Quantum Monte Carlo method for real materials — phase-free random walks in Slater-determinant space

Shiwei Zhang and Henry Krakauer

College of William and Mary

OUTLINE

INTRODUCTION TO QUANTUM MONTE CARLO METHODS

SLATER DETERMINANT RANDOM WALKS

- Formulation as a ground-state method

- Motivation

PHASE/SIGN PROBLEM

APPROXIMATE SOLUTION

APPLICATION TO SILICON

- Calculations on atom, dimer, and bulk (54 atom fcc supercell)

- Binding energy of Si_2 and cohesive energy of bulk in excellent agreement with experiment

SUMMARY AND OUTLOOK

Introduction: Quantum Monte Carlo Methods

Focus on ground-state $(T = 0\,\text{K})$

To project ground state $|\Psi_0\rangle$ of many-body Hamiltonian H,

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

τ: small positive cnst $|\Psi^{(0)}\rangle$: arbitrary

Difference in methods:

different ways of realizing above process stochastically

- Diffusion Monte Carlo (DMC)

- Auxiliary-field methods

Diffusion Monte Carlo (DMC)

Foulkes *et al.*, RMP **73**, 33 (2001); talks by Foulkes and Mitas.

Summary:

- Random walks in coordinate space $|R\rangle \equiv |\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N\rangle$
  ($\mathbf{r}_i$: electronic position)

- Has been applied to atoms, molecules, clusters, solids, etc

- A great deal of success — promising approach

- Outstanding issues:
  - Fermion sign problem (fixed-node approximation)
  - Efficiency: human (e.g., trial w.f. optimization) and machine
  - Accurate calculations of observables (e.g., forces) and
    correlation functions
  - Technical problems with non-local pseudo-potentials:
    locality approximation — overall quality of trial w.f.
    important (not just position of the node)

- Applications to strongly correlated systems not yet widespread

Auxiliary-field quantum Monte Carlo (AFQMC)

- More to follow

- Has been applied to correlated electron lattice models, nuclear
  shell models, etc

- Impurity solver for DMFT closely related

- Outstanding issues:
  - How to go beyond simple Hubbard (beyond U, V)?
  - Sign problem
  ...

Slater determinant random walks

For any given one-particle basis:

$$H = \underbrace{\sum_{i,j} T_{ij} c_i^\dagger c_j}_{\hat{H}_1} + \underbrace{\tfrac{1}{2} \sum_{i,j,k,l} V_{ijkl}\, c_i^\dagger c_j^\dagger c_k c_l}_{\text{one-body} \;\; -\sum_{\gamma=1}^{M} \hat{v}_\gamma^{\,2}}$$

Hubbard-Strotonivich transformation:

$$e^{-\tau H} = \int e^{-\frac{\sigma^2}{2}}\, B(\sigma)\, d\sigma$$

σ: auxiliary fields, M-dimensional vector

$$B(\sigma) \equiv \exp(-\tau \hat{H}_1/2) \exp(\sqrt{\tau}\sigma \cdot \hat{\mathbf{v}}) \exp(-\tau \hat{H}_1/2)$$

$$\hat{\mathbf{v}} \equiv \{\hat{v}_1, \hat{v}_2, \cdots, \hat{v}_M\}$$

Random walk in Slater determinant space:

$$|\Psi^{(0)}\rangle \xrightarrow{\;\; e^{-\tau H} \;\;} |\Psi^{(1)}\rangle \;\; \cdots \; \to |\Psi_0\rangle$$

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

$$|\phi^{(0)}\rangle \xrightarrow{\;\; B(\sigma) \;\times\; |\phi^{(0)}\rangle \;\;} |\phi^{(1)}\rangle \qquad \to |\phi\rangle$$

$$\vdots \qquad\qquad\qquad \vdots \qquad\qquad \vdots$$

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

Each walker $|\phi\rangle$ has anti-symmetry properly imposed.

Slater determinant random walks

Illustration of HS transformation — electronic systems:

$$H = K + V_{\text{e}-\text{I}} + V_{\text{e}-\text{e}} + V_{\text{I}-\text{I}}$$

In plane-wave one-particle basis $|k\rangle \equiv \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}_k \cdot \mathbf{r}}$:

$$V_{\text{e}-\text{I}} = \sum_{i \neq j} V_{\text{local}}(\mathbf{G}_i - \mathbf{G}_j) c_i^\dagger c_j + \sum_{i,j} V_{\text{NL}}(\mathbf{G}_i, \mathbf{G}_j) c_i^\dagger c_j$$

$$V_{\text{e}-\text{e}} = \frac{1}{2\Omega} \sum_{i,j,\mathbf{Q}\neq 0} \frac{4\pi}{|\mathbf{Q}|^2} c_{\mathbf{G}_i+\mathbf{Q}}^\dagger c_{\mathbf{G}_j-\mathbf{Q}}^\dagger c_{\mathbf{G}_j} c_{\mathbf{G}_i}$$

$$\to -\frac{1}{2\Omega} \sum_{\mathbf{Q}\neq 0} \frac{4\pi}{|\mathbf{Q}|^2} \rho^\dagger(\mathbf{Q}) \rho(\mathbf{Q}) \qquad \sum_i c_{\mathbf{G}_i+\mathbf{Q}}^\dagger c_{\mathbf{G}_i}$$

$$\to \sum_{\mathbf{Q}\neq 0} \left(\sqrt{\frac{4\pi}{|\mathbf{Q}|^2}} \right)^{\!2} \Big([\rho^\dagger(\mathbf{Q}) + \rho(\mathbf{Q})]^2 - [\rho^\dagger(\mathbf{Q}) - \rho(\mathbf{Q})]^2 \Big)$$

Slater determinant random walks

Why?

- We would have a QMC approach that shares exactly the same machinery as in mean-field (Hartree-Fock or DFT) calculations, using *any* one-particle basis
  - The one-particle problem would be solved exactly, with no statistical error
  - Correlation effects are obtained by building stochastic ensembles of independent-particle solutions

- Opportunities for better approximations to treat sign problem?

- Each walker is a full mean-field wave function. Could this allow more convenient calculations of observables and correlation functions?

Sign/phase problem

Sign problem (if $\hat{v}$ is real):

- If $\left(\sum |\phi\rangle\right)$ gives ground-state, so does $\left(\sum -|\phi\rangle\right)$.
  Random walk leads to a mixture of the two $\Rightarrow$ sign problem.
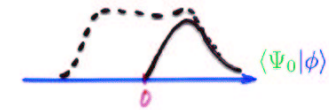
- Constrained path approximation: impose $\langle \Psi_T | \phi \rangle > 0$
  SZ, Carlson, Gubernatis, PRB **55**, 7464 (1997)

- For lattice models, this method has worked well — e.g., better energies than from configuration space fixed-node over a fairly wide range of interaction strengths.

Phase problem (if $\hat{v}$ is complex):

- Except for attractive interactions or special cases (Hubbard), $\hat{v}$ is complex: $\hat{v}_\gamma = i \sum_{ij} v_{ij} c_i^\dagger c_j$

- Simple generalization of the constrained path approximation does not work well:

Jellium, 2 electrons, r_s=10

Nbasis=19, τ=0.01, nwlk=5,000
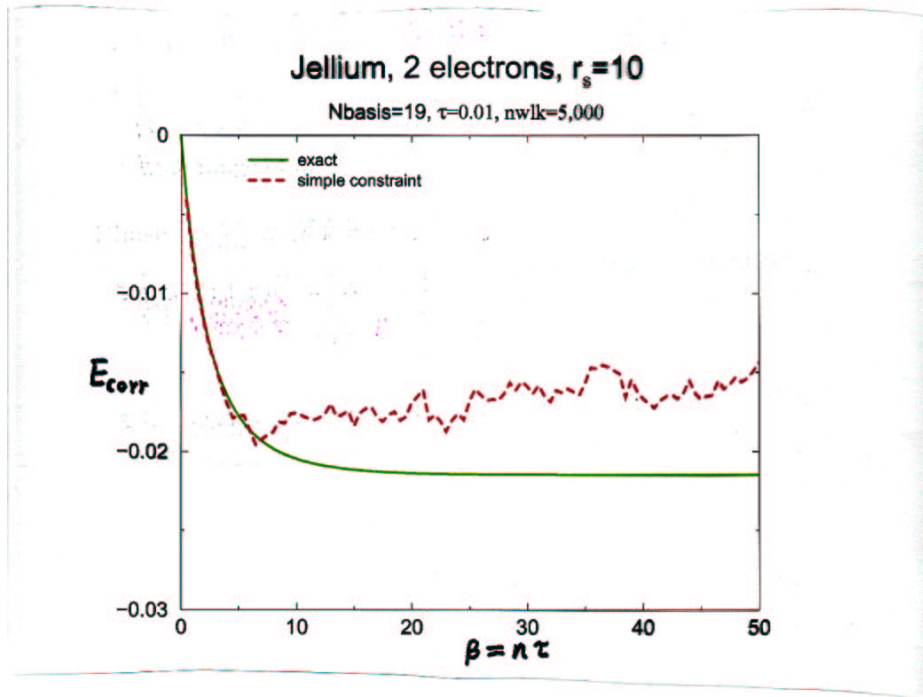
An approximate solution

(a) "Importance-sampling" transformation

- Seek MC representation of $|\Psi_0\rangle$ in the form: $|\Psi_0\rangle \doteq \sum_\phi \frac{|\phi\rangle}{\langle\Psi_T|\phi\rangle}$

  i.e., the contribution of each $|\phi\rangle$ is independent of its phase (if $|\psi_T\rangle$ is exact)

- Modify propagator accordingly, for each $|\phi\rangle \xrightarrow{\sigma} |\phi'(\sigma)\rangle$

$$\int \langle\Psi_T|\phi'(\sigma)\rangle \, e^{-\frac{1}{2}\sigma^2} B(\sigma) \, d\sigma \, \frac{1}{\langle\Psi_T|\phi\rangle}$$

$$\Downarrow$$

$$e^{-\tau\hat{H}_1/2} \int e^{-\frac{1}{2}\sigma^2} e^{(\sigma-\bar{\sigma})\cdot\sqrt{\tau}\,\hat{v}} \, d\sigma \, e^{-\tau\hat{H}_1/2} \, e^{-\tau E_L(\phi)}$$
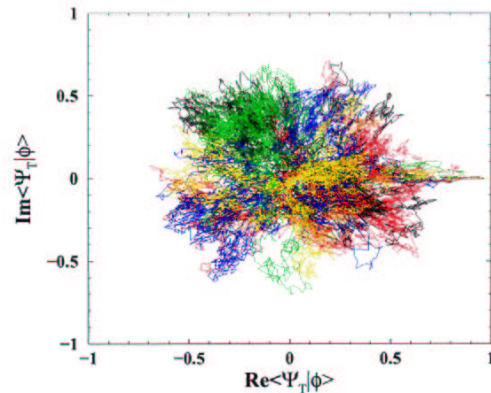
▷ Shift: $\bar{\sigma} \equiv -\frac{\langle\Psi_T|\sqrt{\tau}\,\hat{v}|\phi\rangle}{\langle\Psi_T|\phi\rangle}$ ← complex!

▷ Local energy: $E_L(\phi) \equiv \frac{\langle\Psi_T|H|\phi\rangle}{\langle\Psi_T|\phi\rangle}$

An approximate solution

(b) Projection to break "rotational invariance"

- Even with **(a)**, density of walkers:

Problem!

Trajectories of 5 walkers (color) during the random walk, shown in the complex plane $\langle \Psi_T | \phi \rangle$.

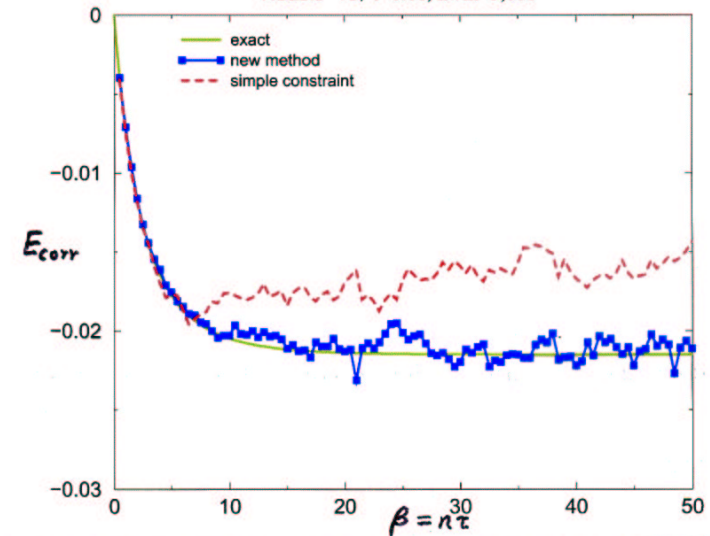Contrast with the case when $\hat{v}$ is real

- Project walker back to real axis in each step according to phase change, e.g., reduce weight by $\cos[Im\{\ln \frac{\langle \Psi_T | \phi' \rangle}{\langle \Psi_T | \phi \rangle}\}]$

An approximate solution

Illustrative results

Jellium, 2 electrons, r_s=10

Nbasis=19, τ=0.01, nwlk=5,000

Comments

- No upper bound property
- The method reduces to constrained path MC when $\hat{v}$ is real
- The formalism leads to fixed-node DMC in real space

First application: silicon atom, dimer, and bulk

- Plane-wave basis

- Kleinman-Bylander norm-conserving non-local pseudopotentials
  — straightforward to implement

- Same set-up as in a DFT calculation $(G, G' < E_{cut})$

- Up to 10,000 plane waves ($\sim$100,000 auxiliary fields per imaginary-time step)

- Trial w.f. $|\psi_T\rangle$: single Slater determinant from LDA

TABLE I: Total valence energies of Si and Si$_2$, and binding energy of Si$_2$. The Si$_2$ ground state is $^3\Sigma_g^-$ (electronic configuration $5\uparrow 3\downarrow$). Calculations were done at the experimental equilibrium bond length of $4.244a_B$, in a cubic supercell with $a = 19a_B$ (4945 plane waves). Energies are in eV. Error bars are in the last digit and are in parentheses.

	Si	Si$_2$	Si$_2$ E_B
LDA	-102.648	-209.175	3.879
QMC	$-103.45(2)$	$-210.03(7)$	3.12(8)
Experiment			3.21(13)

TABLE II: Cohesive energy of bulk Si. Calculations are done for fcc supercells with 16 and 54 atoms, at $a_{exp} = 5.43$Å. QMC result at ∞ is from 54 atoms and includes two finite-size corrections: (i) an independent-particle correction of 0.311 eV from LDA and (ii) an additional Couloumb correction of -0.174 eV from Ref. [20, 22]. A zero-point energy correction of -0.061 eV was also added to the calculated results at ∞. Energies are in eV per atom. Error bars are in the last digit and are in parentheses.

	16	54	∞
LDA	3.836	4.836	5.086
QMC	3.79(4)	4.51(3)	4.59(3)
Experiment			4.62(8)

DMC + psp   4.63(2)

Laura et al (1999)

Summary and outlook

- A QMC method to treat extended-interactions with auxiliary fields without the sign/phase problem (approximate)

- The first "ab initio" ground-state calculations using this framework — promising results:
  - Calculations on silicon atom, dimer, and bulk (54 atom fcc supercell, 216 electrons)
  - Accurate binding energy of Si$_2$ and cohesive energy of bulk, in excellent agreement with experiment

- Potentially a method to systematically go beyond LDA while using much of its existing machinery

- Lots to do:
  - Applications, including to more strongly correlated systems
  - Algorithm
    * Implementing calculation of expectation values (underway)
    * Further improvement? (different choices of one-particle basis, different HS transformations, ...)
    * Finite-T generalization? (real $\hat{v}$: SZ, PRL **83**, 2777 (1999))