Quantum Monte Carlo methods at work for novel phases of matter

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cecam
Centre Européen de Calcul Atomique et Moléculaire

The sign problem & constrained path Monte Carlo methods

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The sign problem & constrained-path Monte Carlo methods

- Better methods for fermion systems: perhaps the most important problem in our field, and in computational physics in general. There are many challenges and opportunities.
  - "but this system has a sign problem ...." is only 1/2 a sentence, and less than 1/2 of the story!
  - new QMC frameworks (+ BIG computers) => opportunities for breakthroughs, for example, in the study of novel phases of matter

The sign problem & constrained-path Monte Carlo methods

- Better methods for fermion systems: perhaps the most important problem in our field, and in computational physics in general. There are many challenges and opportunities.
- Connections with last week:
  - What really is the sign problem?
  - Presently no "approximation-free" general solution. Contrast with bosons: solved! In the sense of classical simulations. (Prof. Troyer)
  - Constrained path/phase-free is a new framework: marrying auxiliary-field (Prof. Assaad) with diffusion MC (Prof. Holzmann)

Outline

- Interacting quantum matter -- a grand challenge:
  - ➢ Standard "first-principles" approach fails when interaction is strong: high-temperature superconductors, magnetic materials, ...
  - ➢ need method with: accuracy, computational scaling
- Constrained path (phase-free) MC: a new framework for simulating quantum fermion (and bose-fermi) systems
  - ➢ Why going to Slater determinant space can reduce the sign problem? How does the sign problem occur? How to control it?
  - ➢ How to formulate for general condensed matter systems?
- Applications
  - ➢ Hubbard models/optical lattice (SDW/FFLO; itinerant ferromag.)
  - ➢ molecules: quantum chemistry
  - ➢ "first-principles" electronic structure calculations in solids

Labs

Instructors: Hao Shi & SZ

- Lab 1 (Wed pm): Jie Xu
  - experimental Matlab code (more direct, and interactive)
  - Fermi Hubbard model
  - exercises range from basic exploration to advanced additions to the code (optional)
- Lab 2 (Th pm): Wirawan Purwanto
  - C++ code
  - Bose Hubbard model: AFQMC for trapped bosons
  - illustrates phase-free constraint which is crucial for calculations of realistic fermion systems (solids, chemistry)
  - exercises range from basic to advanced

Collaborators:

- Wissam Al-Saidi (Pittsburgh)
- Chia-Chen Chang (UC Davis)
- Simone Chiesa
- Henry Krakauer
- Hendra Kwee
- Fengjie Ma
- Wirawan Purwanto (lab2)
- Hao Shi (lab instructor)
- Yudistira Virgus
- Eric Walter
- Jie (Dorothy) Xu (lab1)

Support:

- ARO: optical lattice
- NSF: electronic structure; method development
- DOE ThChem: quantum chemistry
- DOE cmcsn network (Cornell, Rice, W&M)
- NSF PRAC: “Breakthrough QMC calculations on Bluewaters”
  11 members from UIUC, Cornell, MIT, Oak Ridge, ...

The complexity of quantum systems

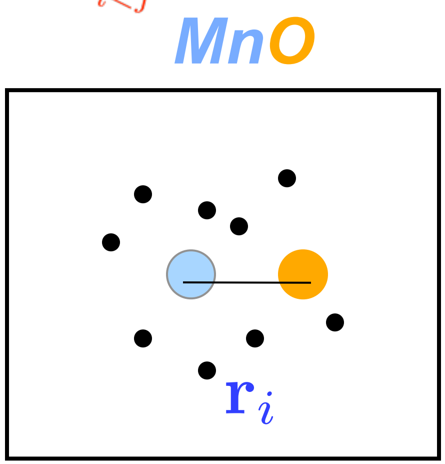
'Simple' theory --- Schrödinger Eq: (Focus on G.S.)

$$H\Psi = E\Psi$$

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

Why hard?

because V_{int} is not separable!



A major success in physics: V_{int} --> V_{mf}

e.g. Density functional theory

The "standard model" for quantum matter

- Density functional theory (DFT) with local-density types of approximate functionals: LDA, GGA, …. (Nobel, Kohn' 98)
- Many applications
- Independent-electron framework

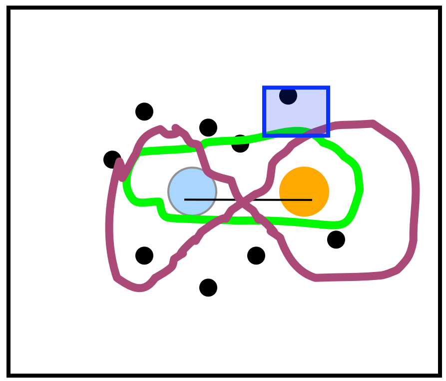
Electronic Hamiltonian: (Born-Oppenheimer)

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

LDA

$$H_{\mathrm{LDA}} = H_{1-\mathrm{body}} + \sum_{i=1}^{N} f_{\mathbf{c}}(n(r_i))$$

MnO



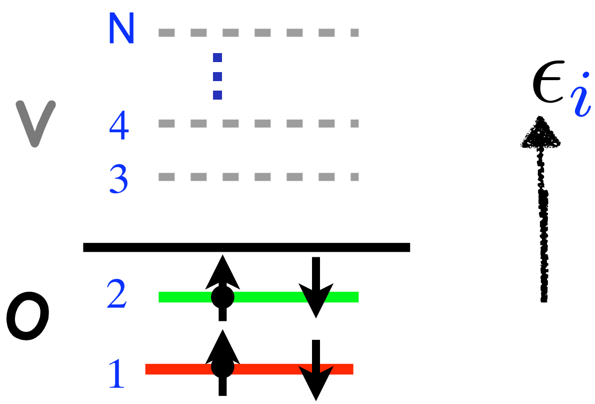
- Almost "routine" tool:

ABINIT, ESPRESSO, GAMESS, Gaussian, VASP, ….

Independent-electron solution

Can always solve 1-body problem: (e.g., grid, Gaussians, ...)

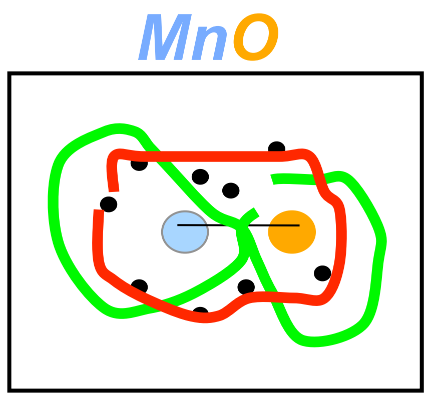
simply occupy levels for many-body solution:



The solution looks like:

$$\begin{pmatrix} \psi_1 & \psi_1 \\ \psi_2 & \psi_2 \\ \cdot & \cdot \\ \cdot & \cdot \\ \psi_N & \psi_N \end{pmatrix}$$

Slater det. - antisymmetric

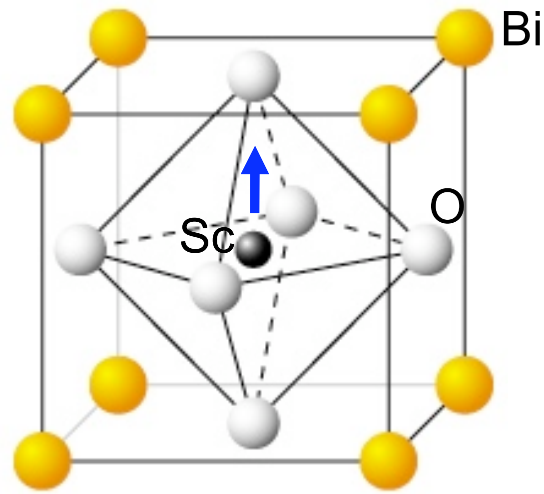


“The standard model” doesn’t always work

- Often incorrect in strongly correlated systems
  - high T_c
  - magnetic systems (spintronics)
  - low dim./nano
  - ...

  e.g., NiO is insulating, but is predicted to be metallic

- Even in moderately-correlated systems, small errors can make qualitative differences



typical DFT error of 1% in lattice cnst

→ no ferroelectricity

Why "the standard model" doesn't always work

"Mean-field" approach: How long does it take to drive A -> B?

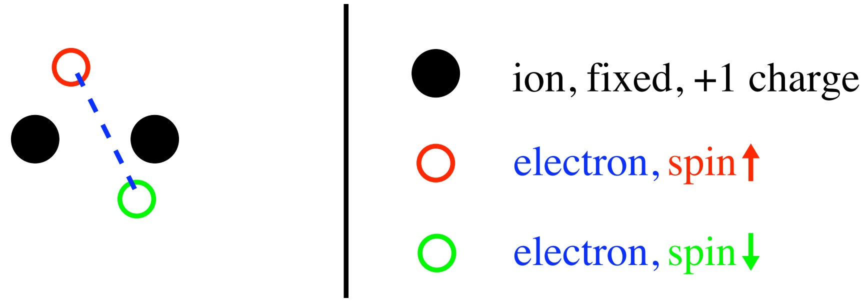
- Williamsburg traffic: yes
- Beijing traffic: no

  (interaction effect strong)

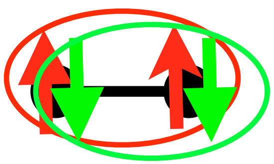
Toy system: Hubbard model

To make connection with CM models, and optical lattices

H_2 molecule:

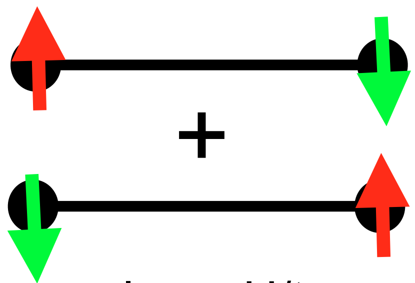


tight binding/minimal basis => 1-band Hubbard model with U/t



small U/t

* 1 determinant



large U/t

* multi determinants
* correlation
* note ‘antiferromagnetism’

The Hubbard model

- ✦ simplest many-body model
- ✦ describe high-Tc SC?

  10,000 papers since '87

- ✦ To solve on GO board:

  "DFT" ("standard model" in CM):

  361×361 matrix

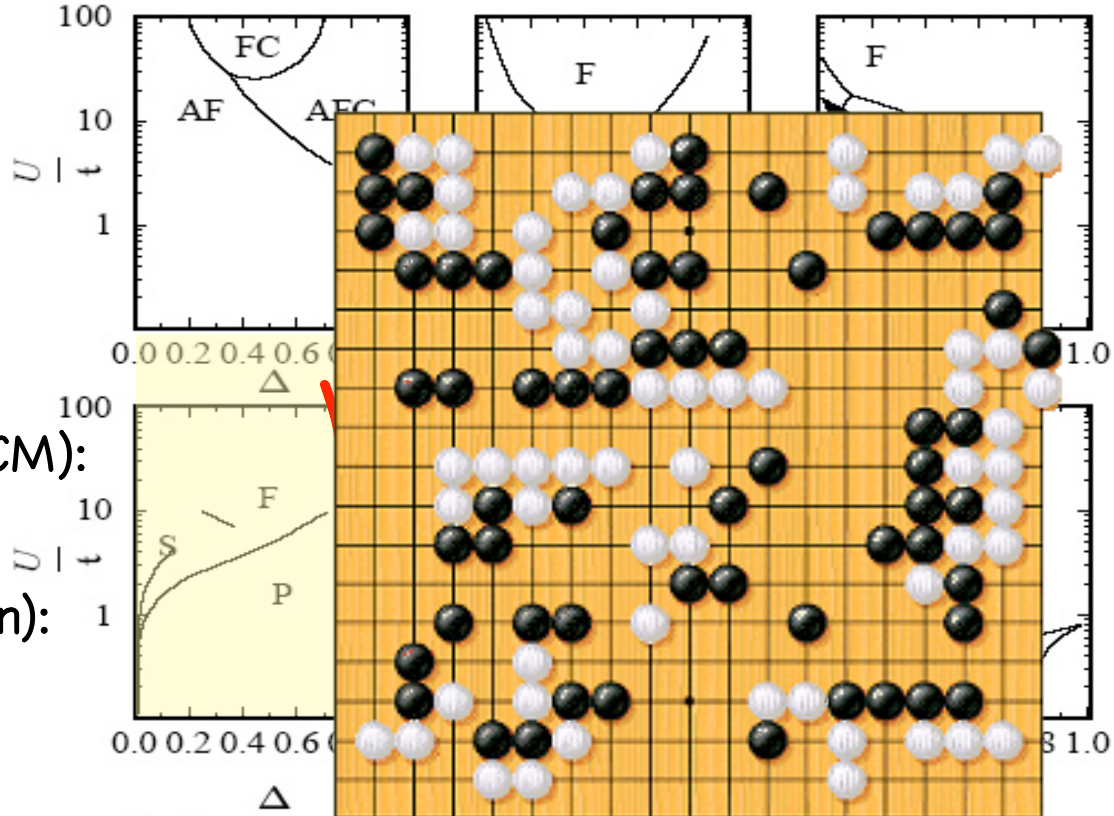
  Many-body (treat correlation):

  $10^{214} \times 10^{214}$ matrix

- ✦ Six (!) possible phase diagrams:

  (ground state)

- ✦ optical lattice emulators?



F=Ferromagnetic
FC=Short-range ferromagnetic correlations
AF=Antiferromagnetic
AFC=Short-range antiferromagnetic correlations
P=Paramagnetic
FI=Ferrimagnetic
IC=Incommensurate, S=Spiral
G=Correlated state of Gutzwiller type

--- From textbook by Mardar

Challenges of the quantum theory

"The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"

--- Paul Dirac, 1929

Solve by simulations?

Classical statistical mechanics: most problems cannot be solved analytically (Ising), but modern MC and MD allow us to solve most classical problems (except turbulance etc) by computer simulations!

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Recall: Monte Carlo methods

We will use two things which are foundations to QMC

1) Monte Carlo is great at evaluating many-dimensional integrals (beyond d>4~6, the only game in town?)

2) Monte Carlo can solve integral equations via random walks

1) Monte Carlo integration

To evaluate many-dimensional integral $G = \int_\Omega f(x) g(x) dx$

$f(x) > 0; \quad \int_\Omega f(x) dx = 1$

$f(x)$: probability density

- Sampling a PDF $f(x)$ means obtaining a sequence $\{x_1, x_2, \cdots, x_i, \cdots\}$ so that

$$\text{Prob}\{x_i \in (x, x + dx)\} = f(x) dx$$

i.e., the probability distribution of the sequence is $f(x)$

- If $f(x)$ is successfully sampled, then $\quad G_M \equiv \frac{1}{M} \sum_{i=1}^{M} g(x_i) \quad \to G$

2) Random walks to solve integral equations:

- An integral equation of the form

$$\Psi'(x) = \int_\Omega G(x,y)w(y)\Psi(y)dy$$

can be viewed as a random walk (transport problem)

- For example,

$$\Psi'(x) = \int_{-\infty}^{\infty} \frac{1}{\sqrt{\pi}} e^{-(x-y)^2} \sqrt{2} e^{-\frac{1}{2}y^2} \Psi(y)dy$$

conditional prob. for particle to jump to x if it is currently at y

"birth/death" at y

prob. for particle to be at y

Q: What is the resulting prob. distribution of particles?

Overview of quantum Monte Carlo

QMC methods *loosely* divide into two catagories according to primary applications:

	Continuum	**Lattice**
Applications	• electronic structure • quantum chemistry • ^{3}He • few-body nuclei	• correlated electron models • nuclear shell model • quantum field theory

cross-fertilization: Sorella et al; SZ et. al.

Algorithm	**Diffusion MC**	**auxiliary-field/projector QMC**
Description	- random walks - 1st quantized form - in configuration space	- auxiliary-fields - 2nd quantized form
Sign problem	fixed-node approximation	constrained path MC ←

SZ, cond-mat/9909090: http://xxx.lanl.gov/abs/cond-mat/9909090v1

Overview of quantum Monte Carlo

QMC methods *loosely* divide into two catagories according to primary applications:

	Continuum	**Lattice**
Applications	• electronic structure • quantum chemistry • ^{3}He • few-body nuclei	• correlated electron models • nuclear shell model • quantum field theory
	FINITE-TEMPERATURE:	
Algorithm	**Path-Integral MC**	**QMC/BSS**
Description	- Mapping to classical ring-polymer system.	- related to above - grand canonical ensemble
Sign problem	restricted path appr.	"new" finite-T method ←

SZ, cond-mat/9909090: http://xxx.lanl.gov/abs/cond-mat/9909090v1

Constrained path MC: basic formalism

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

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

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

(1) We have seen the time evolution operator $U(t_0,t)\equiv\exp(-iH(t-t_0)/\hbar)$ and its matrix representation in x-space, $K(x',t;x,t_0)$. Here we will study the *imaginary-time* evolution operator and its propagator. Specifically, we consider the operator $\exp(-\beta H)$ (β is real) and its matrix representation $K(x',x;\beta)\equiv\langle x'|\exp(-\beta H)|x\rangle$ for a one-dimensional system with the Hamiltonian

$$H=\frac{p^2}{2m}+V(x).$$

For convenience let us set $\hbar=m=1$.

<- HW problem in QM

http://physics.wm.edu/~shiwei

1. Show that

$$K(x',x;\beta)=\sum_n e^{-\beta E_n}\phi_n^\star(x')\phi_n(x),$$

where E_n is an energy eigenvalue and $\phi_n(x)$ is the corresponding eigenfunction. The sum is taken over the complete set of n.

2. Show that the operator $\exp(-\beta H)$ projects out the ground state $|\phi_0\rangle$ from *any* initial state that is not orthogonal to the ground state. That is, given an arbitrary $|\psi^{(0)}\rangle$ that satisfies $\langle\psi^{(0)}|\phi_0\rangle\neq 0$, we have

$$\lim_{\beta\to\infty}\exp[-\beta(H-E_0)]|\psi^{(0)}\rangle\propto|\phi_0\rangle.$$

3. Show that, for a short imaginary-time $\Delta\tau$ (>0),

next →

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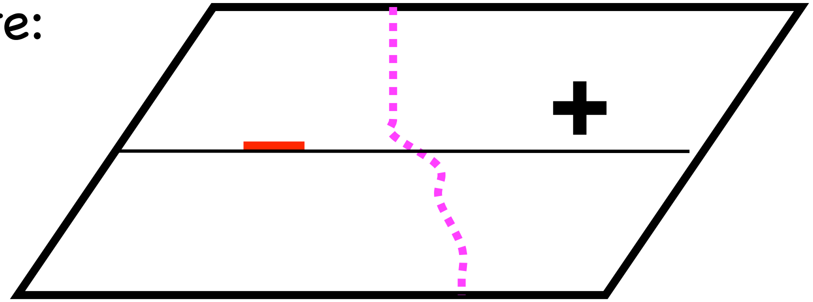
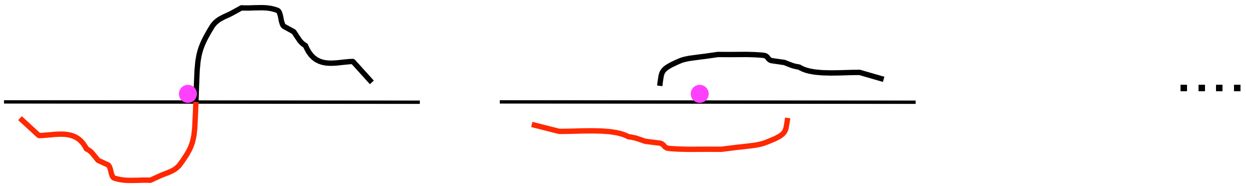
Why marrying DMC with AF methods?

Recall sign problem in diffusion MC:

1 particle, first excited state:



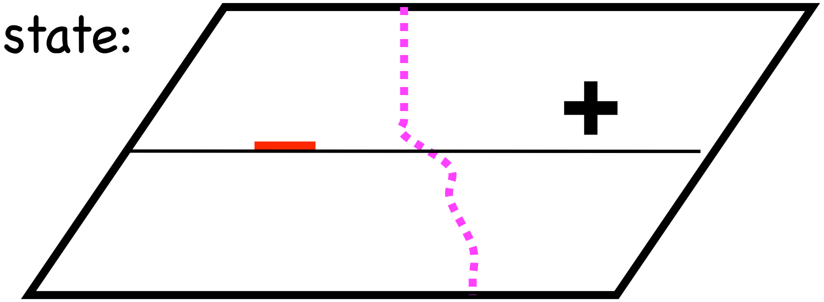
In real-space QMC, we need + and − walkers to cancel



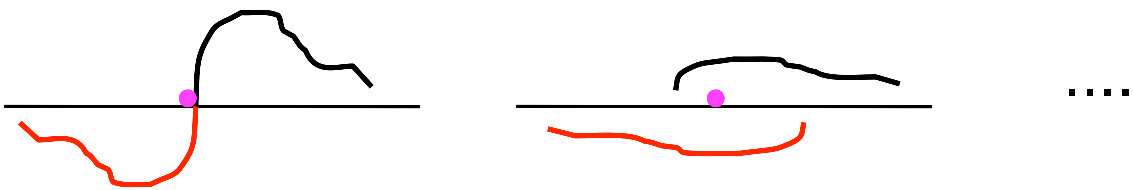
Why marrying DMC with AF methods?

Sign problem – leading obstacle in QMC!

1 particle -- first excited state:

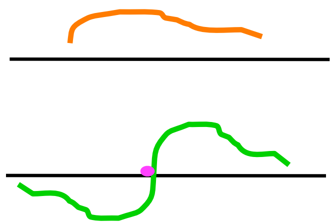


In QMC, we need + and − walkers to cancel



2 fermions -- ground state: same problem

Fermion 1:



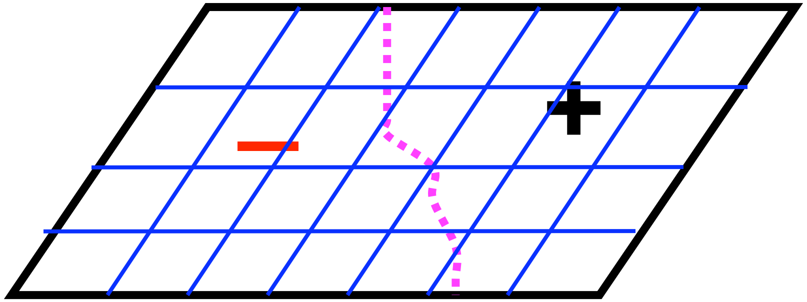
Fermion 2:

Sign problem – a fight against global bosonic state

Why marrying DMC with AF methods?

Recall sign problem:

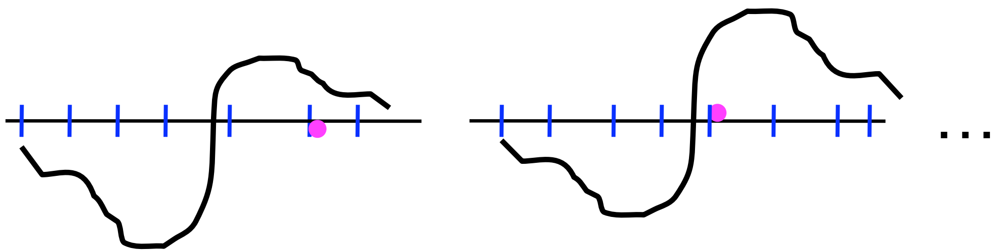
1 particle, first excited state:



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

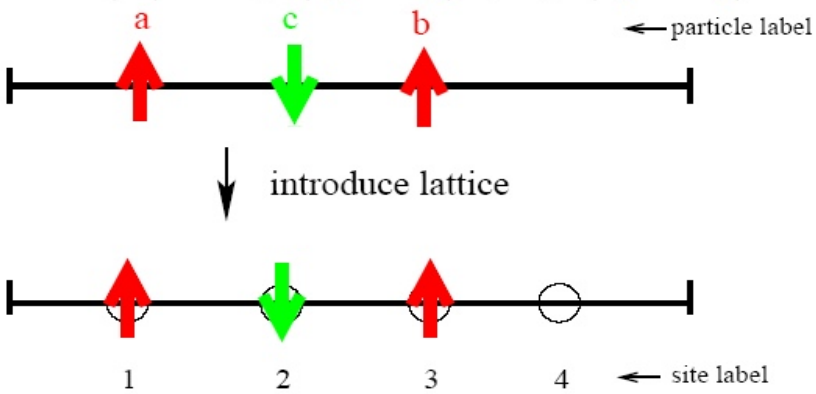
No sign problem

Why marrying DMC with AF methods?

Many particles?

A toy problem – trapped fermion atoms (1-D Hubbard, BC=box)

- 3 fermions in a box, two with ↑ spin and one with ↓ spin; contact interaction $V(R) = a_s\delta(r_a - r_c) + a_s\delta(r_b - r_c)$ (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; $U \propto a_s$

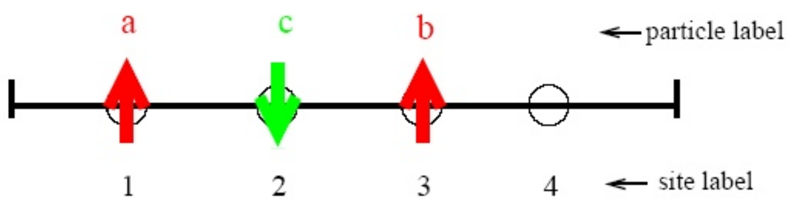
Toy problem – trapped fermions

What is the ground state when U=0 ?

– Diagonalize H directly:

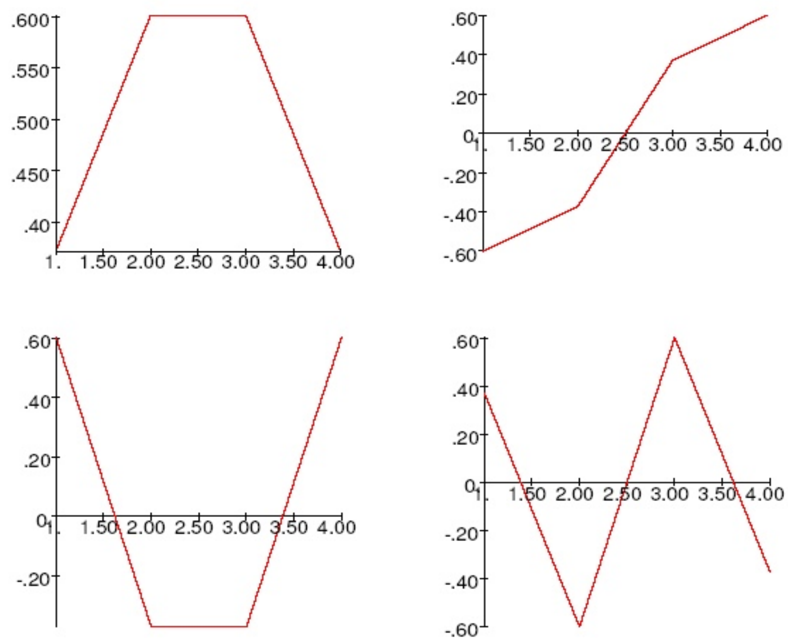
Single-particle Hamiltonian

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



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:

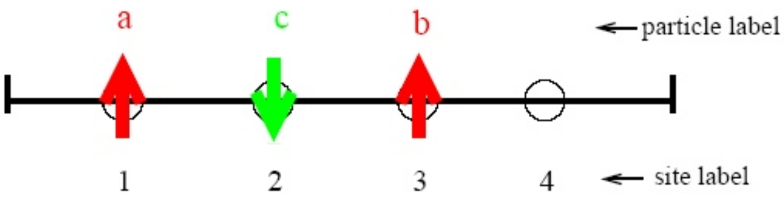
$$\begin{bmatrix} .3717480339 & -.6015009557 \\ .6015009541 & -.3717480349 \\ .6015009553 & .3717480339 \\ .3717480350 & .6015009543 \end{bmatrix} \cdot \begin{bmatrix} .3717480339 \\ .6015009541 \\ .6015009553 \\ .3717480350 \end{bmatrix}$$

Toy problem – trapped fermions

What is the ground state when U=0 ?

- Diagonalize H directly

- Alternatively, power method:



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

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:

> $(v0, v1) = \text{Multiply}(\text{P}(10.), PsiT)$

$$\begin{bmatrix} .8666091211999999999 & -.00006365980000000043740 \\ 1.4022030132999999986 & -.00003934309999999777598 \\ 1.4022030135999999988 & .00003934340000000025819 \\ .8666091210999999991 & .00006365969999999961000 \end{bmatrix}$$

```
> GramSchmidt({v0,v1},normalized);
```

{[-.6015041283, -.3717422466, .3717450812, .6015031834], [.3717488488, .6015014581, .6015004522, .3717472200]}

Same as from direct diag.:

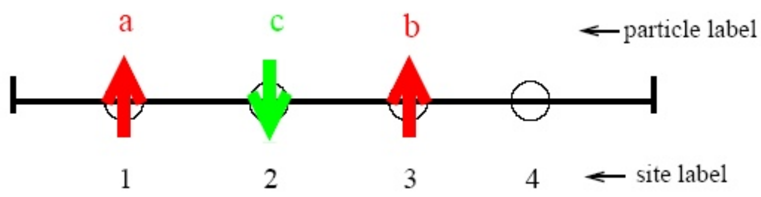
```
ground-state wf:
```

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

Toy problem – trapped fermions

What is the ground state when U=0 ?

- Diagonalize H directly



- Alternatively, power method:

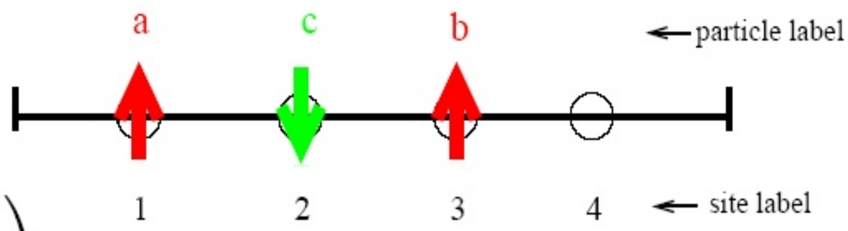
$$e^{-\tau H}: \quad \Big(\ 4 \times 4\ \Big) \otimes \Big(\ 4 \times 4\ \Big) \equiv B_K \ \text{operate on any } |\Psi^{(0)}\rangle \text{ repeatedly} \quad \Rightarrow |\Psi_0\rangle$$

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

-> Eliminates 'sign problem' in all non-interacting systems!

Toy problem – trapped fermions

Properties of Slater determinants:



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

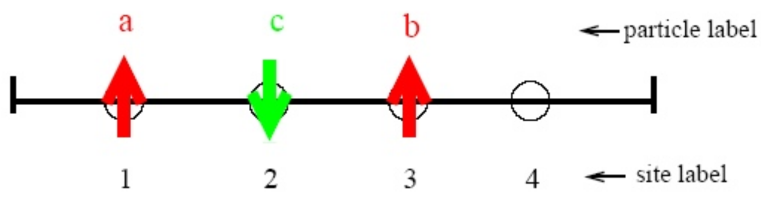
- What is the probability to find the electron configuration shown in the picture? That is, how to calculate $\langle R|\phi\rangle$?
- How to calculate $E_0 = \langle\phi|H|\phi\rangle$ from the wave function?
- How to calculate the density matrix? The spin-spin correlation function?

A: Simple matrix manipulations (See Lab exercises)

Toy problem – trapped fermions

What is the ground state when U=0 ?

- Diagonalize H directly



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

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

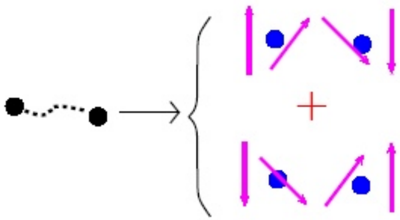
Yes, with Hubbard-Stratonivich transformation

Why marrying DMC with AF 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'):

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



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

- Illustration of HS transformation — Hubbard-like interaction:

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

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

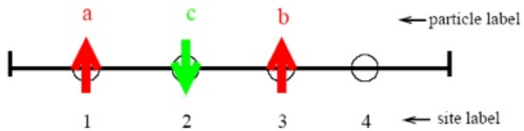
Or trick by Hirsch:

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

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

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

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

- With U, same as U=0, except for integral over $\mathbf{x}$ → Monte Carlo

New AF QMC framework

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:

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

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

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

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

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

iteration →

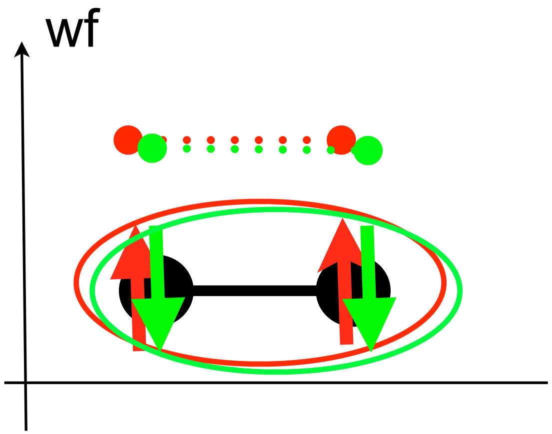
Exact so far (why don't we use path-integral formalism? later)

next →

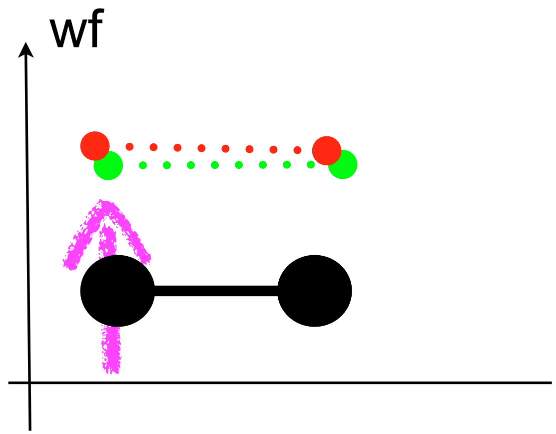
2-site Hubbard model

Illustration of how the new formulation of AFQMC works:

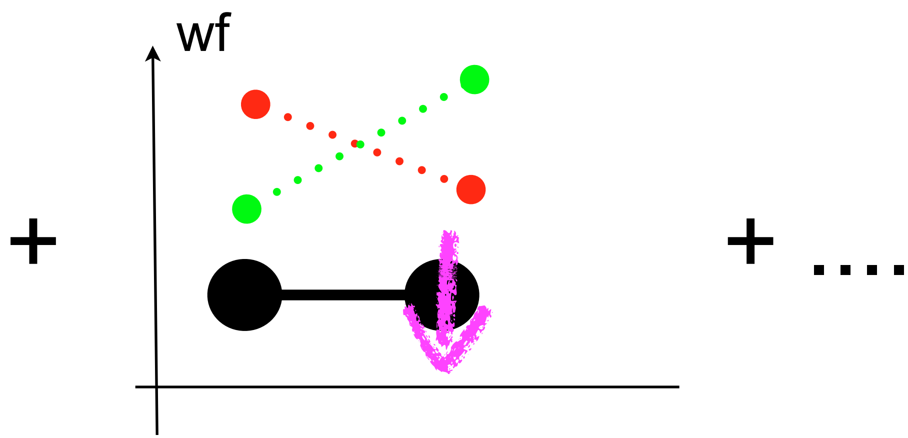
H_2 molecule



mean-field



auxiliary-field QMC



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 $\boxed{B(\mathbf{x})|\phi\rangle = |\phi'\rangle}$

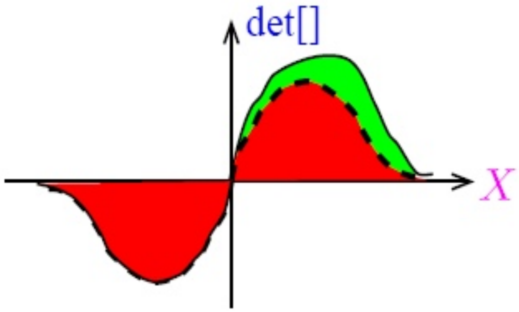
Many-dim integral can be done by Monte Carlo: $\dfrac{\int O_{\mathrm{Gr}}(X) p(X) \det[X] dX}{\int p(X) \det[X] dX}$ $\qquad X \equiv \{\mathbf{x}^{(l)}\}$

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.

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 $\leftarrow \{G_{ij}\}$

Some “lingo” from mean field

- Electronic Hamiltonian: (Born-Oppenheimer)

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

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:

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

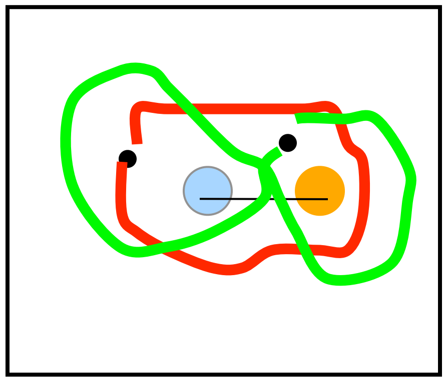
- A Slater determinant:

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

N : basis

M : electrons

MnO



Outline

- Interacting quantum matter -- a grand challenge:
  - ➢ Standard "first-principles" approach fails when interaction is strong: high-temperature superconductors, magnetic materials, ...
  - ➢ need method with: accuracy, computational scaling
- Constrained path (phase-free) MC: a new framework for simulating quantum fermion (and bose-fermi) systems
  - ➢ Why going to Slater determinant space can reduce the sign problem? How does the sign problem occur? How to control it?
  - ➢ How to formulate for general condensed matter systems?
- Applications
  - ➢ Hubbard models/optical lattice (SDW/FFLO; itinerant ferromag.)
  - ➢ molecules: quantum chemistry
  - ➢ "first-principles" electronic structure calculations in solids

Slater determinant random walk (preliminary II)

HS transformation:

For example in electronic systems:

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

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

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

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

derive

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

$$\nwarrow \; \sum_i c^\dagger_{\mathbf{G}_i+\mathbf{Q}} c_{\mathbf{G}_i}$$

'density' decomposition

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

Slater determinant random walk (preliminary II)

HS transformation:

more generally Cholesky decomposition

$$V_{ijkl} \doteq \sum_{\nu=1}^{J_{\max}} L_{ij}^{\nu} \, L_{kl}^{\nu}$$

can be realized with N^3 cost,

with Jmax typically 4--8*N

Summary: AF QMC framework

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:

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

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

apply 1-body propag.

$|\phi^{(0)}\rangle \longrightarrow |\phi^{(1)}(\sigma)\rangle \;\; \to |\phi\rangle$

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

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

iteration

Exact so far (why don't we use path-integral formalism? later)

next →

Connection with DMC

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

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

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

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

$$e^{-\tau\hat{H}} = \int e^{-\vec{\sigma}^2/2}\, e^{i\hat{P}\cdot(\gamma\,\vec{\sigma})}\, d\vec{\sigma}\;\, e^{-\tau\hat{V}}$$

$\vec{\sigma}$: $3M$-dim vector

translation op.

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

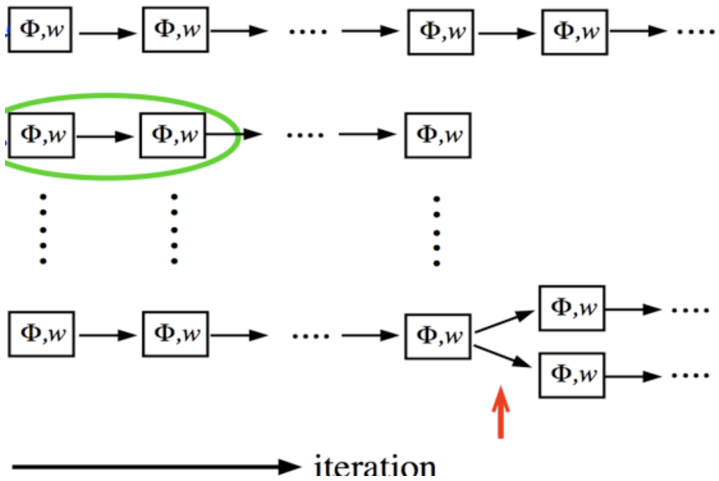
$$|\Psi^{(0)}\rangle \xrightarrow{\quad e^{-\tau H} \quad} |\Psi^{(1)}\rangle \;\; .... \;\; \rightarrow |\Psi_0\rangle$$

$|R^{(0)}\rangle$ —— multiply weight by $e^{-\tau V(R^{(0)})}$; sample $\vec{\sigma}$ from Gaussian; translate $R^{(0)}$ by $(-\gamma\vec{\sigma})$ ——→ $|R^{(1)}\rangle$ $\rightarrow |R\rangle$ diffusion + branching

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

Summary: AF QMC framework

Structure -- loosely coupled RWs of non-orthogonal SDs:



A **step** advances the SD by 'matrix multiplications'

$$e^{\sigma \hat{v}} \begin{pmatrix} \psi_1 & \psi_1 \\ \psi_2 & \psi_2 \\ . & . \\ . & . \\ \psi_N & \psi_N \end{pmatrix} \rightarrow \begin{pmatrix} \psi'_1 & \psi'_1 \\ \psi'_2 & \psi'_2 \\ . & . \\ . & . \\ \psi'_N & \psi'_N \end{pmatrix}$$

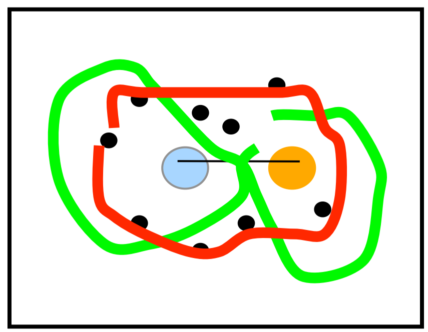
NxN matrix

1-body op

Gaussian, or 'Ising' variable

N is size of 'basis'

MnO



Importance sampling -> better efficiency

Summary: AF QMC framework

How does the weight 'w' come about?

$$\Phi = U{\color{red}D}{\color{green}V}$$

Difference between branching random walk (w) and the standard AFQMC is like that between DMC and path-integral ground state

Importance sampling can be formulated in branching random walk framework (CPMC)

Pairing importance fcn: illustration in Fermi gas

- The unitary Fermi gas: the electron gas, but with $\frac{1}{r_{ij}} \rightarrow -g\delta(r_{ij})$

g	small	unitarity	large
2-body scattering length	<0	infinity	>0
physics	BCS	S.C	BEC of molecules

Experimental measurement of ξ :

0.32(+13)(−10) [9]
0.36(15) [10]
0.51(4) [11]
0.46(5) [12]
0.46(+05)(−12) [13]
0.435(15) [14]
0.41(15) [15]
0.41(2) [16]
0.39(2) [16]
0.36(1) [17]

compiled by D.Lee, 2011

Take $\rho \rightarrow 0$:

no other scale in the system =>

$$E_0 = \xi E_{FG}$$

universal constant:
HF --> 1
BCS --> 0.59

HF wrong (strong corr.!)
int. E/E_k --> 0 as r_s grows
E_H->0, E_{xc}~-0.6E_k

next →

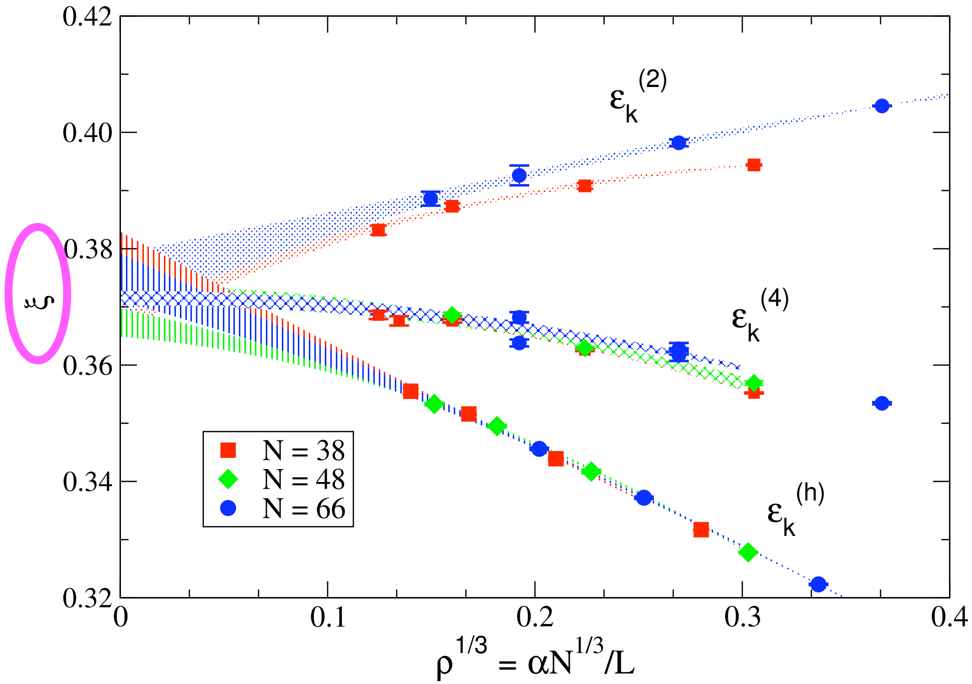
Pairing importance fcn: illustration in Fermi gas

- We have formulated the use of BCS or AGP as trial wf in AFQMC

Need $\langle \Psi_{\rm AGP} | c_i^\dagger c_j | \phi \rangle$ and $\langle \Psi_{\rm AGP} | c_i^\dagger c_j | \phi \rangle$ (**Sorella in DMC**)

Both can be done (**Carlson, Gandolfi, Schmidt, SZ: arXiv:1107.5848**)

same scaling as single Slater determinant



AFQMC has no sign problem in this case

Exact result:

$$\xi = 0.372(5)$$

- new MIT expt (Zwierlein group):

$$0.376(5)$$

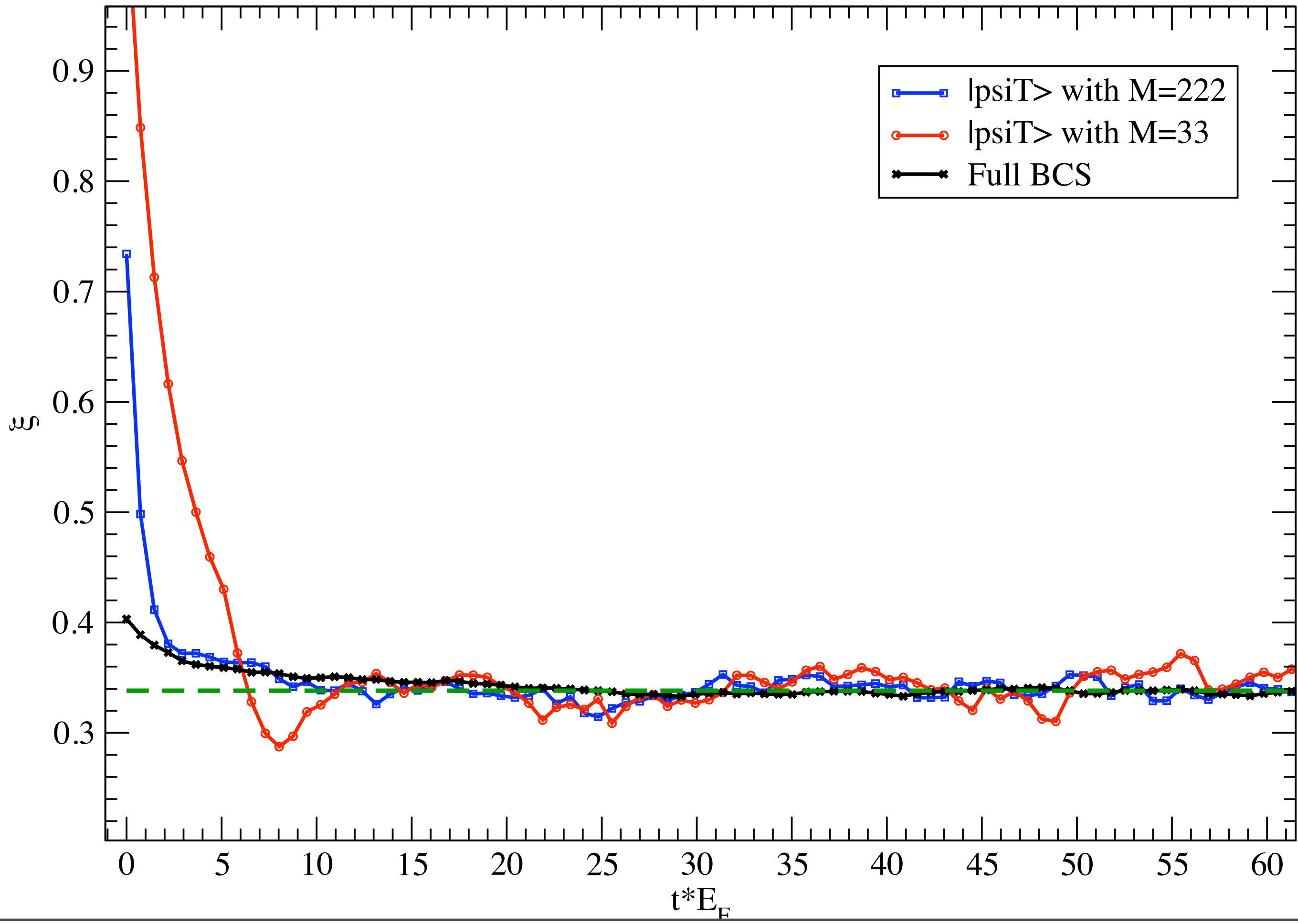
arXiv:1110.3309

next →

Pairing importance fcn: illustration in Fermi gas

- The use of successively better trial wfs as importance function:

Energy vs. projection time



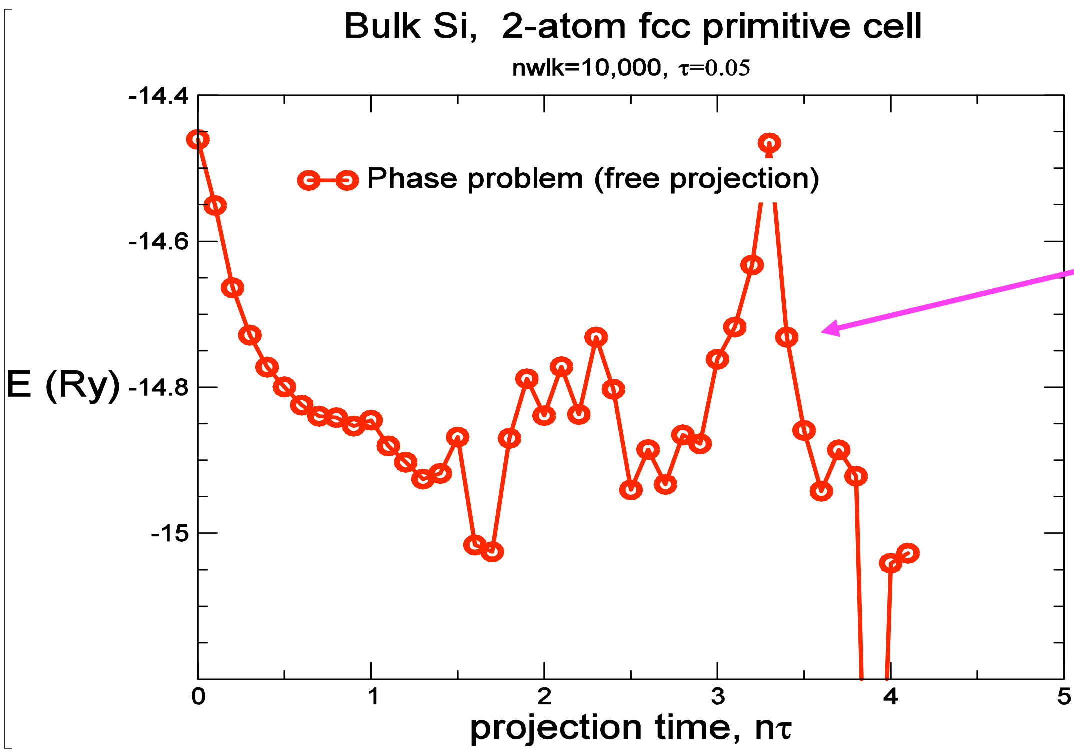
8x8x8

N=14

U=unitarity

Summary: AF QMC framework

Exact, ... but sign problem:



Exponential noise

See p.w. example

$\hat{\mathbf{v}}(\sigma)$ is complex

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

In fact, for general (1/r) interaction, a phase problem

next →

Outline

- Interacting quantum matter -- a grand challenge:
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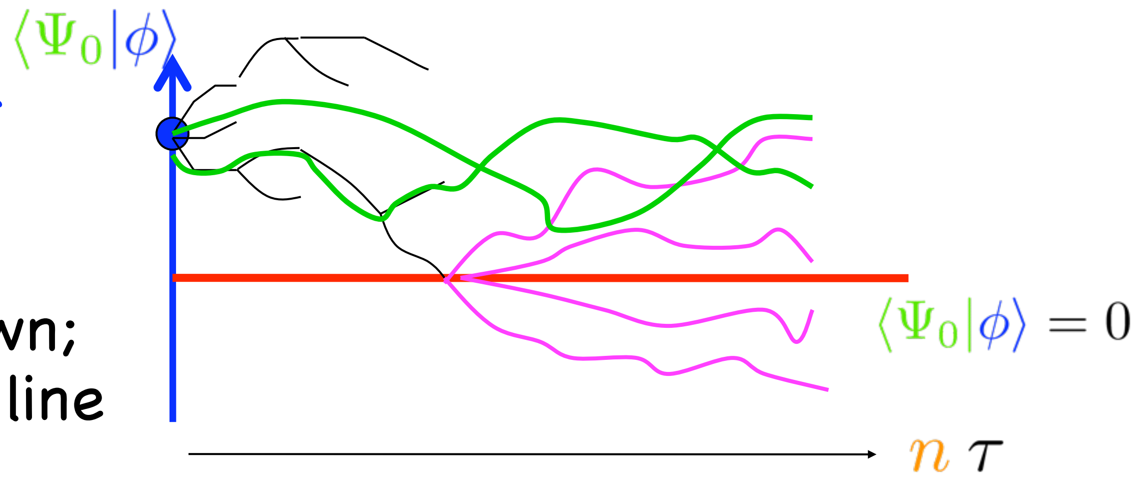
The sign problem

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

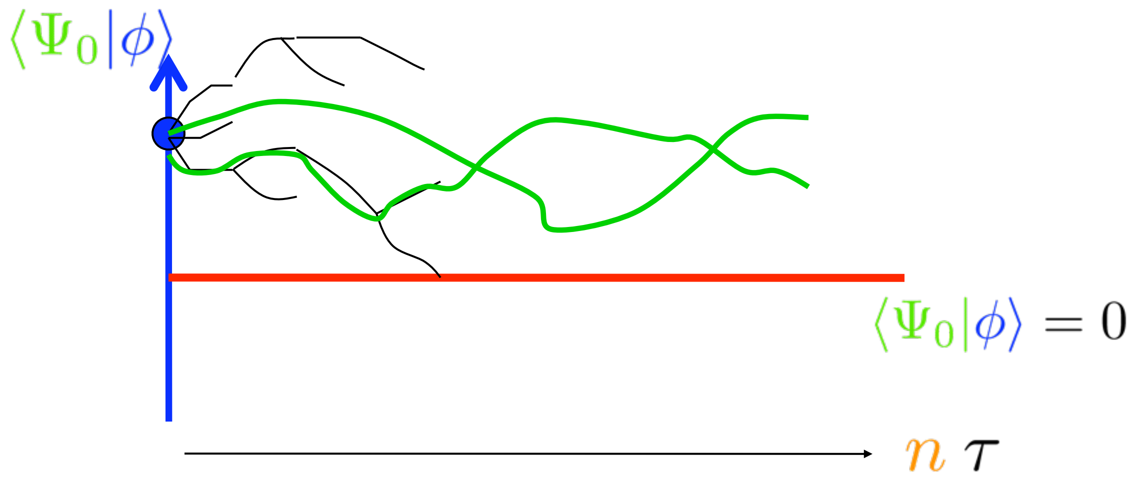
- MC signal is exponentially small compared to noise

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

Zhang, Carlson, Gubernatis, '97

Zhang, '00

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

Trial wave function used to make detection

- Phaseless approximation

Zhang & Krakauer, '03; Chang & Zhang, '08

general interaction: complex HS --> phase problem

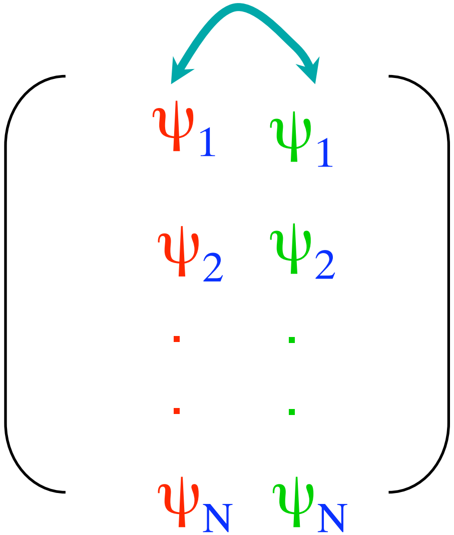
twisted boundary condition: removes shell effects --> complex w.f.

next →

The sign problem

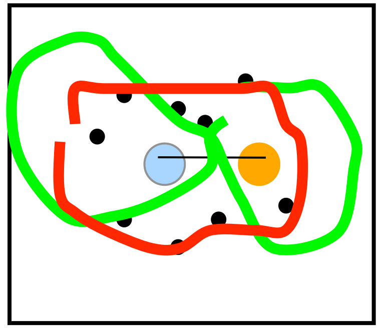
Sign problem is due to --

"superexchange":



Slater det. - antisymmetric

MnO



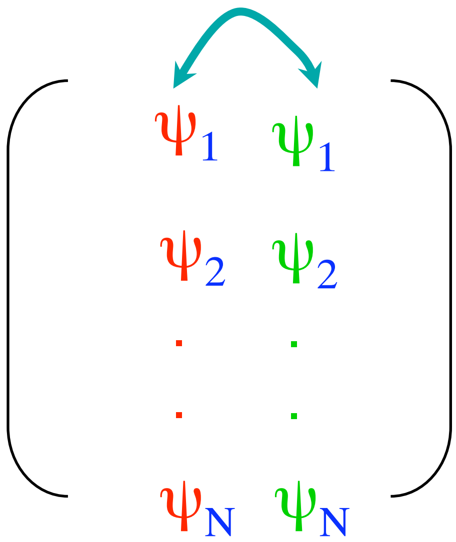
To eliminate sign problem:

Use $\langle \Psi_T | \Psi \rangle = 0$ to determine if **"superexchange"** has occurred

The sign problem

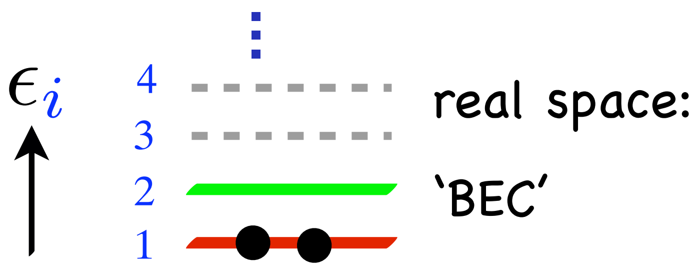
Sign problem is due to --

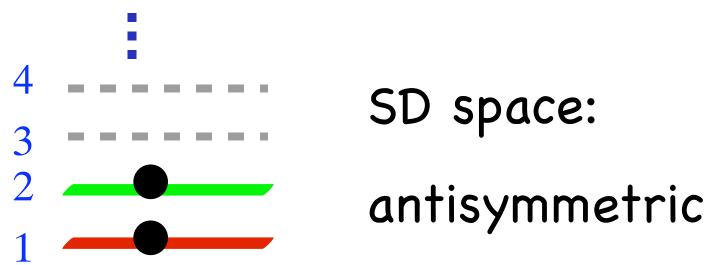
"superexchange":



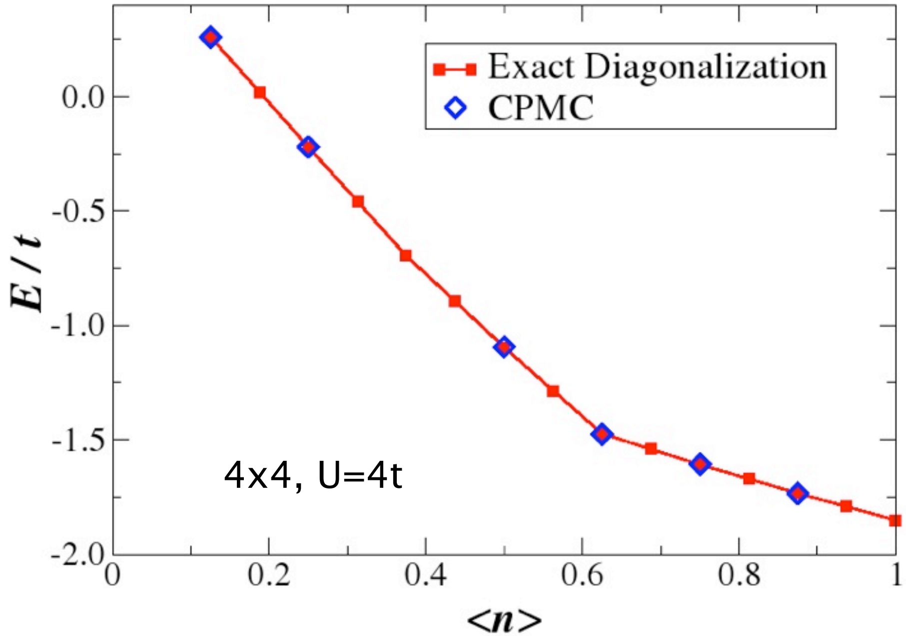
Slater det. - antisymmetric

Reasonable to expect it's reduced compared to DMC --- because tendency for global collapse to bosonic state is removed



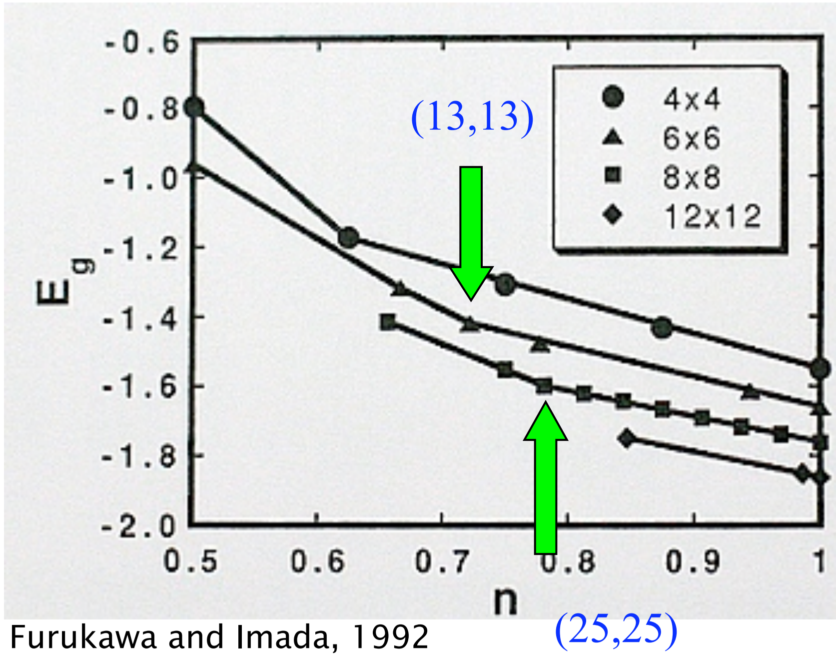


Hubbard model: equation of state



Exact diagonalization: Dagotto et.al. 1992

CPMC: Zhang et.al., 1997



Furukawa and Imada, 1992

- Constrained-path auxiliary field QMC (CPMC) is accurate
- There are **kinks** at closed-shell fillings:

  large shell effects ->

  intrinsic to H, difficult to obtain reliable hole energy (derivative!)
- Solved by twist-average boundary condition (Chang & Zhang, '08)

The phase problem

Sign/phase problem is due to --

"superexchange":

$$\begin{pmatrix} \psi_1 & \psi_1 \\ \psi_2 & \psi_2 \\ \cdot & \cdot \\ \cdot & \cdot \\ \psi_N & \psi_N \end{pmatrix}$$

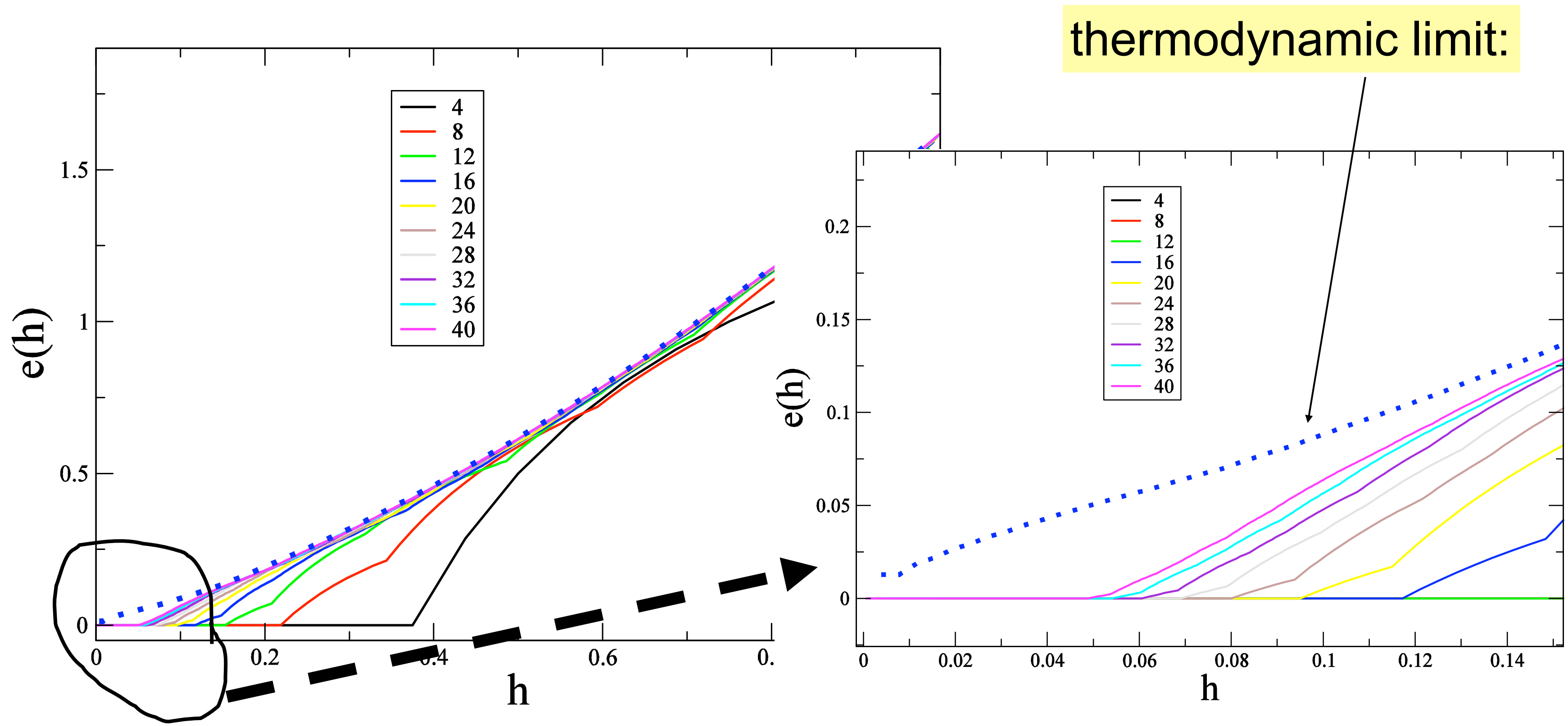
Slater det. - antisymmetric

To eliminate simple phase problem: (twist BC)

Use $\mathcal{R}\frac{\langle \Psi_T | \Phi' \rangle}{\langle \Psi_T | \Phi \rangle} > 0$ to determine if **"superexchange"** has occurred

Hubbard model: persistent shell effects

Non-interacting Hubbard model, *LxL*:



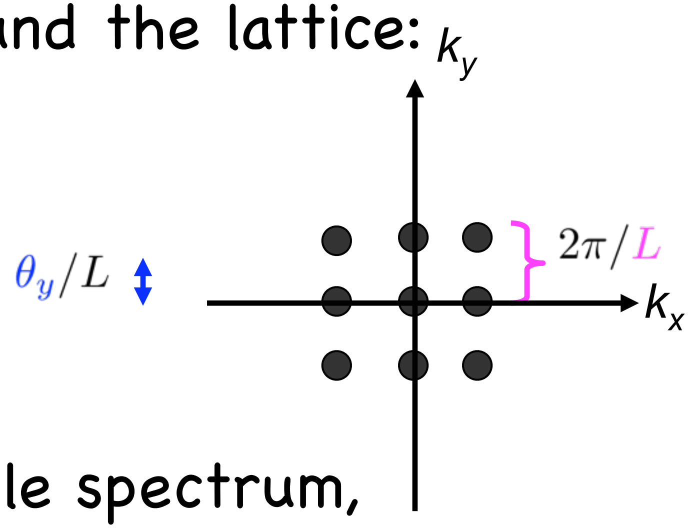
- One signal for phase separation: does e(h) turn ?
- Shell effect persists to >40x40, leads to bias - false signal at U=0!

e(h)=dE/dn, Maxwell constr
h=1-n: doping

Twist averaged boundary conditions (TABC)

- Reduces shell and kinetic energy finite-size effects common in band structure methods; --> many-body
  (Lin, Zhong & Ceperley; Chang & Zhang; ….)

- A phase when electron goes around the lattice:
  $$\Psi(x+L) = e^{i\theta_x}\Psi(x)$$
  - Shifts momentum space grid |k>:
  - Modifies H accordingly



- Breaks degeneracy in free-particle spectrum, **but** introduces **phase problem**

- Averaging over θ greatly reduces finite-size effects

Controlling the phase problem

Generalize constrained path approximation (Chang& Zhang 2008)

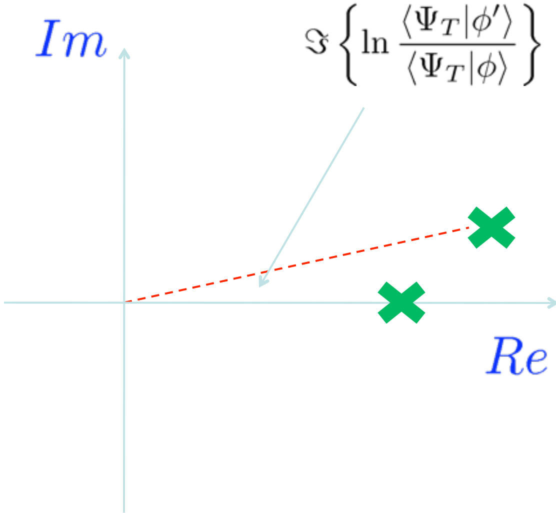
$$H = -t \sum_{\mathbf{j},\delta,\sigma} \left(e^{i\boldsymbol{\Theta}\cdot\delta} c^\dagger_{\mathbf{j}\sigma} c_{\mathbf{j}+\delta,\sigma} + e^{-i\boldsymbol{\Theta}\cdot\delta} c^\dagger_{\mathbf{j}+\delta,\sigma} c_{\mathbf{j}\sigma} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow} \equiv K + V$$

- Propagator: only 1-body part is complex --- deterministic

- Trial state: $|\Psi_T\rangle = |\text{free electrons}\rangle$

- Easier than the standard phaseless method

$$\Re\left\{\frac{\langle\Psi_T|\phi'\rangle}{\langle\Psi_T|\phi\rangle}\right\} \quad \text{and} \quad \left|\Im\left\{\ln\frac{\langle\Psi_T|\phi'\rangle}{\langle\Psi_T|\phi\rangle}\right\}\right| < \frac{\pi}{2}$$



Use real part of ratio, and project

→ constrained path

Benchmark

- Sampling 1000 random TABCs

  3x3: Largest relative error:

  ~ 0.2% for U/t = 4

  ~ 1.0% for U/t = 8

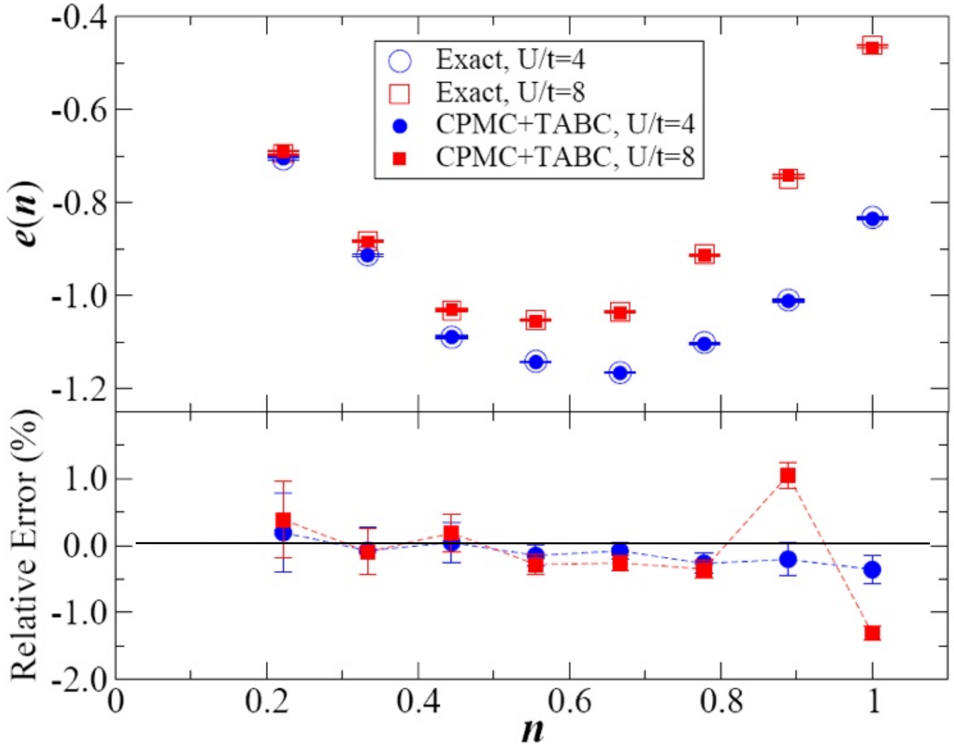
  dilute 4x4 at n=0.25

  ~ 0.2% for U/t = 16

  ~ 0.6% for U/t = 30

- Summary: CPMC + TABCs
  - controls sign problem
  - many benchmarks (including ab initio electronic structure)

Equation of state for 3x3 Hub

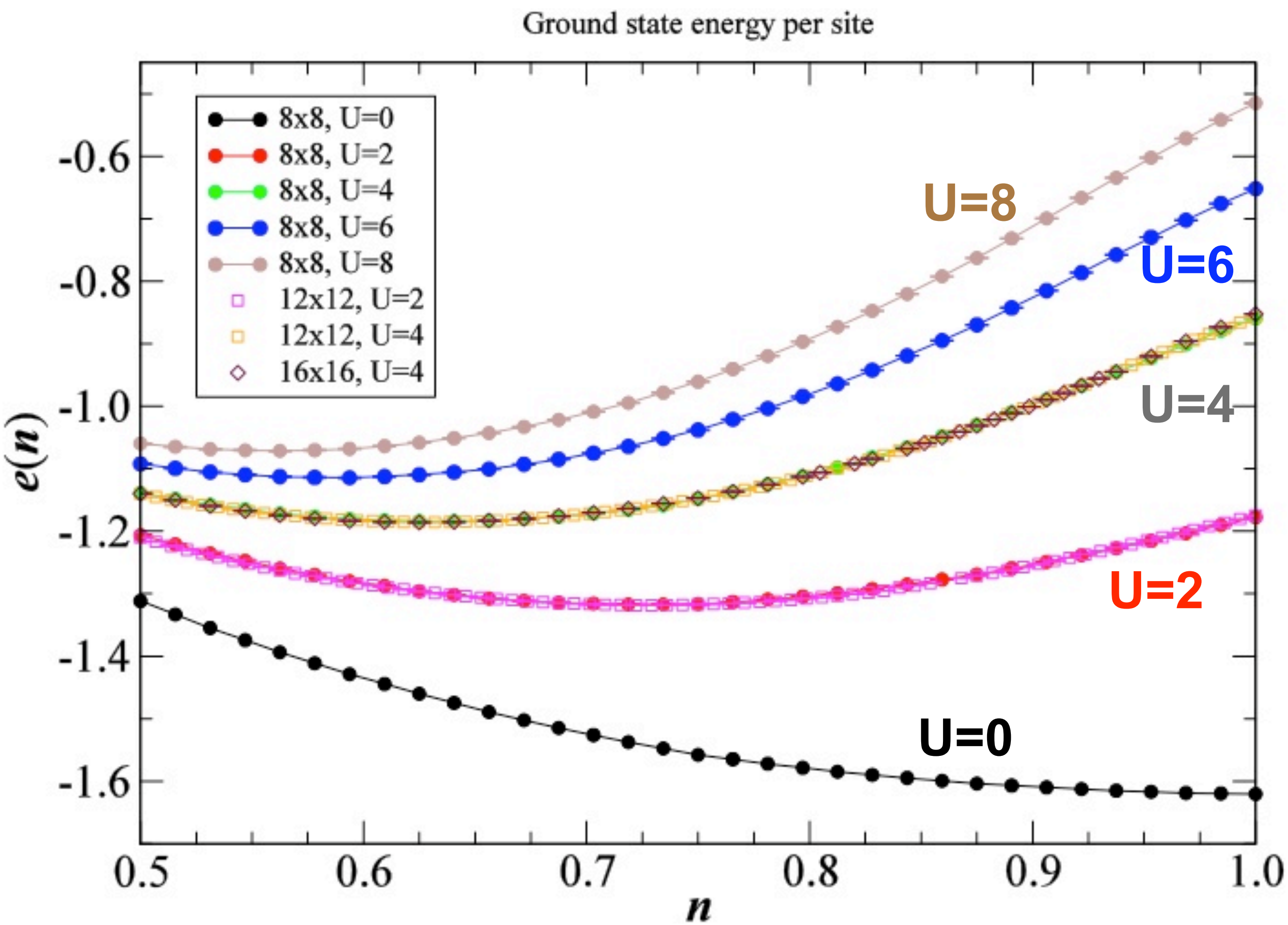


$$\text{Relative error\%} = \frac{e_{QMC}(n) - e_{Exact}(n)}{|e_{Exact}(n)|}$$

Chang & SZ, PRB '08

Hubbard model: equation of state

Phaseless CPMC with TABC:

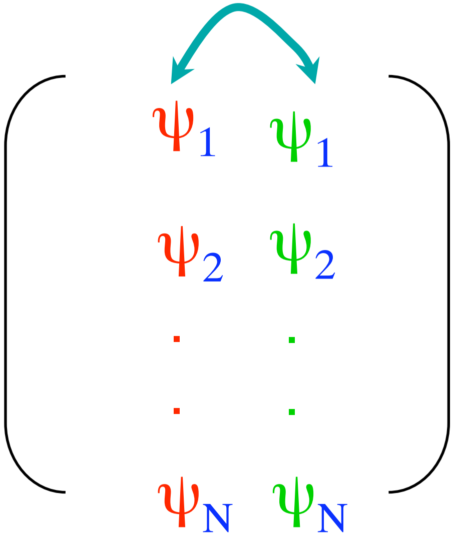


- Smooth, shell effects removed
- Convergence to thermodynamic limit achieved (**except** near n=1 !)

The phase problem

Sign/phase problem is due to --

"superexchange":



Slater det. - antisymmetric

To eliminate simple phase problem: (twist BC)

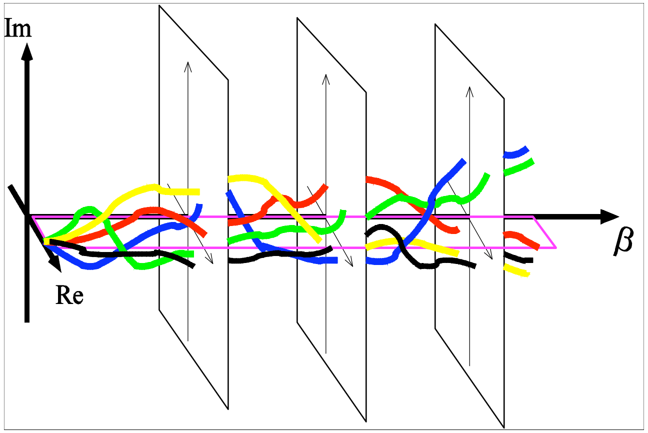
Use $\mathcal{R}\frac{\langle\Psi_T|\Phi'\rangle}{\langle\Psi_T|\Phi\rangle} > 0$ to determine if "superexchange" has occurred

To eliminate 'true' phase problem: (complex HS, e.g., 1/r)

=>

Controlling the phase problem

Sketch of approximate **solution**:



- Modify propagator by “gauge transformation’:
  phase → degeneracy (use trial wf)

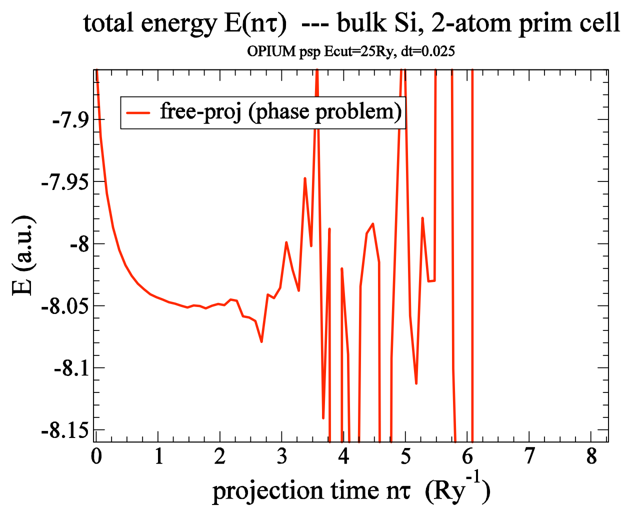
- Project **to one overall phase**:
  break “rotational invariance”

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

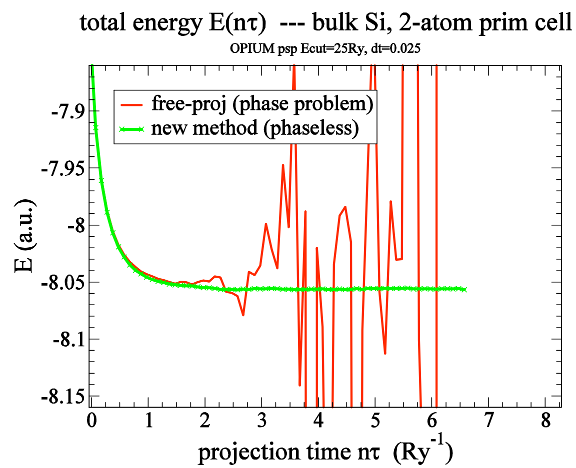
- subtle, but key, difference from: real$<\Psi_T|\phi>$ 0

(Fahy & Hamann; Zhang, Carlson, Gubernatis)

Before:



After:



Controlling the phase problem --- more details

SZ & Krakauer

(a) Phaseless formalism

- 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!

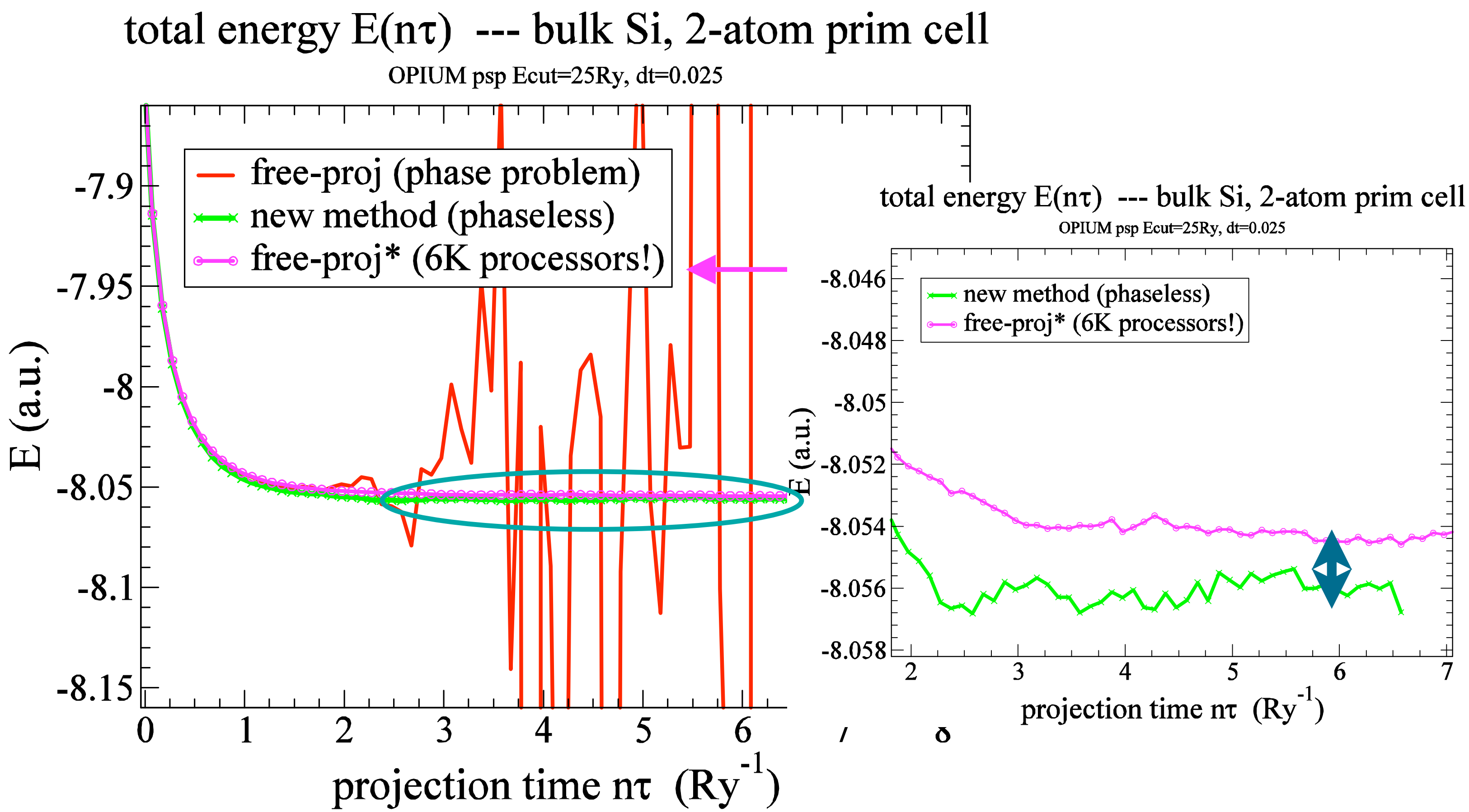
  ⋆ Local energy: $E_L(\phi) \equiv \frac{\langle\Psi_T|\hat{H}|\phi\rangle}{\langle\Psi_T|\phi\rangle}$

(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

Quantify the approximation?



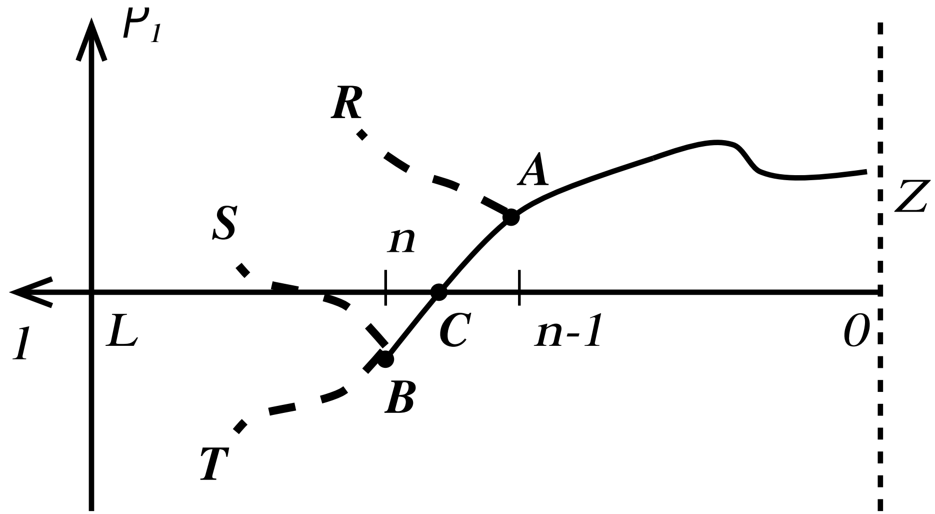
Error in total E < 0.3mH/atom

free-proj: our 'FCI' (8 electrons, Nbasis~570)

1 ~ chemical accuracy

Constrained path method at finite-T

The constraint under finite time-step:



Point of contact:

- Approximate by B
- Approximate by interpolating between A and B (higher order)

Outline

- Interacting quantum matter -- a grand challenge:
  - Standard "first-principles" approach fails when interaction is strong: high-temperature superconductors, magnetic materials, ...
  - need method with: accuracy, computational scaling
- Constrained path (phase-free) MC: a new framework for simulating quantum fermion (and bose-fermi) systems
  - Why going to Slater determinant space can reduce the sign problem? How does the sign problem occur? How to control it?
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  - molecules: quantum chemistry
  - "first-principles" electronic structure calculations in solids

Introduction to *T*>0 method

Standard finite-T method *Blankenbecler, Scalapino, and Sugar, '81*

Partition function for Hamiltonian H is: $(\beta = 1/kT)$

$$\mathrm{Tr}(e^{-\beta H}) = \mathrm{Tr}(e^{-\tau H}\, e^{-\tau H} \cdots e^{-\tau H})$$

Need: $e^{-\tau H} = \sum_{\mathbf{x}} B(\mathbf{x})$

$$\langle O \rangle = \frac{\mathrm{Tr}(O\, e^{-\beta H})}{\mathrm{Tr}(e^{-\beta H})} = \frac{\sum_{\{\mathbf{x}_l\}} \mathrm{Tr}(O B(\mathbf{x}_L) B(\mathbf{x}_{L-1}) \cdots B(\mathbf{x}_1))}{\sum_{\{\mathbf{x}_l\}} \mathrm{Tr}(B(\mathbf{x}_L) B(\mathbf{x}_{L-1}) \cdots B(\mathbf{x}_1))}$$

Analytically evaluate trace: $\mathrm{Tr}(e^{-\beta H}) = \sum_{\{\mathbf{x}_l\}} \det[I + B(\mathbf{x}_L)\, B(\mathbf{x}_{L-1}) \cdots B(\mathbf{x}_1)]$

Sample fields $\{\mathbf{x}_l\}$ by Metropolis Monte Carlo to compute sum.

Sign Problem in standard finite-T AF QMC:

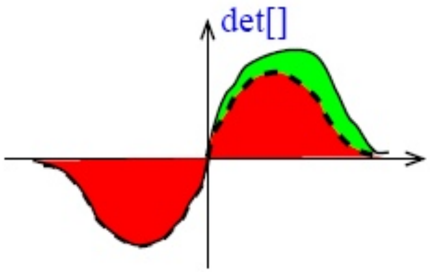
- As T lowers, average sign of $\det[\,]$ $\to 0$ exponentially.
- We need to control the sign problem — focus on real auxiliary fields, i.e., real $\hat{v}$

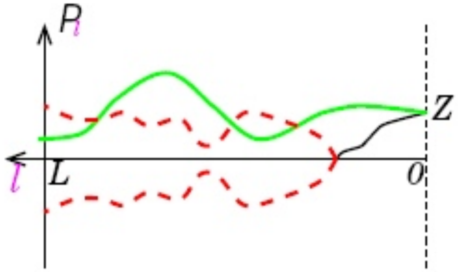
The sign problem at finite-T

Imagine introducing path integrals one time slice at a time: *Zhang, '99*

$$
\begin{aligned}
Z &= \mathrm{Tr}(e^{-\tau H}\, e^{-\tau H} \cdots e^{-\tau H}\, e^{-\tau H}) && P_0 \\
&= \sum_{\{\mathbf{x}_1\}} \mathrm{Tr}(e^{-\tau H}\, e^{-\tau H} \cdots e^{-\tau H}\, B(\mathbf{x}_1)) && P_1(\{\mathbf{x}_1\}) \quad \leftarrow \text{integrand} \\
&= \sum_{\{\mathbf{x}_1,\mathbf{x}_2\}} \mathrm{Tr}(e^{-\tau H}\, e^{-\tau H} \cdots B(\mathbf{x}_2)\, B(\mathbf{x}_1)) && P_2(\{\mathbf{x}_1, \mathbf{x}_2\}) \\
&= \cdots \\
&= \sum_{\{\mathbf{x}_l\}} \det[I + B(\mathbf{x}_L)\, B(\mathbf{x}_{L-1}) \cdots B(\mathbf{x}_1)] && P_L(\{\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_L\})
\end{aligned}
$$

Suppose we know $e^{-\tau H}$. Consider P_l:





- If $P_l = 0$, all future paths $\{\mathbf{x}_{l+1}, \mathbf{x}_{l+2}, \cdots, \mathbf{x}_L\}$ collectively contribute 0 in Z.
- A complete path $\{\mathbf{x}_l\}$ contributes to Z **iff** $P_l > 0$ for all l.

Constrained path method at finite-T

Constraint to control the sign problem

Require: $P_1(\{\mathbf{x}_1\}) > 0$; $P_2(\{\mathbf{x}_1, \mathbf{x}_2\}) > 0$; ....; $P_L(\{\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_L\}) > 0$.

- Constraint eliminates all noise paths ('dashed lines').
- In practice, we use trial B_T for $e^{-\tau H}$ — approximate.

(HF propagator)

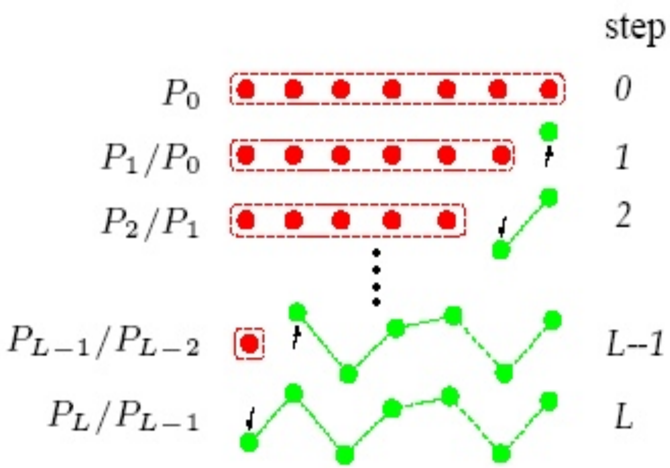
Monte Carlo sampling algorithm to incorporate constraint

If B_T is $\sum$(mean-field), then Tr $\rightarrow$ det[ ] in P_l.

Sampling — random walk of L steps:

Note:

$$P_L = \frac{P_L}{P_{L-1}} \frac{P_{L-1}}{P_{L-2}} \cdots \frac{P_2}{P_1} \frac{P_1}{P_0} P_0$$



Recovery from wrong trial w.f.

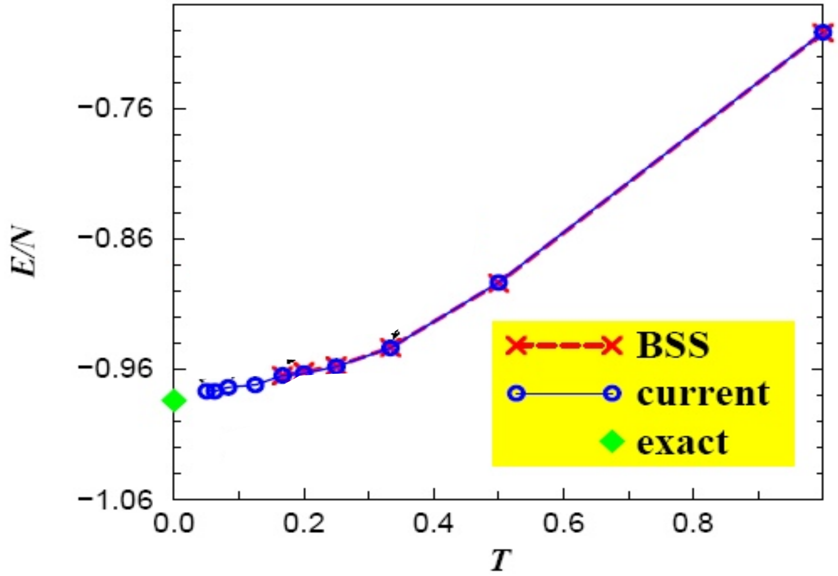
More predictive power requires
reducing reliance on trial wf

2-D Hubbard model: finite-T

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

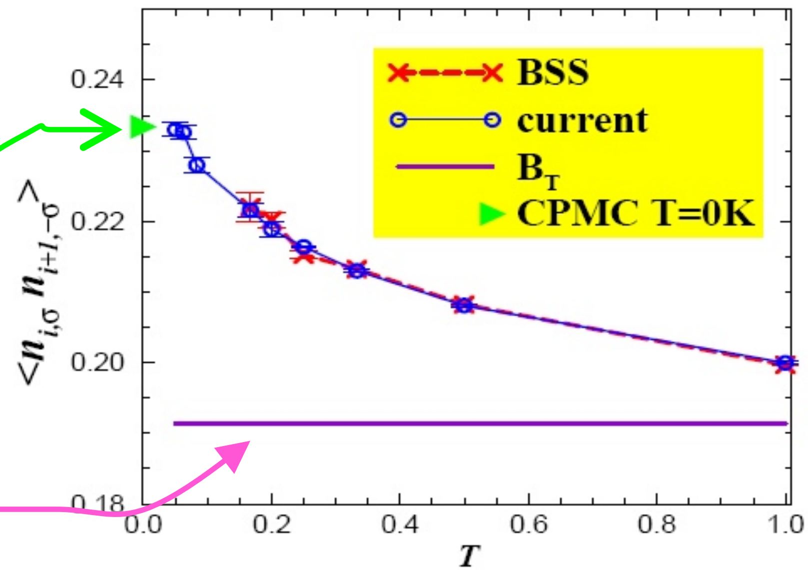
Compare with:

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

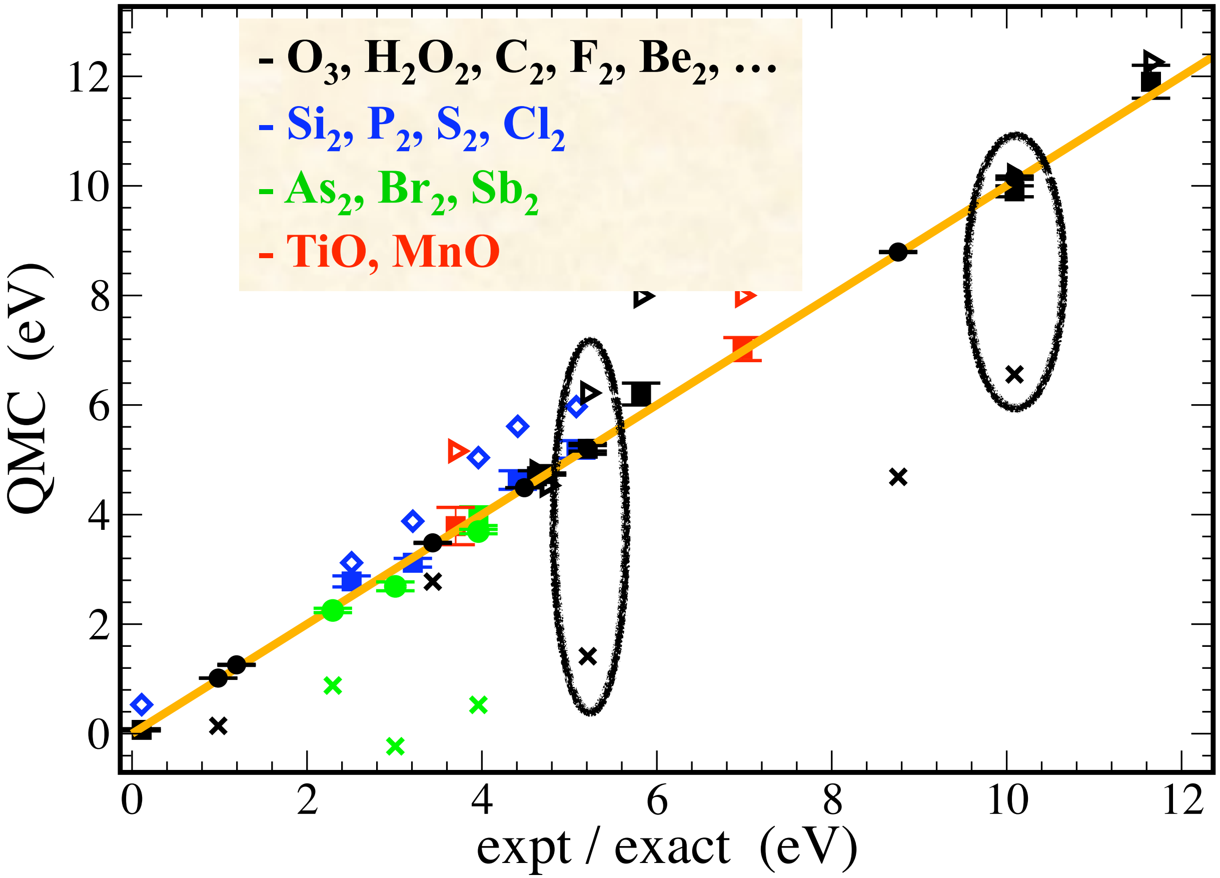


AFM order

wrong trial wf



Test 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 wf
- "automated" post-HF or post-DFT
- HF or LDA trial wf: same result

HF: x

LDA: triangle

GGA: diamond

Constraint less sensitive to trial wf details

MnO solid in antiferromagnetic II phase:

	Ev	*E_QMC/trial wf*
HF	-118.2655	-119.1401(12)
GGA	-118.1929	-119.1387(10)
	-119.0614 (E_GGA)	

Energy in Hartree/unit cell

4-atom cell,

V=21.96A^3

- QMC insensitive to details of the trial wf

RHF vs UHF trial wfs can have effect:e.g., H_2O

Bond length	RHF	UHF	CCSD(T)	FCI	QMC/RHF	QMC/UHF
STO-6G						
$1.5R_e$	−75.440 432	−75.502 069		−75.600 039	−75.5768(3)	−75.5965(6)
$2R_e$	−75.141 587	−75.464 541		−75.486 528	−75.3557(3)	−75.4880(3)

- no upper bound;
- has finite basis error as in QChem methods, but scales much better

Outline

- Interacting quantum matter -- a grand challenge:
  - Standard "first-principles" approach fails when interaction is strong: high-temperature superconductors, magnetic materials, ...
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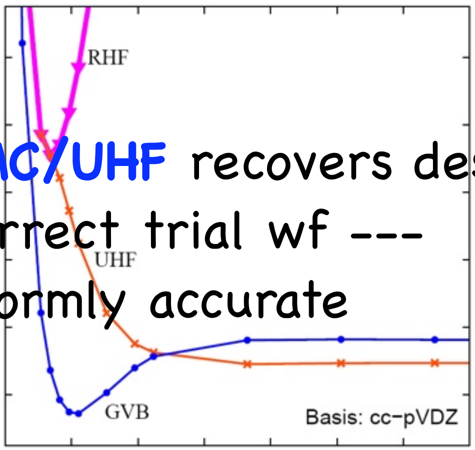
  - "first-principles" electronic structure calculations in solids

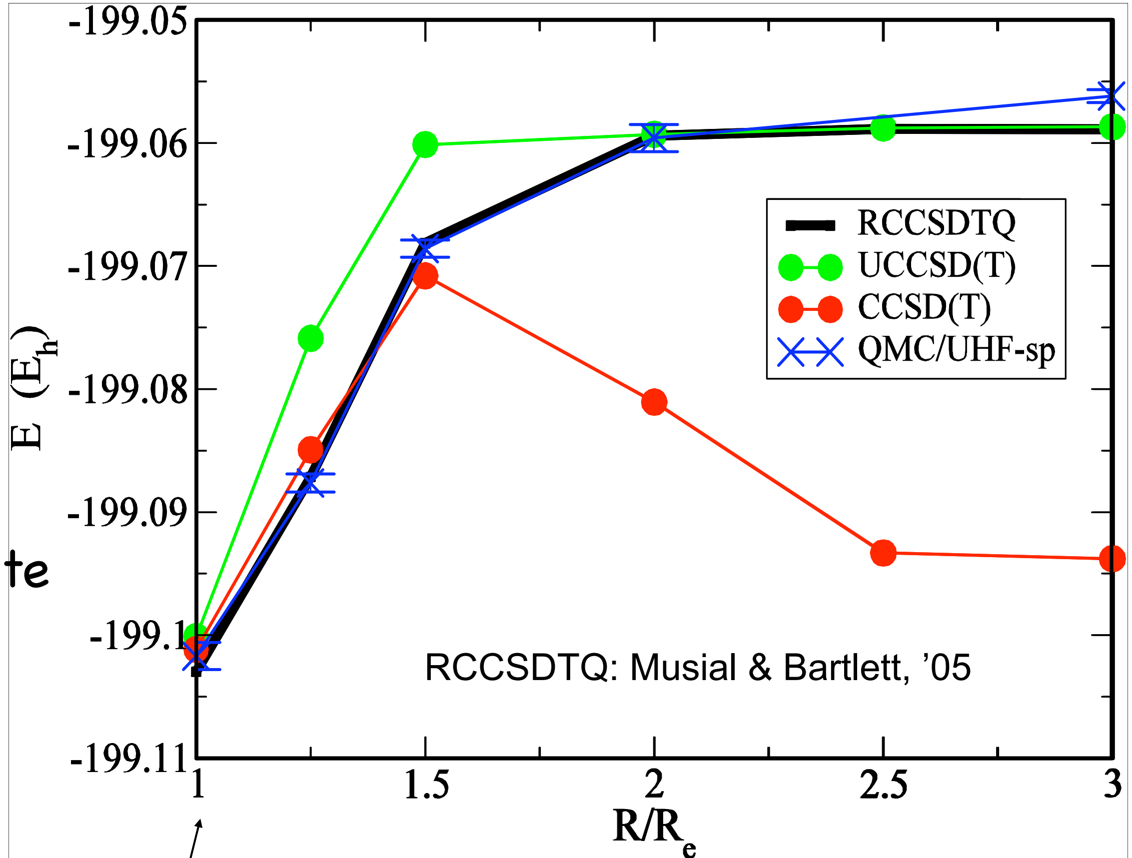
F_2 bond breaking

Mimics increasing correlation effects: F—F

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



(removes spin contamination)



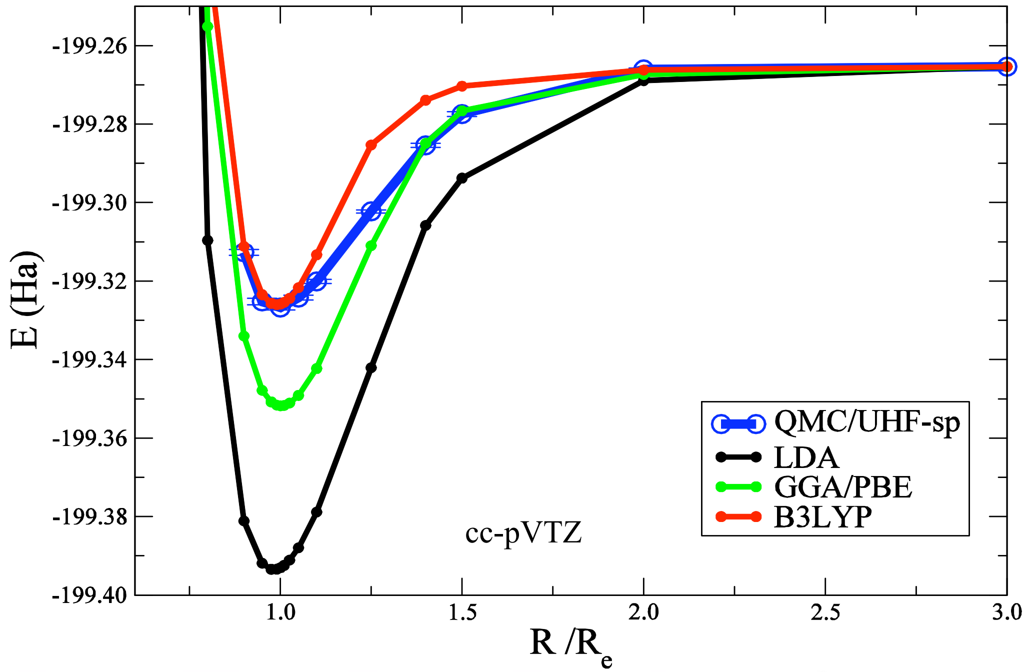
Equilibrium → **Dissoc. limit**

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

F_2 bond breaking --- larger basis

- LDA and GGA/PBE
  - well-depths too deep
- B3LYP
  - well-depth excellent
  - "shoulder" too steep
- Compare with experiment spectroscopic cnsts:

Potential energy curve:

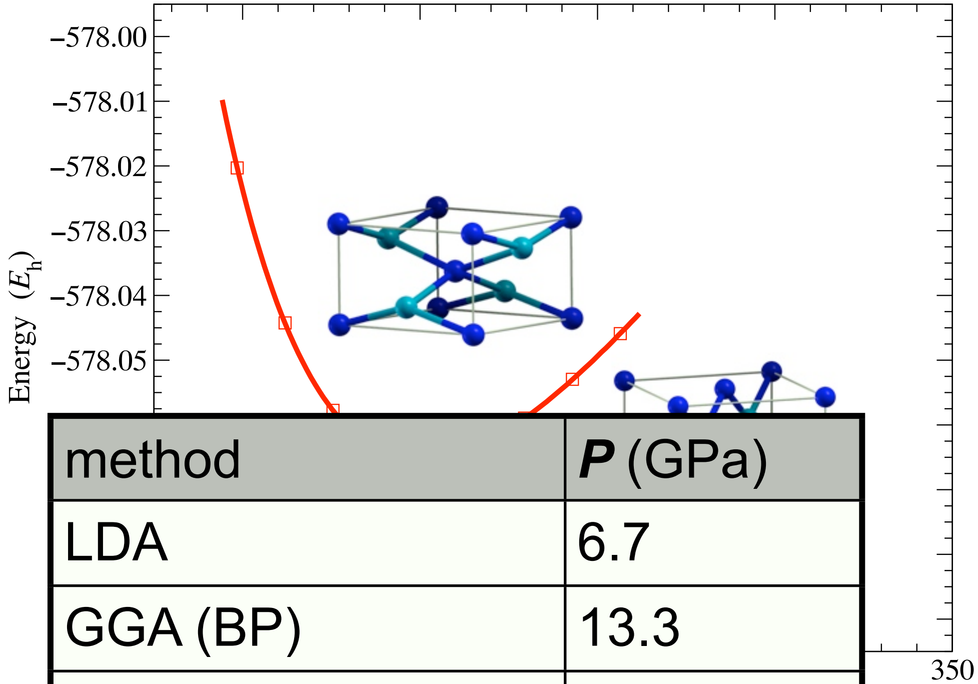


	Expt[a]	AFQMC	RCCSD(T)	UCCSD(T)	LSDA	GGA/PBE	B3LYP
Basis: cc-pVQZ							
r_e (Å)	1.4131(8)	1.411(2)	1.4108	1.3946	1.3856	1.4136	1.3944
ω_0 (cm^{-1})	916.64	912(11)	929	1036	1062	997	1109
D_e (eV)[b]	1.693(5)	1.77(1)	–	1.567	3.473	2.321	1.634
D_e (eV)[c]	1.693(5)	1.70(1)	1.594	1.569			

Purwanto et. al., JCP, '08

Periodic Solids

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



method	***P*** (GPa)
LDA	6.7
GGA (BP)	13.3
GGA (PW91)	10.9
GGA (PBE)	~8.9
DMC (*Alfe et al '04*)	16.5(5)
AFQMC	**12.6(3)**
experiment	**10.3-12.5**

- 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

Excited states

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

C_2 excited state potential energy curves

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

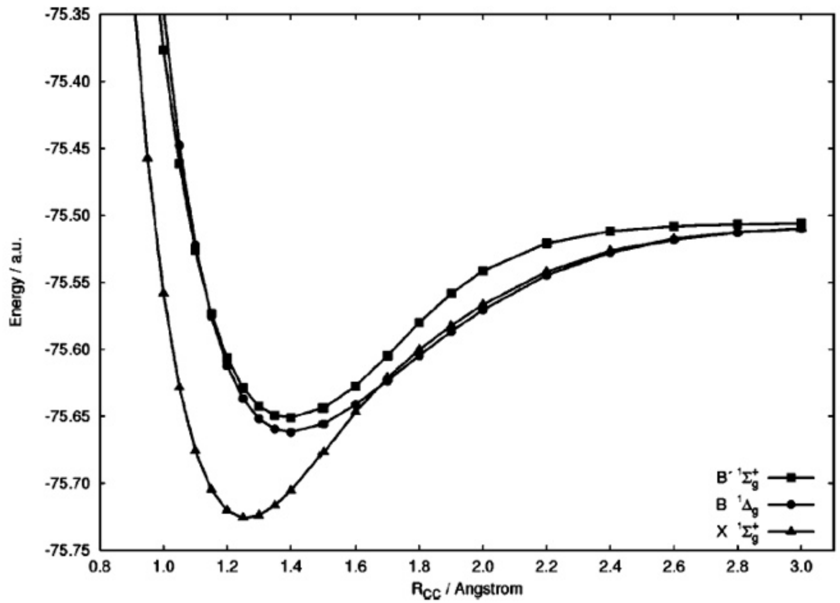
Micah L. Abrams and C. David Sherrill[a)]
Center for Computational Molecular Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

(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

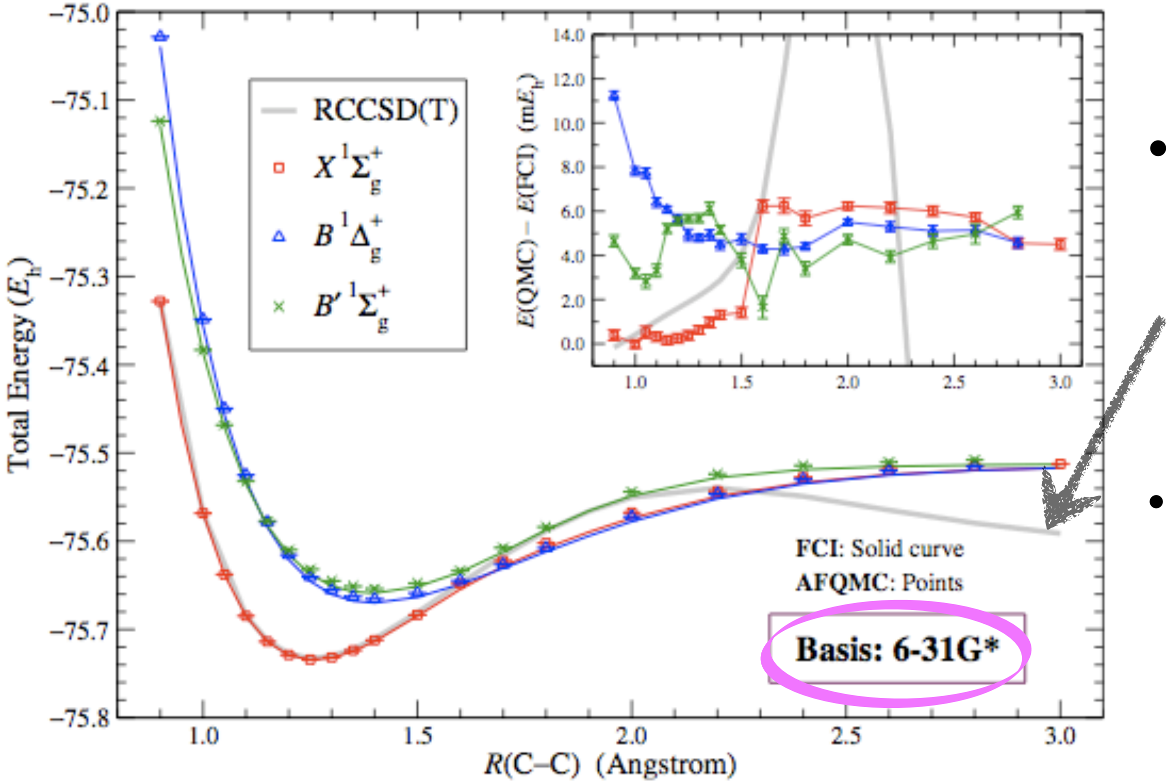


Thursday, February 2, 2012

Bound breaking, and excited states

PECs --- first 3 singlet states in C_2

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



- comparable to CCSD(T) near equilibrium, better for bond breaking (multi-reference)
- first attempt at excitation:
  - level crossing
  - excited state of same symmetry

Truncated CASSCF(8,16) trial wf ~30-50 det's

Bound breaking, and excited states

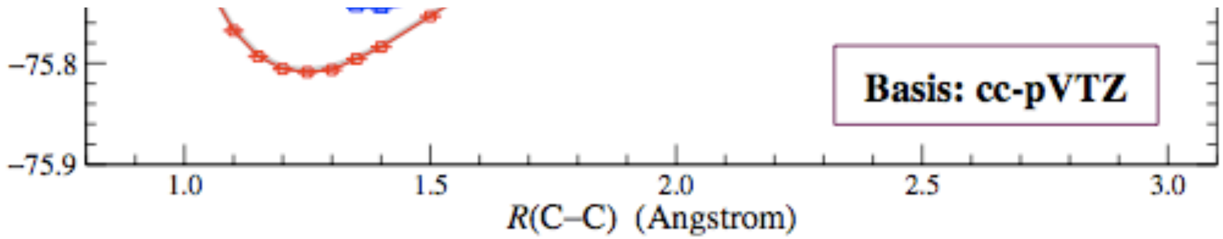
PECs --- first 3 singlet states in C_2

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).

	CASSCF(8,16)					
	Full	Truncated	CCSD(T)	CMRCI[a]	QMC	Expt.
			$X\ {}^1\Sigma_g^+$ ground state			
r_e	1.2452	1.262[3]	1.2459	1.2467	1.244(1)	1.2425
ω_e	1868	1759[29]	1852	1853	1850(21)	1855
D_e	6.57	4.69[1]	6.19	6.29	6.41(1)	6.33

[a]Values from analytical fitting in Ref. 44.



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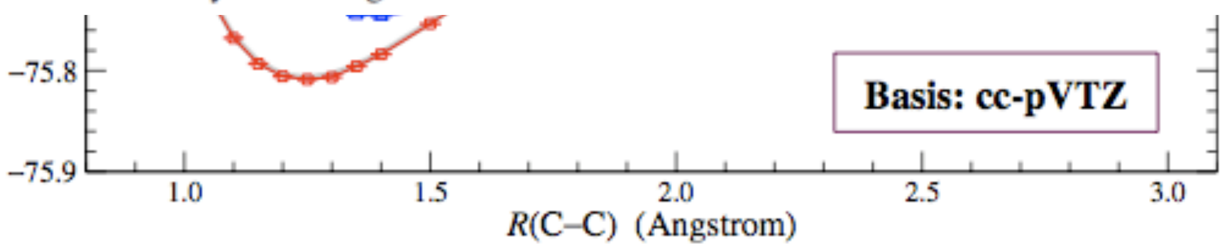
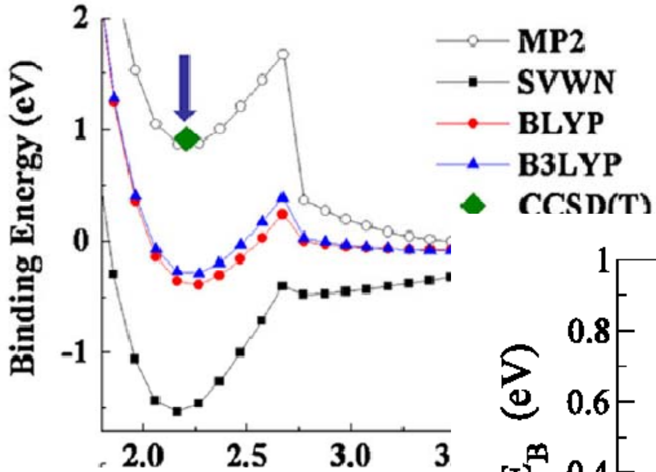
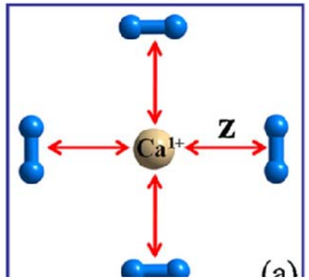


Truncated CASSCF(8,16) trial wf ~30-50 det's

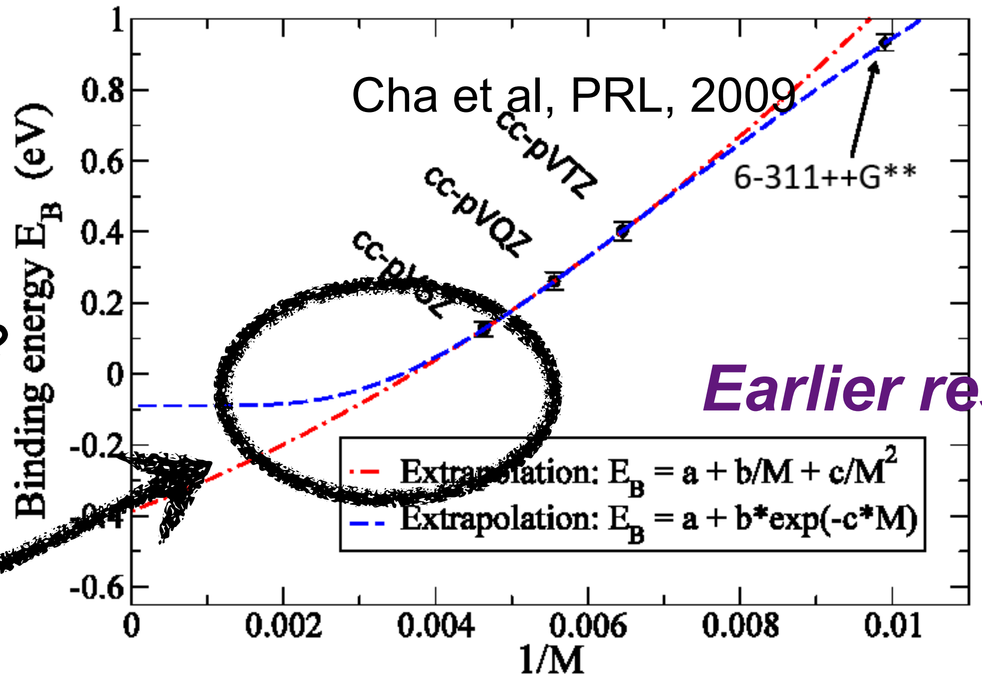
Test: model H-storage problem

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





Finite Basis set error?



Earlier results

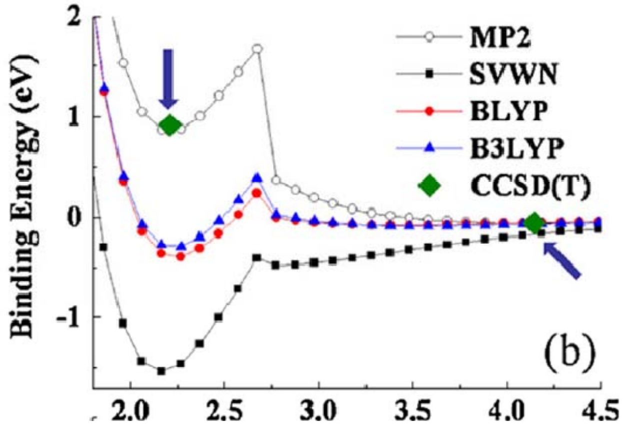
Can now do with modified Cholesky

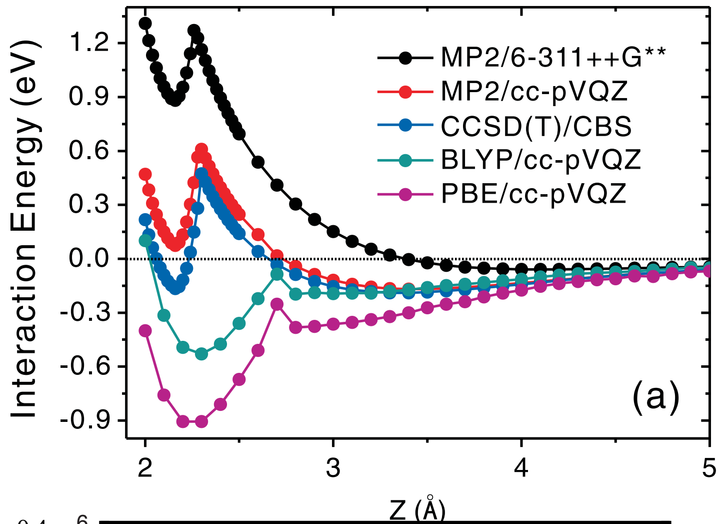
next →

A model H-storage problem

- Finite basis error indeed significant

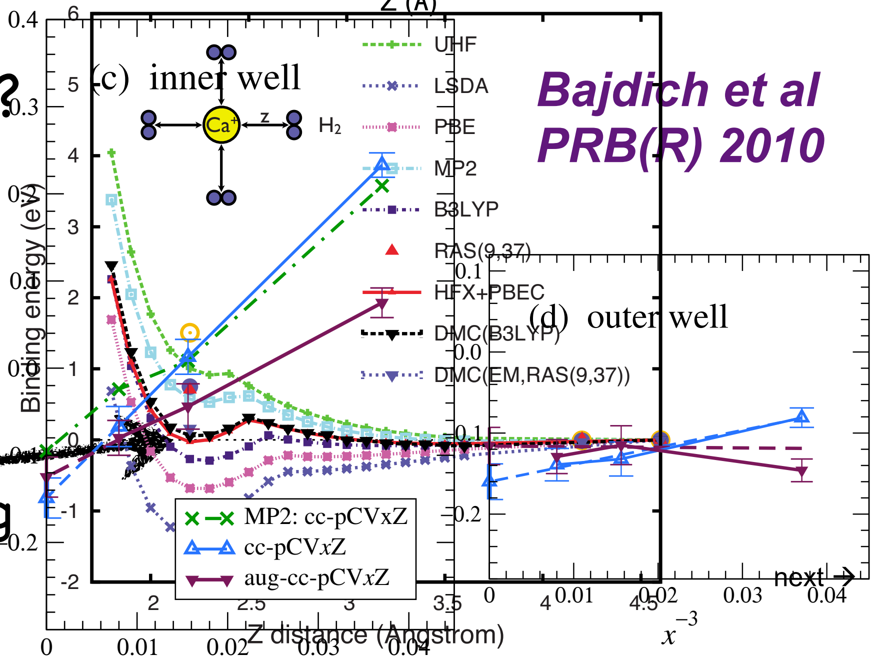
Ohk et al, PRL comment ***2009***





- But are the new results reliable? (given CCSD(T) difficulty in scaling)
  - We find delicate extrapolation with cc-pVxZ (x=3,4,5), up to M=827 (all-electron)
  - New DMC calculation finds no binding
  - EOS curve shape also different

Bajdich et al PRB(R) 2010

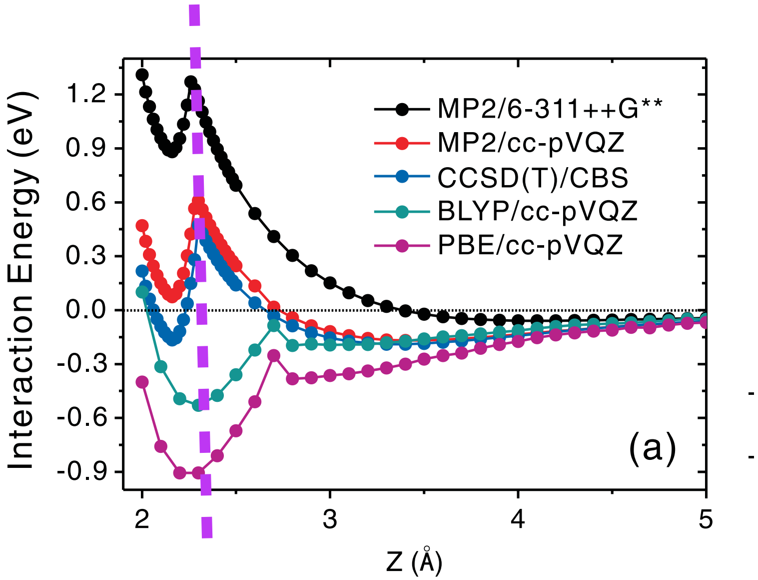


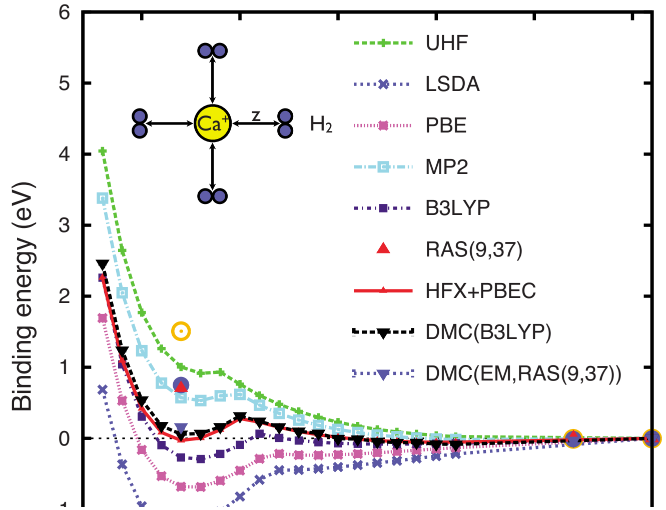
next →

A model H-storage problem

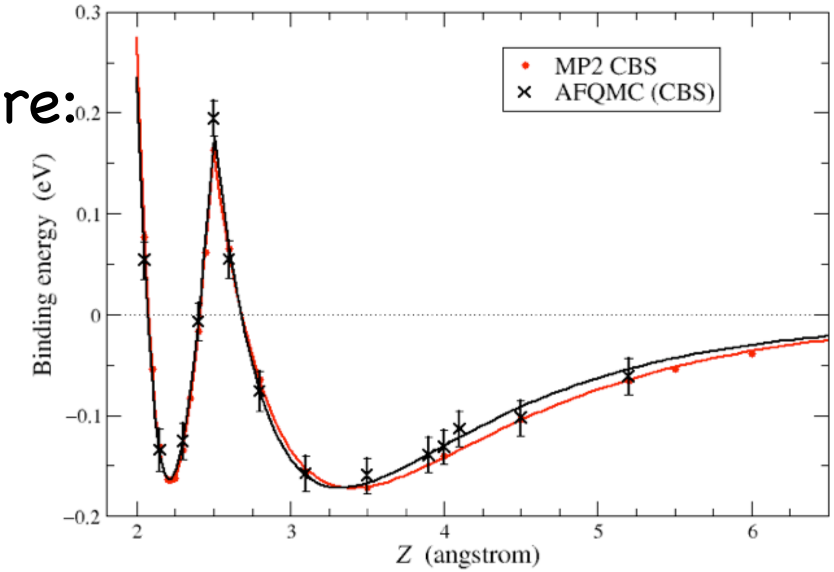
- Finite basis error? Systematic error of

Or fixed-node error in DMC?





- We find double-well structure:
  - large basis: aug-cc-pCVxZ with x=3,4,5
  - careful extrapolation (1/x^3)
  - Note barrier position different



- MP2 is quite accurate here (with careful CBS extrapolation)

t →

Magnetic phases in the Hubbard model:

some recent progress

- Itinerant ferromagnetism
  - ➢ Experiment on dilute Fermi gase
  - ➢ Ferromagnetism in dilute 3-D Hubbard model?
- Antiferromagnetism in Hubbard model (connection with high-Tc?)
  - ➢ Optical lattices: **experimental simulation**?
  - ➢ What happens to the antiferromagnetic order upon doping?

Motivation

- What is the physical basis for ferromagnetism in metals?
- New interests: Expts aimed at emulating the Stoner Hamiltonian: hints of ferromagnetic instability observed in trapped Fermi gas

Jo et. al., Science ('09)

✦ equal mixture of F=1/2 hyperfine states of Li^6

=> 2-component Fermi gas with short-range interaction

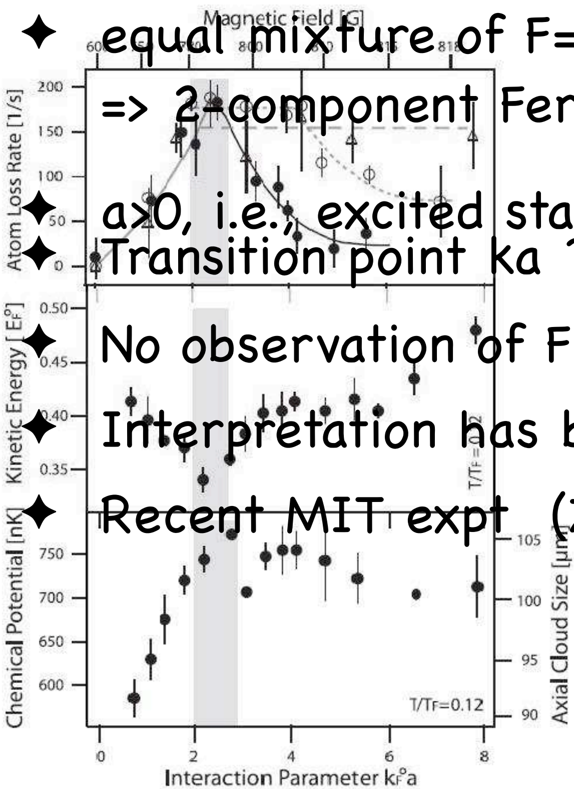
✦ a>0, i.e., excited state branch (molecular bound state below)

✦ Transition point ka ~ 1.9(2)

✦ No observation of FM domains

✦ Interpretation has been debated (Ho, Zhai, ...)

✦ Recent MIT expt (Zwierlein et al)



- At $T/T_F = 0.12$ (lowest used)
- A maximum in atom loss rate: $k_F^0 a \approx 2.5$
- A minimum in kinetic energy: $k_F^0 a \approx 2.2$
- A maximum in cloud size.

$\Downarrow$

Indirect evidence of ferromagnetic ordering

Motivation

- The 3-D Hubbard model is a reasonable representation of the Stoner Hamiltonian:
  itinerant electrons + local interaction

- Caveats!
  - Hubbard model: Ground state, repulsive interaction, equilibrium
    Experiment: Excited states, attractive interaction, dynamic (quench)
  - The scattering length on a lattice is bounded by lattice spacing
    (Castin 2004)
    $$a_{lattice} = \frac{a_s}{1 + 3.173 a_s}$$

- Does it provide a minimal model for itinerant FM in metals?

The Hubbard model

- Simplest model combining band structure and interaction:

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

Electrons on a lattice:

- near-neighbor hopping
- on-site repulsion

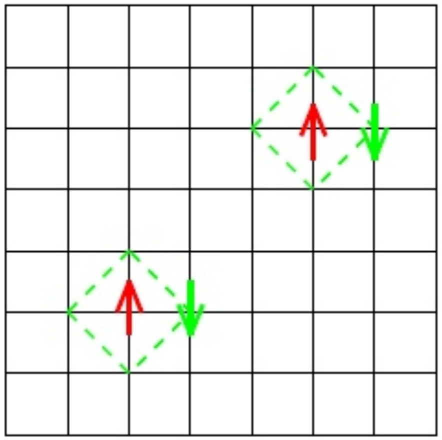
Size N=L^d

Filling $n = \frac{N_\uparrow + N_\downarrow}{N}$

Half-filling: n=1

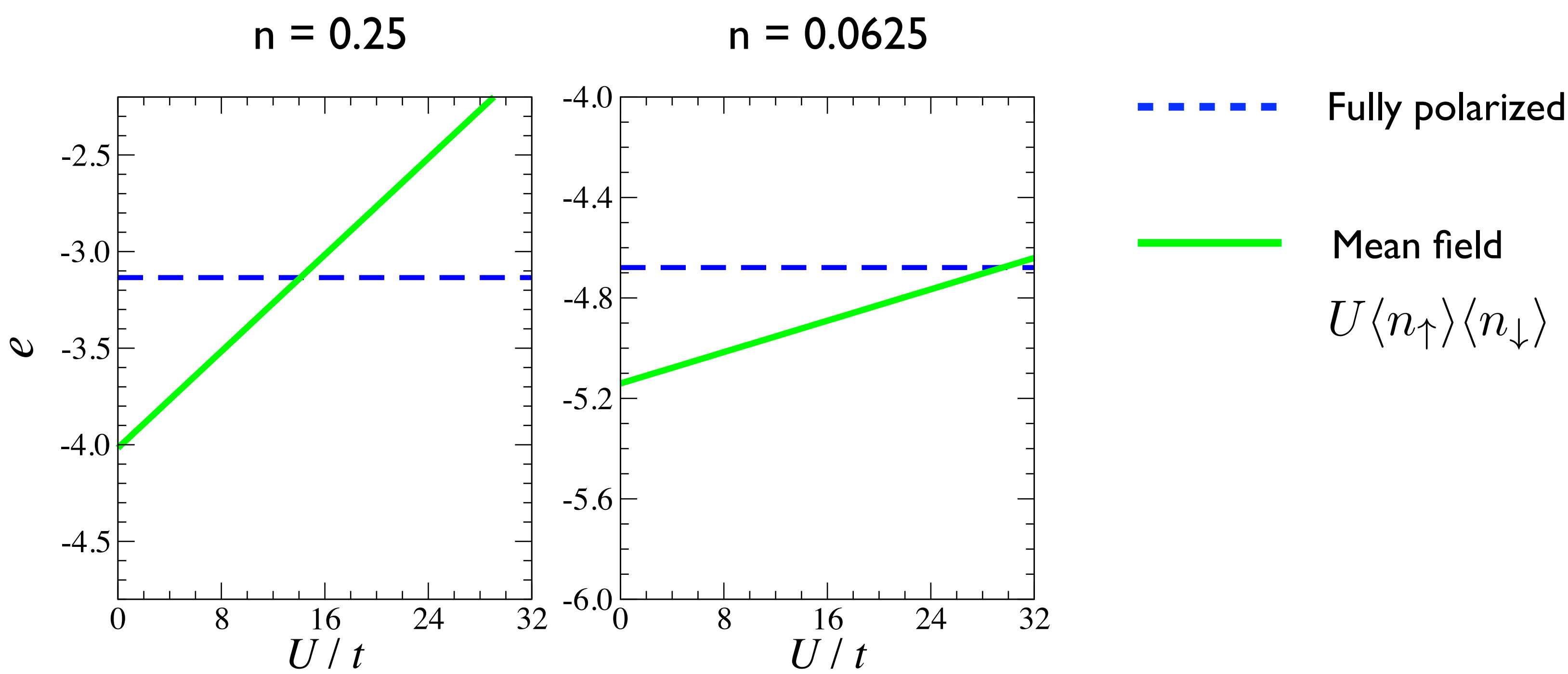
Does it have a ferromagnetic instability?

- Neither K nor V term favors FM alone
- Academic case: Nagaoka-Thouless:
  1 hole, U=infty, bipartite: yes



Mean-field theory

- Stoner's criterion $U \cdot N(\epsilon_F) > 1$

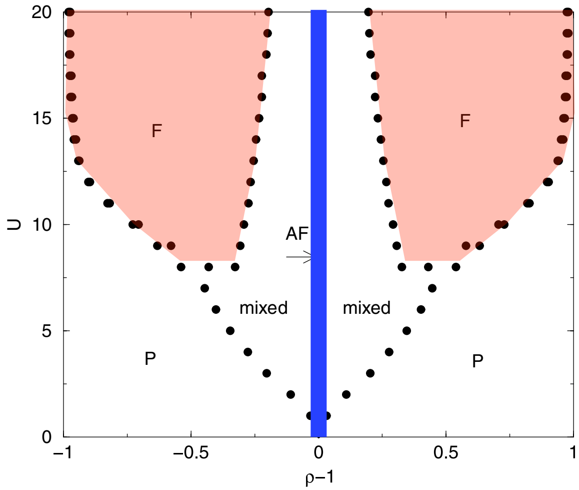


$$H = -t \sum_{\langle \mathbf{i}\,\mathbf{j}\rangle,\sigma} c^\dagger_{\mathbf{i}\sigma} c_{\mathbf{j}\sigma} + U \sum_{\mathbf{i}} n_{\mathbf{i}\uparrow} n_{\mathbf{i}\downarrow}$$

Mean-field theory

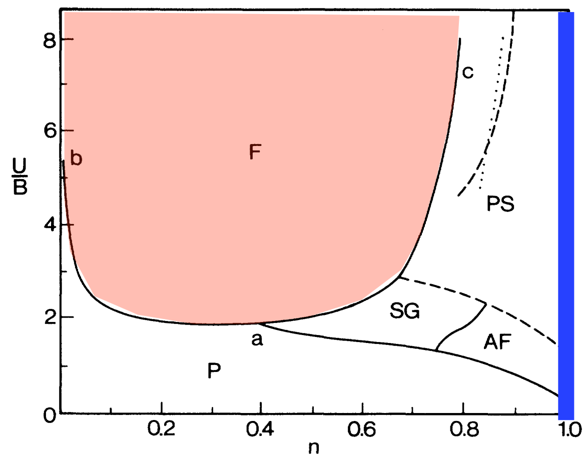
- Stoner's criterion $U \cdot N(\epsilon_F) > 1$

2D Hubbard



Langmann & Wallin (2007)

3D Hubbard



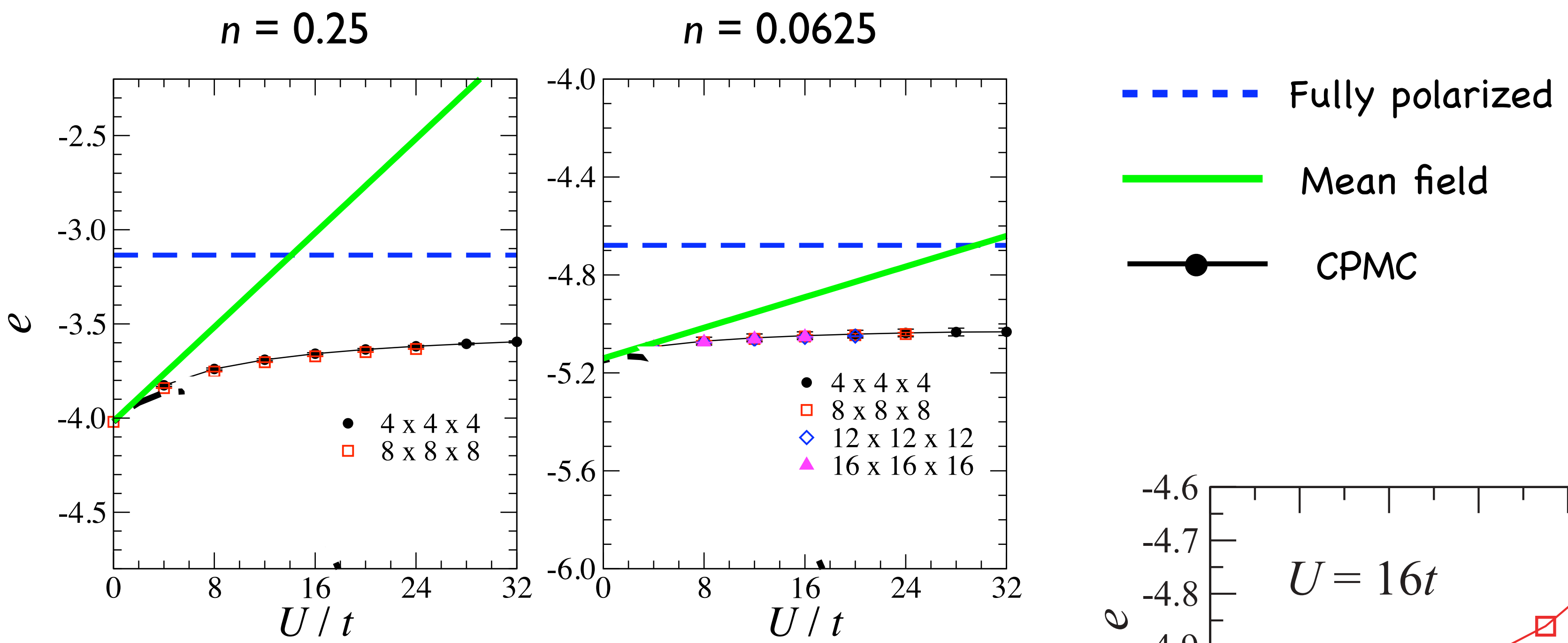
Andriotis et al. (1993)

- The ground state is antiferromagnetic at half-filling n = 1
- Phase diagram has large domain of ferromagnetism

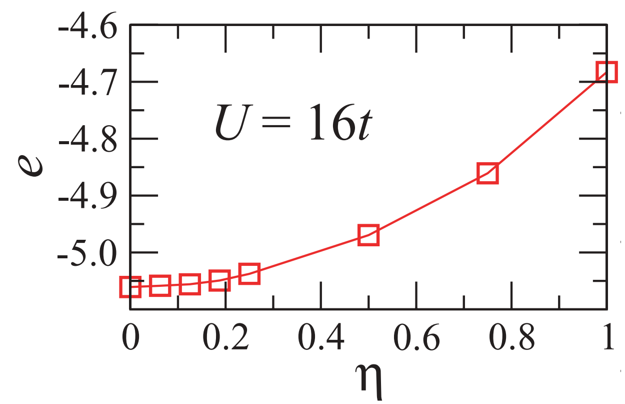
How does correlation modify this?

Ferromagnetism in 3D dilute Hubbard model?

Energy results:



Essentially no finite size effects in the QMC data



- No FM transition was found: $0 < n < 0.5$
- Partially polarized state is unlikely to be stable

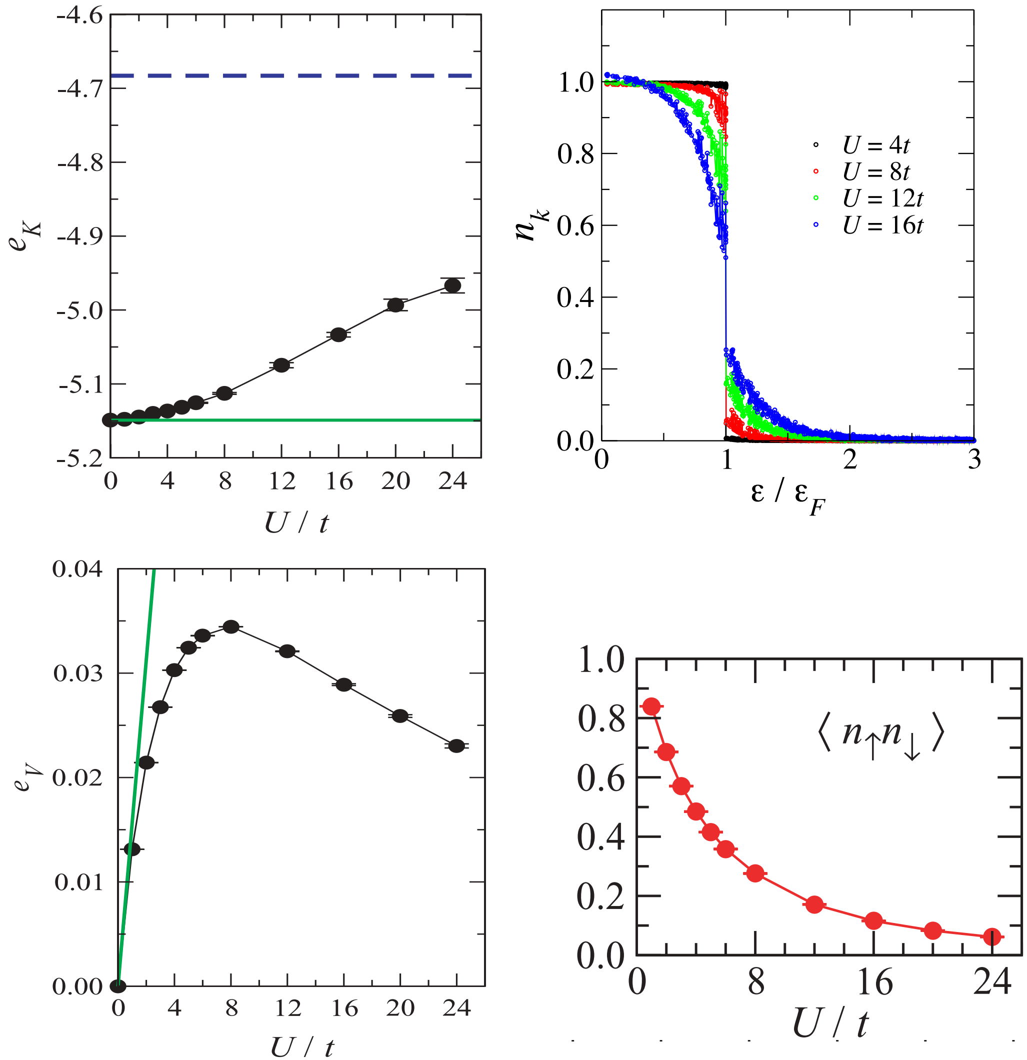
$$\eta = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow}$$

Individual energy components

- Interaction creates excitations beyond the Fermi surface, increasing the kinetic energy
- At large U, the interaction energy is lowered by correlation:

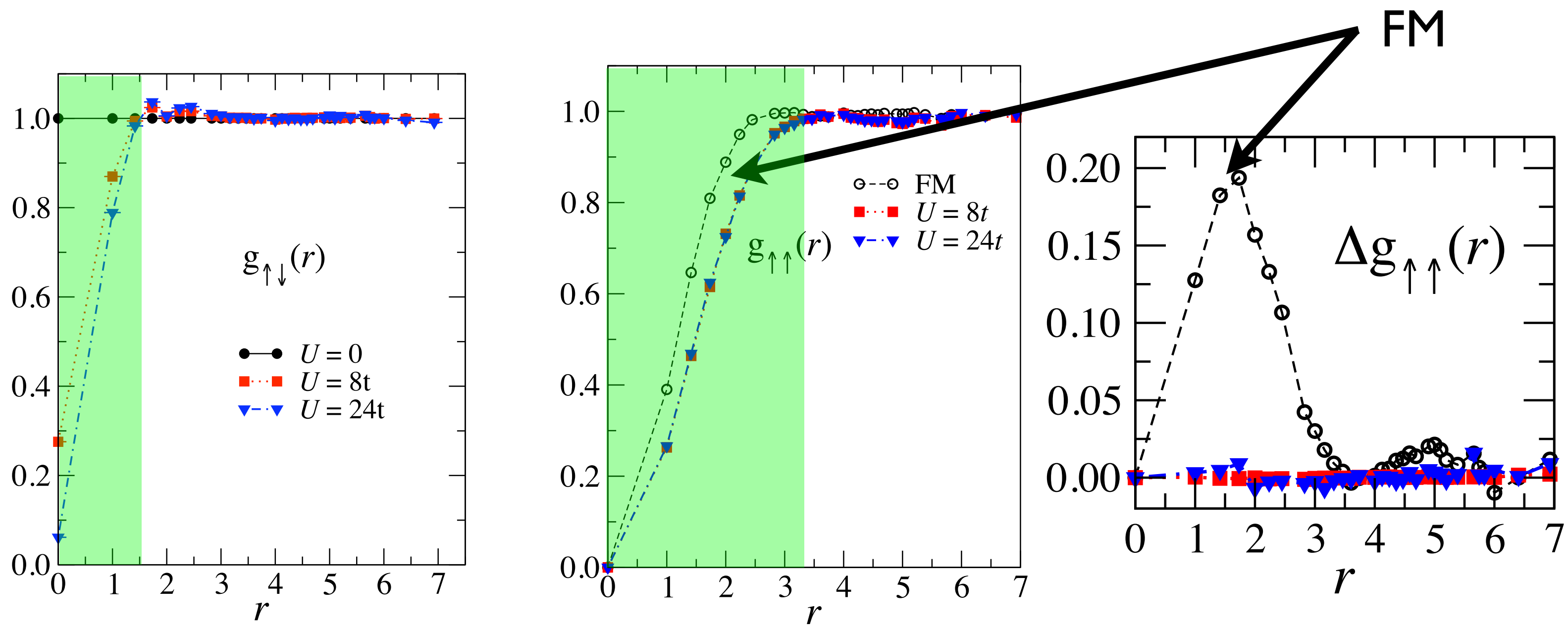
  reduced double occupancy

8x8x8, *n* = 0.0625



Correlation effects

Pair-correlation function:



correlation hole   exchange hole

- Enhanced ferromag. corr, but short-range, weaker than in FM phase
- Consistent with a paramagnetic Fermi liquid

Summary on itinerant FM in Fermi gas

- No ferromagnetism is found in the dilute 3-D Hubbard model up to U~30t, with density up to n=0.5.

- Energy is lowered by creating correlation holes (cf. Wigner, electron gas)

Chang, SZ, Ceperley, PRA, 82, 061603(R) (2010)

- See also commentary in CM Journal Club by C.Varma

Antiferromagnetic order in 2D Hubbard

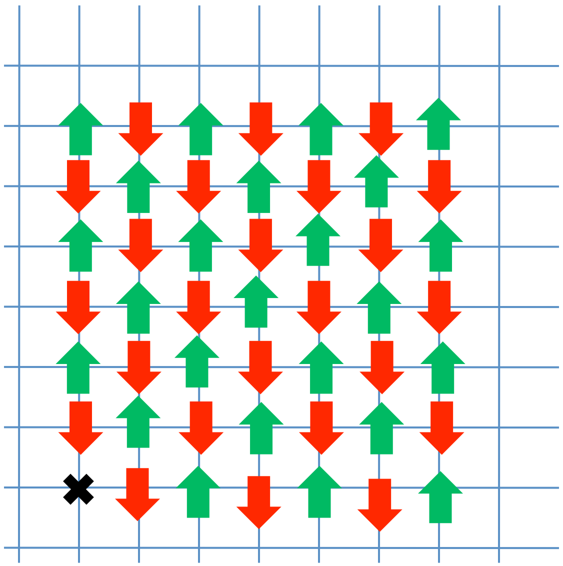
- Half-filling: antiferromagnetic (AF) order

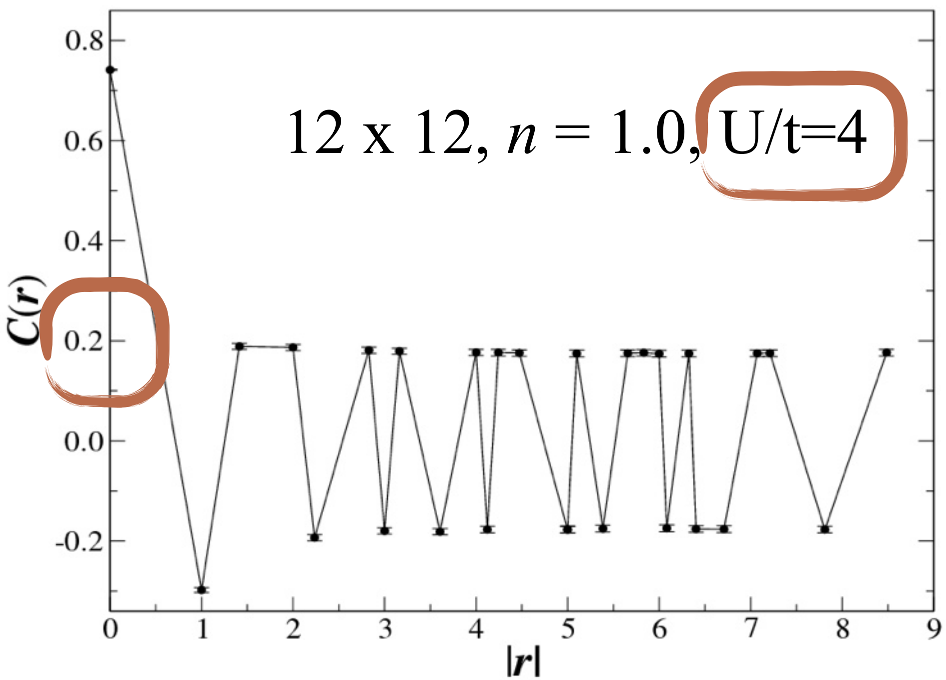
  (Furukawa & Imada 1991; Tang & Hirsch 1983; White et al, 1989; ....)

- Model for high-Tc? Must understand magnetism and its fluctuations first!

Calculate AF correlation:

$$C(\mathbf{r}) = \frac{1}{L \times L} \sum_{\mathbf{r}'} \langle \mathbf{S}_{\mathbf{r}} \cdot \mathbf{S}_{\mathbf{r}+\mathbf{r}'} \rangle$$



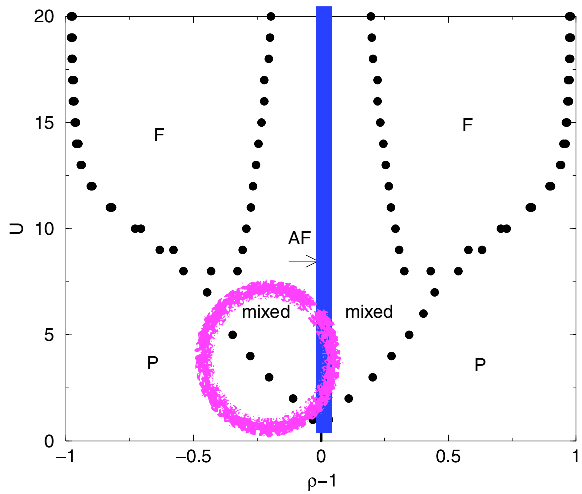


What happens to the AF order with doping?

next →

Mean-field theory

2D Hubbard



Langmann & Wallin (2007)

- Note even the HF answer has not been unambiguous

Xu, Chang, Walter, SZ, 2011

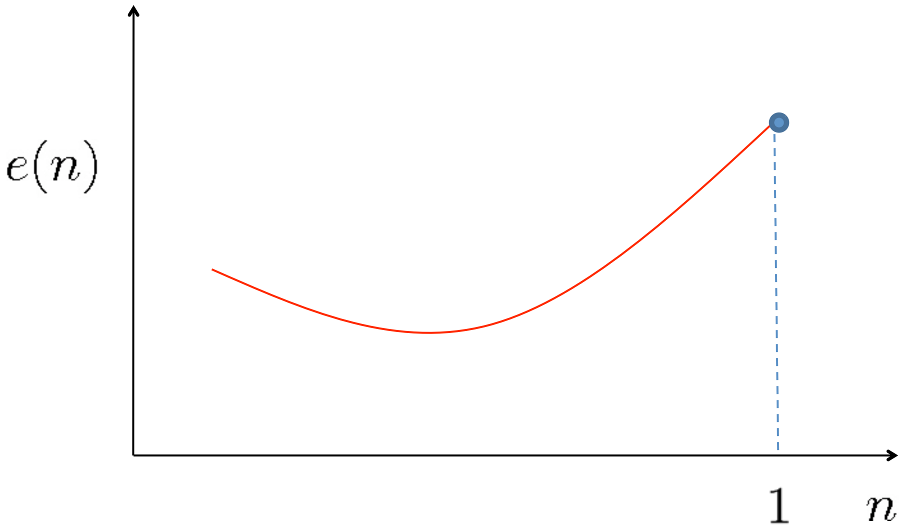
How does correlation modify this?

Phase separation? stripes?.... large body of work

Equation of state

- Equation of state is a convex function for a stable system

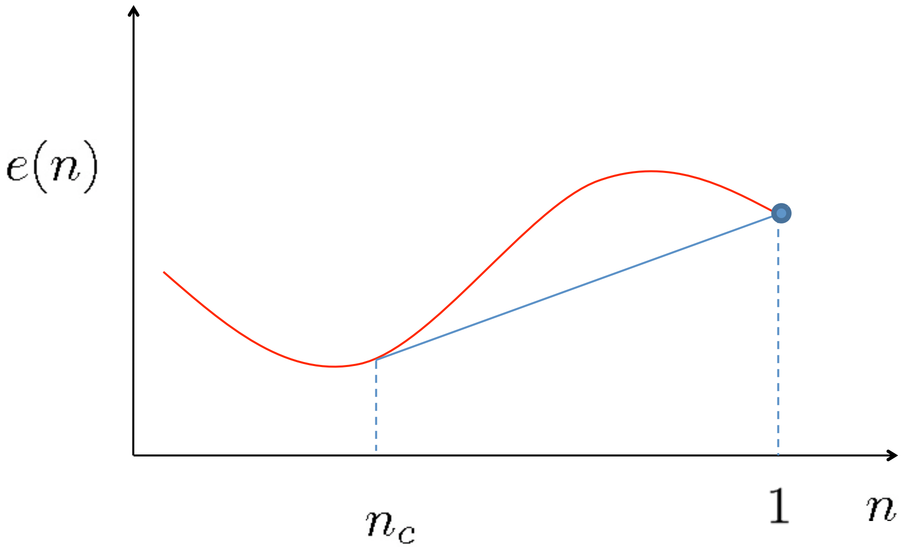
$$\frac{\partial^2 e(n)}{\partial n^2} \geq 0$$



Equation of state

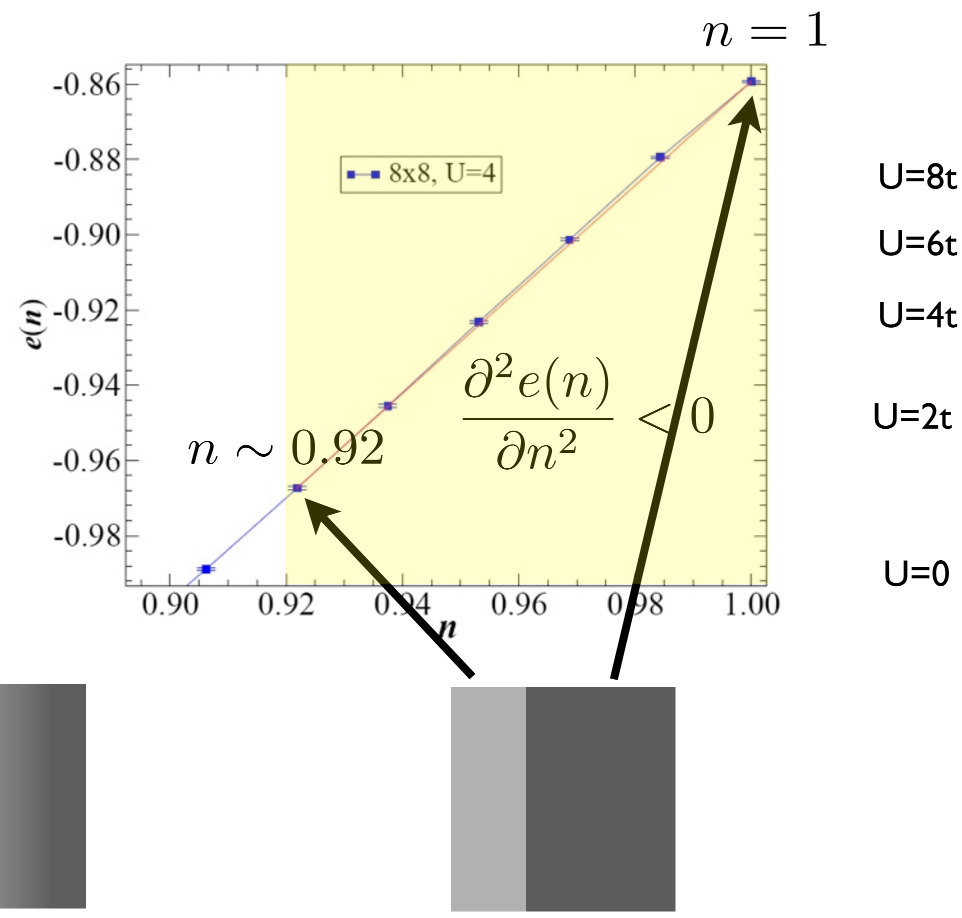
- Instability occurs if the stability condition is violated

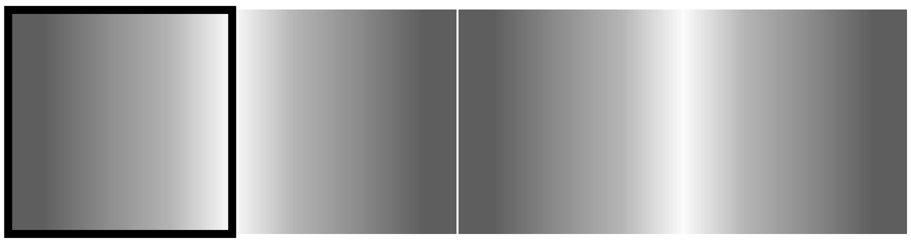
$$\frac{\partial^2 e(n)}{\partial n^2} \geq 0$$



Equation of state in 2D

- Free-electron trial w.f.
- Use 20 ~ 300 random twist angles
- Data of different lattice sizes has good agreement at n < 0.9
- "Unstable" region is found on 8x8, 12x12, 16x16





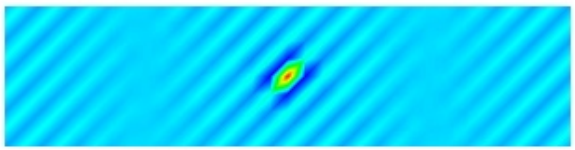
frustrated long wavelength mode ?

phase separation ?

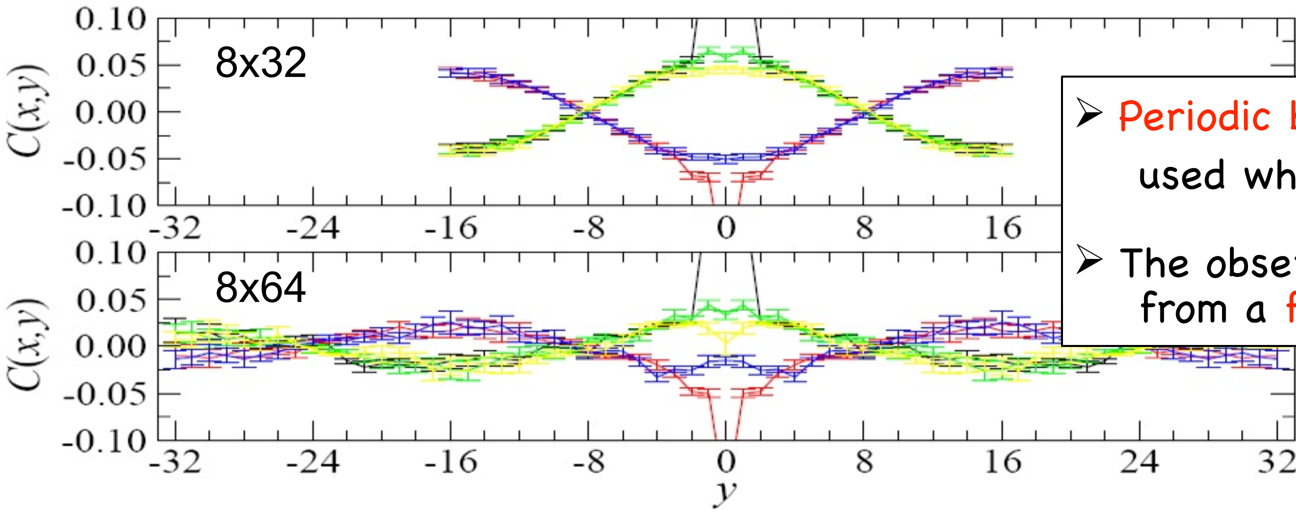
Spin-spin correlation

- Use rectangular lattices to probe correlation length L > 16
- Up to 8x128 supercell (dimension of CI space: 10^600 !)
- Detect spatial structures using correlation functions

8x32
n = 0.9375



$$C(\mathbf{r}) = \frac{1}{N_s}\sum_{\mathbf{r}'}\langle \mathbf{S}_{\mathbf{r}} \cdot \mathbf{S}_{\mathbf{r}+\mathbf{r}'}\rangle$$

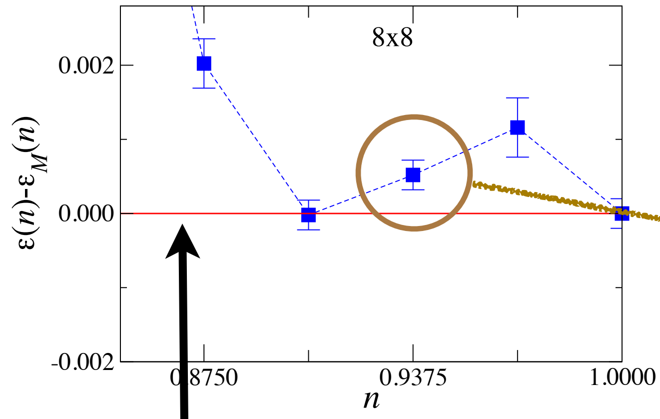


- ➢ Periodic boundary condition is used when calculating C(**r**)
- ➢ The observed structure emerges from a free electron trial state

"staggered": (-1)^y C(x,y)

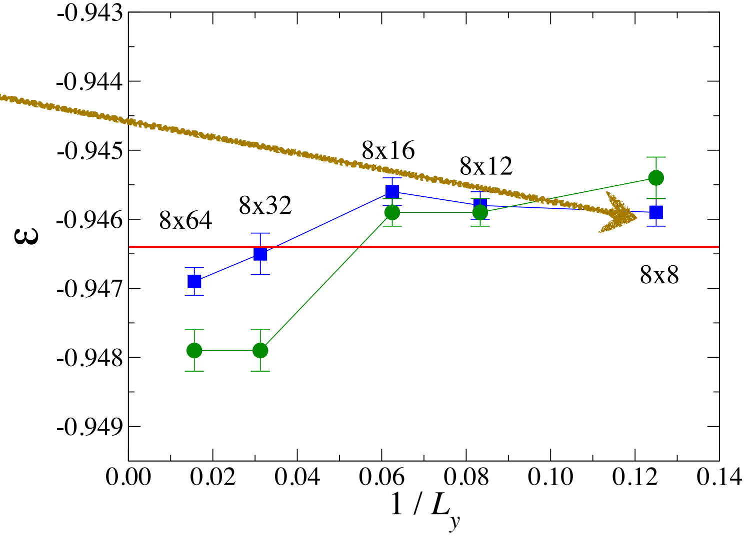
Equation of state, again

- TABC removes one-body shell effects, but not two-body finite-size effects:



Maxwell construction

Rectangular supercells, increasing Ly



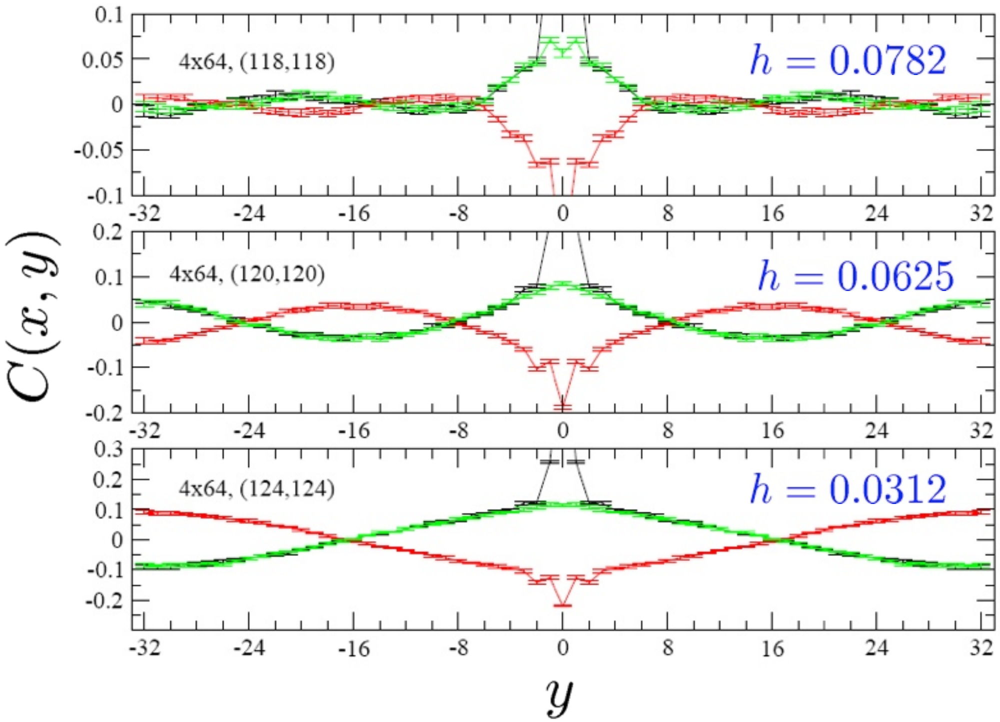
- Instability is from frustration of SDW due to finite size
- At n = 0.9375, need L>~32 to detect SDW state

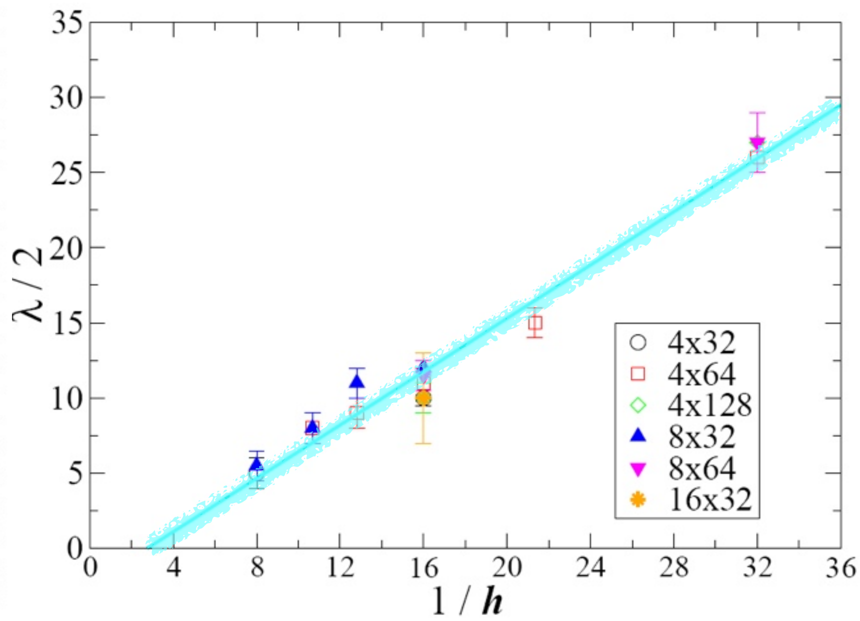
(Previous calculations: Ly~12, with large shell effects)

Wavelength versus doping

Doping h = (1-n) dependence

4x64, U/t = 4.0





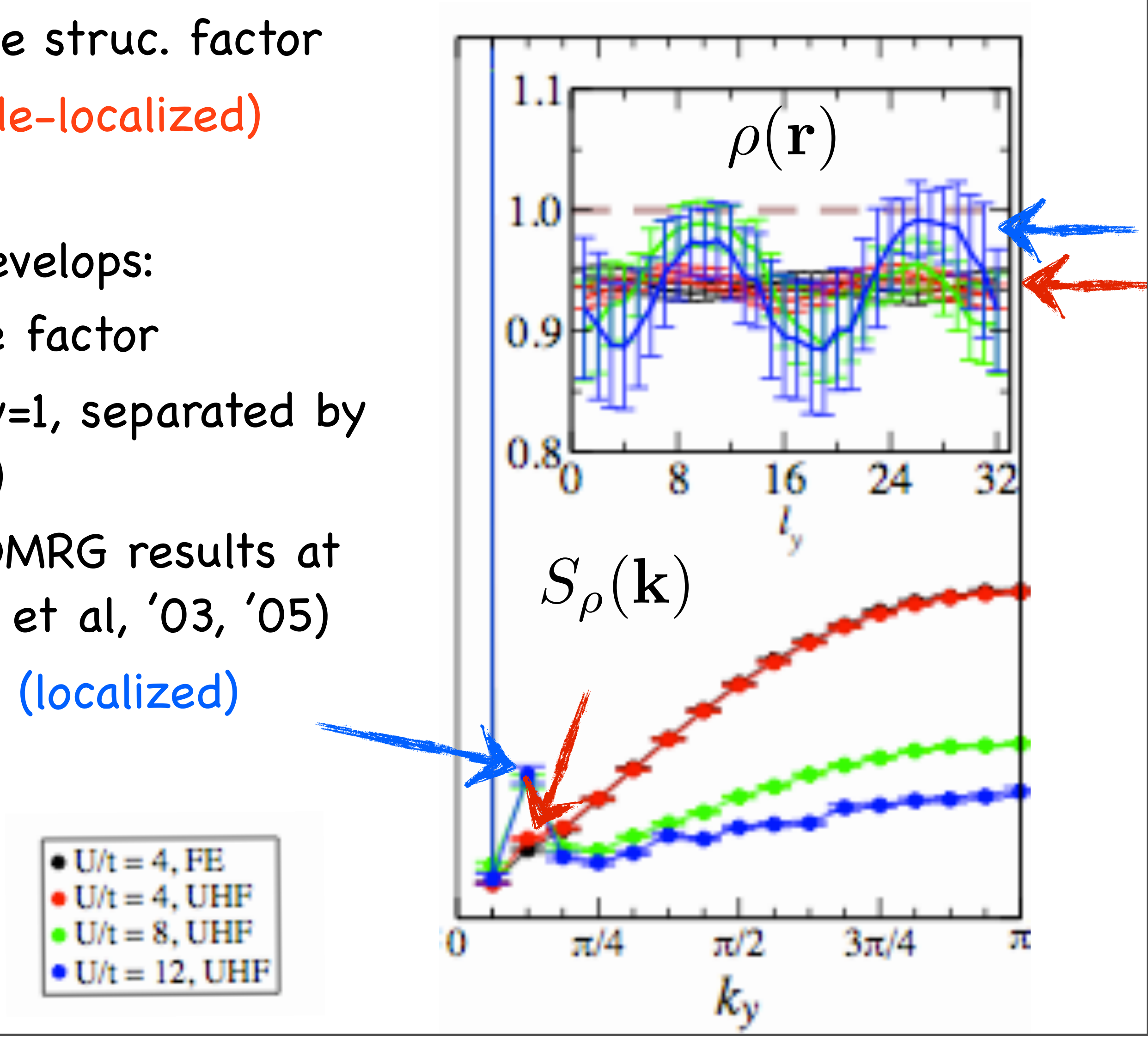
- Wavelength decreases with doping; as does the amplitude
- SDW terminates at finite doping (~0.15), enters paramagnetic state
- Wavelength appears $\propto 1/h$

Chang & SZ, PRL 104, 116402 (2010)

Dependence on U

- At U/t=4, charge is uniform:
  - No peak in charge struc. factor
  - holes fluid-like (de-localized)

- At U/t=8-12, CDW develops:
  - Peak in structure factor
  - Clumps of density=1, separated by dips (SDW nodes)
  - Consistent with DMRG results at large U/t (White et al, '03, '05)
  - holes Wigner-like (localized)



Discussion – constrained path AF QMC

- Pluses
  - Sign problem reduced in many cases
    -> more robust and predictive methods
  - Can do down-folded Hamiltonians (realistic models)
  - Walkers are Slater determinants **(uses a basis)**
    formal connection to DFT:
    k-pts, non-loc psp's, frozen-core, spin-orbit, ...
- Minuses
  - **Uses a basis** --- finite basis-size error
  - Mixed-estimator of total E not variational
  - Not straightforward to include a Jastrow factor in trial w.f. **(....)**
- Also: computing observables requires back-propagation

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) --- crucial for studying `novel phases`

    Hubbard model example
  - Further improvement:
    better constraining wf (BCS/GVB example); free projection or released constraint; frozen-core, SO ....
- Favorable computational scaling ~ O(N^3-N^4)
  - reduce prefactor: (- remove N^4?)
    GTO tricks; better basis; resolution of the identity (modified Cholesky example); .....
  - natural hierarchy in auxiliary-fields, localization, ...

Summary

- Understanding quantum matter by computer simulations (+"theory" and experiment)
- Quantum simulations are a powerful and growing tool in many areas involving quantum physics
- New auxiliary-field quantum Monte Carlo simulation method :
  - Potentially a method to systematically go beyond LDA/HF while directly using much of the existing machinery

    --- **random walks** in **mean-field (Fock) space**
  - Works for both real materials and lattice models
  - Petascale platforms can make this a general tool for a variety of quantum simulations, including in the study of novel phases
- QMC is well positioned to tackle many significant problems on BIG (and small) computers

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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