Auxiliary-field QMC for quantum chemistry: recent progress and open issues

Henry Krakauer
College of William & Mary, USA

Outline

• Introduction
  ➢ Orbital-based QMC --- identical $H$ as in quantum chemistry
  ➢ Random walks in Slater determinant space
    ▪ Any 1-electron basis [planewaves, gaussian type orbitals (GTO), ..]
    ▪ Overall phase constraint on SD: a new way to deal with the sign problem
    ▪ Code naturally builds on top of standard DFT, scales as $N^3-N^4$

• Applications: molecules, bond breaking, solids, ....

• Recent algorithmic developments:
  ➢ Resolution of the identity (RI) --> larger basis sets with GTO
Collaborators:
- Wirawan Purwanto
- Shiwei Zhang
- Eric Walter

Support:
- DOE (ThChem, petascale endstation), NSF, ONR

Some references:
- Zhang & Krakauer, PRL ’03
- Al-Saidi et. al., PRB ’06; JCP, ’06; JCP ’07
- Kwee et. al., PRL ‘08
- Purwanto et. al., JCP ’08; JCP ’09; PRB ’09
- Chang & Zhang, PRL ’10
Quantum chemistry

HF $N$-electron reference state:
Slater determinant of $N$ occupied orbitals.

$$\Phi_0 = A \left[ \tilde{\phi}_1(x_1) \tilde{\phi}_2(x_2) \cdots \tilde{\phi}_N(x_N) \right]$$

The full many-body wave function is spanned by all possible Slater determinants, which can be formed from the $M$ occupied and virtual HF orbitals, where $M$ is the size of the 1-particle basis.
QM chem - e.g. single reference, orthogonal det’s

\[ \Psi = \Phi_0 + \sum_{ia} c_i^a \Phi_i^a + \sum_{ijab} c_{ij}^{ab} \Phi_{ij}^{ab} + \cdots \]

orthogonal determinants
Overview - how does auxiliary-field QMC work?

Random walks of *non-orthogonal* Slater determinants

**quantum chemistry**

AF QMC

A single random walker in AFQMC is a Slater determinant: 

\[ \Phi_0 = A \left[ \phi_1(x_1)\phi_2(x_2)\cdots\phi_N(x_N) \right] \]

- AFQMC is naturally *multi*-reference: *not* the HF orbitals
- any orbital that can be expressed in the basis:

\[ \phi_j(x) = \sum_{i=1}^{M} \alpha_{ji} G_i(x) \]

DMC: \((x_1, x_2, \cdots, x_N)\)
AF QMC: basic formalism

To obtain ground state, use projection in imaginary-time:

$$|\Psi^{(n+1)}\rangle = e^{-\tau \hat{H}} |\Psi^{(n)}\rangle \xrightarrow{n \to \infty} |\Psi_0\rangle$$

$\tau$: cnst, small $|\Psi^{(0)}\rangle$: arbitrary initial state

Electronic Hamiltonian: (2$\text{nd}$ quantization, given any 1-particle basis)

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i,j}^{M} T_{ij} c_i^\dagger c_j + \sum_{i,j,k,l}^{M} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l$$

$M$ basis functions

(textbooks: $M = \infty$)

QM chemistry: $M \propto N$

Recall

$$H = H_1 + H_2 = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{\text{ext}}(r_i) + \sum_{i < j}^{N} V_{\text{int}}(|r_i - r_j|)$$
AF QMC: basic formalism

To obtain **ground state**, use projection in imaginary-time:

\[
|\Psi^{(n+1)}\rangle = e^{-\tau \hat{H}} |\Psi^{(n)}\rangle \xrightarrow{n\to\infty} |\Psi_0\rangle
\]

\(\tau\): cnst, small  \(|\Psi^{(0)}\rangle\): arbitrary initial state

**Electronic Hamiltonian:** (2\(^{nd}\) quantization, given any 1-particle basis)

\[
\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i,j}^M T_{ij} c_i^\dagger c_j + \sum_{i,j,k,l}^M V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l
\]

\(M\): basis size

\[
\hat{H}_2 \rightarrow -\sum \hat{v}^2 \quad \text{with} \quad \hat{v} = 1\text{-body}
\]

Hubbard-Strotonivich transf.

\[
e^{-\tau \hat{H}} \rightarrow e^{-\tau \hat{H}_1} \int e^{-\frac{\sigma^2}{2}} e^{\sigma \sqrt{\tau} \hat{v}} d\sigma
\]

interacting system \(\rightarrow\) \(\sum\) **(non-interacting system in auxiliary fields)**

DFT: \(\hat{H}_2 \rightarrow \sum_i f_c(n_i) \hat{n}_i\)

HF: \(c_i^\dagger c_j^\dagger c_k c_l \rightarrow \langle c_i^\dagger c_i \rangle c_j^\dagger c_k + \cdots\)
Auxiliary-field methods: some background

• Applied in models in condensed matter, nuclear physics, (lattice QCD), ....

  *Scalapino, Sugar, Hirsch, White et al.; Koonin; Sorella,* ....

  *interacting → \( \sum \) (non-interacting in fields)*

  basic idea: Monte Carlo to do sum (path integral)

• Potential for real materials well recognized

  *Fahy & Hamann; Silvestreli, Baroni & Car; Wilson & Gyorffy; Baer et al.;* ....

• However,
  
  ➢ sign problem for “simple” interactions (Hubbard)
  ➢ phase problem for realistic interaction

• Our reformulation gives a way to control the problem by an approximation to have a \(N^3\) or \(N^4\) scaling algorithm
AF QMC - schematic implementation

Random walks in Slater determinant space:

Recall $|\Psi^{(n+1)}\rangle = e^{-\tau \hat{H}} |\Psi^{(n)}\rangle \xrightarrow[n \to \infty]{} |\Psi_0\rangle$

H-S transformation

$$\int e^{-\sigma^2/2} e^{\hat{\psi}(\sigma)} d\sigma$$

1-body: $\sum_{i,j} v_{ij}(\sigma) c_i^\dagger c_j$

Schematically:

$$|\Psi^{(0)}\rangle \xrightarrow{e^{-\tau \hat{H}}} |\Psi^{(1)}\rangle \quad \ldots \quad \xrightarrow{} |\Psi_0\rangle$$

Sample $\sigma$ from $e^{-\frac{\sigma^2}{2}}$;

Apply 1-body propag.

$$|\phi^{(0)}\rangle \xrightarrow{\text{1-body propag.}} |\phi^{(1)}(\sigma)\rangle \quad \rightarrow \quad |\phi\rangle$$

$$\vdots \quad \vdots \quad \vdots$$

$$|\Psi_0\rangle \doteq \sum_{\phi} |\phi\rangle$$

Slater det.
AF QMC - schematic implementation

Random walks in Slater determinant space:

\[ |\Psi^{(n+1)}\rangle = e^{-\tau \hat{H}} |\Psi^{(n)}\rangle \xrightarrow{n \to \infty} |\Psi_0\rangle \]

H-S transformation

\[ \int e^{-\sigma^2/2} e^{\hat{v}(\sigma)} d\sigma \]

1-body: \[ \sum_{i,j} v_{ij}(\sigma) c_i^\dagger c_j \]

Exact, but phase problem:

\[ \hat{v}(\sigma) \text{ is complex} \]

\[ \sum_{MC} |\phi\rangle \to 0 \]
AF QMC - schematic implementation

Random walks in Slater determinant space:

Recall $|\Psi^{(n+1)}\rangle = e^{-\tau \hat{H}} |\Psi^{(n)}\rangle \xrightarrow{n \to \infty} |\Psi_{0}\rangle$

H-S transformation

$$\int e^{-\frac{\sigma^2}{2}} e^{\hat{V}(\sigma)} d\sigma$$

1-body: $\sum_{i,j} v_{ij}(\sigma) c_i^\dagger c_j$

Exact, but phase problem:

Exponential noise

Problem! $\sum_{MC} |\phi\rangle \to 0$
The sign problem

Sign/phase problem is due to --

"superexchange":

\[ \Phi_0 = A[\phi_1(x_1)\phi_2(x_2)\cdots\phi_N(x_N)] \]

Reasonable to expect that problem is reduced, since tendency for global collapse to bosonic state is removed

To eliminate sign problem:

Use \( \langle \Psi_T|\Psi \rangle = 0 \) to determine if "superexchange" has occurred
The sign problem and the constraint

- The constraint is exact when \( \text{sgn}[\langle \Psi_T | \Psi \rangle] = \text{sgn}[\langle \Psi_{GS} | \Psi \rangle] \)
  - similar to fixed-node in DMC, but the global sign of a \( \Psi \) (fermionic) is less demanding than that of \( R \) (bosonic)
- “Mixed estimate” of total energy not an upper bound
- The method is exact if \( \langle \Psi_T | \Psi \rangle \) is always non-negative
Controlling the phase problem

Sketch of approximate solution:

- Modify propagator by "gauge transformation":
  \[ \text{phase} \rightarrow \text{degeneracy} \quad \text{(use trial wf)} \]

- Project to one overall phase:
  break "rotational invariance"

- Subtle, but key, difference from: real \( \left< \Psi_T | \phi \right> \)
  
  \( (\text{Fahy & Hamann; Zhang, Carlson, Gubernatis}) \)

Before:

After:
Controlling the phase problem

Quantify the approximation?

**total energy \( E(\tau) \) --- bulk Si, 2-atom prim cell**

Error in total \( E < 0.3 \text{mH/atom} \)

free-proj: our ‘FCI’ (8 electrons, Nbasis~570)
Test application: molecular binding energies

- O$_3$, H$_2$O$_2$, C$_2$, F$_2$, Be$_2$, ...
- Si$_2$, P$_2$, S$_2$, Cl$_2$
- As$_2$, Br$_2$, Sb$_2$
- TiO, MnO

3 types of calc’s:
- PW + psp:
- Gaussian/AE:
- Gaussian/sc-ECP:

N$_{val}$ up to ~ 60

• All with single mean-field determinant as trial wf
• “automated” post-HF or post-DFT
• HF or LDA trial wf: same result
**Constraint independent of trial wf details**

**MnO solid in antiferromagnetic II phase:**

<table>
<thead>
<tr>
<th></th>
<th>(E_{\text{var}})</th>
<th>(E_{\text{QMC/trial \text{wf}}})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HF</strong></td>
<td>-118.2655</td>
<td>-119.1401(12)</td>
</tr>
<tr>
<td><strong>GGA</strong></td>
<td>-118.1929</td>
<td>-119.1387(10)</td>
</tr>
<tr>
<td></td>
<td>-119.0614 (E\text{GGA})</td>
<td></td>
</tr>
</tbody>
</table>

Energy in Hartree/unit cell

4-atom cell,

\(V=21.96 \text{ A}^3\)

**QMC insensitive to details of the trial wave function**

**Spin restriction (R vs U type of trial wfs) does have effect:**

E.g., water molecule:

<table>
<thead>
<tr>
<th>Bond length</th>
<th>RHF</th>
<th>UHF</th>
<th>CCSD(T)</th>
<th>FCI</th>
<th>QMC/RHF</th>
<th>QMC/UHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-6G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.5R_e)</td>
<td>-75.440432</td>
<td>-75.502 069</td>
<td></td>
<td>-75.600 039</td>
<td>-75.5768(3)</td>
<td>-75.5965(6)</td>
</tr>
<tr>
<td>(2R_e)</td>
<td>-75.141 587</td>
<td>-75.464 541</td>
<td></td>
<td>-75.486 528</td>
<td>-75.3557(3)</td>
<td>-75.4880(3)</td>
</tr>
</tbody>
</table>

no upper bound!
**F₂ bond breaking**

Mimics increasing correlation effects:

- CCSD(T) methods have problems (excellent at equilibrium)
- UHF unbound
- QMC/UHF recovers despite incorrect trial wf --- uniformly accurate

(removes spin contamination)
F₂ bond breaking --- larger basis

- LDA and GGA/PBE
  - well-depths too deep

- B3LYP
  - well-depth excellent
  - “shoulder” too steep

- Compare with experiment spectroscopic cnsts:

<table>
<thead>
<tr>
<th></th>
<th>Expt⁹</th>
<th>AFQMC</th>
<th>RCCSD(T)</th>
<th>UCCSD(T)</th>
<th>LSDA</th>
<th>GGA/PBE</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis: cc-pVQZ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_e) (Å)</td>
<td>1.4131(8)</td>
<td>1.411(2)</td>
<td>1.4108</td>
<td>1.3946</td>
<td>1.3856</td>
<td>1.4136</td>
<td>1.3944</td>
</tr>
<tr>
<td>(\omega_0) (cm⁻¹)</td>
<td>916.64</td>
<td>912(11)</td>
<td>929</td>
<td>1036</td>
<td>1062</td>
<td>997</td>
<td>1109</td>
</tr>
<tr>
<td>(D_e) (eV)ᵇ</td>
<td>1.693(5)</td>
<td>1.77(1)</td>
<td>–</td>
<td>1.567</td>
<td>3.473</td>
<td>2.321</td>
<td>1.634</td>
</tr>
<tr>
<td>(D_e) (eV)ᶜ</td>
<td>1.693(5)</td>
<td>1.70(1)</td>
<td>1.594</td>
<td>1.569</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Purwanto et. al., JCP, ‘08
Excited states

• Excited states are more difficult
• For QMC, this is manifested as a more severe sign/phase problem, especially for excited states with the same symmetry as the GS
• A first attempt, using the same approach as in GS
Excited states

Benchmark  (FCI: Abrams & Sherrill, JCP ’04)

Truncated CASSCF(8,16) trial wf ~30-50 det’s
Excited states

TZ and QZ basis:

TABLE IV. AFQMC/CASSCF calculated $C_2$ ground state spectroscopic constants compared to experiment. Conventions are as in Table II. Calculations used the cc-pVQZ basis set (except CMRCI which used the cc-pV5Z basis).

<table>
<thead>
<tr>
<th></th>
<th>CASSCF(8,16)</th>
<th>CCSD(T)</th>
<th>CMRCI(^a)</th>
<th>QMC</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Full</td>
<td>Truncated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_e$</td>
<td>1.2452</td>
<td>1.262[3]</td>
<td>1.2459</td>
<td>1.2467</td>
<td>1.244(1)</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>1868</td>
<td>1759[29]</td>
<td>1852</td>
<td>1853</td>
<td>1850(21)</td>
</tr>
</tbody>
</table>

\(^a\)Values from analytical fitting in Ref. 44.

Basis: cc-pVTZ

Truncated CASSCF(8,16) trial wf ~30-50 det’s
Larger basis size with GTOs

- Computational scaling of phaseless AF QMC

<table>
<thead>
<tr>
<th>basis</th>
<th>start-up</th>
<th>propagating</th>
</tr>
</thead>
<tbody>
<tr>
<td>planewave/psp</td>
<td>$\sim 0$</td>
<td>$N^2 M \log(M)$</td>
</tr>
<tr>
<td>GTO</td>
<td>$M^6$ (brute force)</td>
<td>$M^3$ &amp; $M^4$ (energy calc)</td>
</tr>
</tbody>
</table>

- We’ve implemented a modified Cholesky to remove $M^6$

Table: Comparison of diagonalization vs. modified Cholesky method. $M$ is the basis size. Times are reported in seconds. Calculations were done on an AMD workstation with 8-core OpenMP parallelism.

<table>
<thead>
<tr>
<th>$M$</th>
<th>Time (diagonalization)</th>
<th>Time (mod-Cholesky)</th>
<th>$J_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>3608</td>
<td>11</td>
<td>592</td>
</tr>
<tr>
<td>155</td>
<td>33649</td>
<td>66</td>
<td>1044</td>
</tr>
<tr>
<td>180</td>
<td>67194</td>
<td>108</td>
<td>1247</td>
</tr>
<tr>
<td>216</td>
<td>---</td>
<td>112</td>
<td>1480</td>
</tr>
<tr>
<td>344</td>
<td>---</td>
<td>1066</td>
<td>2255</td>
</tr>
</tbody>
</table>
$M^6$ bottleneck? - AFQMC with GTO basis:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{\mu \nu} T_{\mu \nu} \tilde{c}_\mu \tilde{c}_\nu + \sum_{\alpha \beta \mu \nu} V_{\alpha \beta \mu \nu} \tilde{c}_\alpha \tilde{c}_\mu \tilde{c}_\beta \tilde{c}_\nu$$

Hubbard-Stratonivich transformation requires:

$$\hat{H}_2 = \sum_{\lambda} \hat{v}_\lambda^2 \quad \hat{v}_\lambda = 1\text{-body}$$

Brute force solution - diagonalize $M^2 \times M^2$ matrix:

$$V_{\alpha \beta \mu \nu} = V_{\{\alpha \beta\},\{\mu \nu\}}$$

*
Avoid bottleneck: resolution of identity (RI)

2-body Coulomb: \((\mu \nu | \lambda \sigma) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_\mu(\mathbf{r}_1) \chi_\nu(\mathbf{r}_1) r_{12}^{-1} \chi_\lambda(\mathbf{r}_2) \chi_\sigma(\mathbf{r}_2)\)

RI: \(r_{12}^{-1} = \sum_n \phi_n(\mathbf{r}_1) \phi_n(\mathbf{r}_2)\)

e.g., PW’s: \(\frac{1}{2\Omega} \sum_{Q \neq 0} \frac{4\pi}{Q^2} \hat{\rho}^\dagger(Q) \hat{\rho}(Q) \sim O(8M)\)

I) density fitting:

|\mu \nu) \approx |\widetilde{\mu} \nu) = \sum_P C_{\mu \nu}^P |P) \quad P \ll M^2

pre-defined

auxiliary basis

\((\mu \nu | \lambda \sigma) \approx \sum_{PQ} C_{\mu \nu}^P (P | Q) C_{\lambda \sigma}^Q\)

II) modified Cholesky*:

accuracy controlled by one \((\mu \nu | \lambda \alpha) \approx \sum_{j=1}^J L^{(j)}_{\mu \nu} L^{(j)}_{\lambda \alpha} \quad J \ll M^2\)

parameter - unbiased

Test: model H-storage problem

- Model system of Ca$^{1+}$/4H2
- Possible high-density H storage by dispersed alkaline-earth metals?

6-311+G**

Finite Basis set error?

Can now do with modified Cholesky
Discussion and open issues

- Approximate (global phase condition) --- how accurate?
  - method relatively new, but quite extensive tests in GS (~100 systems: atomization, IP, EA, Re, ....)
  - can recover from wrong constraining trial wf (eg F₂)
  - Further improvement:
    better constraining wf; back propagation; release; ....

- Favorable computational scaling \( \sim O(M^3-M^4) \)
  - reduce prefactor: (remove \( M^4 \)?)
    GTO tricks; better basis; resolution of the identity
    (modified Cholesky example); ..... 
  - natural hierarchy in auxiliary-fields, localization, ....
Summary

- **AF QMC**: random walks in mean-field space
  - Orbital-based, non-perturbative, many-body method
  - Approximate: (exact without constraint -- FCI-like)
    - QMC’s only source of error reduced --> making QMC more a “blackbox”, for more problems
    - encouraging accuracy and robustness

- Applications & benchmarks
  - comparable to CCSD(T) around equilibrium geometry
  - better for stronger correlations, e.g. bond-breaking in molecules

- Modified Cholesky for GTOs

- Various opportunities to import techniques from QC

- A new wf-based method which can directly use much of the existing machinery from DFT/HF:
  --- superposition of independent-particle calculations
Thank you!
Periodic Solids

Silicon structural phase transition (diamond --> β-tin):

- transition pressure is sensitive: small dE
- AFQMC
  - 54-atom supercells + finite-size correction
  - PW + psp
  - uses LDA trial wf
- Good agreement w/ experiment --- consistent w/ exact free-proj checks