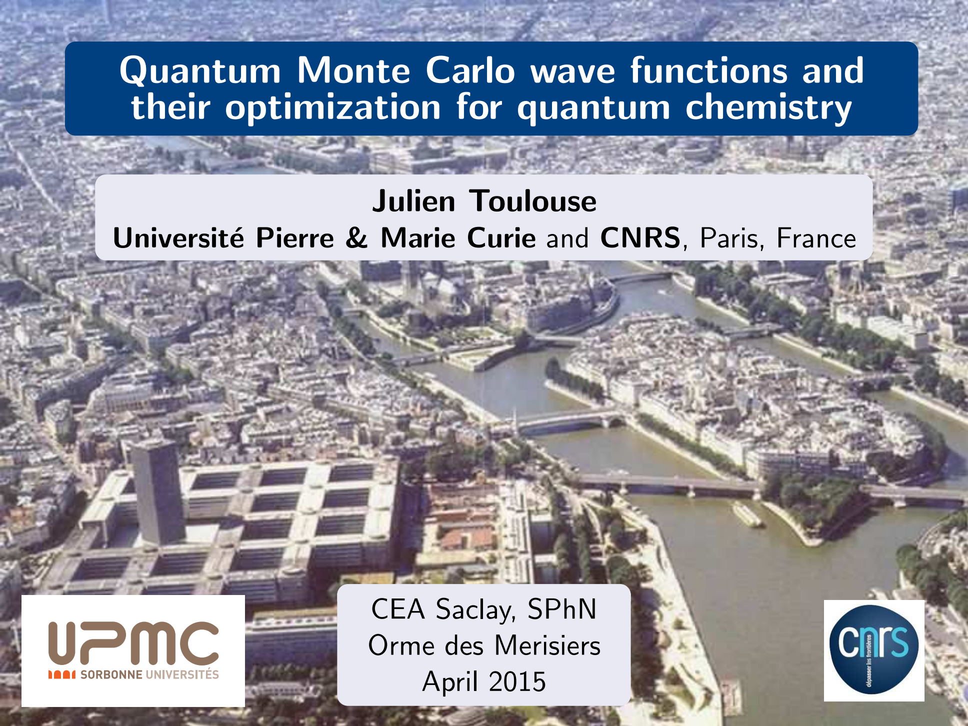

Quantum Monte Carlo wave functions and their optimization for quantum chemistry

Julien Toulouse
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CEA Saclay, SPhN
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April 2015

Outline

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

$$\langle \Psi | \hat{H} | \Psi \rangle = \int d\mathbf{R} \left(\frac{H(\mathbf{R})\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \right) \Psi(\mathbf{R})^2$$

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

$\uparrow$

Metropolis sampling: M points $\mathbf{R}_k$

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↑

Metropolis sampling: M points $\mathbf{R}_k$

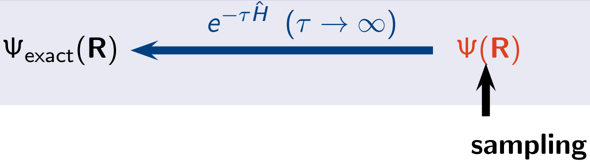
Advantage: can use a flexible explicitly correlated $\Psi(\mathbf{R})$

In practice, 2 types of error:

- unknown **systematic error** due to approximate wave function
- known **statistical uncertainty** (finite sampling) $\propto 1/\sqrt{M}$

Diffusion Monte Carlo (DMC)

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



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

sampling

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

$$\Psi_{\text{exact}}(\mathbf{R}) \xleftarrow{\quad e^{-\tau\hat{H}} \ (\tau \to \infty) \quad} \underset{\underset{\textbf{sampling}}{\uparrow}}{\Psi(\mathbf{R})}$$

but:

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

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In practice: fixed-node (FN) approximation

$$\Psi_{\text{FN}}(\mathbf{R}) \xleftarrow{\;e^{-\tau\hat{H}_{\text{FN}}}\quad(\tau\to\infty)\;} \Psi(\mathbf{R})$$

$E_{\text{DMC}} \geq E_{\text{fermionic gs}}$

diffusion with nodes of $\Psi(\mathbf{R})$ fixed

Standard Jastrow-Slater wave functions

$$\Psi(\mathbf{R},\mathbf{p}) = J(\mathbf{R},\alpha) \sum_m c_m \Phi_m(\mathbf{R})$$

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

- $\sum_m c_m \Phi_m(\mathbf{R})$: **linear combination of Slater determinants or CSFs** of given spatial and spin symmetry
  $\Longrightarrow$ **long-range strong/static correlation**

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Slater determinants made of orbitals expanded on a Slater basis:

$$\phi_k(\mathbf{r}) = \sum_\mu \lambda_{k\mu} \chi_\mu(\mathbf{r})$$

$$\chi(\mathbf{r}) = N(\zeta) \, r^{n-1} \, e^{-\zeta r} \, S_{l,m}(\theta,\phi)$$

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Parameters to optimize $\mathbf{p} = \{\alpha, \mathbf{c}, \boldsymbol{\lambda}, \zeta\}$: **Jastrow parameters α**, **CSF coefficients c**, **orbital coefficients λ** and **basis exponents ζ**

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"Linear" optimization method

- **Wave function is linearly expanded in $\Delta\mathbf{p} = \mathbf{p} - \mathbf{p}^0$:**

$$\boxed{|\Psi^{(1)}(\mathbf{p})\rangle = |\Psi_0\rangle + \sum_j \Delta p_j \, |\Psi_j\rangle}$$

where $|\Psi_0\rangle = |\Psi(\mathbf{p}^0)\rangle$ and $|\Psi_j\rangle = \left.\dfrac{\partial|\Psi(\mathbf{p})\rangle}{\partial p_j}\right|_{\mathbf{p}=\mathbf{p}^0}$

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

$$\min_{\mathbf{p}} \frac{\langle \Psi^{(1)} | \hat{H} | \Psi^{(1)} \rangle}{\langle \Psi^{(1)} | \Psi^{(1)} \rangle} \Longrightarrow \boxed{\mathbf{H} \cdot \Delta \mathbf{p} = E \, \mathbf{S} \cdot \Delta \mathbf{p}}$$

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: $\mathbf{p}^0 \rightarrow \mathbf{p}^0 + \Delta \mathbf{p}$**

Toulouse, Umrigar, JCP, 2007
Umrigar, Toulouse, Filippi, Sorella, Hennig, PRL, 2007
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"Linear" optimization method in VMC

- **Estimators on a finite sample**:

$$H_{ij} = \frac{1}{M} \sum_{k=1}^{M} \frac{\Psi_i(\mathbf{R}_k)}{\Psi_0(\mathbf{R}_k)} \frac{H(\mathbf{R}_k)\Psi_j(\mathbf{R}_k)}{\Psi_0(\mathbf{R}_k)} \quad , \quad S_{ij} = \frac{1}{M} \sum_{k=1}^{M} \frac{\Psi_i(\mathbf{R}_k)}{\Psi_0(\mathbf{R}_k)} \frac{\Psi_j(\mathbf{R}_k)}{\Psi_0(\mathbf{R}_k)}$$

non-symmetric !

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non-symmetric !

$\Longrightarrow$ **Zero-variance principle**:

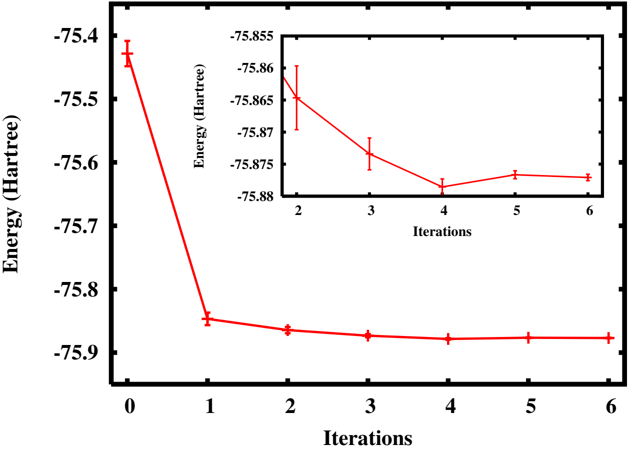
If there is some $\Delta\mathbf{p}$ so that $\Psi_0 + \sum_j \Delta p_j \, \Psi_j = \Psi_{\text{exact}}$ **then** $\Delta\mathbf{p}$ is found from $\mathbf{H} \cdot \Delta\mathbf{p} = E \, \mathbf{S} \cdot \Delta\mathbf{p}$ with **zero variance**

In practice, this non-symmetric estimator greatly reduces the fluctuations on $\Delta\mathbf{p}$

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 **$\mathbf{C_2}$ molecule** :

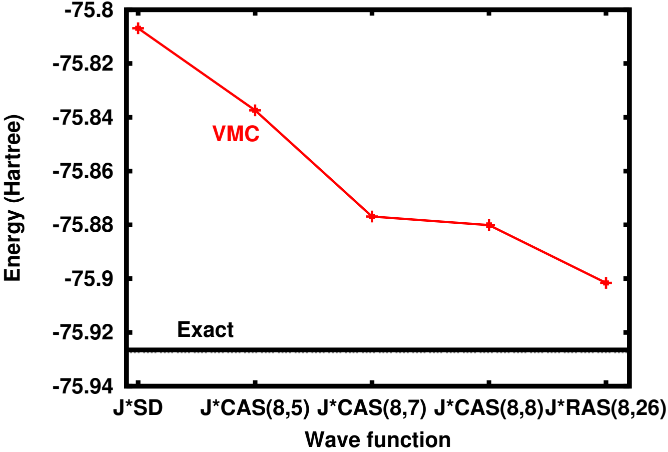


⟹ **Energy converges within error bars in a few iterations**

Toulouse, Umrigar, JCP, 2008

Systematic improvement in QMC

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



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Toulouse, Umrigar, JCP, 2007

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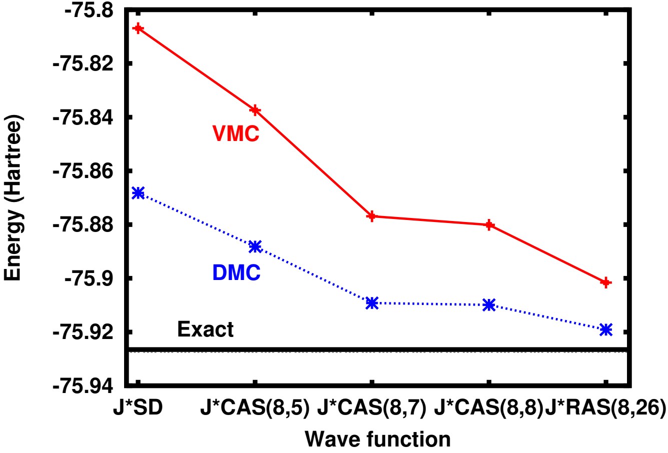
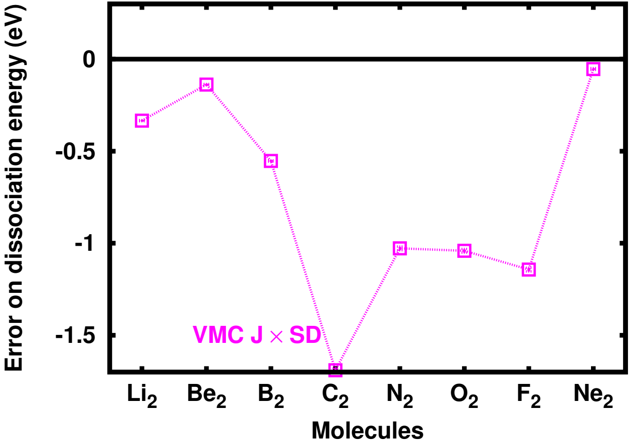


$\Longrightarrow$ **Systematic improvement in VMC and DMC**

Toulouse, Umrigar, JCP, 2007

Dissociation energies of diatomic molecules

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



Toulouse, Umrigar, JCP, 2008

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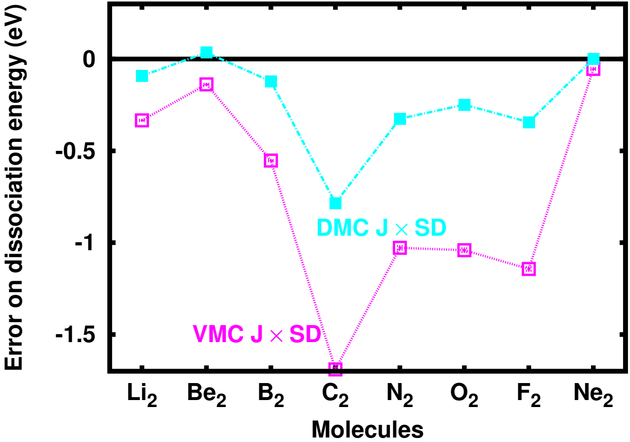

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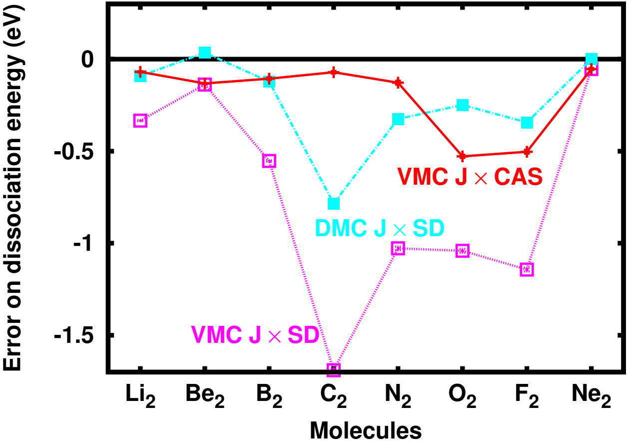

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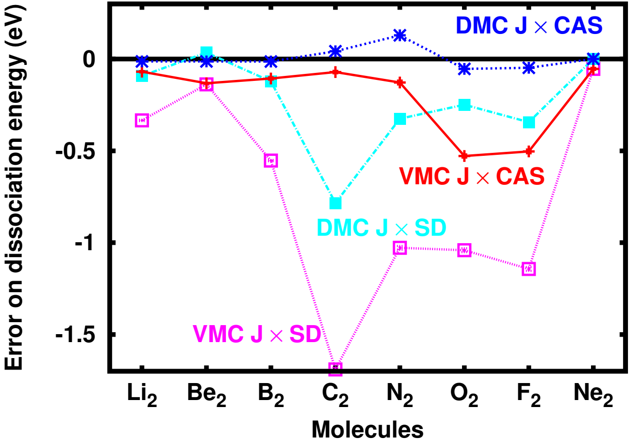

⟹ **Near chemical accuracy in DMC with Jastrow × CAS**

Toulouse, Umrigar, JCP, 2008

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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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- 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 $\Delta\mathbf{p}$ in the linear optimization method

  (Zimmerman, Toulouse, Zhang, Musgrave, Umrigar, JCP, 2009)

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DMC excited-state calculation with VMC-optimized wave function

Fixed-node approximation prevents collapse on the ground state

Example of methylene CH_2

Adiabatic excitation energies (eV) with full-valence CAS wave functions:

	VMC	**DMC**	**CR-CC**	**Exp.**
$^1\mathbf{A}_1$	2.550(8)	2.524(4)	2.633	
$^1\mathbf{B}_2$	1.460(8)	1.416(4)	1.464	1.415
$^1\mathbf{A}_1$	0.430(8)	0.406(4)	0.430	0.406
$^3\mathbf{B}_2$	0.000	0.000		

Zimmerman, Toulouse, Zhang, Musgrave, Umrigar, JCP, 2009

Gour, Piecuch,Wloch, MP, 2010

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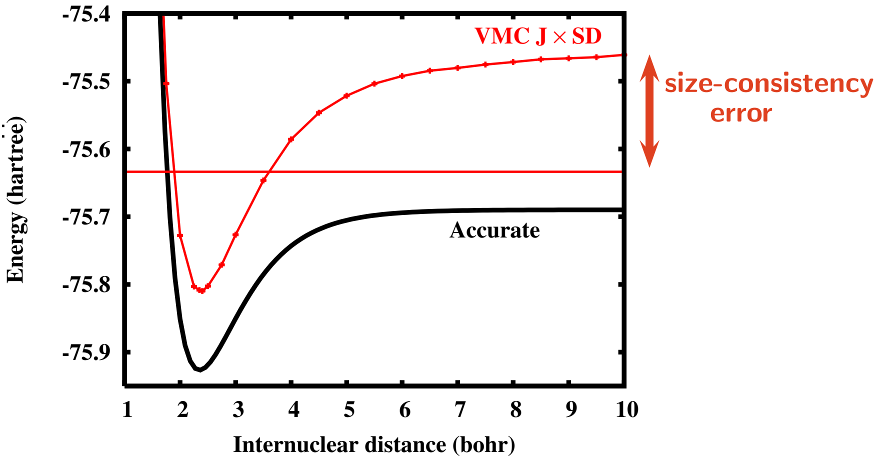
Ground-state potential energy curve of C_2 molecule ($^1\Sigma_g^+$)

Jastrow × single determinant wave function



Toulouse, Umrigar, JCP, 2008

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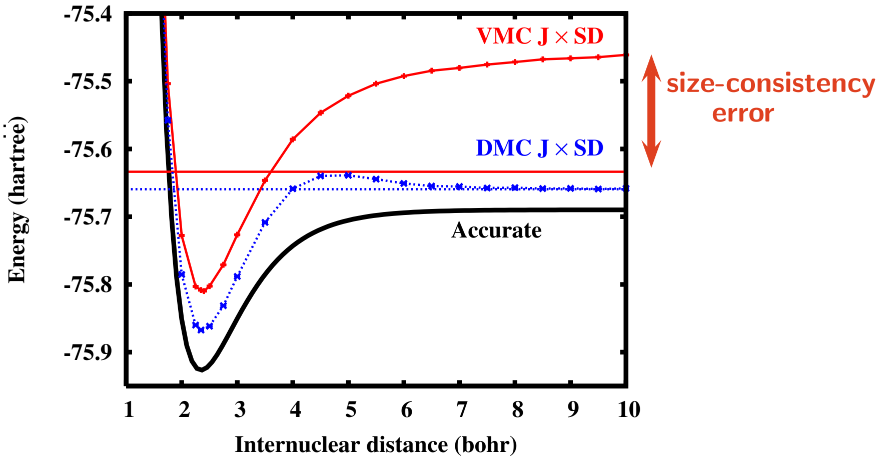


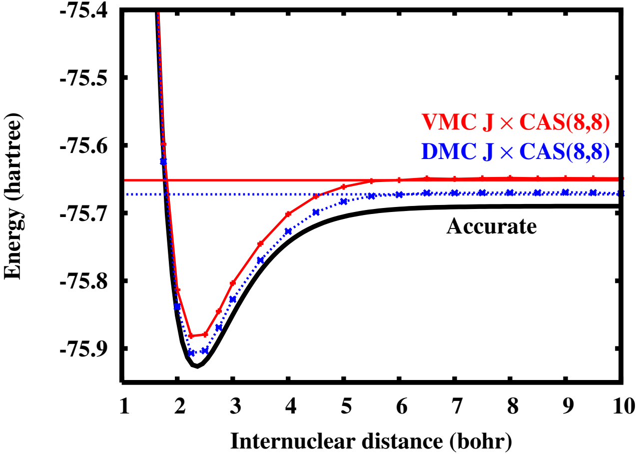
$\Longrightarrow$ **Single-determinant DMC is size consistent**

but with broken spin symmetry at dissociation, $\langle \Psi_{\mathbf{FN}} | \hat{S}^2 | \Psi_{\mathbf{FN}} \rangle = 2$

Toulouse, Umrigar, JCP, 2008

Ground-state potential energy curve of C_2 molecule $(^1\Sigma_g^+)$

Jastrow × multideterminant wave function:



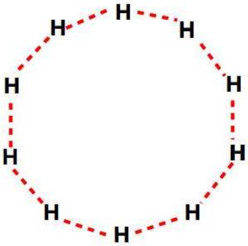
⟹ VMC and DMC are now size consistent without symmetry breaking

Toulouse, Umrigar, JCP, 2008

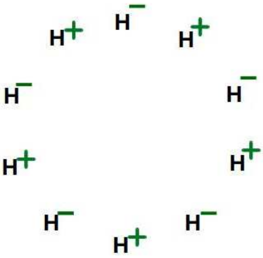
Spatial symmetry breaking in hydrogen rings

For large enough rings, three Hartree-Fock solutions:

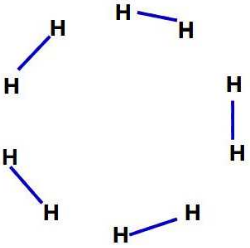
symmetry adapted (SA)



symmetry broken atom-centered (SB-AC)



symmetry broken bond-centered (SB-BC)

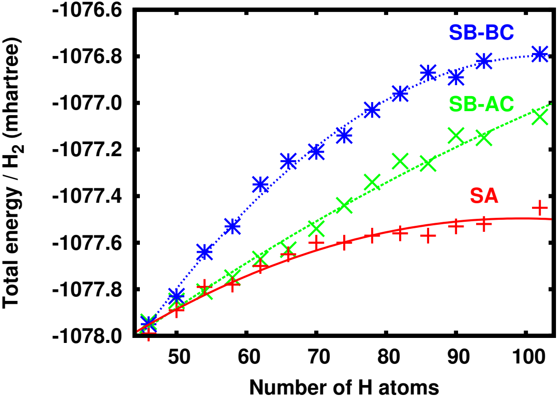


Which Hartree-Fock wave function should we use in DMC ?

Reinhardt, Toulouse, Assaraf, Umrigar, Hoggan, ACS Proceedings, 2012

Spatial symmetry breaking in hydrogen rings

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



$\Longrightarrow$ **Symmetry-adapted wave function has better nodes**

Reinhardt, Toulouse, Assaraf, Umrigar, Hoggan, ACS Proceedings, 2012

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Jastrow-Valence-Bond wave functions

$$|\Psi_{\mathrm{J\times VB}}\rangle = \hat{J} \sum_m c_m \, |\Phi_{\mathrm{VB},m}\rangle$$

where $|\Phi_{\mathrm{VB},m}\rangle$ are **VB structures**:

$$|\Phi_{\mathrm{VB},m}\rangle = \overset{\text{inactive}}{\prod_p} \hat{a}^\dagger_{p\uparrow}\hat{a}^\dagger_{p\downarrow} \overset{\substack{\text{active}\\\text{pairs}}}{\prod_{(ij)}} \left(\hat{a}^\dagger_{i\uparrow}\hat{a}^\dagger_{j\downarrow} - \hat{a}^\dagger_{i\downarrow}\hat{a}^\dagger_{j\uparrow}\right) \overset{\substack{\text{unpaired}\\\text{active}}}{\prod_q} \hat{a}^\dagger_{q\uparrow}|\mathrm{vac}\rangle$$

with nonorthogonal active orbitals localized on single atom

$\Longrightarrow$ **Compact wave functions from chemical picture**

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011

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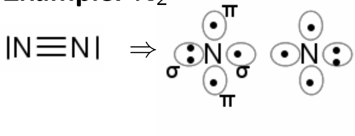

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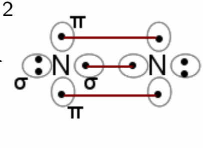

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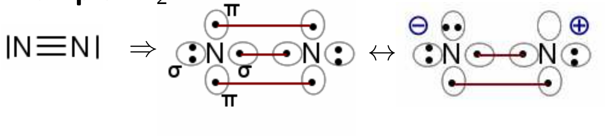


Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011

Jastrow-Valence-Bond wave functions

$$|\Psi_{\mathrm{J\times VB}}\rangle = \hat{J} \sum_m c_m \, |\Phi_{\mathrm{VB},m}\rangle$$

where $|\Phi_{\mathrm{VB},m}\rangle$ are **VB structures**:

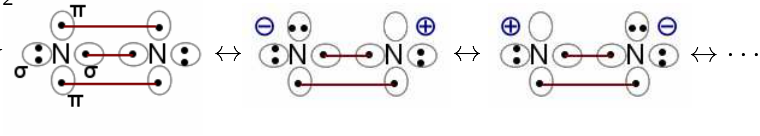
$$|\Phi_{\mathrm{VB},m}\rangle = \overset{\text{inactive}}{\prod_{p}} \hat{a}^{\dagger}_{p\uparrow}\hat{a}^{\dagger}_{p\downarrow} \overset{\text{active pairs}}{\prod_{(ij)}} \left(\hat{a}^{\dagger}_{i\uparrow}\hat{a}^{\dagger}_{j\downarrow} - \hat{a}^{\dagger}_{i\downarrow}\hat{a}^{\dagger}_{j\uparrow}\right) \overset{\text{unpaired active}}{\prod_{q}} \hat{a}^{\dagger}_{q\uparrow}|\mathrm{vac}\rangle$$

with nonorthogonal active orbitals localized on single atom

$\Longrightarrow$ **Compact wave functions from chemical picture**

Example: N_2

$|N\equiv N|$ $\Rightarrow$



Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011

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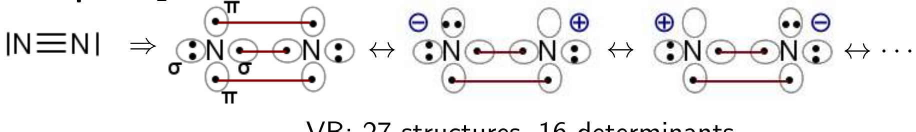
Example: N$_2$



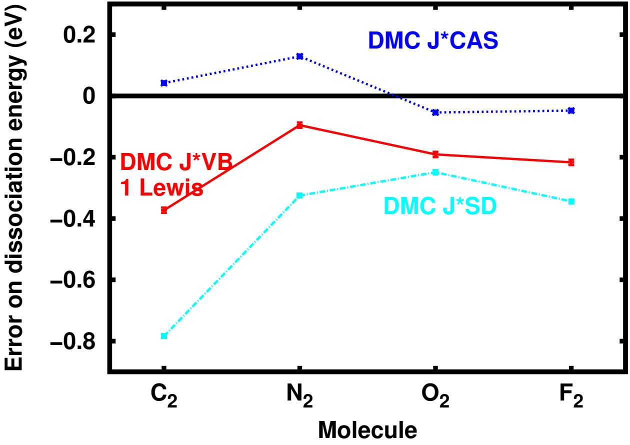
VB: 27 structures, 16 determinants

CAS: 112 determinants

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011

Dissociation energies of diatomic molecules with J×VB

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



⟹ **Compromise between compactness and accuracy**

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011

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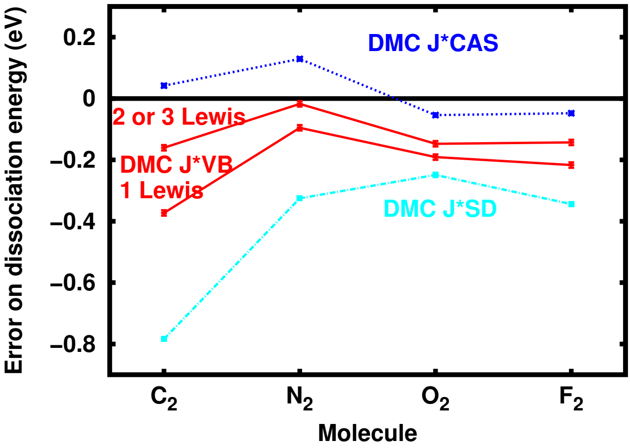


$\Longrightarrow$ **Compromise between compactness and accuracy**

Braïda, Toulouse, Caffarel, Umrigar, JCP, 2011

New basis function form for nondivergent pseudopotentials

Gauss-Slater basis function

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

- For $r \ll 1$, its reduces to a Gaussian function

  $$\chi_{nlm}(\mathbf{r},\zeta) \approx N_n(\zeta)\; r^{n-1} e^{-(\zeta r)^2}\; S_{l,m}(\theta,\phi)$$

  which is appropriate since no e-n cusp with nondivergent pseudopotentials

- For $r \gg 1$, its reduces to a Slater function

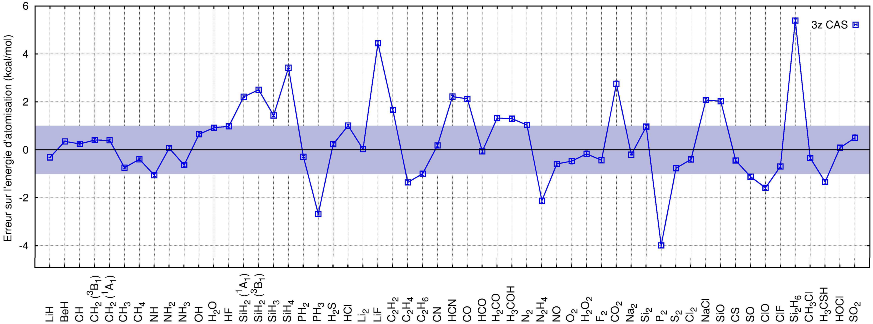
  $$\chi_{nlm}(\mathbf{r},\zeta) \approx N_n(\zeta)\; r^{n-1} e^{-\zeta r}\; S_{l,m}(\theta,\phi)$$

  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:



$\Longrightarrow$ **Mean absolute deviation in DMC = 1.2 kcal/mol**

Petruzielo, Toulouse, Umrigar, JCP, 2012

Summary and acknowledgements

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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