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Quantum Monte Carlo: From Minerals and Materials to Molecules
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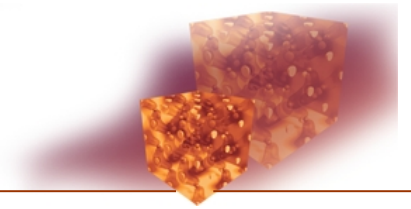
http://www.mcc.uiuc.edu/summerschool/2007/qmc/



Introduction to auxiliary-field quantum Monte Carlo methods

Shiwei Zhang

College of William & Mary

[shiwei@physics.wm.edu]

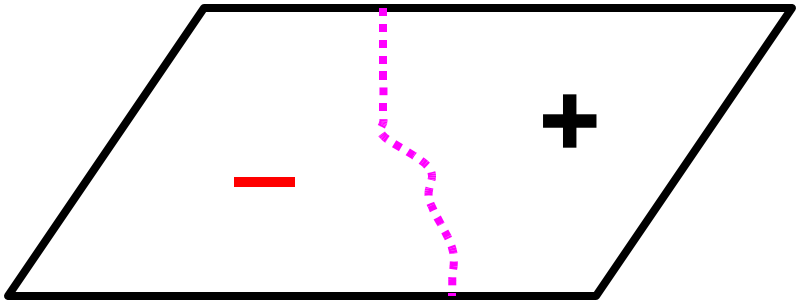
Outline

- Why auxiliary-field QMC?
  - A new approach: stochastic mean-field theory
  - Motivation: reduce QMC error & increase predictive power;
    more "black-box" like LDA or HF?
- Random walks in Slater determinant space
  - Understanding the sign (phase!) problem in this framework
  - How to control it? (approximate)
- What applications are possible?
  - Molecules and solids: T=0K
    plane-wave+Psps **or** Gaussians
  - Models for strongly correlated systems: T =0 and T>0K

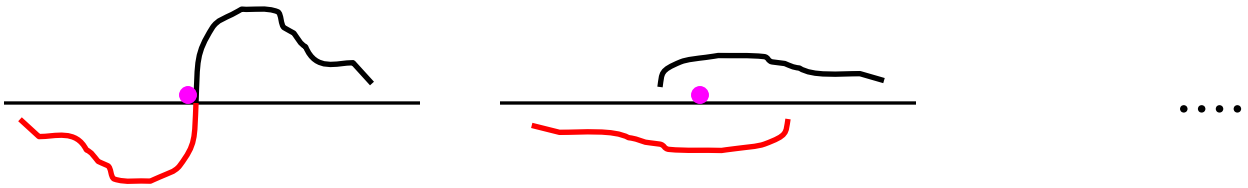
Introduction: why auxiliary-field methods?

Recall sign problem:

1 particle, first excited state:



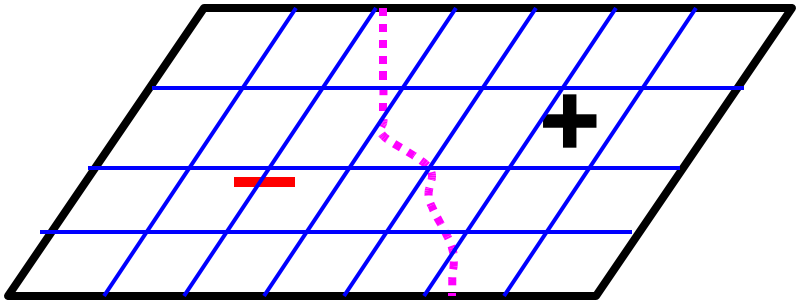
In real-space QMC, we need + and − walkers to cancel



Why auxiliary-field methods?

Recall sign problem:

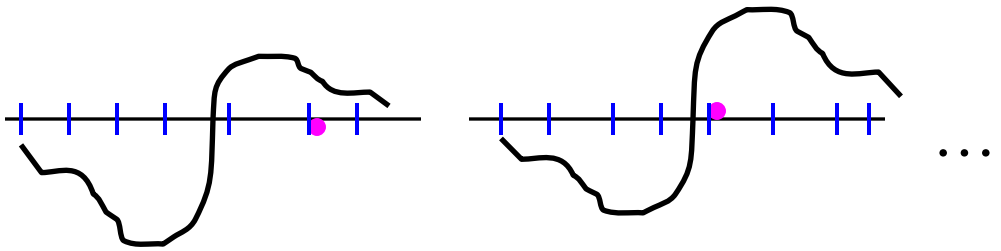
1 particle, first excited state:



Solid state or quantum chemistry?

➔ **basis**

$$e^{-\tau H} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \cdot \\ \cdot \\ \psi_N \end{pmatrix}$$



Explicit --- matrix x vec

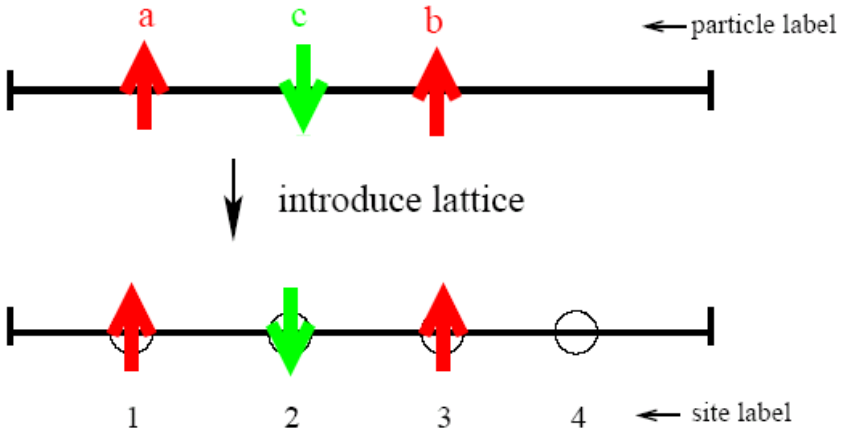
No sign problem

Why auxiliary-field methods?

Many particles?

A toy problem – trapped fermion atoms:

- 3 fermions in a box, two with $\uparrow$ spin and one with $\downarrow$ spin;
  contact interaction $V(R) = a_s\delta(r_{\rm a} - r_{\rm c}) + a_s\delta(r_{\rm b} - r_{\rm c})$ (no s-wave bt. a & b)



- Use a crude lattice basis with $i = 1, 2, 3, 4$ sites (circles). In second quantized form:

$$H = K + V = -t \sum_{\langle ij\rangle\sigma} (c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

near-neighbor

- Parameters: t; $U \propto a_s$

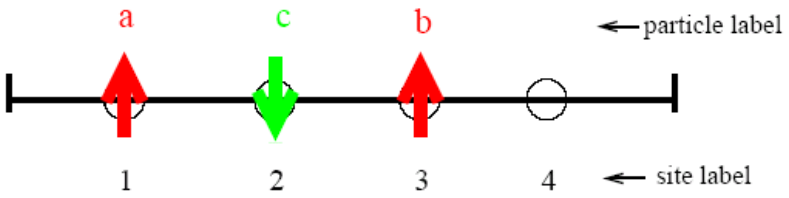
Toy problem – trapped fermions

What is the ground state when *U=0* ?

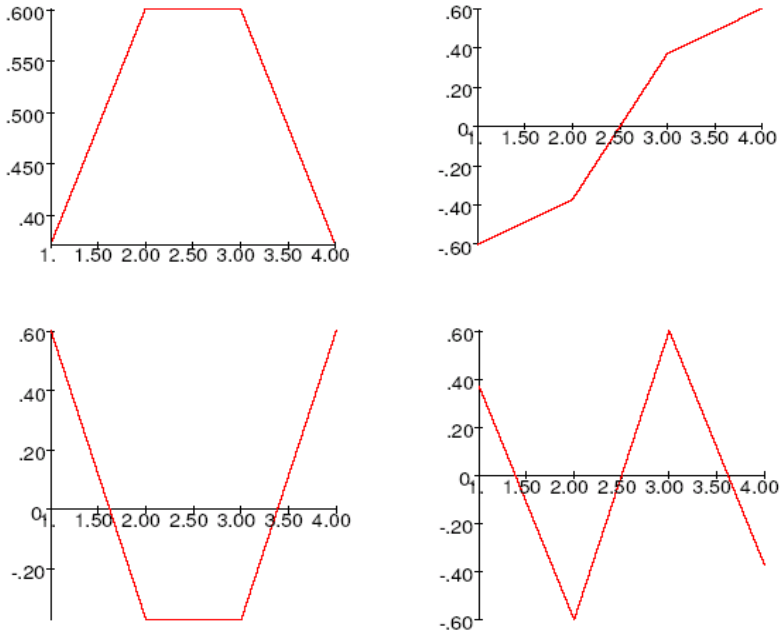
- Diagonalize *H* directly:

Single-particle Hamiltonian

$$H := \begin{bmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & -1 & 0 \\ 0 & -1 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix}$$



Diagonalize H to find single-particle energies and w.f's
Plot wf in order of 1 , 2, 3, 4



Put fermions in lowest levels:

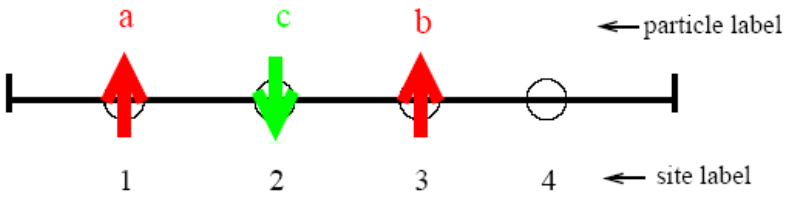
➔ many-body wf:

$$\begin{bmatrix} .3717480339 & -.6015009557 \\ .6015009541 & -.3717480349 \\ .6015009553 & .3717480339 \\ .3717480350 & .6015009543 \end{bmatrix} \cdot \begin{bmatrix} .3717480339 \\ .6015009541 \\ .6015009553 \\ .3717480350 \end{bmatrix}$$

Toy problem – trapped fermions

What is the ground state when *U=0* ?

- Diagonalize *H* directly
- Alternatively, power method:



$$e^{-\tau H}: \quad \left(4 \times 4 \right) \otimes \left(4 \times 4 \right) \equiv B_K \ \text{operate on any } |\Psi^{(0)}\rangle \text{ repeatedly} \quad \Rightarrow |\Psi_0\rangle$$

Theorem: For any $\hat{v} = \sum_{ij} v_{ij} c_i^\dagger c_j$,
$e^{\hat{v}} |\phi\rangle = |\phi'\rangle$ where $\Phi' \equiv e^v \Phi$ in matrix form

Toy problem – trapped fermions

[Define projection operator exp(-tau*H):

```
[ > P := tau -> convert(evalf(exponential((H+1.6),-tau)),Matrix);
```

For example exp(-0.1*H) looks like: (tau=0.1)

```
> P(0.1);
```

$$\begin{bmatrix} .8564116151 & .08549878210 & .004271380206 & .0001422371517 \\ .08549878209 & .8606829955 & .08564101925 & .004271380206 \\ .004271380206 & .08564101925 & .8606829955 & .08549878210 \\ .0001422371517 & .004271380206 & .08549878210 & .8564116153 \end{bmatrix}$$

[>

Pick an arbitrary initial wf to project from:

```
>      --- note we're only writing out the up component
```

$$PsiT := \begin{bmatrix} 1. & -1. \\ 1. & -1. \\ 1. & 1. \\ 1. & 1. \end{bmatrix}$$

[

[Project for a beta of 10, i.e. exp(-n*tau*H)|Psi_T>, with n*tau=10:

```
> (v0, v1) = Multiply(P(10.), PsiT)
```

$$\begin{bmatrix} .866609121199999999 & -.0000636598000000043740 \\ 1.40220301329999986 & -.0000393430999999777598 \\ 1.40220301359999988 & .0000393434000000025819 \\ .866609121099999991 & .0000636596999999961000 \end{bmatrix}$$

```
> GramSchmidt({v0,v1},normalized);
{[-.6015041283, -.3717422466, .3717450812, .6015031834],
    [.3717488488, .6015014581, .6015004522, .3717472200]}
```

Same as from direct diag.:

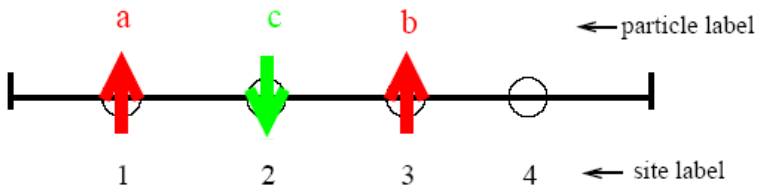
ground-state wf:

$$\begin{bmatrix} .3717480339 & -.6015009557 \\ .6015009541 & -.3717480349 \\ .6015009553 & .3717480339 \\ .3717480350 & .6015009543 \end{bmatrix} \cdot \begin{bmatrix} .3717480339 \\ .6015009541 \\ .6015009553 \\ .3717480350 \end{bmatrix}$$

Toy problem – trapped fermions

What is the ground state when *U=0* ?

- Diagonalize *H* directly
- Alternatively, power method:



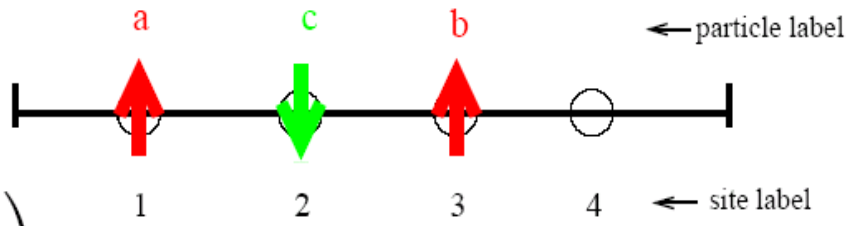
$$e^{-\tau H}: \quad \left(\begin{array}{c} 4\times 4 \end{array} \right) \otimes \left(\begin{array}{c} 4\times 4 \end{array} \right) \equiv B_K \quad \text{operate on any } |\Psi^{(0)}\rangle \text{ repeatedly} \quad \Rightarrow |\Psi_0\rangle$$

- Applies to any non-interacting system
- Re-orthogonalizing the orbitals prevents fermions from collapsing to the bosonic state

→ Eliminates ‘sign problem’ in non-interacting systems

Toy problem – trapped fermions

Properties of Slater determinants:



$$|\phi\rangle: \quad \Phi = \begin{pmatrix} 0.37 & -0.60 \\ 0.60 & -0.37 \\ 0.60 & 0.37 \\ 0.37 & 0.60 \end{pmatrix} \otimes \begin{pmatrix} 0.37 \\ 0.60 \\ 0.60 \\ 0.37 \end{pmatrix} \quad \leftarrow \text{matrix rep.}$$

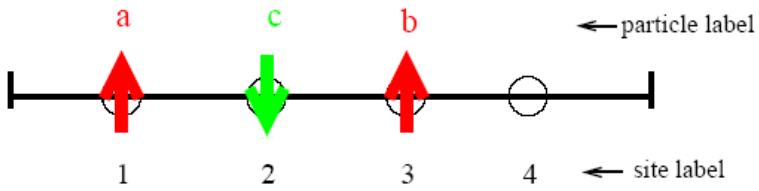
- What is the probability to find the electron configuration shown in the picture? That is, how to calculate $\langle R|\phi\rangle$?
- How to calculate $E_0 = \langle\phi|H|\phi\rangle$ from the wave function?
- How to calculate the density matrix? The spin-spin correlation function?

A: Simple matrix manipulations (See Lab exercises)

Toy problem – trapped fermions

What is the ground state when *U=0* ?

- Diagonalize *H* directly
- Alternatively, power method:



$$e^{-\tau H}: \quad \left(\; 4 \times 4 \; \right) \otimes \left(\; 4 \times 4 \; \right) \equiv B_K \;\; \text{operate on any } |\Psi^{(0)}\rangle \text{ repeatedly} \quad \Rightarrow |\Psi_0\rangle$$

What is the ground state, if we turn on *U* ?

- Lanczos (scaling !)
- Can we still write $e^{-\tau H}$ in one-body form?

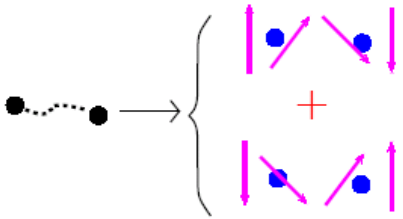
  Yes, with Hubbard-Stratonivich transformation

Introduction – why auxiliary-field methods?

Hubbard-stratonivich transformation

- Interacting two-body problem can be turned into a linear combination of non-interacting probems living in fluctuating external fields ('completion of square'):

$$e^{\tau \hat{v}^2} \xrightarrow{\text{Hubbard}-\text{Strotonivich transformation}} \int e^{-\sigma^2/2}\, e^{\sigma \sqrt{\tau}\, \hat{v}}\, d\sigma \qquad \sigma: \text{auxiliary field}$$



$$\hat{v} = \sum v_{ij} c_i^\dagger c_j : \text{one-body operator}$$

- Illustration of HS transformation — Hubbard-like interaction:

$$e^{-\tau U n_{i\uparrow} n_{i\downarrow}} \to e^{\tau U (n_{i\uparrow} - n_{i\downarrow})^2/2} = \text{factor} \times \int e^{-\frac{1}{2}x^2}\, e^{\sqrt{\tau U}\, x\, (n_{i\uparrow} - n_{i\downarrow})}\, dx$$

$$e^{-\tau U n_{i\uparrow} n_{i\downarrow}} \to e^{-\tau U (n_{i\uparrow} + n_{i\downarrow})^2/2} = \text{factor} \times \int e^{-\frac{1}{2}x^2}\, e^{\sqrt{\tau U}\, \mathrm{i}\, x\, (n_{i\uparrow} + n_{i\downarrow})}\, dx$$

Or trick by Hirsch:

$$e^{-\tau U n_{i\uparrow} n_{i\downarrow}} = e^{-\tau U (n_{i\uparrow} + n_{i\downarrow})/2} \cdot \sum\nolimits_{x=\pm 1} \frac{1}{2}\, e^{\gamma\, x\, (n_{i\uparrow} - n_{i\downarrow})} \qquad \cosh \gamma = e^{\tau U/2}$$

Back to toy problem

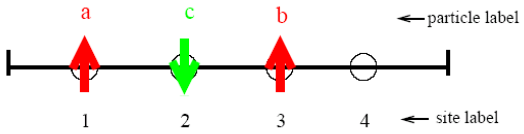
What is the ground state, if we turn on *U* ?

$$e^{-\tau U n_{i\uparrow} n_{i\downarrow}} = \text{factor} \times \sum_{x=\pm 1} \frac{1}{2}\; e^{\gamma\, x\, n_{i\uparrow}}\; e^{-\gamma\, x\, n_{i\downarrow}} \qquad \cosh\gamma = e^{\tau U/2}$$

$$e^{-\tau H} = \int d\mathbf{x}\; p(\mathbf{x}) \begin{pmatrix} e^{\gamma x_1} & 0 & 0 & 0 \\ 0 & e^{\gamma x_2} & 0 & 0 \\ 0 & 0 & e^{\gamma x_3} & 0 \\ 0 & 0 & 0 & e^{\gamma x_4} \end{pmatrix} \cdot B_{K,\uparrow}$$

$$\otimes \begin{pmatrix} e^{-\gamma x_1} & 0 & 0 & 0 \\ 0 & e^{-\gamma x_2} & 0 & 0 \\ 0 & 0 & e^{-\gamma x_3} & 0 \\ 0 & 0 & 0 & e^{-\gamma x_4} \end{pmatrix} \cdot B_{K,\downarrow}$$

$B(\mathbf{x})$ 1-particle propagator



$$\boxed{e^{-\tau H} = \int p(\mathbf{x}) B(\mathbf{x}) d\mathbf{x}}$$

$$\mathbf{x} \equiv \{x_1, x_2, x_3, x_4\}$$

- With *U*, same as *U=0*, except for **integral** over **x** → Monte Carlo

Introduction to AF QMC

Standard ground-state AF QMC *Sugiyama & Koonin '86*

$$\langle \hat{O} \rangle = \frac{\langle \Psi^{(0)} | e^{-\tau H} \cdots e^{-\tau H} \, \hat{O} \, e^{-\tau H} \cdots e^{-\tau H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | e^{-\tau H} \cdots e^{-\tau H} \;\; e^{-\tau H} \cdots e^{-\tau H} | \Psi^{(0)} \rangle}$$

$$\Downarrow \qquad \boxed{e^{-\tau H} = \int p(\mathbf{x}) B(\mathbf{x}) d\mathbf{x}}$$

$$\frac{\int p(\mathbf{x}^{(1)}) \cdots p(\mathbf{x}^{(2L)}) \, \langle \Psi^{(0)} | B(\mathbf{x}^{(2L)}) \cdots B(\mathbf{x}^{(L+1)}) \, \hat{O} \, B(\mathbf{x}^{(L)}) \cdots B(\mathbf{x}^{(1)}) | \Psi^{(0)} \rangle \, d\mathbf{x}^{(1)} \cdots d\mathbf{x}^{(2L)}}{\int p(\mathbf{x}^{(1)}) \cdots p(\mathbf{x}^{(2L)}) \, \langle \Psi^{(0)} | B(\mathbf{x}^{(2L)}) \cdots B(\mathbf{x}^{(L+1)}) \;\; B(\mathbf{x}^{(L)}) \cdots B(\mathbf{x}^{(1)}) | \Psi^{(0)} \rangle \, d\mathbf{x}^{(1)} \cdots d\mathbf{x}^{(2L)}}$$

Choose $|\Psi^{(0)}\rangle$ as a Slater determinant $\boxed{B(\mathbf{x})|\phi\rangle = |\phi'\rangle}$

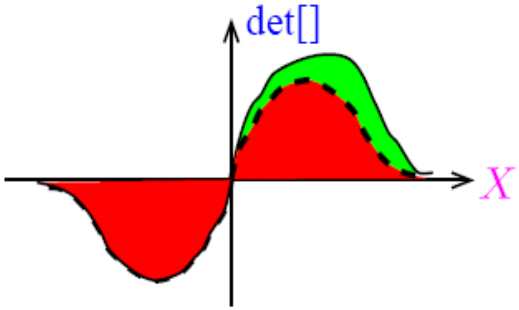
Many-dim integral can be done by Monte Carlo: $\dfrac{\int O_{\mathrm{Gr}}(X) p(X) \det[X] dX}{\int p(X) \det[X] dX}$ $\qquad X \equiv \{\mathbf{x}^{(l)}\}$

Applications mostly to "simple models":

- Hubbard model, impurity models in condensed matter
- nuclear shell model
- lattice QCD

Introduction to AF QMC

Sign problem in standard AF QMC:



As system size grows, average sign of det[ ] $\rightarrow 0$ exponentially.

$\Rightarrow$ exponential scaling

- Sign problem is often most severe where the physics is most interesting, for example, in 2-D Hubbard model when number of electrons $\sim 85\%$ number of lattice sites, where it is thought to model the CuO planes of high-T_c cuprates
- In fact, a phase (not just sign) problem appears for general 2-body interactions.

Some "lingo" from mean field

- Electronic Hamiltonian: (Born-Oppenheimer)

$$H = H_{1-\mathrm{body}} + H_{2-\mathrm{body}} = -\frac{\hbar^2}{2m}\sum_{i=1}^{M}\nabla_i^2 + \sum_{i=1}^{M} V_{\mathrm{ext}}(\mathbf{r}_i) + \sum_{i<j}^{M} V_{\mathrm{int}}(|\mathbf{r}_i - \mathbf{r}_j|)$$

can choose any single-particle basis $\{|\chi_i\rangle\}$

$$\hat{H} = \sum_{i,j}^{N} T_{ij} c_i^\dagger c_j + \sum_{i,j,k,l}^{N} V_{ijlk} c_i^\dagger c_j^\dagger c_k c_l$$

$$\int \chi_i^\star(\mathbf{r}_1)\chi_j^\star(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_1)\, d\mathbf{r}_1 d\mathbf{r}_2$$

- An orbital:

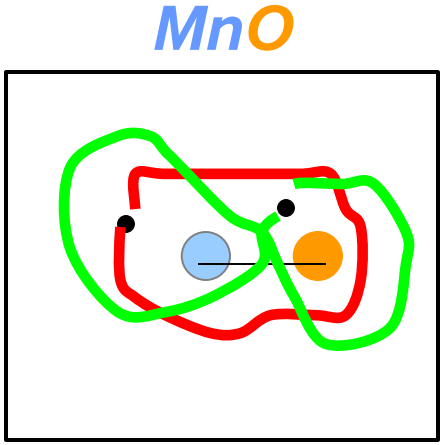
$$|\varphi_m\rangle = \sum_{i=1}^{N} \varphi_{i,m}|\chi_i\rangle$$

- A Slater determinant:

$$\begin{pmatrix} \varphi_{1,1} & \varphi_{1,2} & \cdots & \varphi_{1,M} \\ \varphi_{2,1} & \varphi_{2,2} & \cdots & \varphi_{2,M} \\ \vdots & \vdots & & \vdots \\ \varphi_{N,1} & \varphi_{N,2} & \cdots & \varphi_{N,M} \end{pmatrix}$$

N : basis

M : electrons



Summary: basic formalism of AF methods

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

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

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

Electronic Hamiltonian: (2nd quantization, given any 1-particle basis)

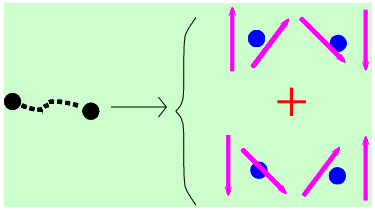
$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i,j}^{M} T_{ij} c_i^\dagger c_j + \sum_{i,j,k,l}^{M} V_{ijlk} c_i^\dagger c_j^\dagger c_k c_l$$

M : basis size

$\hat{H}_2 \to -\sum \hat{v}^2$ with $\hat{v}$ = 1-body

Hubbard-Strotonivich transf.

$$e^{-\tau \hat{H}} \quad \to \quad e^{-\tau \hat{H}_1} \int e^{-\sigma^2/2} \; e^{\sigma \sqrt{\tau}\, \hat{v}} \; d\sigma$$



interacting system $\to \sum$ (non-interacting system in auxiliary fields)

next →

AF methods: some background

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

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

  $$\text{interacting} \rightarrow \sum (\text{non-interacting in fields})$$

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

- However,
  - sign problem for "simple" interactions (Hubbard)
  - phase problem for realistic interaction

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

- Reformulate ---

Slater determinant random walk (preliminary I)

- In general, we can choose any single-particle basis $\{|\chi_i\rangle\}$, with $i = 1, 2, \cdots, N$
- A single-particle orbital (labeled by m) is given by $\hat{\varphi}_m{}^\dagger|0\rangle \equiv \sum_{i=1}^{N} \varphi_{i,m}|\chi_i\rangle$
- If we have M identical fermions ($M \leq N$), a Slater determinant $|\phi\rangle$ is given by:

$$|\phi\rangle \equiv \hat{\varphi}_1{}^\dagger \hat{\varphi}_2{}^\dagger \cdots \hat{\varphi}_M{}^\dagger |0\rangle$$

- $|\phi\rangle$ is represented by an $N \times M$ matrix:

$$\Phi \equiv \begin{pmatrix} \varphi_{1,1} & \varphi_{1,2} & \cdots & \varphi_{1,M} \\ \varphi_{2,1} & \varphi_{2,2} & \cdots & \varphi_{2,M} \\ \vdots & \vdots & & \vdots \\ \varphi_{N,1} & \varphi_{N,2} & \cdots & \varphi_{N,M} \end{pmatrix}$$

- E.g., $\langle\phi|\phi'\rangle = \det(\Phi^{\mathrm{T}}\Phi')$; $\quad G_{ij} \equiv \frac{\langle\phi|c_i^\dagger c_j|\phi'\rangle}{\langle\phi|\phi'\rangle} = [\Phi'(\Phi^{\mathrm{T}}\Phi')^{-1}\Phi^{\mathrm{T}}]_{ij}$;
  any 2-body correlation $\leftarrow \{G_{ij}\}$

Slater determinant random walk (preliminary II)

HS transformation:

For example in electronic systems:

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

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

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

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

$$\rightarrow -\frac{1}{2\Omega} \sum_{\mathbf{Q}\neq 0} \frac{4\pi}{|\mathbf{Q}|^2} \rho^\dagger(\mathbf{Q})\, \underline{\rho(\mathbf{Q})}$$

$$\underline{\rho(\mathbf{Q})} \nwarrow \sum_i c^\dagger_{\mathbf{G}_i+\mathbf{Q}} c_{\mathbf{G}_i}$$

$$\rightarrow \sum_{\mathbf{Q}\neq 0} \sqrt{\frac{4\pi}{|\mathbf{Q}|^2}} \left([\, \underbrace{\rho^\dagger(\mathbf{Q}) + \rho(\mathbf{Q})}_{i\,\hat{v}} \,]^2 - [\, \underbrace{\rho^\dagger(\mathbf{Q}) - \rho(\mathbf{Q})}_{\hat{v}'} \,]^2 \right)$$

'density' decomposition

New AF QMC approach

Random walks in Slater determinant space:

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

SZ, Carlson, Gubernatis

SZ, Krakauer

H-S transformation

$\int e^{-\sigma^2/2} \; e^{\hat{\mathbf{v}}(\sigma)} d\sigma$

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

Schematically:

$|\Psi^{(0)}\rangle \xrightarrow{e^{-\tau \hat{H}}} |\Psi^{(1)}\rangle \;\; .... \;\; \rightarrow \; |\Psi_0\rangle$

sample σ from $e^{-\frac{\sigma^2}{2}}$;
apply 1-body propag.

$|\phi^{(0)}\rangle \rightarrow |\phi^{(1)}(\sigma)\rangle \rightarrow |\phi\rangle$

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

Exact so far

next →

Connection with DMC

Many-dim. electronic configuration space: $R = \{ \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_M \}$

$$\hat{H} = \sum_i^M \frac{\hat{\mathbf{p}}_i^2}{2m} + \hat{V}$$

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

$$e^{-\tau \hat{\mathbf{p}}_i^2/2m} = \int e^{-\sigma^2/2} \; e^{i \hat{\mathbf{p}}_i \cdot (\gamma \, \sigma)} \; d\sigma \qquad \gamma = \sqrt{\tfrac{\tau}{m}}$$

$$e^{-\tau \hat{H}} = \int e^{-\vec{\sigma}^2/2} \; e^{i \hat{P} \cdot (\gamma \, \vec{\sigma})} \; d\vec{\sigma} \; e^{-\tau \hat{V}} \qquad \vec{\sigma}\text{: } 3M\text{-dim vector}$$

translation op.

Random walk realization of $\cdots$: basic idea (importance sampling can also be derived)

$$|\Psi^{(0)}\rangle \xrightarrow{\quad e^{-\tau H} \quad} |\Psi^{(1)}\rangle \; .... \; \rightarrow \; |\Psi_0\rangle$$

$$|R^{(0)}\rangle \xrightarrow[\text{sample } \vec{\sigma} \text{ from Gaussian;}]{\text{multiply weight by } e^{-\tau V(R^{(0)})}} |R^{(1)}\rangle \; \rightarrow \; |R\rangle \quad \text{diffusion + branching}$$

$$\text{translate } R^{(0)} \text{ by } (-\gamma\vec{\sigma})$$

. . . .

Random walks in Slater determinant space

Standard DMC

$|R\rangle = |\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_M\rangle$

$|\Psi_0\rangle = \sum_R \Psi_0(R)|R\rangle$

$\Downarrow$

$|\Psi_0\rangle \doteq \sum_{\mathrm{MC}} |R\rangle$

Slater determinant RW

$|\phi\rangle = |\psi_1, \psi_2, \cdots, \psi_M\rangle$

$\sum_k c_{k,i}|\chi_k\rangle$ basis

$|\Psi_0\rangle = \sum_\phi \Psi_\phi|\phi\rangle$

$\Downarrow$

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

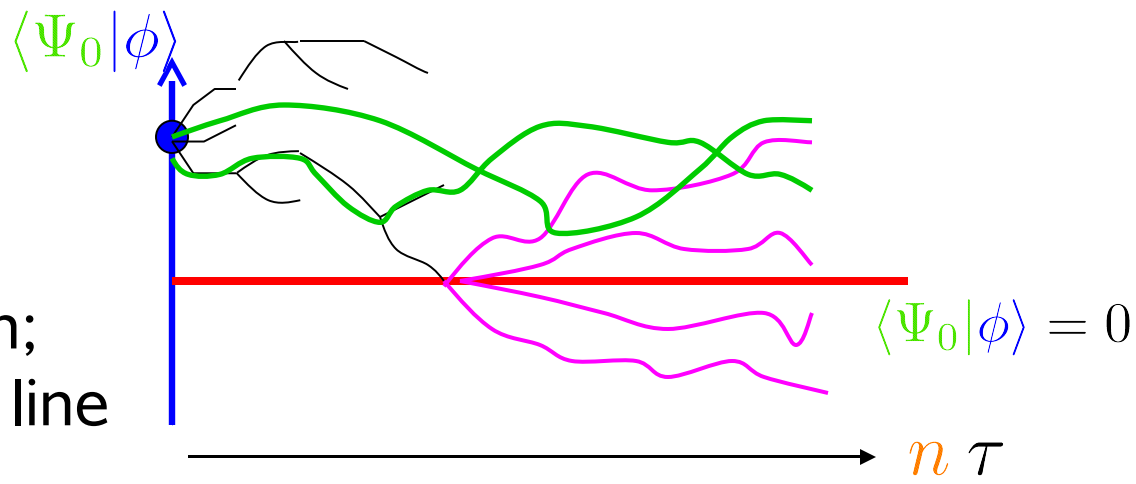
- The formalism is appealing — each random walker is a full Slater determinant
- Close formal relation to mean-field approaches. The QMC thus shares the same machinery as DFT or Hartree-Fock, using *any* one-particle basis
  - Second-quantization, antisymmetry automatically imposed
  - The single-particle problem ($\hat{H}_1$) is solved exactly, with no statistical error
  - Correlation effects are obtained by building stochastic ensembles of independent-particle solutions
- Core-electron problem: non-local pseudopotential can be implemented straightforwardly — *locality approximation* eliminated

But … sign problem

E.g., in Hubbard:

- $e^{-\tau \hat{H}}$ → paths in Slater determinant space

- Suppose $|\Psi_0\rangle$ is known; consider "**hyper-node**" line



- If path reaches **hyper-node**

$$\langle \Psi_0 | \phi \rangle = 0$$
$$\Rightarrow \langle \Psi_0 | e^{-n\tau \hat{H}} | \phi \rangle = 0$$

then its descendent paths collectively contribute 0

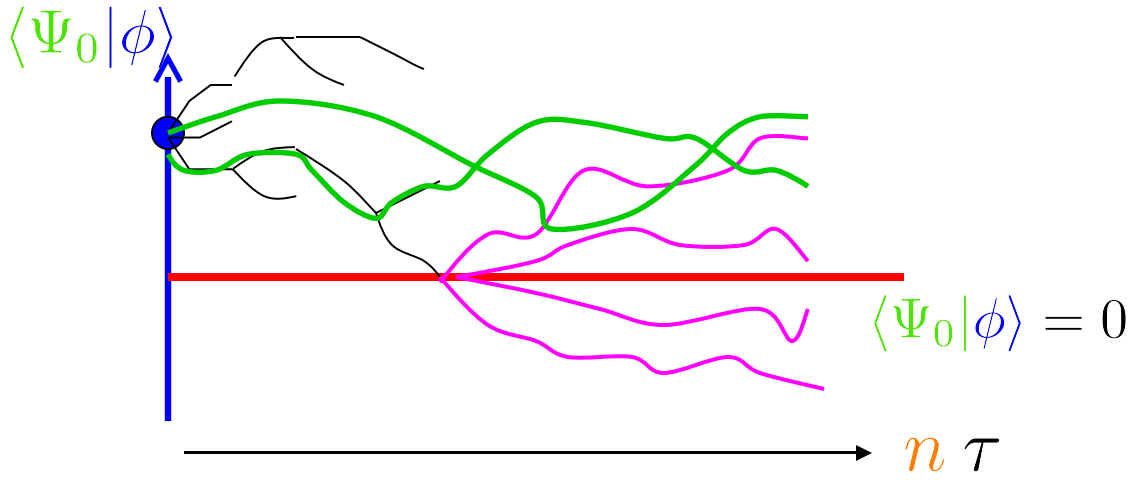
- MC signal is exponentially small compared to noise

In special cases (1/2 filling, or U<0), symmetry keeps paths to one side → no sign problem

next →

How to control the sign problem?

Constrained path appr.



keep only **paths that never reach the node**

require $\langle \Psi_{\mathbf{T}} | \phi \rangle > 0$

Trial wave function

Zhang, Carlson, Gubernatis, '97

Zhang, '00

next →

Recovery from wrong trial w.f.

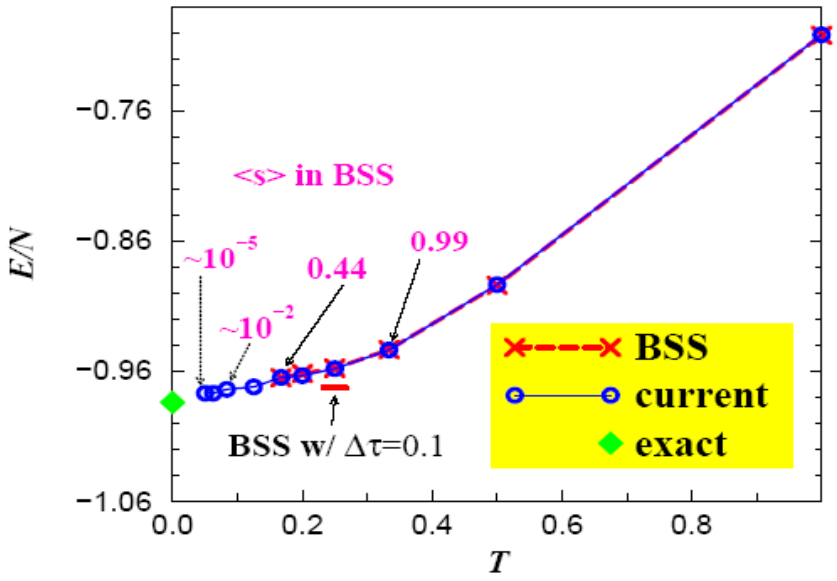
More predictive QMC: requires reducing reliance on trial wf

2-D Hubbard model: **finite-*T***

- *U*>0; 12% doping, 4x4
- Sign problem severe <s>~10^-5

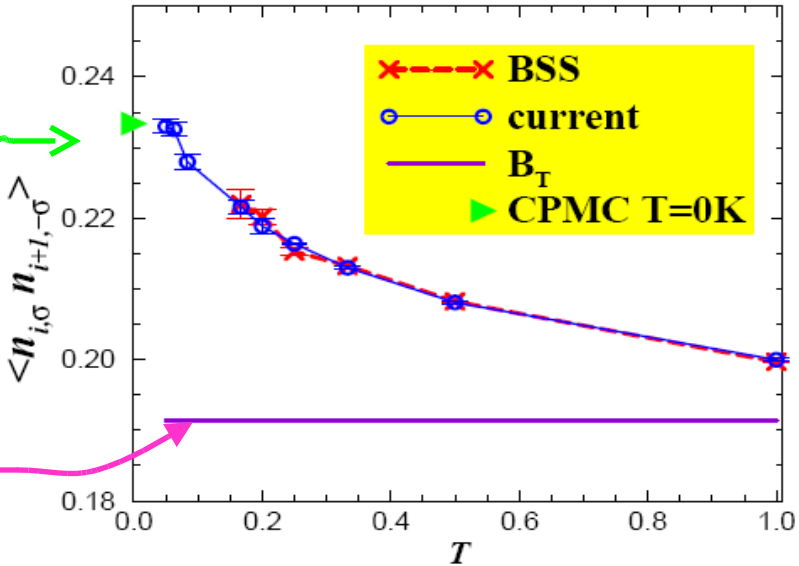
Compare with:

- high T: exact calculation with sigr problem
- T=0K: exact diag.



AFM order

wrong trial



New AF QMC approach

Random walks in Slater determinant space:

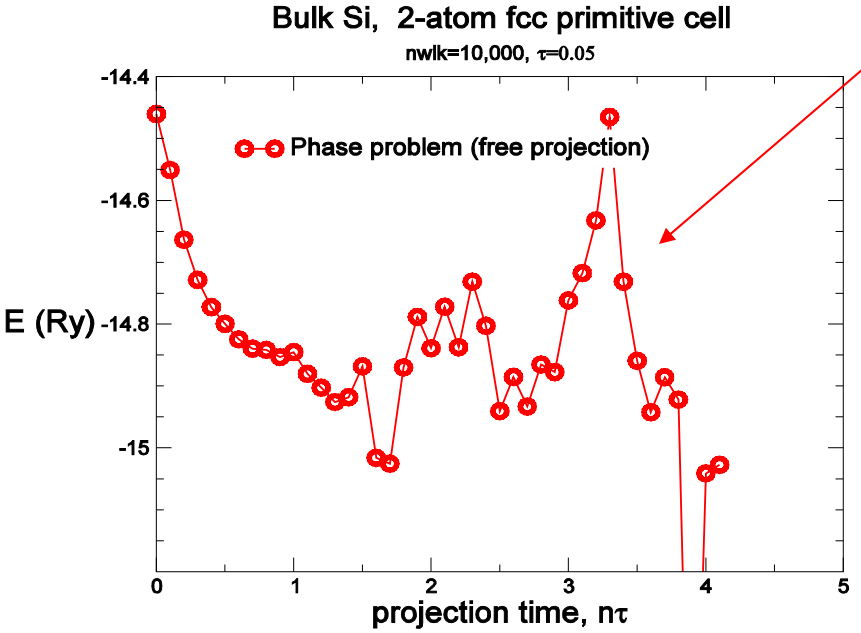
$$\text{Recall } |\Psi^{(n+1)}\rangle = e^{-\tau \hat{H}} \; |\Psi^{(n)}\rangle \xrightarrow{n\to\infty} |\Psi_0\rangle$$

H-S transformation

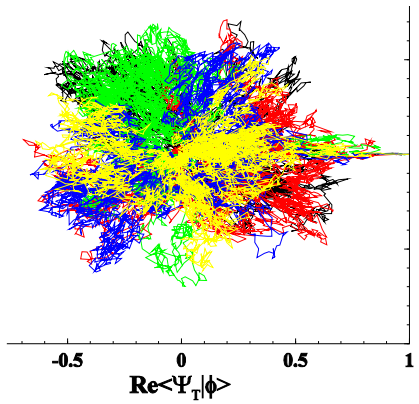
$$\int e^{-\sigma^2/2} \; e^{\hat{\mathbf{v}}(\sigma)} d\sigma$$

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

For general interaction, phase problem:



Exponential noise



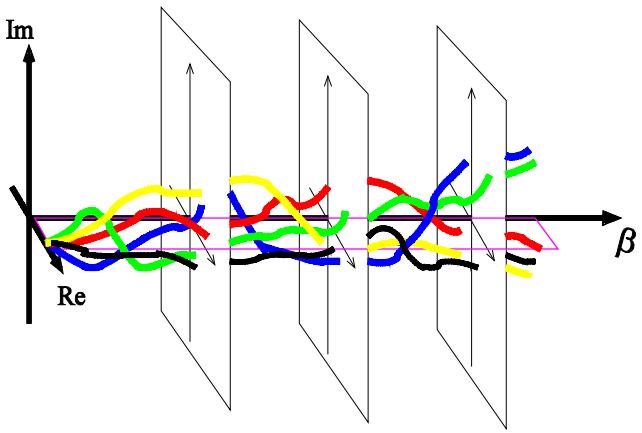
problem!

$\sum_{\text{MC}} |\phi\rangle \to 0$

next →

Controlling the phase problem

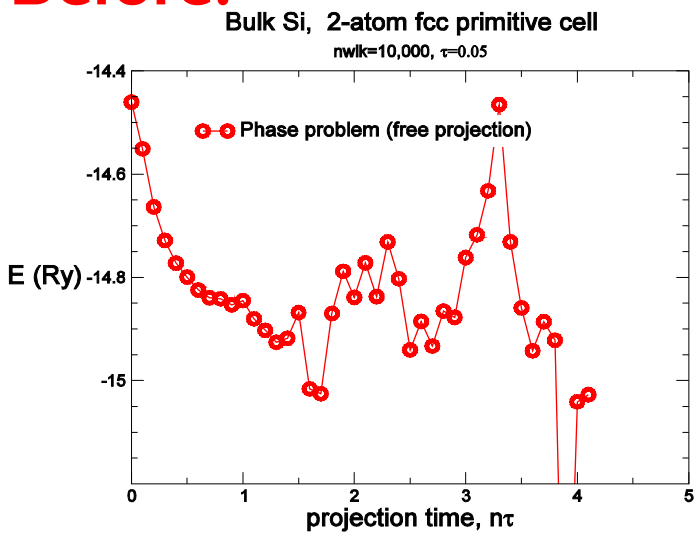
Sketch of approximate **solution**:



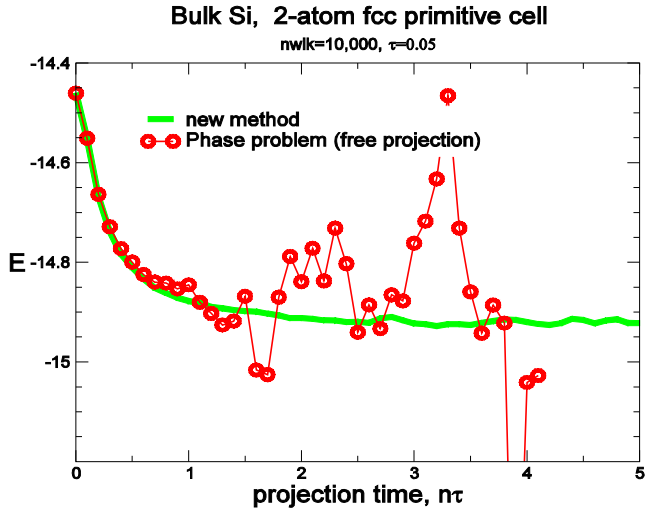
- Modify propagator by "importance sampling":
  phase → degeneracy (use trial wf)
- Project **to one overall phase**:
  break symmetry (+/- → rotation)

$$\sum_\phi \frac{|\phi\rangle}{\langle \Psi_T | \phi \rangle}$$

Before:



After:



Controlling the phase problem --- more details

(a) Phaseless formalism

SZ & Krakauer

- 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)

- This is accomplished by an "importance-sampling" transformation to modify the propagator:

$$\int \langle\Psi_T|\phi'(\sigma)\rangle\, e^{-\frac{1}{2}\sigma^2} B(\sigma)\, d\sigma\, \frac{1}{\langle\Psi_T|\phi\rangle} = e^{-\tau\hat{H}_1} \int e^{-\sigma^2/2}\, e^{(\sigma-\bar{\sigma})\sqrt{\tau}\,\hat{v}}\, d\sigma\; e^{-\tau Re\{E_L(\phi)\}}$$

  ⋆ Force bias: $\bar{\sigma} \equiv -\frac{\langle\Psi_T|\sqrt{\tau}\,\hat{v}|\phi\rangle}{\langle\Psi_T|\phi\rangle}$ ← complex!

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

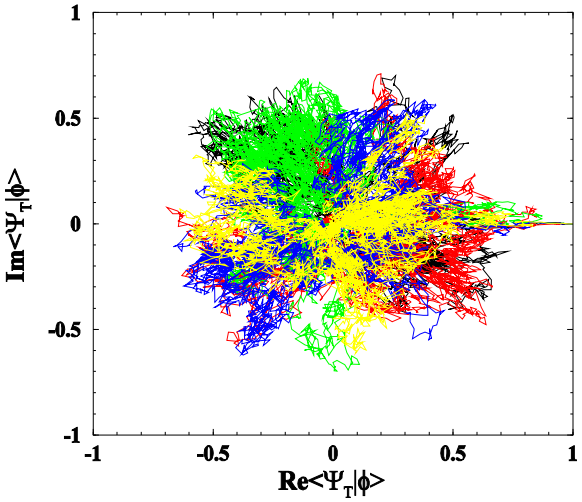
(b) Projection to break "rotational invariance"

- With **(a)**, we can confine the RW to one overall phase (e.g., 0)
- This is accomplished by projecting the RW onto 1D: reducing the weight of a walker according to its phase change, e.g., by $\cos(\Delta\theta)$

Controlling the phase problem: some comments

Subtleties:

- Constraint **before** importance sampling:
  $\mathrm{Re}\langle\Psi_T|\phi\rangle > 0,$
  then use $\mathrm{Re}\langle\Psi_T|\phi\rangle$ as importance function
  --- natural (!?), but does not work well
- Instead, project **after** "importance sampling":
  use complex importance function $\langle\Psi_T|\phi\rangle$



It helps to subtract "mean-field background" in HS:

$$\hat{v}^2 \rightarrow (\hat{v} - \langle\hat{v}\rangle)^2 + 2\hat{v}\langle\hat{v}\rangle - \langle\hat{v}\rangle^2$$

If $\hat{v}$ is real, method reduces to constrained path MC

Two-dimensionality unique -
connection and difference(!) with fixed-phase

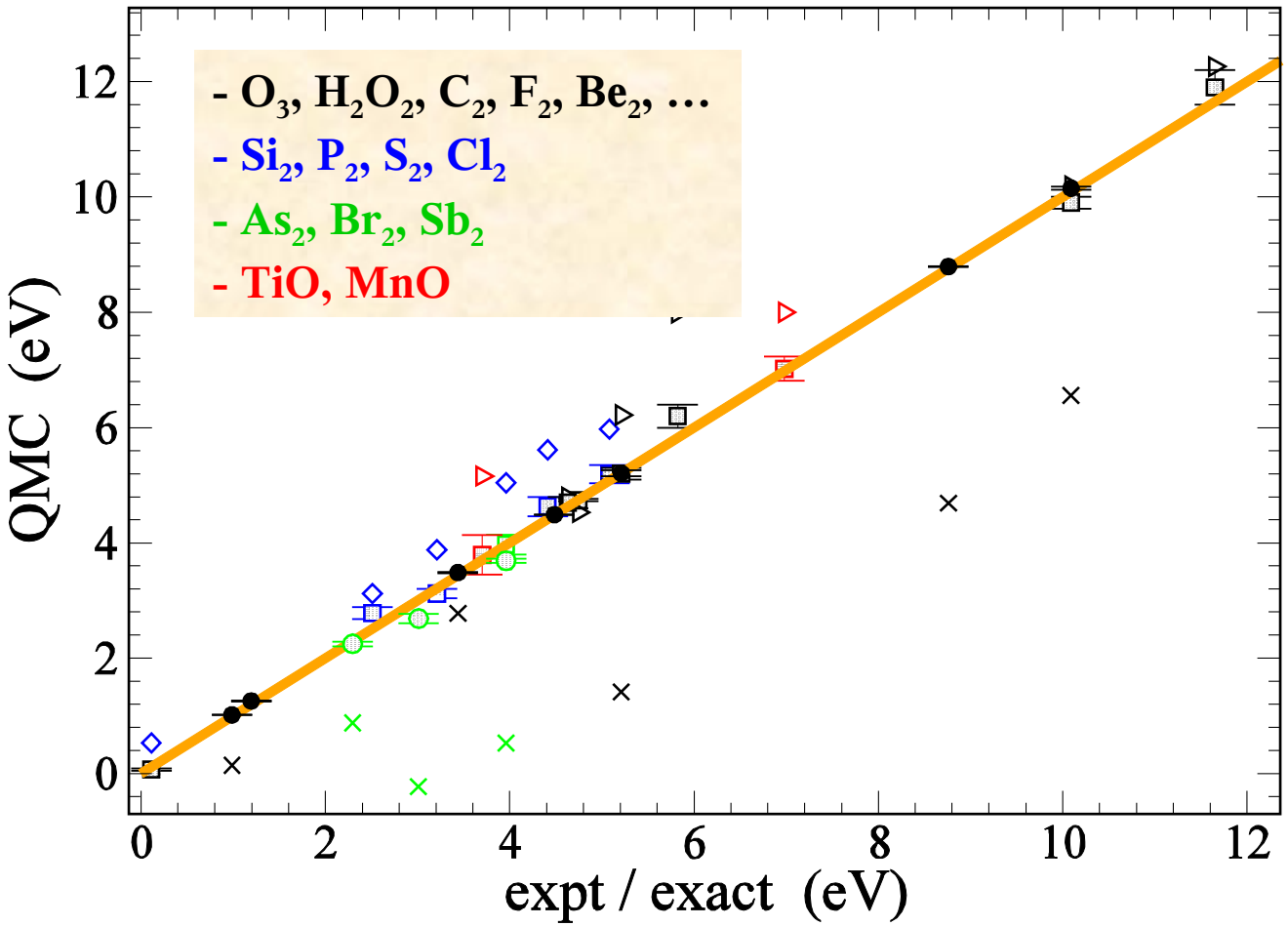
Discussion – new AF QMC

- Pluses
  - **Sign problem** is often found to be reduced

    ← more robust and predictive methods
  - Can do down-folded Hamiltonians (realistic models)
  - **Uses a basis** --- walkers are Slater determinants

    formal connection to DFT --- k-pts, non-loc psp's, PAW's, ….
- Minuses
  - **Uses a basis** --- finite basis-size error
  - Mixed-estimator of total energy is not variational
  - Not straightforward to include a Jastrow factor in trial w.f. **(….)**

Application: molecular binding energies



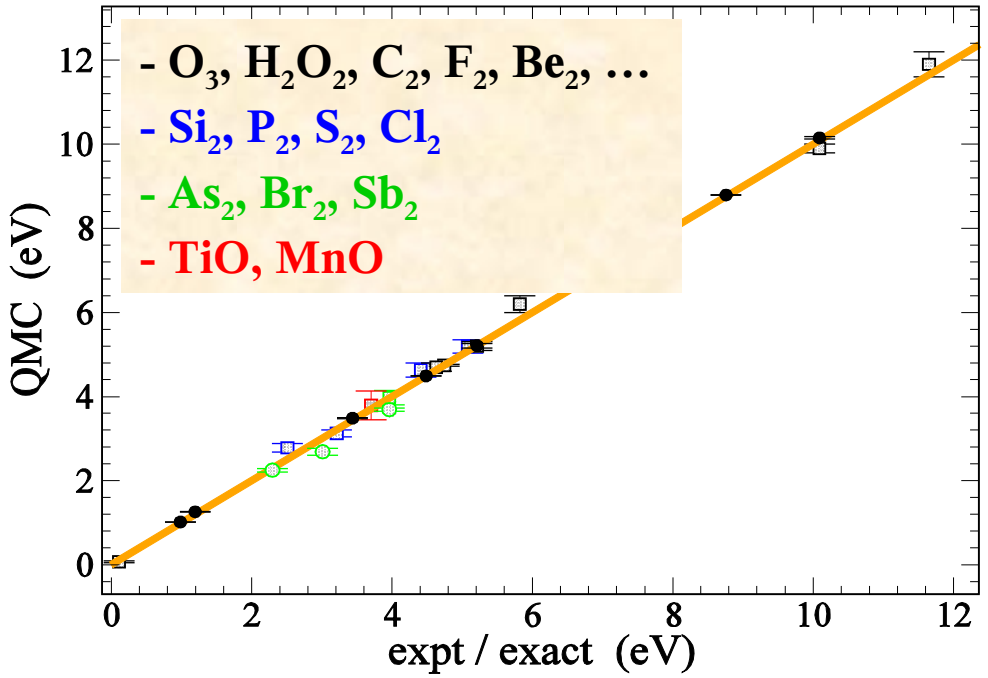
3 types of calc's:

- PW +psp:
- Gaussian/AE:
- Gaussian/sc-ECP:

N_{val} up to ~ 60

- All with single mean-field determinant as trial w.f.
- "automated" post-HF or post-DFT

Molecular binding energies



3 types of calc's:

- PW +psp:
- Gaussian/AE:
- Gaussian/sc-ECP:

N*val* up to ~ 60

- ~ 100 systems (also IP, EA, a_B, ω): eq. geom., moderate correlation
- Error < a few mHa (0.1 eV)
- Accuracy ~ CCSD(T) (gold standard in chemistry, but N^7)
- A QMC algorithm that complements DMC/GFMC
- reduced dependence on trial wf

- **Larger systems? strong correlation?**

Large extended systems

Cohesive energies: (eV/atom)

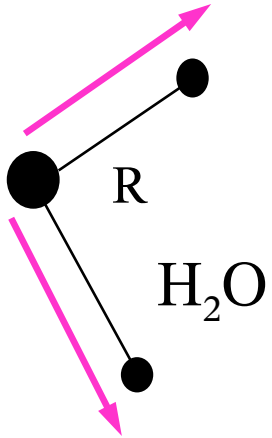
	diamond Si	bcc Na
LDA	5.086	1.21
DMC	4.63(2)	0.991(1) w/o CPP
		1.022(1) w/ CPP
present	4.59(3)	1.143(7)
expt.	4.62(8)	1.13

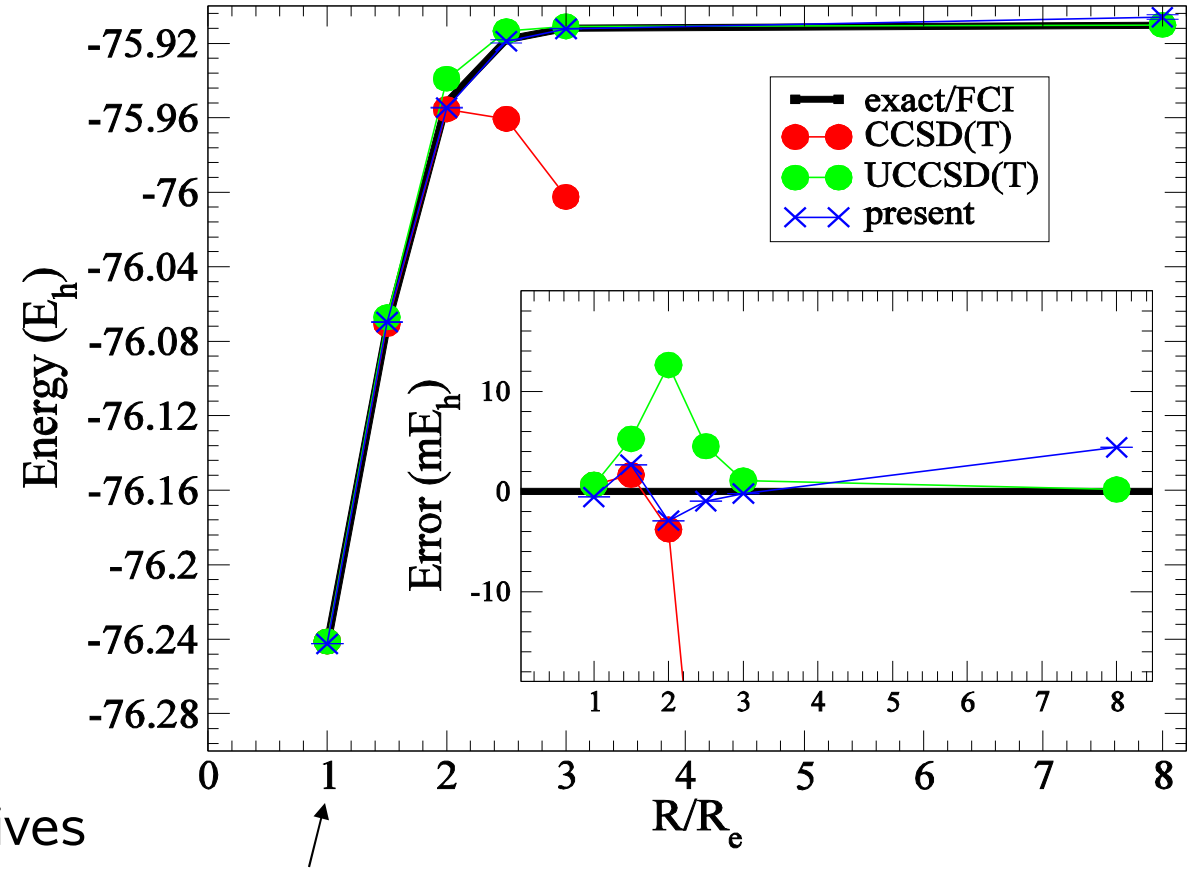
- **Na** (*preliminary*):
  - metal
  - new finite-size correction scheme
- plane-wave + pseudopotential calculations
- DMC -- Needs *et al* (Cambridge group)

Benchmark: H_2O bond breaking

Mimics increasing correlation effects:

(Quantum-chemistry-like calculation with **Gaussian basis**)





- CCSD(T) methods (excellent at eq.) have problems
- The new method gives more uniform accuracy (error < 4 mHa)

Equilibrium → **Dissoc. limit**

"bonding" ***"insulating"***

F_2 bond breaking

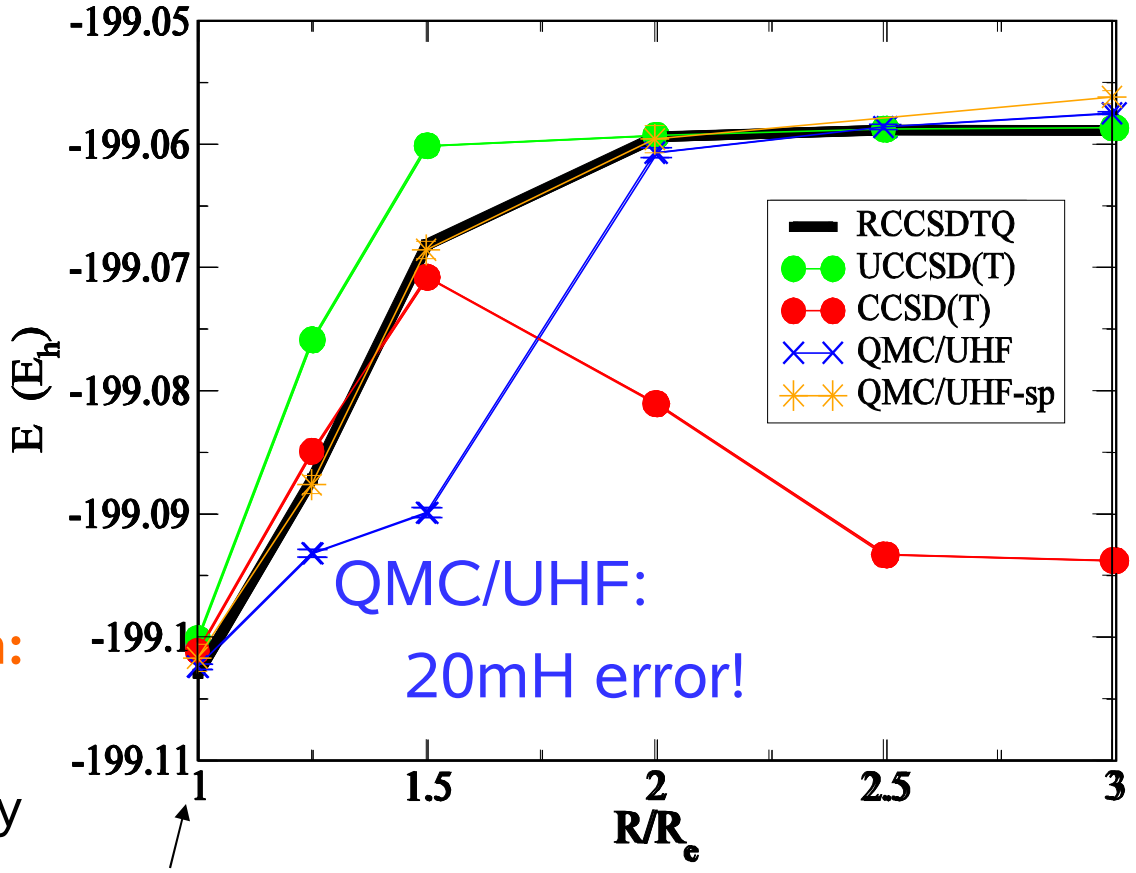
Mimics increasing correlation effects:

- UHF unbound.
  Nonetheless, large dependence on trial wf??

- **No. Spin-contamination:**
  - $|\Psi_{UHF}\rangle$: not eigenstate of S^2
  - low-lying triplet in F_2

- **Simple fix – spin-projection:**
  - Let $|\Psi^{(0)}\rangle = |\Psi_{RHF}\rangle$
  - HS preserves spin symmetry
  - each walker determinant:

  free of contamination



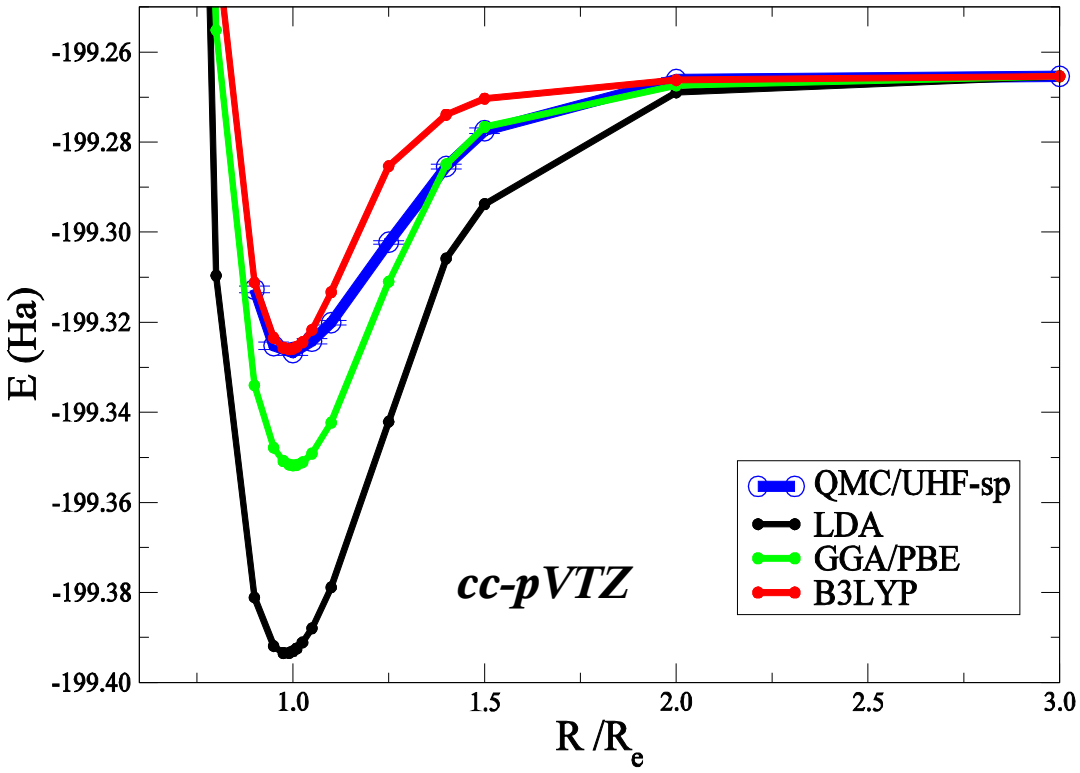
Equilibrium → **Dissoc. limit**

"bonding" ***"insulating"***

F_2 bond breaking --- larger basis

How well does DFT do?

- LDA and **GGA/PBE** well-depths too deep
- **B3LYP** well-depth excellent
- "Shoulder" too steep in all 3



C_2 potential energy curve

JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 19 15 NOVEMBER 2004

ARTICLES

Full configuration interaction potential energy curves for the $X^1\Sigma_g^+$, $B^1\Delta_g$, and $B'^1\Sigma_g^+$ states of C_2: A challenge for approximate methods

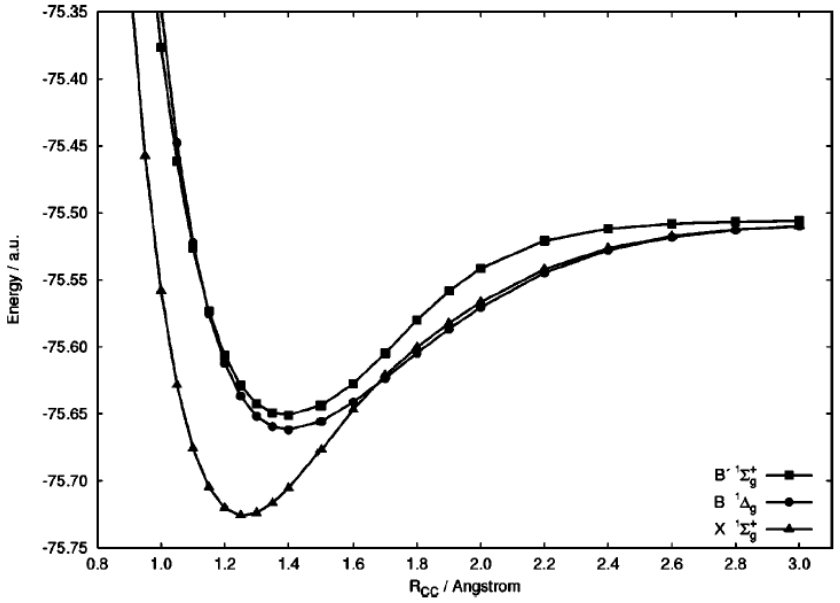
Micah L. Abrams and C. David Sherrill[a)]
Center for Computational Molecular Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

(Received 7 July 2004; accepted 17 August 2004)

The C_2 molecule exhibits unusual bonding and several low-lying excited electronic states, making the prediction of its potential energy curves a challenging test for quantum chemical methods. We

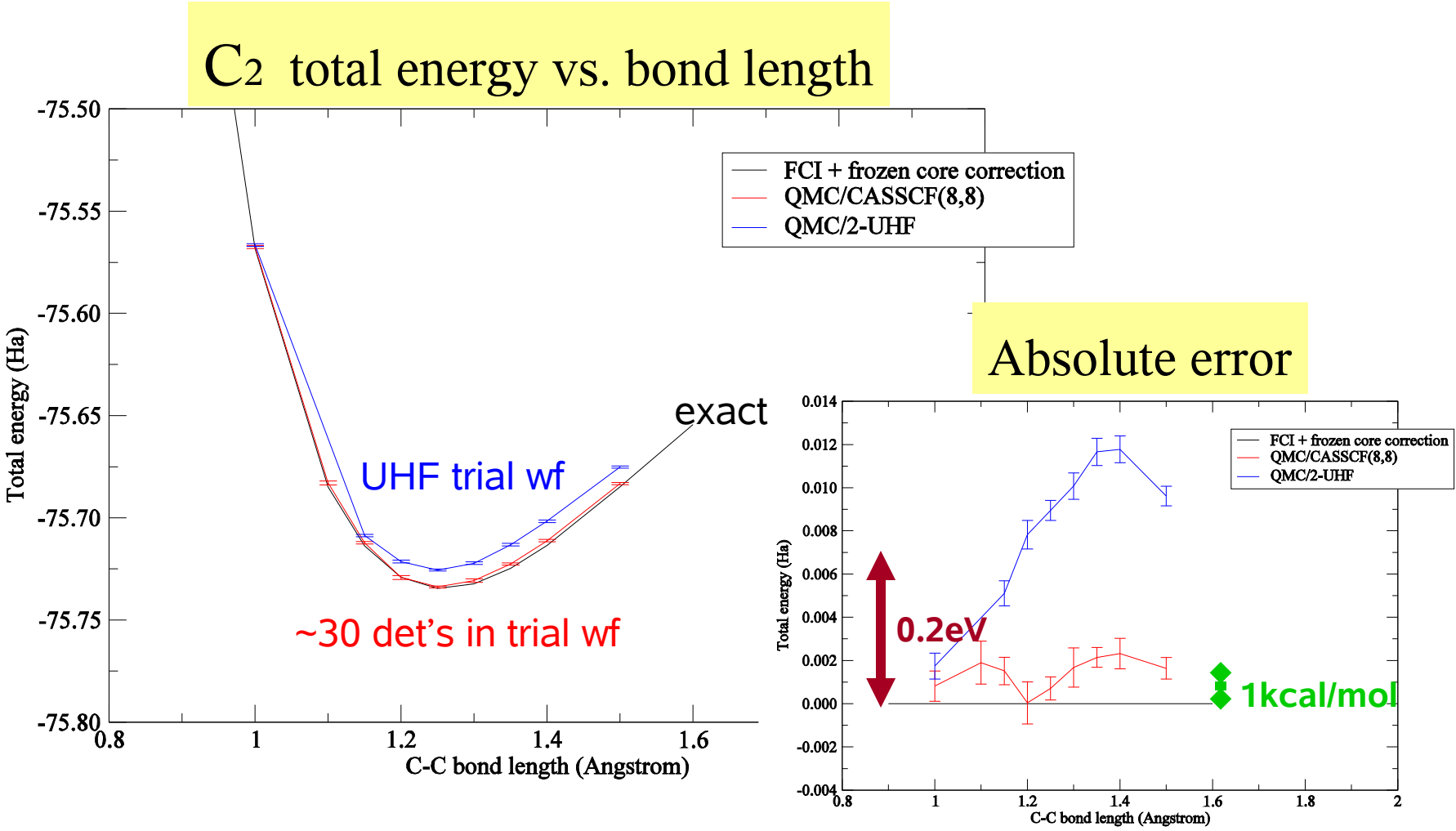
. . . .

benchmark results. Unfortunately, even couple
unrestricted Hartree–Fock reference exhibits l
ground state. The excited states are not accurat



C_2 potential energy curve

- QMC with multi-determinant MCSCF trial wf (*preliminary*)



Metal-insulator transition in H-chain

Stretching bonds in H_{50}:

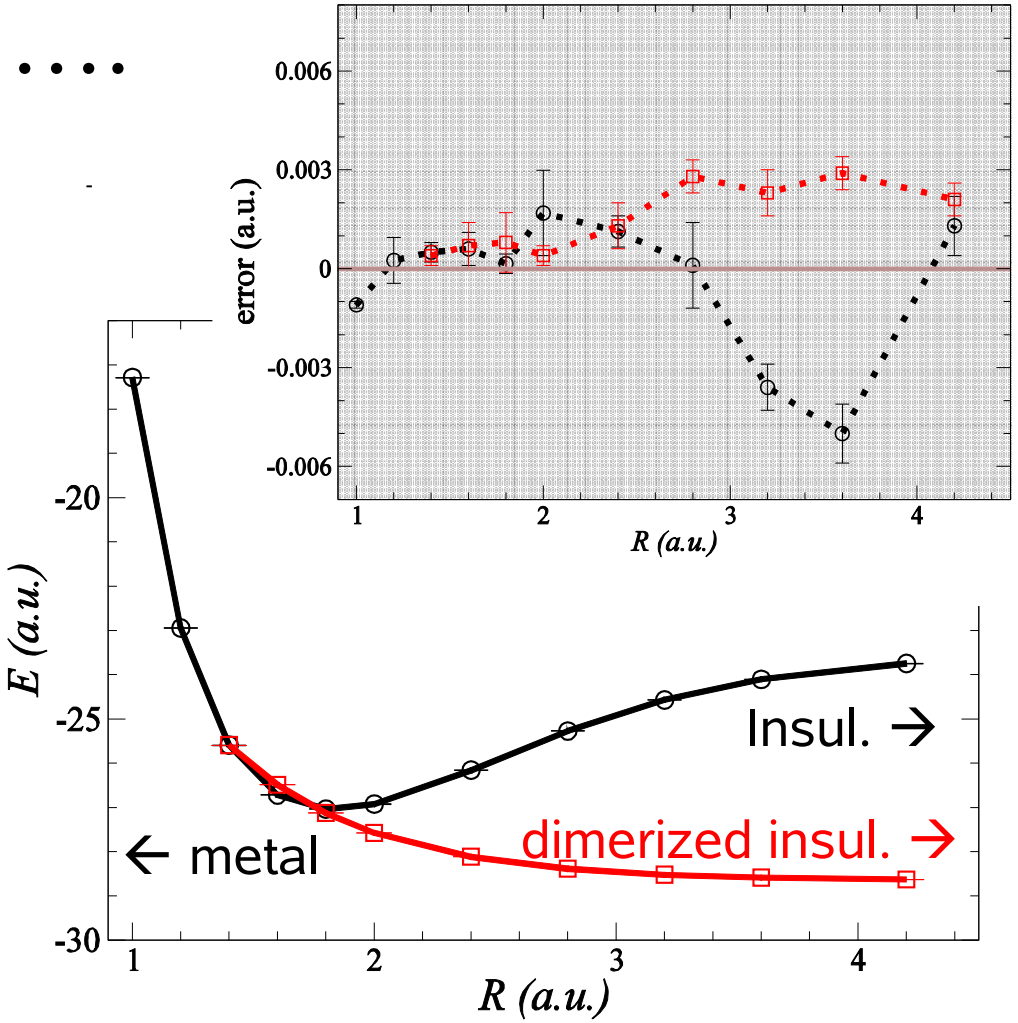
Symmetric: stretch each b

Asymmetric: stretch red bonds only

- Near-exact DMRG (solid lines)

  Chan *et. al.*, '06

- QMC agrees with DMRG to 0.002 eV/electron



Thanks:

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- Wissam Al-Saidi
- Chia-Chen Chang
- Henry Krakauer
- Hendra Kwee
- Wirawan Purwanto

Support:

- NSF, ARO, DOE-cmsn

Lecture Notes: (missing recent developments – see papers below)

- Shiwei Zhang, ``*Constrained Path Monte Carlo For Fermions*," in ``*Quantum Monte Carlo Methods in Physics and Chemistry*," Ed.M. P. Nightingale and C. J. Umrigar, NATO ASI Series (Kluwer Academic Publishers, 1998).
  (cond-mat/9909090: http://xxx.lanl.gov/abs/cond-mat/9909090v1)

- Shiwei Zhang, ``*Quantum Monte Carlo Methods for Strongly Correlated Electron Systems*," in ``*Theoretical Methods for Strongly Correlated Electrons*," Ed. by D. Senechal, A.-M. Tremblay, and C. Bourbonnais, Springer-Verlag (2003).
  (available at my website:
  http://www.physics.wm.edu/~shiwei/Preprint/Springer03.pdf)

Some references: (incomplete!)

In addition to the general QMC references from previous lectures:

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15. W. A. Al-Saidi, S. Zhang, and H. Krakauer, J. Chem. Phys. **124**, 224101 (2006)

What we have not covered (see references)

- Finite-T method (ref 8)
  - Model systems
  - Connection with PIMC
- Ground state method for boson systems (Ref 10))
- Back-propagation to calculate observables other than the energy (refs 7, 10)
- Finite-size correction for solids
  - Twist-averaging (k-point sampling) (Ceperley) easy to do
  - Two-body finite-size correction scheme (Kwee *et al*)
- Applications (Al-Saidi, Chang, Kwee, Purwanto, …)
  - Van der waals, post-d atoms & molecules, TM molecules, electron affinities, more bond-breaking, trapped atoms, ….

    (my website)

Summary

- New AF QMC approach: random walks in Slater det. space
  - Potentially a method to systematically go beyond independent-particle methods while using much of its machinery

    --- **superposition** of **independent-particle calculations**
  - Phaseless approximation (→ constrained path if sign problem)
  - Hybrid of real-space QMC and 'mean-field' methods
- Towards making QMC more robust, capable, black-box:
  - Benchmarks in ~ 100 systems (w/ increased correlation effects)
  - Simple trial wfs

    QMC 'recovery' ability important for strong correlation
  - accuracy seems systematic
- **Many opportunities** for further development
- and applications!