Quantum Monte Carlo wave functions and their optimization for quantum chemistry

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1. Quantum Monte Carlo (QMC) in a nutshell

2. Wave function optimization

3. Calculation of excited states

4. Symmetry breaking

5. New forms of wave functions
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Variational Monte Carlo (VMC)

a method for calculating multidimensional integrals

e.g., the energy

\[ \langle \Psi | \hat{H} | \Psi \rangle = \int dR \left( \frac{H(R)\psi(R)}{\psi(R)} \right) \psi(R)^2 \]
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\[
\langle \psi | \hat{H} | \psi \rangle = \int d\mathbf{R} \left( \frac{H(\mathbf{R})\psi(\mathbf{R})}{\psi(\mathbf{R})} \right) \psi(\mathbf{R})^2 \approx \frac{1}{M} \sum_{k=1}^{M} \frac{H(\mathbf{R}_k)\psi(\mathbf{R}_k)}{\psi(\mathbf{R}_k)}
\]

Metropolis sampling: \( M \) points \( \mathbf{R}_k \)
Variational Monte Carlo (VMC)

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\]

Metropolis sampling: \( M \) points \( R_k \)

Advantage: can use a flexible explicitly correlated \( \psi(R) \)

In practice, 2 types of error:
- unknown systematic error due to approximate wave function
- known statistical uncertainty (finite sampling) \( \propto 1/\sqrt{M} \)
Basic idea: diffusion in imaginary time $\tau = i t$

$$\Psi_{\text{exact}}(R) \xleftarrow{\text{sampling}} e^{-\tau \hat{H}} (\tau \to \infty) \xrightarrow{\text{sampling}} \Psi(R)$$
Diffusion Monte Carlo (DMC)

Basic idea: diffusion in imaginary time $\tau = i t$

$\Psi_{\text{exact}}(R) \xrightarrow{e^{-\tau \hat{H}} (\tau \to \infty)} \Psi(R)$

but:

**sign problem**: “converges” to the *bosonic* ground-state!
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but:

**sign problem**: “converges” to the *bosonic* ground-state!

In practice: **fixed-node (FN) approximation**

$$\Psi_{\text{FN}}(R) \xleftarrow{\exp(-\tau \hat{H}_{\text{FN}}) \ (\tau \to \infty)} \Psi(R)$$

$E_{\text{DMC}} \geq E_{\text{fermionic gs}}$  diffusion with nodes of $\Psi(R)$ fixed
Standard Jastrow-Slater wave functions

\[ \psi(R, p) = J(R, \alpha) \sum_m c_m \Phi_m(R) \]

- \( J(R, \alpha) \): **Jastrow factor** = exponential of a function depending explicitly on e-n and e-e distances
  \[ \implies \text{short-range weak/dynamic correlation} \]

- \( \sum_m c_m \Phi_m(R) \): linear combination of **Slater determinants** or **CSFs** of given spatial and spin symmetry
  \[ \implies \text{long-range strong/static correlation} \]
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Slater determinants made of orbitals expanded on a Slater basis:

\[ \phi_k(r) = \sum_{\mu} \lambda_{k\mu} \chi_\mu(r) \]

\[ \chi(r) = N(\zeta) r^{n-1} e^{-\zeta r} S_{l,m}(\theta, \phi) \]
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Parameters to optimize \( p = \{ \alpha, c, \lambda, \zeta \} \): Jastrow parameters \( \alpha \), CSF coefficients \( c \), orbital coefficients \( \lambda \) and basis exponents \( \zeta \)
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"Linear" optimization method

Wave function is linearly expanded in $\Delta p = p - p^0$:

$$|\psi^{(1)}(p)\rangle = |\psi_0\rangle + \sum_j \Delta p_j |\psi_j\rangle$$

where $|\psi_0\rangle = |\psi(p^0)\rangle$ and $|\psi_j\rangle = \left. \frac{\partial |\psi(p)\rangle}{\partial p_j} \right|_{p=p^0}$

Toulouse, Umrigar, JCP, 2007
Umrigar, Toulouse, Filippi, Sorella, Hennig, PRL, 2007
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- Minimization of energy $\Rightarrow$ generalized eigenvalue equation

$$\min_p \frac{\langle \psi^{(1)} | \hat{H} | \psi^{(1)} \rangle}{\langle \psi^{(1)} | \psi^{(1)} \rangle} \Rightarrow H \cdot \Delta p = E S \cdot \Delta p$$

where $H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle$ and $S_{ij} = \langle \psi_i | \psi_j \rangle$

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- Update of parameters: $p^0 \rightarrow p^0 + \Delta p$

Toulouse, Umrigar, JCP, 2007
Umrigar, Toulouse, Filippi, Sorella, Hennig, PRL, 2007
Toulouse, Umrigar, JCP, 2008
Estimators on a finite sample:

$$H_{ij} = \frac{1}{M} \sum_{k=1}^{M} \frac{\psi_i(R_k)}{\psi_0(R_k)} \frac{H(R_k) \psi_j(R_k)}{\psi_0(R_k)}$$,

$$S_{ij} = \frac{1}{M} \sum_{k=1}^{M} \frac{\psi_i(R_k)}{\psi_0(R_k)} \frac{\psi_j(R_k)}{\psi_0(R_k)}$$

non-symmetric!
Estimators on a finite sample:

\[ H_{ij} = \frac{1}{M} \sum_{k=1}^{M} \frac{\psi_i(R_k) H(R_k) \psi_j(R_k)}{\psi_0(R_k) \psi_0(R_k)} , \quad S_{ij} = \frac{1}{M} \sum_{k=1}^{M} \frac{\psi_i(R_k) \psi_j(R_k)}{\psi_0(R_k) \psi_0(R_k)} \]

non-symmetric!

\[ \implies \text{Zero-variance principle:} \]

If there is some \( \Delta p \) so that \( \psi_0 + \sum_j \Delta p_j \psi_j = \psi_{\text{exact}} \) then

\( \Delta p \) is found from \( H \cdot \Delta p = E S \cdot \Delta p \) with zero variance

In practice, this non-symmetric estimator greatly reduces the fluctuations on \( \Delta p \)

Toulouse, Umrigar, JCP, 2007
Umrigar, Toulouse, Filippi, Sorella, Hennig, PRL, 2007
Toulouse, Umrigar, JCP, 2008
Simultaneous optimization of all parameters

Optimization of 149 parameters = 24 (Jastrow) + 49 (CSF) + 64 (orbitals) + 12 (exponents) for C₂ molecule:

\[
\begin{array}{cccccc}
\text{Energy (Hartree)} & -75.9 & -75.8 & -75.7 & -75.6 & -75.5 \\
\text{Iterations} & 0 & 1 & 2 & 3 & 4 \\
\end{array}
\]

⇒ Energy converges within error bars in a few iterations

Toulouse, Umrigar, JCP, 2008
Systematic improvement in QMC

For \( \text{C}_2 \) molecule: total energies for a **series of fully optimized Jastrow-Slater wave functions:**

<table>
<thead>
<tr>
<th>Wave function</th>
<th>Energy (Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J*SD</td>
<td>-75.94</td>
</tr>
<tr>
<td>J*CAS(8,5)</td>
<td>-75.92</td>
</tr>
<tr>
<td>J*CAS(8,7)</td>
<td>-75.90</td>
</tr>
<tr>
<td>J*CAS(8,8)</td>
<td>-75.88</td>
</tr>
<tr>
<td>J*RAS(8,26)</td>
<td>-75.84</td>
</tr>
<tr>
<td>J*RAS(8,26)</td>
<td>-75.82</td>
</tr>
</tbody>
</table>

⇒ Systematic improvement in VMC

Toulouse, Umrigar, JCP, 2007
Systematic improvement in QMC

For $C_2$ molecule: total energies for a series of fully optimized Jastrow-Slater wave functions:

$$\begin{array}{c|c|c|c|c}
\text{Wave function} & \text{exact} & \text{VMC} & \text{DMC} \\
\hline
J^*SD & -75.94 & & \\
J^{CAS}(8,5) & -75.92 & & \\
J^{CAS}(8,7) & -75.9 & & \\
J^{CAS}(8,8) & -75.88 & & \\
J^{RAS}(8,26) & -75.86 & & \\
\end{array}$$

$\Rightarrow$ Systematic improvement in VMC and DMC

Toulouse, Umrigar, JCP, 2007
Dissociation energies of diatomic molecules

Single-determinant (SD) and multideterminant (full valence CAS) wave functions:

![Graph showing the dissociation energies for various diatomic molecules. The graph plots the error on dissociation energy in eV against the molecules Li₂, Be₂, B₂, C₂, N₂, O₂, F₂, and Ne₂. The error values range from -1.5 to 0. The graph indicates that the error generally decreases as the molecule's atomic number increases, with the exception of F₂ and Ne₂.]
Dissociation energies of diatomic molecules

Single-determinant (SD) and multideterminant (full valence CAS) wave functions:

Molecules

Li$_2$, Be$_2$, B$_2$, C$_2$, N$_2$, O$_2$, F$_2$, Ne$_2$

Error on dissociation energy (eV)

VMC J $\times$ SD

DMC J $\times$ SD

Toulouse, Umrigar, JCP, 2008
Dissociation energies of diatomic molecules

Single-determinant (SD) and multideterminant (full valence CAS) wave functions:

![Graph showing dissociation energy errors for various diatomic molecules.](image)

Molecules

Toulouse, Umrigar, JCP, 2008
Dissociation energies of diatomic molecules

Single-determinant (SD) and multideterminant (full valence CAS) wave functions:

\[
\begin{align*}
\text{Li}_2 & \quad -1.5 \\
\text{Be}_2 & \quad -1 \\
\text{B}_2 & \quad -0.5 \\
\text{C}_2 & \quad 0 \\
\text{N}_2 & \quad 0.5 \\
\text{O}_2 & \quad 1 \\
\text{F}_2 & \quad 1.5 \\
\text{Ne}_2 & \quad 2
\end{align*}
\]

Error on dissociation energy (eV)

Molecules

\[
\begin{align*}
\text{VMC J} \times \text{SD} & \quad \text{VMC J} \times \text{CAS} \\
\text{DMC J} \times \text{SD} & \quad \text{DMC J} \times \text{CAS}
\end{align*}
\]

\[\Rightarrow \text{Near chemical accuracy in DMC with Jastrow } \times \text{ CAS}\]

Toulouse, Umrigar, JCP, 2008
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VMC excited-state calculation with wave-function optimization

- For lowest energy state of a given symmetry: same as ground state calculation
VMC excited-state calculation with wave-function optimization

- For lowest energy state of a given symmetry: same as ground state calculation

- For a state that is not the lowest one in a given symmetry, two strategies:
  - **state-average** approach: minimization of a weighted average of the energies of $n$ states (C. Filippi *et al.*)
  - **state-specific** approach: minimization of the energy of the targeted state by selecting the $n^{th}$ eigenvector $\Delta p$ in the linear optimization method (Zimmerman, Toulouse, Zhang, Musgrave, Umrigar, JCP, 2009)
Calculation of excited states in QMC

VMC excited-state calculation with wave-function optimization

- For lowest energy state of a given symmetry: same as ground state calculation
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DMC excited-state calculation with VMC-optimized wave function

Fixed-node approximation prevents collapse on the ground state
### Adiabatic excitation energies (eV) with full-valence CAS wave functions:

<table>
<thead>
<tr>
<th></th>
<th>VMC</th>
<th>DMC</th>
<th>CR-CC</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1$</td>
<td>2.550(8)</td>
<td>2.524(4)</td>
<td>2.633</td>
<td></td>
</tr>
<tr>
<td>$^1B_2$</td>
<td>1.460(8)</td>
<td>1.416(4)</td>
<td>1.464</td>
<td>1.415</td>
</tr>
<tr>
<td>$^1A_1$</td>
<td>0.430(8)</td>
<td>0.406(4)</td>
<td>0.430</td>
<td>0.406</td>
</tr>
<tr>
<td>$^3B_2$</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zimmerman, Toulouse, Zhang, Musgrave, Umrigar, JCP, 2009
Gour, Piecuch, Wloch, MP, 2010
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Ground-state potential energy curve of $C_2$ molecule ($^{1}Σ_g^+$)

Jastrow $\times$ single determinant wave function

![Graph showing the ground-state potential energy curve of $C_2$ molecule. The graph includes a plot of energy (in hartree) against internuclear distance (in bohr). The graph illustrates the Jastrow $\times$ single determinant wave function and compares it with an accurate size-consistency error. The reference is to Toulouse and Umrigar, JCP, 2008.]
Ground-state potential energy curve of $\text{C}_2$ molecule ($^1\Sigma_g^+$)

Jastrow $\times$ single determinant wave function

$$\begin{array}{c}
\begin{array}{cccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\
-75.9 & -75.8 & -75.7 & -75.6 & -75.5 & -75.4 \\
\end{array}
\end{array}$$

Internuclear distance (bohr)

- $\text{VMC J} \times \text{SD}$
- $\text{DMC J} \times \text{SD}$

Accurate

$\Rightarrow$ Single-determinant DMC is size consistent but with broken spin symmetry at dissociation, $\langle \Psi_{\text{FN}} | \hat{S}^2 | \Psi_{\text{FN}} \rangle = 2$

Toulouse, Umrigar, JCP, 2008
Ground-state potential energy curve of C$_2$ molecule ($^1\Sigma^+_g$)

**Jastrow × multideterminant wave function:**

-75.9
-75.8
-75.7
-75.6
-75.5
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<table>
<thead>
<tr>
<th>Internuclear distance (bohr)</th>
<th>Energy (hartree)</th>
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</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-75.9</td>
</tr>
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<td>2.0</td>
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</tr>
<tr>
<td>3.0</td>
<td>-75.7</td>
</tr>
<tr>
<td>4.0</td>
<td>-75.6</td>
</tr>
<tr>
<td>5.0</td>
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</tr>
<tr>
<td>6.0</td>
<td>-75.4</td>
</tr>
<tr>
<td>7.0</td>
<td>-75.3</td>
</tr>
<tr>
<td>8.0</td>
<td>-75.2</td>
</tr>
<tr>
<td>9.0</td>
<td>-75.1</td>
</tr>
<tr>
<td>10.0</td>
<td>-75.0</td>
</tr>
</tbody>
</table>

VMC J × CAS(8,8)

DMC J × CAS(8,8)

Accurate

⇒ VMC and DMC are now size consistent without symmetry breaking

Toulouse, Umrigar, JCP, 2008
Spatial symmetry breaking in hydrogen rings

For large enough rings, three Hartree-Fock solutions:

- symmetry adapted (SA)
- symmetry broken atom-centered (SB-AC)
- symmetry broken bond-centered (SB-BC)

Which Hartree-Fock wave function should we use in DMC?

DMC total energies with symmetry-adapted (SA) or symmetry-broken (SB) Hartree-Fock wave functions:

![Graph showing total energy vs. number of H atoms for SA, SB-AC, and SB-BC wave functions.]

⇒ Symmetry-adapted wave function has better nodes

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Jastrow-Valence-Bond wave functions

\[ |\psi_{J \times VB} \rangle = \hat{J} \sum_{m} c_m |\Phi_{VB,m} \rangle \]

where \( |\Phi_{VB,m} \rangle \) are VB structures:

\[ |\Phi_{VB,m} \rangle = \prod_{p} \hat{a}_{p \uparrow}^{\dagger} \hat{a}_{p \downarrow}^{\dagger} \prod_{ij} \left( \hat{a}_{i \uparrow}^{\dagger} \hat{a}_{j \downarrow}^{\dagger} - \hat{a}_{i \downarrow}^{\dagger} \hat{a}_{j \uparrow}^{\dagger} \right) \prod_{q} \hat{a}_{q \uparrow}^{\dagger} |\text{vac} \rangle \]

with nonorthogonal active orbitals localized on single atom

\[ \implies \text{Compact wave functions from chemical picture} \]
Jastrow-Valence-Bond wave functions

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\textbf{Example: } N_2

\[ |N \equiv N| \]

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011
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**Example: N\(_2\)**

\[ |N \equiv N| \Rightarrow \begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\end{array} \leftrightarrow \begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{N}
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with nonorthogonal active orbitals localized on single atom

\[ \longrightarrow \text{Compact wave functions from chemical picture} \]

**Example: N}_2

\[ |N \equiv N\rangle \Rightarrow \]

\[ \text{\includegraphics[width=0.2\textwidth]{example1.png}} \quad \leftrightarrow \quad \text{\includegraphics[width=0.2\textwidth]{example2.png}} \quad \leftrightarrow \quad \text{\includegraphics[width=0.2\textwidth]{example3.png}} \quad \leftrightarrow \cdots \]

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with nonorthogonal active orbitals localized on single atom

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Example: \( \text{N}_2 \)

\[ |\text{N} \equiv \text{N}| \Rightarrow \]

VB: 27 structures, 16 determinants

CAS: 112 determinants

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011
Dissociation energies of diatomic molecules with $J \times VB$

Comparison with single-determinant (SD) and full-valence CAS wave functions:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>DMC J*SD</th>
<th>DMC J*VB</th>
<th>DMC J*CAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)</td>
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<tr>
<td>N(_2)</td>
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<td>O(_2)</td>
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<tr>
<td>F(_2)</td>
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</tr>
</tbody>
</table>

Error on dissociation energy (eV)

$\Rightarrow$ Compromise between compactness and accuracy

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011
Dissociation energies of diatomic molecules with $J \times VB$

Comparison with single-determinant (SD) and full-valence CAS wave functions:

![Graph showing error on dissociation energy (eV) for different molecules (C$_2$, N$_2$, O$_2$, F$_2$) using DMC J*SD, DMC J*VB, and DMC J*CAS wave functions.]

$\Rightarrow$ **Compromise between compactness and accuracy**

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011
**Gauss-Slater basis function**

\[ \chi_{nlm}(r, \zeta) = N_n(\zeta) \, r^{n-1} e^{-\frac{(\zeta r)^2}{1+\zeta r}} \, S_{l,m}(\theta, \phi) \]

- For \( r \ll 1 \), it reduces to a Gaussian function
  \[ \chi_{nlm}(r, \zeta) \approx N_n(\zeta) \, r^{n-1} e^{-\zeta^2 r^2} \, S_{l,m}(\theta, \phi) \]
  which is appropriate since no e-n cusp with nondivergent pseudopotentials

- For \( r \gg 1 \), it reduces to a Slater function
  \[ \chi_{nlm}(r, \zeta) \approx N_n(\zeta) \, r^{n-1} e^{-\zeta r} \, S_{l,m}(\theta, \phi) \]
  which is the correct asymptotic behavior in finite systems

Petruzielo, Toulouse, Umrigar, JCP, 2011
Petruzielo, Toulouse, Umrigar, JCP, 2010
Atomization energies of 55 molecules (G2 set)

DMC calculations with reoptimized truncated multideterminant CAS wave functions with pseudopotentials and Gauss-Slater basis:

Mean absolute deviation in DMC = 1.2 kcal/mol

Petruzielo, Toulouse, Umrigar, JCP, 2012
Summary

- QMC methods can handle weak and strong correlation
- Efficient wave function optimization method by minimization of VMC energy
- Near chemical accuracy on energy differences
- Calculation of excited states possible
- Must be careful with symmetry breaking in DMC
- Exploration of new forms of compact wave functions

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