Efficient Multi-reference DMC and Insight from QMC

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Benchmark calculations

- experimental atomization energies of 55 small molecules (G2 set)
- previous DMC benchmark calculations by J. C. Grossman and Nemec/Towler/Needs
  - Grossman: natural orbitals, SBK PP, FN-DMC
  - Nemec/Towler/Needs: HF orbitals from GTO and STO basis, all electron, cusp correction, FN-DMC
Our benchmark methodology

- standard FN-DMC code with drift-diffusion propagator, Metropolis step, local energy, and drift cut-off
- Slater-Jastrow one determinant guide function with standard Schmidt-Moskowitz Jastrow
- cc-pVTZ-f basis set (standard TZP GTO basis set without f functions)
- 1s and 2s Cusp correction (Manten/Lüchow, JCP 115, 5362 (2001))
- Comparison of KS (BP86, B3LYP) and HF orbitals.
- Time step extrapolation
- experimental geometries
benchmark results: details

$\Delta E_A$ DMC/BP86 - extrapoliert

![Graph showing $\Delta E_A$ for various molecules](image-url)
benchmark results: conclusions

errors of FN-DMC atomization energies in kJ/mol for 55 molecules of G2 set using different MOs

<table>
<thead>
<tr>
<th></th>
<th>R(O)HF</th>
<th>UHF</th>
<th>B3LYP</th>
<th>BP86</th>
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<tbody>
<tr>
<td>MAD</td>
<td>13.4</td>
<td>12.2</td>
<td>10.4</td>
<td>9.4</td>
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<tr>
<td>MD</td>
<td>−6.7</td>
<td>−3.7</td>
<td>−4.8</td>
<td>−3.5</td>
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<td>RMS</td>
<td>19.2</td>
<td>18.6</td>
<td>15.1</td>
<td>13.4</td>
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</tbody>
</table>

- Grossman: MAD=11.6, MD=−7.8, RMS=16.4 kJ/mol
- Nemec/Towler/Needs: MAD for STOs is 13.4, for GTOs 21.3 kJ/mol

Conclusion

No obvious advantage of STO compared with cusp-corrected GTOs, but significant gain from GGA MOs.
further results on second row molecules

- all-electron calculations on 50 molecules with second row atoms Na – Ar
- time-step needs to decrease with nuclear charge $Z$
- calculations with time-step down to 0.00025 a.u.

all-electron FN-DMC for second-row molecules

No loss in accuracy for all-electron FN-DMC calculations using GTO with cusp-correction.
Do we really need accurate energies?

- Why are traditional ab initio methods so successful in spite of lousy total energies?

**systematic error cancellation**

- Traditional ab initio method have a systematic basis set error
- Wave function based method have a systematic higher-level correlation error
- DFT methods have a systematic $E_{XC}$ functional bias
Error cancellation in DMC

- FN-DMC accuracy of 10 kJ/mol for atomization energies
- Errors in total energies often 100 kJ/mol
- Goal: how to improve error cancellation of
  - Node location error
  - Time-step error

Visualization of error cancellation in FN-DMC
Example: ring opening of bicyclo[1.1.0]butane

isomerization of bicyclo[1.1.0]butane to trans-1,3-butadiene
Example: ring opening of bicyclo[1.1.0]butane

isomerization of bicyclo[1.1.0]butane to *trans*-1,3-butadiene

Woodward-Hoffmann rules

conrotatory ring closure
reaction path

- two possible transition state: conrotatory and disrotatory
- rearrangement of gauche-butadiene to trans-butadiene
Multireference-DMC

- To account for non-dynamical correlation CASSCF guide functions are calculated
- truncated CASSCF functions are employed (with optimized Jastrow) in FN-DMC
MR-DMC: bicylcobutane

- FN-DMC increases as CASSCF wave function improves!
MR-DMC: transition states

- only initial decrease then increase of energy, mostly in dis_TS
MR-DMC: products

significant decrease only with second CSF
Optimal Multi-Reference (OMR-)DMC

- Well known fact: FN-DMC increases with improving MCSCF (Flad, Lüchow, Caffarel,...)

Why?

- CASSCF accounts for non-dynamical as well as partially for the dynamical electron correlation
- The dynamical correlation is accounted for by Jastrow: CASSCF deteriorates nodes
- The non-dynamical correlation contribution improves nodes and FN-DMC

Best compromise: Use minimum of FN-DMC vs # CSF curve
- in this example: only 3 CSFs in the dis_Ts system, 1 CSF in educt, 2 CSFs in rest

Alternative: reoptimize CI coefficients (Umrigar, Toulouse, Sorella, Filippi, Hennig...). Cost?
Results for OMR-DMC
in kcal/mol relative to bicyclobutane

<table>
<thead>
<tr>
<th></th>
<th>con_TS</th>
<th>dis_TS</th>
<th>g-but</th>
<th>gt_TS</th>
<th>t-but</th>
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<tbody>
<tr>
<td>experiment</td>
<td>40(2.5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-25.9(4)</td>
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<td>DFT/B3LYP</td>
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<td>-22.8</td>
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<td>CCSD(T)</td>
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<td>21.8</td>
<td>-25.1</td>
<td>-22.3</td>
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<td>CR-CCSD(T)</td>
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<td>-24.8</td>
<td>-22.1</td>
<td>-27.7</td>
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<td>CR-CC(2,3)</td>
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<td>-22.1</td>
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<td>OMR1-DMC</td>
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<td>-22.8(5)</td>
<td>-27.0(5)</td>
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<td>59.4(5)</td>
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<td>DMC/HF</td>
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<td>DMC/B3LYP</td>
<td>54(1)</td>
<td>85.1(8)</td>
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<td>DMC/CASSCF</td>
<td>47(1)</td>
<td>91.7(9)</td>
<td>-22.5(9)</td>
<td>-19.4(9)</td>
<td>-25.5(9)</td>
</tr>
</tbody>
</table>

OMR1: small CAS; OMR2: CAS(10,10); OMR3: DMC-optimized
DMC/CASSCF: first det from CAS(10,10)
Discussion of OMR-DMC

- CCSD(T) fails to predict a conrotatory TS
- B3LYP has too small difference between conrotatory and disrotatory TS
- SR-DMC overestimates both TS
- OMR-DMC has excellent agreement with sophisticated CR-CC calculation (and experiment)
- OMR-DMC also improves significantly for small non-dynamical contributions (products)
- Reoptimization of CI coefficients (with DMC!) does not yield significant improvements
- OMR-DMC is very efficient in accounting for dynamical and non-dynamical electron correlation
Insight from QMC

- QMC produces samples from accurate many-body wave functions
  - $|\Psi_G|^2$ in VMC and $|\Psi_G \Psi_0^{(FN)}|$ in FN-DMC
  - $3n$ dimensional probabilities
  - contain information about antisymmetry (Fermi hole, “Pauli repulsion”) and electron correlation

- insight from simple model or a posteriori from accurate wave functions?

- binding energies, lone pair energies, orbitals, etc.: no observables

How to visualize many-body effects like antisymmetry?

- QMC emphasizes “real space” analysis (rather than “orbital space”)
Most probable electron arrangement

The maximum of $|\Psi(x_1, x_2, \ldots, x_n)|^2$ yields the most probable electron arrangement of all $n$ electrons simultaneously. The arrangement contains considerable information about the bonding in the molecule.

- Due to antisymmetry, same spin electrons avoid each other more than unlike spin electrons
- For eight electrons ($4\alpha, 4\beta$) around an atom, the most probable arrangement consists of two tetrahedra
  - Linnett's double quartet theory (1960), Artmann (1940)

Determination of the maximum of $|\Psi|^2$ is a global optimization problem: today easy

- Metropolis-Monte Carlo random walk combined with local gradient optimization.
Ethane

Most probable electron arrangement for ethane (HF/cc-pVTZ):
- connected tetrahedra
- symmetry breaking!
Water

Maximum with correlated wave function (Slater-Jastrow):
Water II
Single electron densities

- Electrons are mostly not at the maximum position
- Partition the total density $\rho(r)$ into *single electron densities* that are obtained by assigning electrons from the many-body distribution $|\Psi|^2$ to the maximum.

$$\rho(r) = \sum_{i=1}^{n} \rho_i^{SED}(r)$$

**Single electron densities (SED)**

Assign electrons of many-body distribution $|\Psi|^2$ to a reference arrangement by finding the permutation that minimizes the distance (in $\mathbb{R}^{3n}$) to the reference. Single electron densities are the densities of the assigned electrons.
Single electron densities (SED)

Compare:

- electron density (integrating to electron number $n$)

$$\rho(r_1) = n \int |\Psi(R)|^2 dr_2 \ldots dr_n, \quad R = (r_1, r_2, \ldots, r_n)$$

- single electron density for electron 1:

$$\rho_{1}^{SED}(r_1) = \int |\Psi(\mathcal{P}R)|^2 dr_2 \ldots dr_n, \quad R = (r_1, r_2, \ldots, r_n)$$

where the permutation $\mathcal{P}$ depends on $R$ and a reference arrangement $R_{ref}$

- Currently we require: $|\mathcal{P}R - R_{ref}| \overset{!}{=} \text{min}$
Ethane

- uncorrelated wave function
Water

- correlated wave function
Water
Water: “electron pairs”

- add SEDs to pairs, use symmetry (invariant maxima)
- obvious relation to VSEPR model
Comparison to ELF

- Electron structure is mostly determined by antisymmetry of electronic wave function – and by attraction from the nuclei.
- Antisymmetry is an inherently many-body effect – difficult to visualize
- ELF measures the *excess kinetic energy* due to antisymmetry
- SEDs contain the many-body information because the assignment to a SED *depends on all electrons*
- ELF and SED show similar spatial topology (?)
double bond: ethene

- splitting of $\alpha$ and $\beta$ maximum already at uncorrelated level
- “banana” type bonds with distorted tetrahedral arrangement
double bond: ethene

- double bond “electron pairs” after adding upper and lower SEDs (of all invariant maxima)
fluorine dimer $F_2$
strong left-right correlation (55 % LR vs. 52% in H₂O₂, N₂H₄, C₂H₆)
nitrogen monoxide NO

- regular tetrahedral, triangular or linear arrangement for $6\alpha$ and $5\beta$ electrons
\( \alpha, \beta \) systems avoid building electron pairs due to Coulomb interaction
Benzene
Conclusions

- partitioning of density based on physically meaningful max of $|\psi|^2$
- like ELF role of antisymmetry in electron structure is visualized
- structure of SEDs easily understood in terms of Fermi holes and Coulomb interaction
- electrons of *unlike* spin *separate* rather than unite if possible (ethene, benzene, etc.)
- energy partitioning based on SEDs is intuitive and simple: SED pair energies
- many-body real space analysis independent of models (MO, VB)