forces and response functions in QMC

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1) NEB calculation of minimum energy pathways

   Collaborators: Sebastiano Saccani (Trieste), Claudia Filippi (Twente)
   Special thanks to: Stefano Baroni

2) AFQMC calculation of imaginary-time correlations

   Collaborators: Ettore Vitali, Mario Motta, Davide Galli (Milano)
Nudged Elastic Band

A local search method to find the minimum-energy path:

\[
F_\perp = (F \cdot n_\perp) \ n_\perp \\
F_\parallel = (F_s \cdot n_\parallel) \ n_\parallel
\]

After convergence, find transition state by climbing image:

\[
F_\perp = (F \cdot n_\perp) \ n_\perp \\
F_\parallel = - (F \cdot n_\parallel) \ n_\parallel
\]

Nudged Elastic Band

- Extensively used for catalysis problems
- Mostly within DFT (especially GGA)

- Feasible/accurate with QMC?

Test on reaction paths of small molecules

- Reasonably automatic
- Reasonably accurate (VMC, fixed-node DMC)
- Presumably scalable
Reasonably automatic: 1) finite-variance estimators of forces

\[ I = \int_0^c p(x) f(x) \, dx \]

Monte Carlo evaluation requires that \( \int_0^c p(x) f^2(x) \, dx \) be finite

If \( p \propto x^2, \quad f \propto 1/x \), MC evaluation of \( I \) is OK (e.g. energy); but \( \nabla I = \int_0^c p(x) [\nabla f(x) + \cdots ] \, dx \) and \( \nabla f \propto 1/x^2, \quad (\nabla f)^2 \propto 1/x^4 \)

MC evaluation of this estimator of \( \nabla I \) is not possible (e.g. forces).

- A finite-variance estimator (S. Sorella and C. Attaccalite, PRL, 2008):

\[ I = \int_0^c \tilde{p}(x) \left[ p(x)/\tilde{p}(x) f(x) \right] \, dx \quad \text{with} \quad \lim_{x \to 0} \tilde{p}(x) = \text{const} \]

\( \tilde{p} \sim \text{const.,} \quad \tilde{f} = p/\tilde{p} f \propto x \), MC evaluation of both \( I \) and \( \nabla I \) is OK

- finite-variance estimator available in both VMC and DMC
Reasonably automatic: 2) low-enough variance in DMC

\[ \prod_{i=1}^{k} G_{dd}(R_i, R_{i-1}) e^{-\tau[E_L(R_i) + E_L(R_{i-1})]/2} \]

The drift-diffusion term \( G_{dd} \) gives high statistical noise in the calculation of forces.

A low-variance estimator of the DMC forces: replace

\[ \nabla \prod_{i=1}^{k} G_{dd}(R_i, R_{i-1}) \rightarrow \nabla \Psi_T^2(R_k) \]

Approximate but accurate (exact if \( \Psi_T \) is exact)

C.Filippi and C.J.Umrigar, PRB 61, R16291 (2000)
Reasonably automatic: 3) forces as partial derivatives

\[
\frac{dE}{d\lambda} = \frac{\partial E}{\partial \lambda} + \sum_i \frac{\partial E}{\partial c_i} \frac{\partial c_i}{\partial \lambda}
\]

\(c_i\) variational parameters in \(\Psi_T\)

Optimize all variational parameters \(\rightarrow \frac{dE}{d\lambda} = \frac{\partial E}{\partial \lambda}\)

In the present study of reactions, optimization* and calculation of forces take approximately the same CPU time.

Test of force as partial derivative in VMC: Carbon dimer

HF orbitals, optimized Jastrow

optimized orbitals, optimized Jastrow
Test of approximation to DMC forces: Carbon dimer

DMC forces with replacement

\[ \nabla \prod_{i=1}^{k} G_{dd}(R_i, R_{i-1}) \rightarrow \nabla \Psi_T^2(R_k) \]
Reasonably accurate:

DMC atomization energies for the G2 data set


Fixed-node DMC with multideterminant wavefunction approaches chemical accuracy

- For scalability we will use 2z one-determinant SJ wavefunction
- Expected accuracy ~a few kcal/mol: is that enough?
Barrier heights calculated by LSDA, GGA and Meta DFT methods:

<table>
<thead>
<tr>
<th>Reactions</th>
<th>VSXC</th>
<th>BB95</th>
<th>mPWPW91</th>
<th>TFSS</th>
<th>BLYP</th>
<th>LSDA</th>
<th>BP86</th>
<th>TPSSK CIS</th>
<th>PBE</th>
<th>mPWLYP</th>
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<tbody>
<tr>
<td><strong>Heavy atom transfer reactions</strong></td>
<td></td>
<td></td>
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<tr>
<td>H + N₂O → OH + N₂</td>
<td>V_f</td>
<td>16.02</td>
<td>11.65</td>
<td>10.77</td>
<td>8.41</td>
<td>8.94</td>
<td>3.16</td>
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<tr>
<td></td>
<td>V_r</td>
<td>71.18</td>
<td>55.36</td>
<td>55.34</td>
<td>60.77</td>
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<td>52.20</td>
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<tr>
<td>H + FH → HF + H</td>
<td>V_f</td>
<td>36.75</td>
<td>29.71</td>
<td>28.57</td>
<td>27.53</td>
<td>26.77</td>
<td>19.40</td>
<td>26.00</td>
<td>29.15</td>
<td>27.98</td>
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<td>19.40</td>
<td>26.00</td>
<td>29.15</td>
<td>27.98</td>
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<tr>
<td>H + CIH → HCl + H</td>
<td>V_f</td>
<td>17.40</td>
<td>12.25</td>
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<td>8.51</td>
<td>10.57</td>
<td>3.02</td>
<td>8.41</td>
<td>11.59</td>
<td>10.45</td>
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<td></td>
<td>V_r</td>
<td>17.40</td>
<td>12.25</td>
<td>10.92</td>
<td>8.51</td>
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<td>8.41</td>
<td>11.59</td>
<td>10.45</td>
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<tr>
<td></td>
<td>V_r</td>
<td>21.79</td>
<td>19.78</td>
<td>18.94</td>
<td>17.35</td>
<td>16.33</td>
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<td>16.25</td>
<td>18.98</td>
<td>18.74</td>
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<td></td>
<td>V_r</td>
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<td>80.78</td>
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<tr>
<td>CH₃ + FCl → CH₃F + Cl</td>
<td>V_f</td>
<td>-6.99</td>
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<td>36.87</td>
<td>43.03</td>
<td>43.36</td>
<td>42.71</td>
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</tbody>
</table>

Mean error:  

-14.66  

-14.93
QMC calculation:

- Reactions studied [S. Saccani, C. Filippi and SM, JCP 138, 084109 (2013)]

  H transfer: \( H + OH \rightarrow H_2 + O \)
  Heavy atom transfer: \( H + N_2O \rightarrow OH + N_2 \)
  \( H + F_2 \rightarrow HF + F \)
  Nucleophilic substitution: \( F^- \cdots CH_3F \rightarrow FCH_3 \cdots F \)
  Association reaction: \( H + CO \rightarrow HCO \)

- Initial one-particle orbitals from GAMESS
- Pseudopotentials and optimized GTO VDZ basis from BFD*
- QMC energy and force calculations with CHAMP

* M. Burkatzki, C. Filippi and M. Dolg, JCP 126, 234105 (2007)
QMC results: Mean Unsigned Deviation from best estimates

<table>
<thead>
<tr>
<th></th>
<th>MUD</th>
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</thead>
<tbody>
<tr>
<td><strong>forward barrier:</strong></td>
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<tr>
<td>VMC</td>
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<tr>
<td>DMC</td>
<td>0.4</td>
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<td><strong>reverse barrier:</strong></td>
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<td>VMC</td>
<td>8.1</td>
</tr>
<tr>
<td>DMC</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Significant improvement over GGA DFT

...but there exist better functionals
Y. Zhao, N. Gonzalez-Garcia, and D. G. Truhlar, JPC A 109, 2012 (2005)

Barrier heights calculated by hybrid methods:

<table>
<thead>
<tr>
<th>Reactions</th>
<th>MPW1K</th>
<th>B97-2</th>
<th>BHandHLYP</th>
<th>mPW1PW91</th>
<th>B98</th>
<th>B97-1</th>
<th>PBE1PBE</th>
<th>X3LYP</th>
<th>B3LYP</th>
<th>O3LYP</th>
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<tr>
<td><strong>Heavy-atom transfer reactions</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$H + N_2O \rightarrow OH + N_2$</td>
<td>$V_t^#$ 17.16</td>
<td>18.69</td>
<td>16.08</td>
<td>14.65</td>
<td>15.43</td>
<td>16.37</td>
<td>14.44</td>
<td>11.74</td>
<td>11.81</td>
<td>12.65</td>
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<tr>
<td></td>
<td>$V_r^#$ 81.63</td>
<td>72.36</td>
<td>91.27</td>
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<td>74.10</td>
<td>72.62</td>
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<td>66.93</td>
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<tr>
<td>$H + FH \rightarrow HF + H$</td>
<td>$V_t^#$ 39.72</td>
<td>41.01</td>
<td>39.28</td>
<td>35.17</td>
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<td>41.01</td>
<td>39.28</td>
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<td>34.71</td>
<td>31.79</td>
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<td>32.45</td>
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<tr>
<td>$H + FCH_3 \rightarrow HF + CH_3$</td>
<td>$V_t^#$ 30.90</td>
<td>29.76</td>
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<td>26.07</td>
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<td>$V_r^#$ 56.53</td>
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<tr>
<td>$H + F_2 \rightarrow HF + F$</td>
<td>$V_t^#$ -2.21</td>
<td>-0.57</td>
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<td>-2.72</td>
<td>-2.13</td>
<td>-4.32</td>
<td>-7.32</td>
<td>-7.32</td>
<td>-6.25</td>
</tr>
<tr>
<td></td>
<td>$V_r^#$ 110.28</td>
<td>101.10</td>
<td>112.76</td>
<td>99.61</td>
<td>99.50</td>
<td>97.99</td>
<td>98.41</td>
<td>95.79</td>
<td>95.57</td>
<td>96.40</td>
</tr>
<tr>
<td>$CH_3 + FCl \rightarrow CH_3F + Cl$</td>
<td>$V_t^#$ 5.83</td>
<td>-0.07</td>
<td>5.71</td>
<td>1.35</td>
<td>-1.35</td>
<td>-2.06</td>
<td>0.84</td>
<td>-1.66</td>
<td>-1.55</td>
<td>0.38</td>
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<tr>
<td></td>
<td>$V_r^#$ 62.74</td>
<td>54.92</td>
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<td>54.56</td>
<td>52.24</td>
<td>52.00</td>
<td>53.03</td>
</tr>
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</table>

Mean unsigned error: 1.58 11.51
QMC results: geometries for the reaction $H + F_2 \rightarrow HF + F$

Root mean square deviation of all interatomic distances from best estimate in Å

<table>
<thead>
<tr>
<th></th>
<th>VMC</th>
<th>DMC</th>
<th>BLYP</th>
<th>PBE</th>
<th>B3LYP</th>
<th>PBE0</th>
<th>M06</th>
</tr>
</thead>
<tbody>
<tr>
<td>React</td>
<td>0.008</td>
<td>0.007</td>
<td>0.037</td>
<td>0.018</td>
<td>0.002</td>
<td>0.019</td>
<td>0.020</td>
</tr>
<tr>
<td>Prod</td>
<td>0.002</td>
<td>0.008</td>
<td>0.029</td>
<td>0.017</td>
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<td>0.001</td>
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<tr>
<td>TS</td>
<td>0.028</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.216</td>
</tr>
</tbody>
</table>

- Within DFT only the M06 functional* does find a barrier
- VMC improves the geometry of the transition state significantly
- Further geometrical improvement with DMC is marginal

*constructed to fit (also) accurate barrier heights for the NHTBH38/04 database
QMC vs DFT geometries

- QMC marginally better for reactants and products
- QMC significantly better for transition states
QMC vs DFT energies

- **MUD**
  - VMC: 4.5
  - DMC: 0.4
  - B3LYP: 3.1
  - PBE0: 2.0
  - M06: 0.7

- **VMC**
  - VMC: 8.1
  - DMC: 3.0
  - B3LYP: 5.2
  - PBE0: 5.9
  - M06: 3.5

- **DMC ~ M06**
QMC vs DFT energies

- VMC: 4.5
- DMC: 0.4
- B3LYP: 3.1
- PBE0: 2.0
- M06: 0.7

- VMC: 8.1
- DMC: 3.0 (1.8)
- B3LYP: 5.2
- PBE0: 5.9
- M06: 3.5

- DMC ~ M06
- DMC improves with a small CAS (~ten determinants)
- Presumably scalable (algorithmic differentiation, large optimizations):

S. Sorella and L. Capriotti, JCP 133, 234111 (2010)

extra factor in CPU time to compute forces independent of the number of atoms


optimization of ~10,000 variational parameters
Summary part 1

- NEB calculation with full QMC forces reasonably automatic and stable

- Based on a few reactions:
  - VMC geometry improves DFT results
  - DMC energy at least as good as M06 with simple SJ wavefunctions

- At this level of accuracy, presumably scalable to large systems

- Improvements possible in specific situations using better wavefunctions
Response functions (work in progress)

\[ F_{AB}(\tau) = \langle \hat{A}(\tau) \hat{B}(0) \rangle \quad \text{QMC simulation} \]

\[ F_{AB}(\tau) = \int d\omega e^{-\omega \tau} S_{AB}(\omega) \quad \text{Inverse Laplace transform} \]

An example for a Bose system:

\[ C(\tau) = \langle \mathbf{d}(\tau) \cdot \mathbf{d}(0) \rangle \rightarrow \text{rotational spectrum with J=1} \]

Effective rotational constant of CO2 in 4He clusters vs cluster size. Circles, experiment; crosses, simulation.
• In particular cases, for small enough systems this works well also for Fermions. An example: the dynamic structure factor of 2D 3He at freezing density (N=26)

![Histograms with errorbars: simulation; points: experiment](image)

but in general Fermi systems require approximations to avoid the sign problem.
fixed node approximation not good for imaginary-time correlations

Static susceptibility

\[ \chi(q) = \int F(q, \tau) d\tau, \quad F(q, \tau) = \langle \rho_{-q}(\tau) \rho_q(0) \rangle \]

2D jellium, rs=5

Non interacting

\[ \Phi \text{ From fixed-node } F(q, \tau) \]

\[ \bullet \text{ “exact”} \]
a different nodal constraint: phaseless AFQMC  
[S.Zhang and H.Krakauer, PRL 90, 136401 (2003)]

- Hubbard-Stratonovich transformation maps many-body propagator into one-body propagator with fluctuating auxiliary fields
- Imaginary time evolution simulated by a random walk in the space of Slater determinants
- Importance sampling enhances overlap between random walker \( |\phi\rangle \) and trial function \( |\Psi_T\rangle \)
- Phaseless approximation: branching weight approximated by
  \[
  \exp(-\tau \text{Re}[E_L(\phi)])
  \]
  - Very good results for ground-state energy even with poor trial functions

How good for imaginary-time correlation functions?
Summary part 2:

- Phaseless AFQMC looks good for imaginary-time correlations
- Tests still very preliminary