Potential Energy Surfaces with Quantum Monte Carlo

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Outline

• Motivation
• Potential Energy Surfaces
• Preliminary Vibrational Calculations
• Conclusions
Motivation

• “DMC is the most accurate electronic structure method”
• “No forces, no geometries, no vibrational frequencies”
Accuracy of FN-DMC

• Almost as good as CCSD(T)/cc-pVTZ for isogyric reactions (S. Manten, and A. Luchow, J. Chem. Phys. 115 (2001) 5362)


Recent Developments

• Accurate Wave Function Optimization

Alleviation of the Fermion-Sign Problem by Optimization of Many-Body Wave Functions

C. J. Umrigar,¹ Julien Toulouse,¹ Claudia Filippi,² S. Sorella,³ and R. G. Hennig⁴

Full optimization of Jastrow–Slater wave functions with application to the first-row atoms and homonuclear diatomic molecules

Julien Toulouse¹,²,ᵃ and C. J. Umrigar³,ᵇ
Accuracy of FN-DMC


Accuracy

- “Chemical accuracy” $\approx 1$ kcal/mol $\approx 350$ cm$^{-1}$
- “Spectroscopic accuracy” $< 1$ cm$^{-1}$

- Binding energies, atomization energies, etc are dependent on well depth
- Vibrational frequencies dependent on curvature about minimal geometry.
Recent Developments

• Forces

Methods for calculating forces within quantum Monte Carlo simulations

A Badinski¹, P D Haynes¹,², J R Trail¹,³ and R J Needs¹

Algorithmic differentiation and the calculation of forces by quantum Monte Carlo

Sandro Sorella¹,²,a) and Luca Capriotti³,b)
Recent Developments

• Geometry Optimization

Structural Optimization by Quantum Monte Carlo: Investigating the Low-Lying Excited States of Ethylene
Matteo Barborini, Sandro Sorella, and Leonardo Guidoni

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Potential Energy Surfaces

H + H₂ reaction barrier: A fixed-node quantum Monte Carlo study

R. N. Barnett, b) P. J. Reynolds, and W. A. Lester, Jr. b)
Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Quantum chemistry by random walk: Application to the potential energy surface for F + H₂ → HF + H

David R. Garmer and James B. Anderson
Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

(Received 18 February 1987; accepted 8 April 1987)

The potential energy surface for the reaction F + H₂ → HF + H has been the subject of repeated theoretical studies for which the predicted barrier height has had its ups and downs. ¹ We report here a study which, in yielding for an F–H–H configuration in the general region of the saddle point an energy of 3.2 ± 1.3 kcal/mol relative to F + H₂, demonstrates a way in which accurate potential energies can be obtained for the system.

We have applied the random walk method of solving the Schrödinger equation to determine energies of the following
Two Aspects of Quantum Monte Carlo: Determination of Accurate Wavefunctions and Determination of Potential Energy Surfaces of Molecules

C. J. UMRGBAR


Spectroscopic data for the LiH molecule from pseudopotential quantum Monte Carlo calculations

J. R. Trail and R. J. Needs
Reasonable agreement already with RHF-Jastrow Trial Wave Functions
Potential Energy Surfaces

• Barrier height more stringent than binding energy
• Anharmonic vibrational frequency more stringent than harmonic frequency.
• Sometimes cancellation of errors can allow one to get away with overly simple wave functions.
• What is needed to obtain reasonable vibrational frequencies?
Practicalities

• Ab initio SCF convergence usually $10^{-6}$ Hartrees and often $10^{-8}$ Hartrees for frequency calculations.
• QMC optimization thresholds usually $10^{-3} - 10^{-4}$ Hartrees.
• Can QMC benefit from correlations that makes the convergence threshold less important?
When things go wrong...
DMC Calculation Details

• RHF/ROHF using the Burkatzki-Filippi-Dolg triple Zeta ECP basis sets (J. Chem. Phys. 126, 234105)

• Linear optimization method of Toulouse and Umrigar (J. Chem. Phys. 99, 2865) (with 1% variance and 99% energy).
  – Initially, the energy was converged to 0.5 mHartrees but it was found that for weaker bonds 0.1 mHartree convergence criteria was necessary.
Calculation Details continued

• Single electron move version of Umrigar-Nightingale-Runge DMC algorithm (J. Chem. Phys. 99, 2865(1993)) with 800 walkers, time-step=0.02Hartree$^{-1}$, and 1,000,000 steps.

• Frequencies calculated from 16 discrete energy points around the minimum geometry using the Fourier-Grid Hamiltonian method (J. Chem. Phys. 91, 3571 (1989))
Ideal Frequency Error Bar Dependency on Energy Error Bar

Frequency Error Bar as a Fraction of the Vibrational Frequency

Energy Error Bar (Hartrees)

- N2
- F2
- He2 +
Vibrational Frequency Error Bar

• Non-zero vibrational frequency error bar even if DMC energy bar could be converged to zero.
  – Approx. ±10cm\(^{-1}\) in the examined cases
• Systematic error due to choice of trial wave function.
• Partially due to the choice of optimization criteria.
• Possible metric for evaluating the quality of a wave function?
N₂ Anharmonic Vibrational Frequency and Equilibrium Bond Length

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>DMC (jast)</th>
<th>VMC (jast + orb)</th>
<th>DMC (Jast+orb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν (cm⁻¹)</td>
<td>2330</td>
<td>2389</td>
<td>2308</td>
<td>2442(10)</td>
<td>2404(13)</td>
<td>2364(10)</td>
</tr>
<tr>
<td>Req (Å)</td>
<td>1.098</td>
<td>1.096</td>
<td>1.102</td>
<td>1.091(1)</td>
<td>1.090(1)</td>
<td>1.092(1)</td>
</tr>
</tbody>
</table>

The curvature obtained from DMC using simple Hartree-Fock Jastrow wave functions is worse than CCSD and requires optimisation of the orbitals to perform a little bit better than CCSD. (but at 150,000x cost of CCSD(T))

The geometry on the other hand is in reasonable agreement (<1% error) for all the methods.
Importance of time-step?
DMC Time-Step bias ($F_2$ molecule)

Interatomic Distance (Angstroms)

Energy (Hartree)

- $\tau = 0.02$
- $\tau = 0.01$
- $\tau = 0.0$ (linear extrapolation)
F$_2$ Anharmonic Vibrational Frequencies

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>DMC (jast)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (cm$^{-1}$)</td>
<td>894</td>
<td>994</td>
<td>895</td>
<td>1000(10)</td>
</tr>
</tbody>
</table>

Again one sees that DMC with a simple Hartree-Fock trial wave function is no better than CCSD.

There is no substantial bias due to the selected time step.
Sensitivity to basis set?
As expected DMC is not very sensitive to basis set effects.

<table>
<thead>
<tr>
<th></th>
<th>VMC (jast)</th>
<th>DMC (jast)</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal basis</td>
<td>428(13)</td>
<td>424(10)</td>
</tr>
<tr>
<td>diffuse basis</td>
<td>420(13)</td>
<td>427(10)</td>
</tr>
</tbody>
</table>
Conclusions

- The curvature of a QMC potential energy surface is relatively insensitive to time-step and basis sets.
- Weaker bonds require tighter convergence threshold than stronger bonds.
- Optimization criteria that are sufficient for thermochemical properties may not be sufficient for spectroscopic properties.
- Single determinant trial wave functions are not sufficiently accurate for determining vibrational frequencies.
Acknowledgements

• David M. Benoit
• DFG/SFB 569
• Universität Ulm

• Julien Toulouse and Cyrus Umrigar