

\[
\Psi_{GVB} = \left| \cdots \Phi_a \Phi_b \right| + \left| \cdots \Phi_b \Phi_a \right|
\]

- Explicitly writing covalent and ionic structures with localized orbitals is *another way*:

- Combining *both ways* leads to *redundancy*
  - no consequences in VBSCF
  - artefactual energy lowering in BOVB
Delocalizing also the active orbitals in BOVB?

No! Never! No way! By no means!

Test case: the dissociation of $F_2$

1) BOVB with *strictly local* active orbitals
   - L-BOVB: $D_e = 29.1$ kcal/mol
   - SD-BOVB: $D_e = 36.2$ kcal/mol

2) BOVB with delocalized active orbitals
   - L-BOVB: $D_e = 51.5$ kcal/mol
   - SD-BOVB: $D_e = 102$ kcal/mol (!)

Experiment
   - $D_e = 38$ kcal/mol

Alternative means to include dynamic correlation into VB

The VBCI method

1) Start from VBSCF \( \Psi_{VB} = \sum C_i \Phi_i \)

2) For each \( \Phi_i \), define a set of \( i \) strictly localized virtual orbitals (localized on the same centers as the occupied orbitals of \( \Phi_i \))

3) Improve \( \Phi_i \) by post-VBSCF configuration interaction:

\[
\Phi_{CI} = \sum C_K^i \Phi_K^i
\]

All \( \Phi_K^i \) are excitations that correspond to the same VB structure \( \Phi_{CI} \) is a multi-determinant description of a unique VB structure

4) Do the configuration interaction:

\[
\Psi^{VBCI} = \sum K C_K^{CI} \Phi_K^{CI}
\]
Alternative means to include dynamic correlation into VB

• The VBPT2 method

1) Start from VBSCF \( \Psi_{VB} = \sum C_i \Phi_i \)

2) Same principle as VBCI, but 2\textsuperscript{nd}-order perturbation instead of CI

VBCI and VBPT2 will be taught in VB lecture III by Prof. Wei Wu

• The VB-QMC method (QMC = Quantum Monte Carlo)

1) Start from VBSCF \( \Psi_{VB} = \sum C_i \Phi_i \)

2) Each determinant is multiplied by a Jastrow factor
Summary: the two great families of VB methods

Example: the H₂ molecule

Static correlation

Classical VB
Local approach

\[ \Psi_{\text{VB}} = H\cdot - \cdot H + H^-H^+ + H^+H^- \]

- Keep strictly local orbitals
- Explicit inclusion of ionic structures

Coulson-Fischer
Semi-delocal approach

\[ \Psi_{\text{CF}} = \begin{array}{c}
\text{Ionic structures}
\end{array} \]

- Use semi-delocalized orbitals
- Implicit inclusion of ionic structures

Dynamic correlation

BOVB, VBCI, VBPT2, VB-QMC

CCCI, VB-QMC
Calculation of diabatic energies

What for?

*Resonance energies*

\[ \text{RE} = E(1) - E(1 \leftrightarrow 2) \]

*VB-state-crossing diagrams*

See VB lecture V by Prof. S. Shaik
Calculation of diabatic energies

Example: Covalent-ionic resonance energy in H$_2$

\[ \Psi_{VB} = C_1 \Phi_{cov} + C_2 \Phi_{ion-1} + C_2 \Phi_{ion-2} \]

\[ \text{RE} = E(\Phi_{cov}) - E(\Psi_{VB}) \]

**How does one calculate** $E(\Phi_{cov})$?

First method: «Consistent Diabatic Configuration»

$$\Phi_{cov}$$ is simply extracted from the Hamiltonian matrix

\[
\begin{array}{ccc}
1 & 2 & 3 \\
1 & -1.853879 & -1.579215 & -1.579215 \\
2 & -1.579215 & -1.578592 & -1.163000 \\
3 & -1.579215 & -1.163000 & -1.578592 \\
\end{array}
\]

\[ E(\Psi_{VB}) = -1.86452 \text{ au} \]

\[ \text{RE(CDC)} = -1.85388 + 1.86452 = 0.01064 \text{ au} = 6.7 \text{ kcal/mol} \]
Calculation of diabatic energies

Example: Covalent-ionic resonance energy in H₂

\[ \Psi_{\text{VB}} = C_1 \Phi_{\text{cov}} + C_2 \Phi_{\text{ion-1}} + C_2 \Phi_{\text{ion-2}} \]

\[ \text{RE} = E(\Phi_{\text{cov}}) - E(\Psi_{\text{VB}}) \]

Second method: «Variational Diabatic Configuration»

\( \Phi_{\text{cov}} \) is calculated separately: \( E(\Phi_{\text{cov}}) = -1.85778 \text{ au} \)

\Rightarrow \Phi_{\text{cov}} \text{ is variationally optimized}

\[
\begin{array}{ccc}
1 & 2 & 3 \\
1 & -1.853879 & -1.579215 & -1.579215 \\
2 & -1.579215 & -1.578592 & -1.163000 \\
3 & -1.579215 & -1.163000 & -1.578592
\end{array}
\]

\( E(\Psi_{\text{VB}}) = -1.86452 \text{ au} \)

\( \text{RE(VDC)} = -1.85778 + 1.86452 = 0.00674 \text{ au} = 4.2 \text{ kcal/mol} \)

(\(< \text{RE(CDC)}\))
An alternative way to calculate diabatic energies: The block-localized wave function (BLW) method

**Example:** Energy of a single Kekulé structure of benzene

\[ \Psi_{BLW} \]

\( \pi \)-MOs are optimized with the constrain to be localized on either of 1-2, 3-4 or 5-6 carbons: 
\( \Psi_{BLW} = \) energy of a Kekulé structure

Then we do a normal Hartree-Fock calculation: We get \( \Psi_{RHF} \)

Resonance energy = \( E(\Psi_{BLW}) - E(\Psi_{RHF}) \)

Exists also at the DFT level

See VB lecture VIII by Prof. Yirong Mo
Variational diabatic energies and basis set dependency: a warning

\[ \text{DZ}+ \text{P} \quad \text{TZ}+ \text{P} \quad \text{aug-TZ}+ \text{P} \quad \text{aug-QZ}+ \text{P} \quad \text{aug-5Z}+ \text{P} \]

In infinite basis set, any one-center AO can take the shape of a fully delocalized MO

⇒ The concepts of localized AO and of VB structure become meaningless
⇒ Variational diabatic energies (BLW method, VB calculation of VDC type) tend to collapse to the energy of the ground state
⇒ Resonance energies tend to collapse to unrealistic small values
Example: variational calculation of the vertical resonance energy of benzene

Block-localized wave function method:
VRE = E(Kekulé) - E(ground state)

\begin{align*}
\text{6-31G(d)} & \quad 6-311+G(d) & \quad \text{cc-pVTZ} & \quad \text{aug-cc-pVTZ} \\
\hline
\text{BLW-RHF} & 87.9 & 91.6 & 90.7 & 79.0 \\
\text{BLW-DFT} & 88.8 & 92.2 & 89.1 & 80.9 \\
\end{align*}

Moderate basis sets \(\Rightarrow\) consistent values,
Match experimentally measured quantities \(\Rightarrow\) too small values…
Variational diabatic energies: which basis set to choose?

**Strategy:**

- Avoid diffuse orbitals if not necessary (keep only for anions)
- **Choose a basis set** sufficiently large to yield good energetics (bonding energies, reaction energies, reaction barriers, etc., but no larger (typically DZ+P or TZ+P)
- Calculate the diabatic states and resonance energies in the **same basis set**
To be implemented in the very near future: CAS-VBSCF
• millions of VB structures allowed
• same cost and computational scaling as CASSCF

Current capabilities of the XMVB code

Can do: classical VB, GVB, SCVB, BLW, VBCI, VBPT2, + solvent effects

Current size limitations: Recent VB-QMC study:

• 22 non-hydrogen atoms
• 90 valence electrons
• accuracy matching CASPT2 or CCSD(T)
And now do it yourself!
(hands-on labs)