Auxiliary-field quantum Monte Carlo for correlated electron systems

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Outline

- Interacting quantum matter -- a grand challenge
  - need methods with: accuracy, computational scaling
- A general framework for correlated electron systems: Constrained path (phase-free) AFQMC
  - An ``emergent" of independent-electron solutions
  - How does the sign problem occur? How to control it?
- Applications
  - Hubbard models/optical lattice
  - both molecules and solids

Labs

Packages for both Labs at

http://www.democritos.it/montecarlo2012/index.php/Main/Program

Revised version of Lab 1 will be available: physics.wm.edu/~shiwei

- Lab 1: Jie Xu, Huy Ngyen, Hao Shi, SZ
  - Matlab code (more direct and interactive, slow!)
  - Fermi Hubbard model
  - exercises range from basic exploration to advanced additions to the code (optional)
- Lab 2: Wirawan Purwanto, SZ
  - C++ code
  - Bose Hubbard model: AFQMC for trapped bosons
  - exercises range from basic to advanced

Collaborators:

- Wissam Al-Saidi (Pittsburgh)
- Chia-Chen Chang (UC Davis)
- Simone Chiesa
- Henry Krakauer
- Wirawan Purwanto
- Hao Shi
- Jie Dorothy Xu (Citi Group)
- Fengjie Ma
- Yudis Virgus

Support:

- NSF: electronic structure; method development
- DOE ThChem: quantum chemistry
- DOE SciDAC (UIUC, W&M, Princeton); DOE cmcsn network (Cornell, W&M, Rice, LLNL)
- Computing: DOE INCITE (Oak Ridge) and NSF Blue Waters (UIUC)

The electronic problem

'Simple' theory --- Schrödinger Eq:

$$H\Psi = E\Psi$$

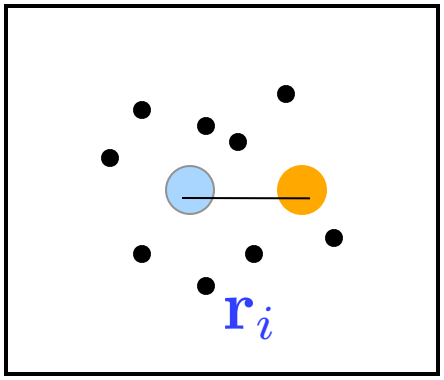
with $H = H_{1-\mathrm{body}} + H_{2-\mathrm{body}} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} V_{\mathrm{ext}}(\mathbf{r}_i) + \sum_{i<j}^{N} V_{\mathrm{int}}(|\mathbf{r}_i - \mathbf{r}_j|)$

Why hard?

because V_{int} is not separable! ($\sum_i$ ...)

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

e.g. Density functional theory



"Bread and butter" calculations

- Density functional theory (DFT) with local-density types of approximate functionals: LDA, GGA, ….
- Independent-electron framework

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

$$\Downarrow$$

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

LDA

- In 2nd quantization:

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

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

HF: $c_i^\dagger c_j^\dagger c_k c_l \rightarrow \langle c_i^\dagger c_l \rangle c_j^\dagger c_k + \cdots$

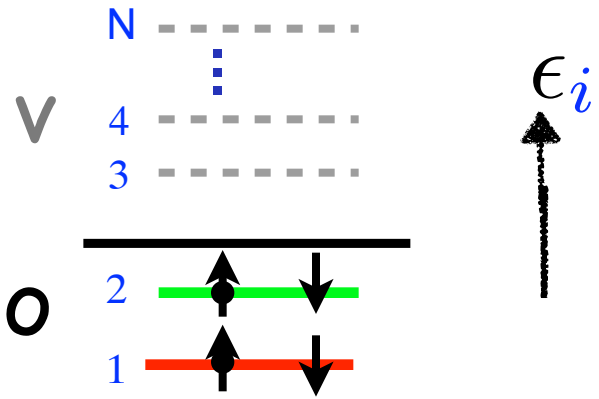
ABINIT, ESPRESSO, VASP,

GAMESS, Gaussian, ….

Independent-electron solution

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

Simply occupy levels for many-body solution:

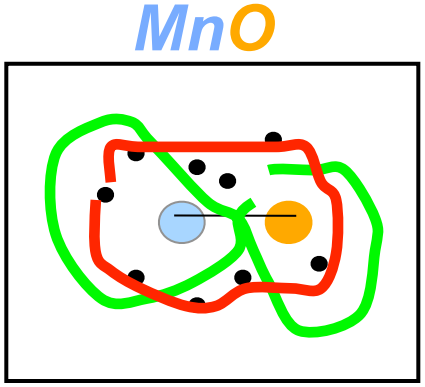


ϵ_i

Note: can break spin symmetry
- non-trivial differences

The solution looks like:

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



Slater det. - antisymmetric

"Bread and butter" calculations

- Independent-electron:

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

HF: $c_i^\dagger c_j^\dagger c_k c_l \rightarrow \langle c_i^\dagger c_l \rangle c_j^\dagger c_k + \cdots$

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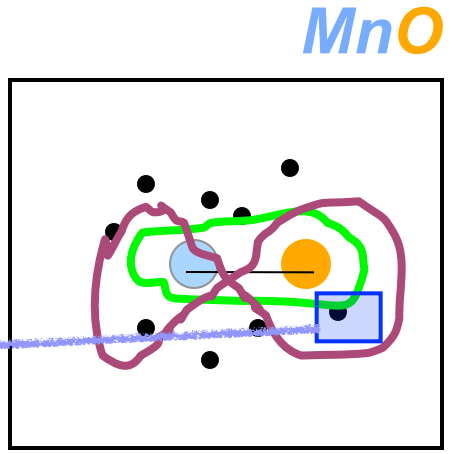
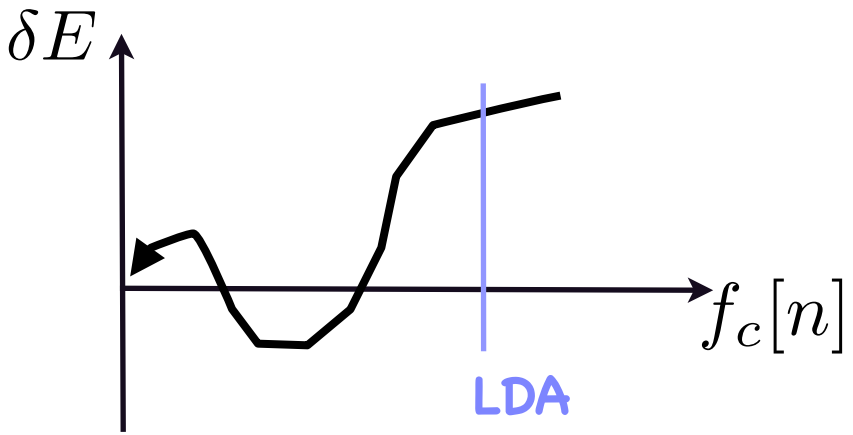


- Change the Hamiltonian "If you don't like the answer, change the question!"
- Demand a single-determinant solution



DFT:

If one has the right functional

--> correct n

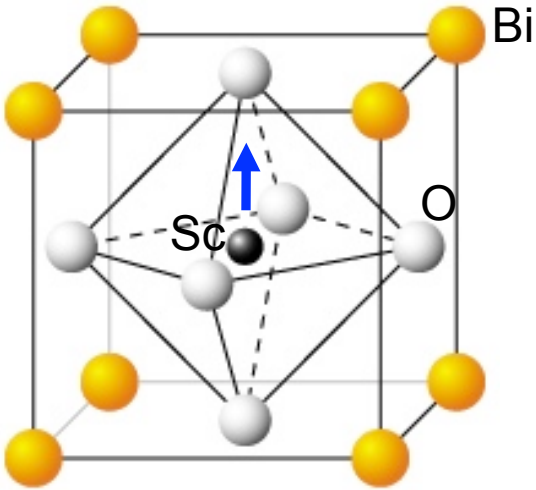
--> correct E

Difficulties with correlated electrons

- Often incorrect in strongly correlated systems
  - high T_c
  - magnetic systems
  - low dim./nano
  - …

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

- Even in 'conventional' systems, small errors can make qualitative differences



typical DFT error of 1% in lattice cnst

→ no ferroelectricity

Why doesn't it always work

How long does it take to drive A -> B?

``mean-field'':

- Williamsburg traffic: yes
- Beijing traffic: no

Sensitivity of functional:

Many-body solution?

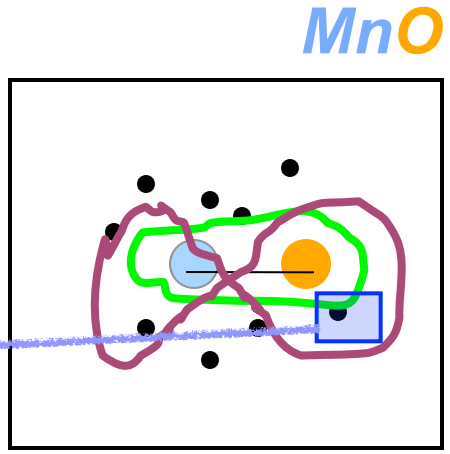
"Bread and butter" calculations

- Independent-electron:

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

HF: $c_i^\dagger c_j^\dagger c_k c_l \rightarrow \langle c_i^\dagger c_l \rangle c_j^\dagger c_k + \cdots$

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



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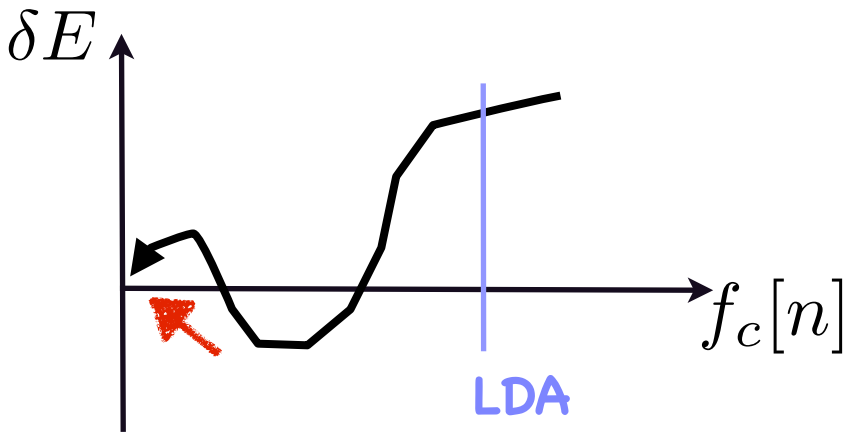


DFT:

If one has the right functional

--> correct n

--> correct E

QMC to climb Jacob's ladder

An auxiliary-field perspective

- Independent-electron:

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

HF: $c_i^\dagger c_j^\dagger c_k c_l \rightarrow \langle c_i^\dagger c_l \rangle c_j^\dagger c_k + \cdots$

- Change the Hamiltonian
- Demand a single-determinant solution

- Can we turn the Hamiltonian **blue** without changing it?

Yes. Consider the propagator $e^{-\tau \hat{H}}$

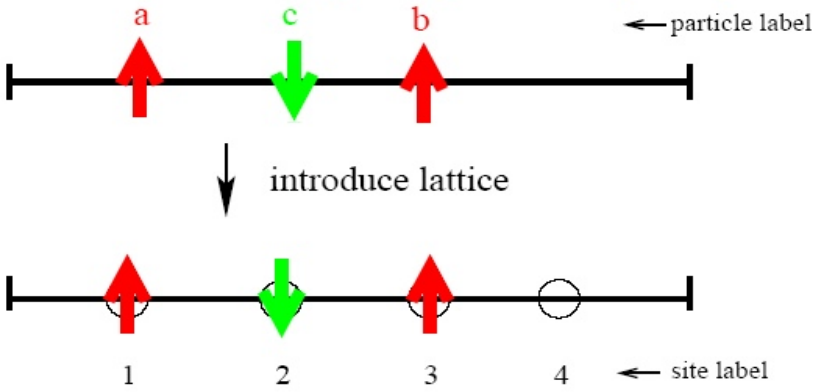
$$\doteq e^{-\tau \hat{H}_1} e^{-\tau \hat{H}_2} + \mathcal{O}(\tau^2)$$

An exact many-body formalism **as an emergent phenomenon** of independent-electron solutions

AFQMC: "emergent" mean-field solutions

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

- 3 fermions in a box, two with $\uparrow$ spin and one with $\downarrow$ 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; $U \propto a_s$

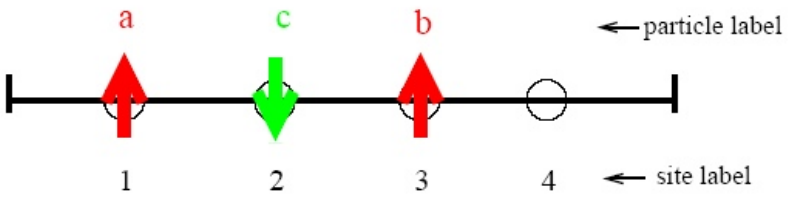
Toy problem – trapped fermions

What is the ground state when U=0 ?

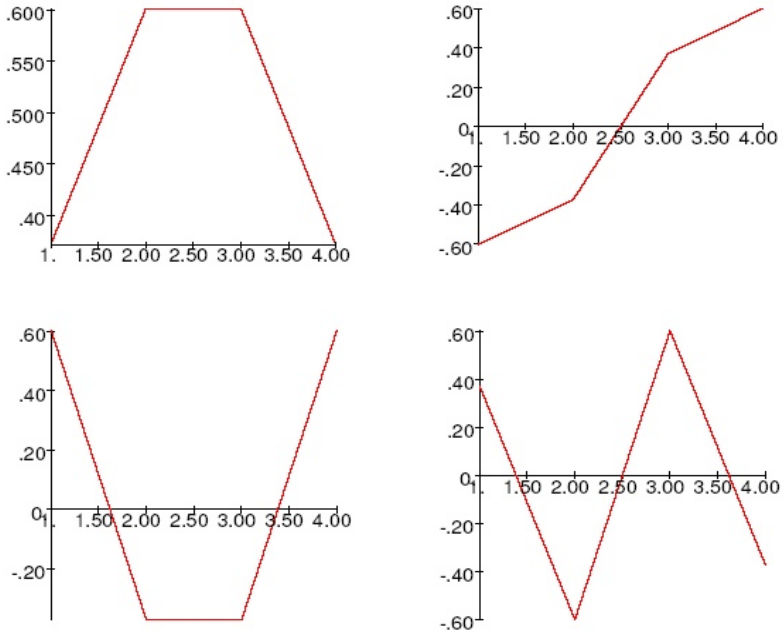
- Diagonalize H directly:

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:

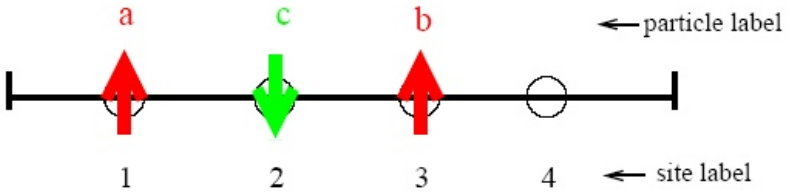
➔ many-body wf:

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

Toy problem – trapped fermions

What is the ground state when U=0 ?

- Diagonalize H directly
- Alternatively, power method:



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 $\qquad$ $|\Psi^{(0)}\rangle$: arbitrary initial state

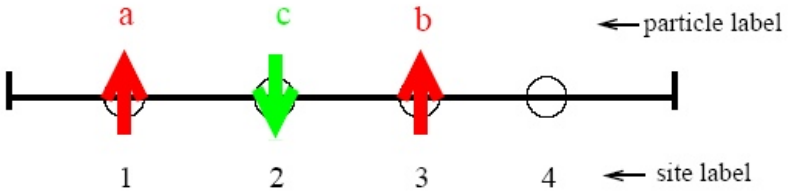
2. Show that the operator $\exp(-\beta H)$ projects out the ground state $|\phi_0\rangle$ from *any* initial state that is not orthogonal to the ground state. That is, given an arbitrary $|\psi^{(0)}\rangle$ that satisfies $\langle\psi^{(0)}|\phi_0\rangle \neq 0$, we have

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

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.:

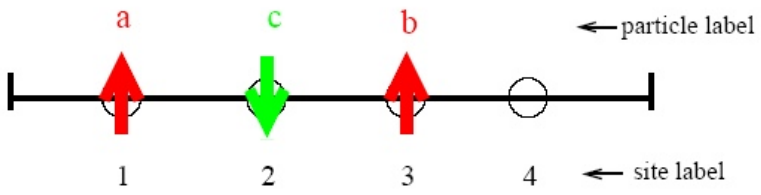
ground-state wf:

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

Toy problem – trapped fermions

What is the ground state when U=0 ?

- Diagonalize H directly
- Alternatively, power method:



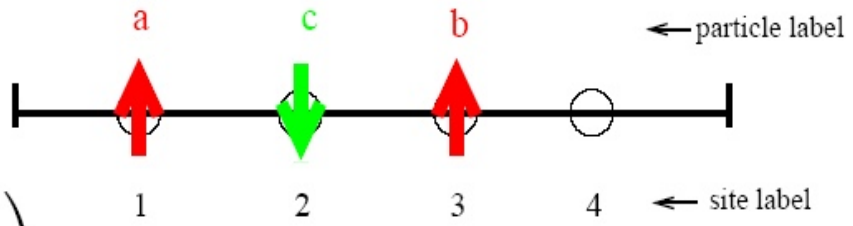
$$e^{-\tau H}: \quad \left(4 \times 4 \right) \otimes \left(4 \times 4 \right) \equiv B_K \ \text{operate on any } |\Psi^{(0)}\rangle \text{ repeatedly} \quad \Rightarrow |\Psi_0\rangle$$

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

-> i.e., no 'sign problem' in non-interacting systems

Toy problem – trapped fermions

Properties of Slater determinants:



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

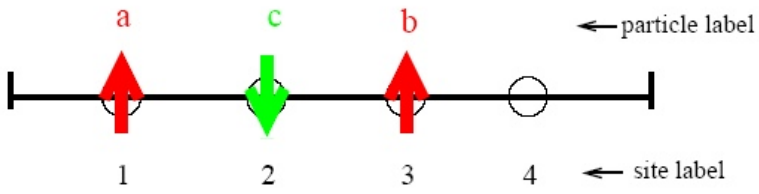
- What is the probability to find the electron configuration shown in the picture? That is, how to calculate $\langle R|\phi\rangle$?
- How to calculate $E_0 = \langle\phi|H|\phi\rangle$ from the wave function?
- How to calculate the density matrix? The spin-spin correlation function?

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?

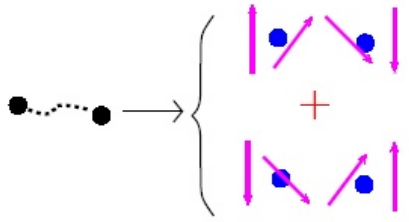
  Yes, with Hubbard-Stratonivich transformation

AFQMC: "emergent" mean-field solutions

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:

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

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

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

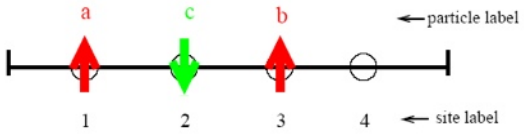
What is the ground state, if we turn on U ?

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

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

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

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



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

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

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

Recall: Monte Carlo methods

We will use two things which are foundations to QMC

1) Monte Carlo is great at evaluating many-dimensional integrals (most efficient beyond d>4~6)
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" prob. for particle to be at y

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

Summary: an auxiliary-field perspective

Consider the propagator $e^{-\tau \hat{H}} \doteq e^{-\tau \hat{H}_1} e^{-\tau \hat{H}_2} + \mathcal{O}(\tau^2)$

- Independent-electron: $e^{-\tau \hat{H}_{\rm LDA}(n)} \doteq e^{-\tau \hat{H}_1} e^{-\tau \hat{H}_{\rm xc}(n)}$

Thus, LDA calculation:

$$e^{-\tau \hat{H}_{\rm LDA}(n^{(1)})} \cdots \leftarrow e^{-\tau \hat{H}_{\rm LDA}(n^{(1)})} |SD^{(1)}\rangle \leftarrow |SD^{(0)}\rangle$$

Single-determinant solution

- Many-body: $\hat{H}_2 = -\sum_\gamma \hat{v}_\gamma^2$

$$e^{v^2} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\sigma^2} e^{2\sigma v} d\sigma$$

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

Propagation leads to multi-determinants

Importance sampling to make practical

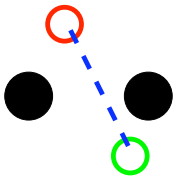
Different form --> Hartree, HF, pairing, ..

SZ & Krakauer, '03
Purwanto & SZ, '05

Two-site Hubbard model

An illustration:

H_2 molecule:

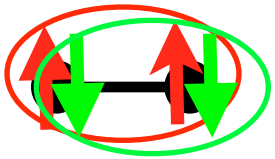


ion, fixed, +1 charge

electron, spin ↑

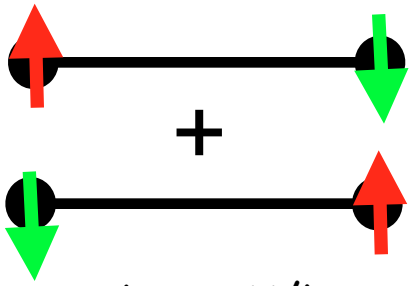
electron, spin ↓

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



small U/t

* 1 determinant



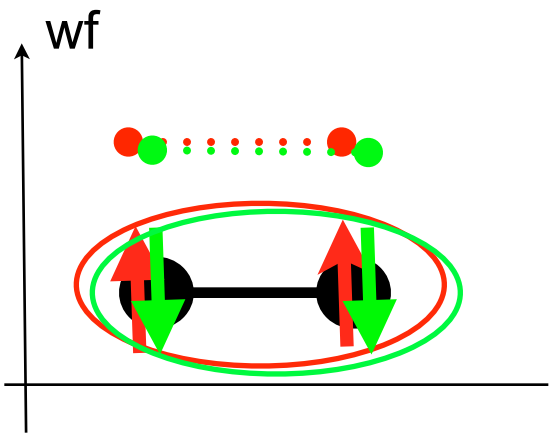
large U/t

* multi determinants
* correlation
* note 'antiferromagnetism'

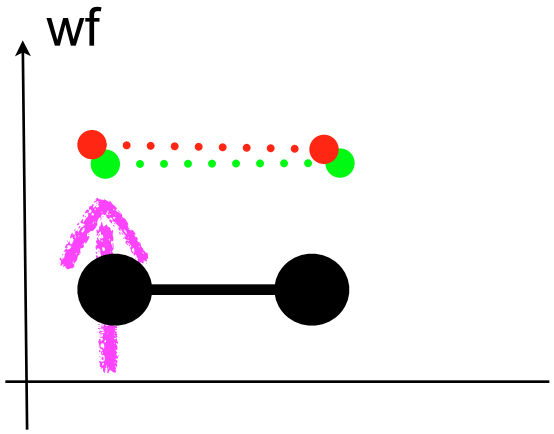
Two-site Hubbard model

How AFQMC works:

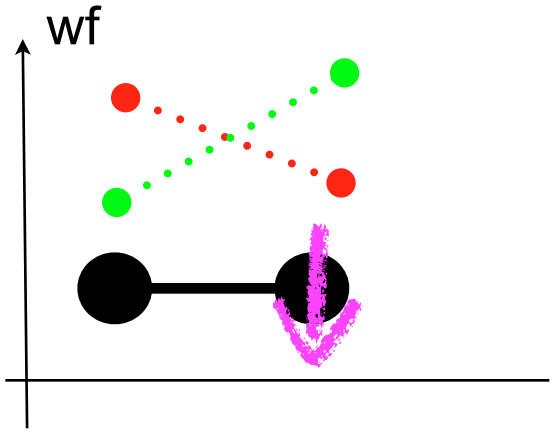
H2 molecule



mean-field



auxiliary-field QMC



+ + ...

- Formalism similar to LGT
- But this formulation allows a natural way to control sign problem

Full electronic Hamiltonians

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

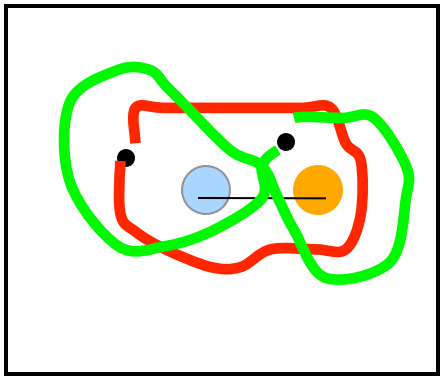
- A Slater determinant:

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

N : basis

M : electrons

MnO



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 $|k\rangle \equiv \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}_k \cdot \mathbf{r}}$:

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

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

derive

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

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

'density' decomposition

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

Slater determinant random walk (preliminary II)

HS transformation for full V-matrices (e.g. Gaussian basis sets)

modified 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

Purwanto et al, J. Chem. Phys. 135, 164105 (2011)

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

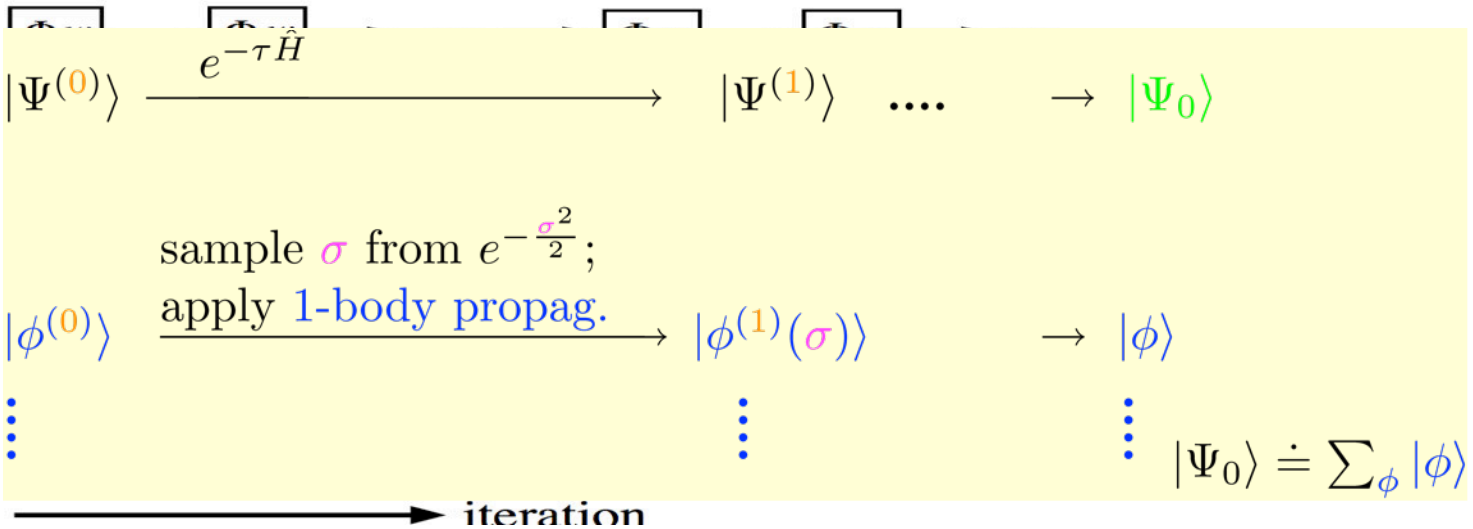
SZ, Krakauer

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:

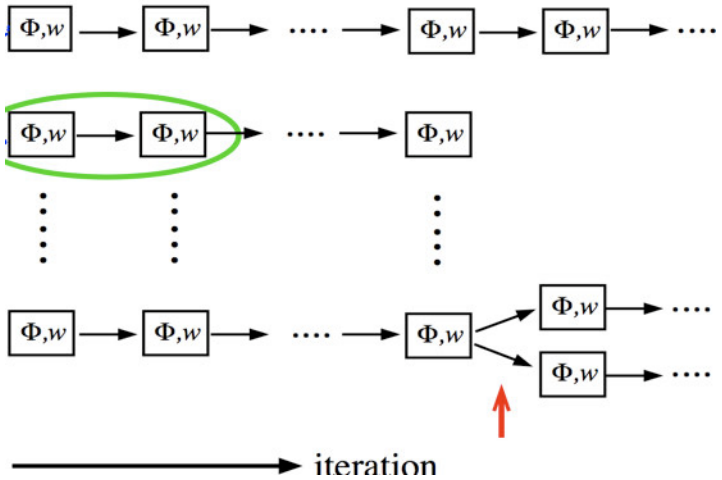


Exact so far (why don't we use path-integral formalism? later)

next →

Summary: AF QMC framework

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



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

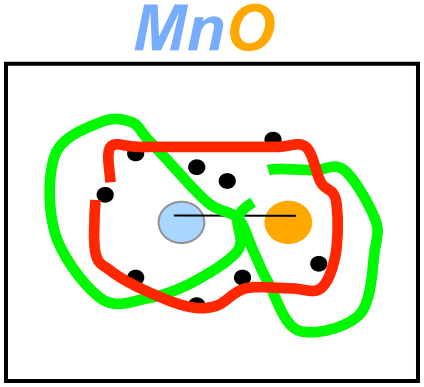
$$e^{\sigma \hat{v}} \begin{pmatrix} \psi_1 & \psi_1 \\ \psi_2 & \psi_2 \\ \cdot & \cdot \\ \cdot & \cdot \\ \psi_N & \psi_N \end{pmatrix} \rightarrow \begin{pmatrix} \psi'_1 & \psi'_1 \\ \psi'_2 & \psi'_2 \\ \cdot & \cdot \\ \cdot & \cdot \\ \psi'_N & \psi'_N \end{pmatrix}$$

NxN matrix

1-body op

Gaussian, or 'Ising' variable

N is size of 'basis'



Importance sampling -> better efficiency

Summary: AF QMC framework

How does the weight 'w' come about?

$$\Phi = UDV$$

We have formulated this as branching random walks

Basic idea of AFQMC, done with path-integrals over AF paths, has been around since the '80s.

Koonin; Scalapino, Sugar, White; Hirsch; Baroni & Car; Sorella; Fahy & Hamann; Baer et. al. ....

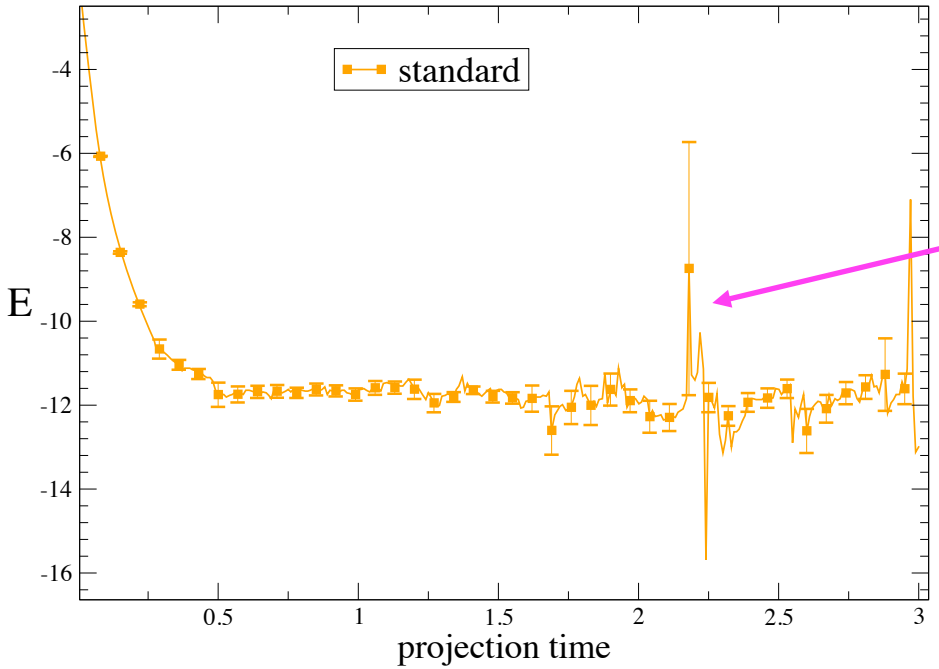
The new formulation

- allows a close connection with DFT and HF
- makes possible a way to control the sign problem

The sign/phase problem

Hubbard model

4x4, n=0.875, U/t=8 (strongly corr)



Exponential noise

- More severe at lower T, larger system size
- or in the most correlated regime

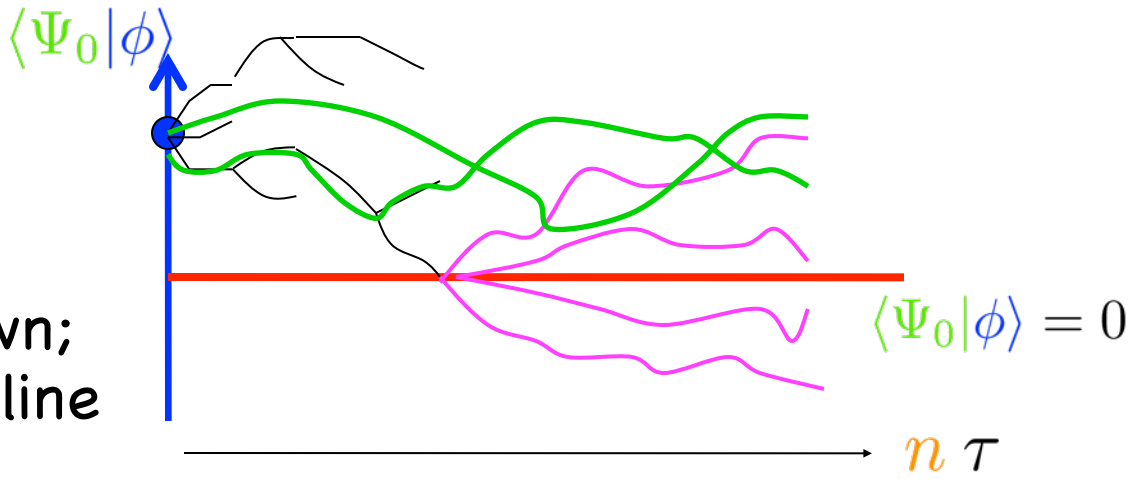
Koonin; Scalapino & White et al; Baroni & Car; Fahy & Hamman; Baer et al;

How does the sign problem happen?

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

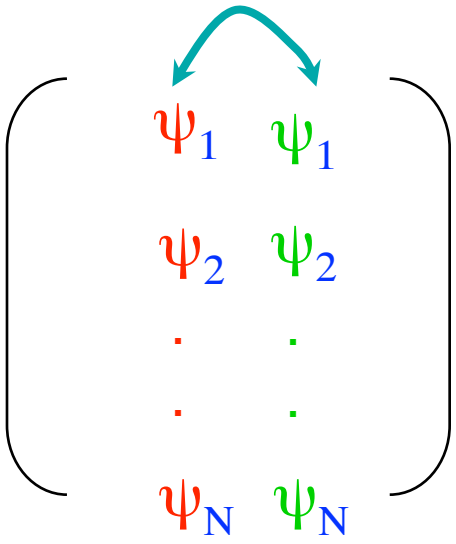
In special cases (1/2 filling, or U<0), symmetry keeps paths to one side → no sign problem

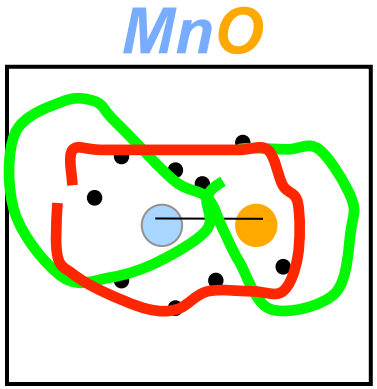
next →

The sign problem

Sign/phase problem is due to --

"superexchange":





Slater det. - antisymmetric

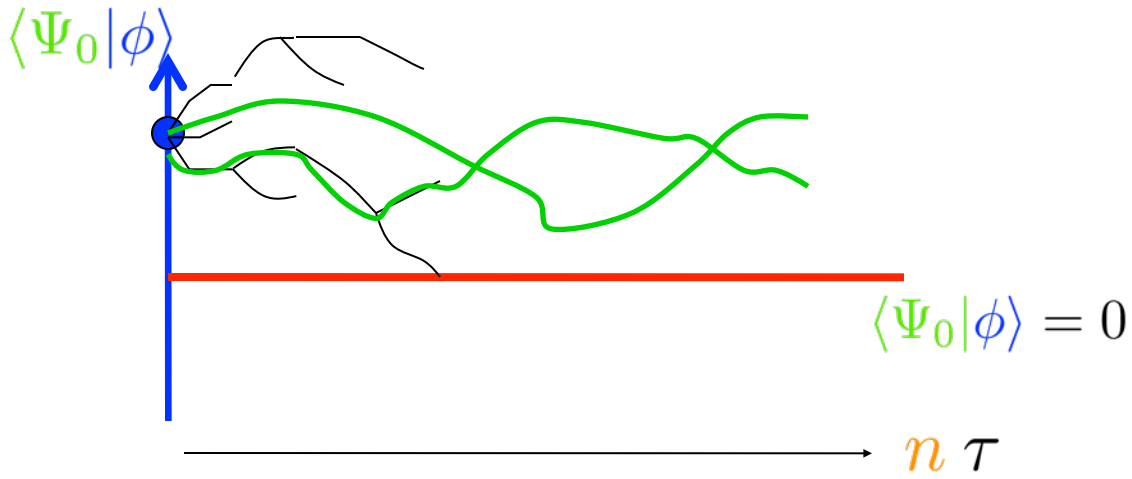
To eliminate sign problem:

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

SZ, Carlson, Gubernatis, '97; SZ '00; Chang & SZ '10

How to control the sign problem?

- Constrained path appr.



keep only paths that never reach the node

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

Zhang, Carlson, Gubernatis, '97

Zhang, '00

Trial wave function used to make detection

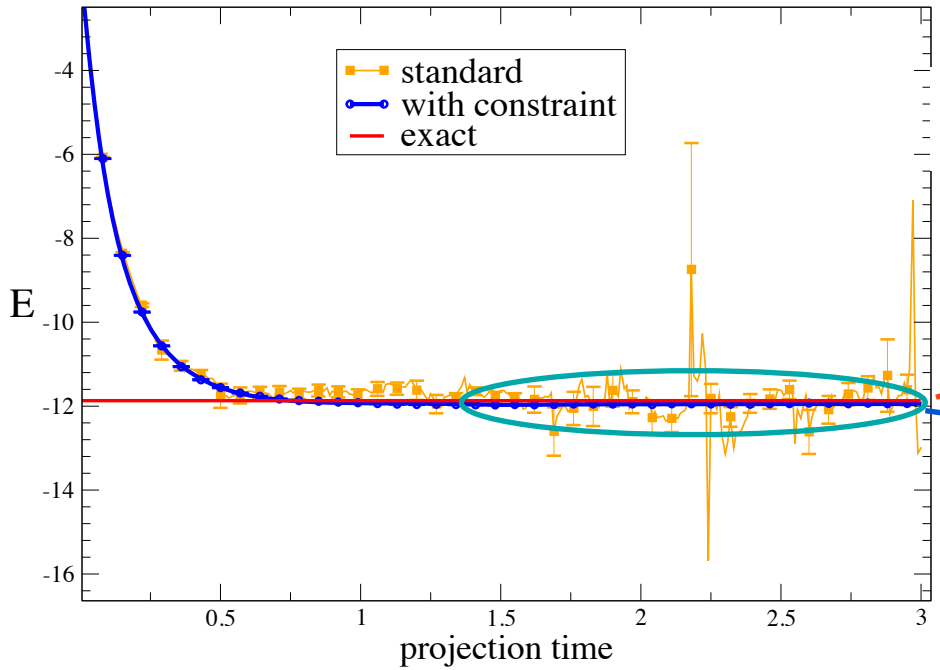
Connection to fixed-node, or restricted path (Ceperley),

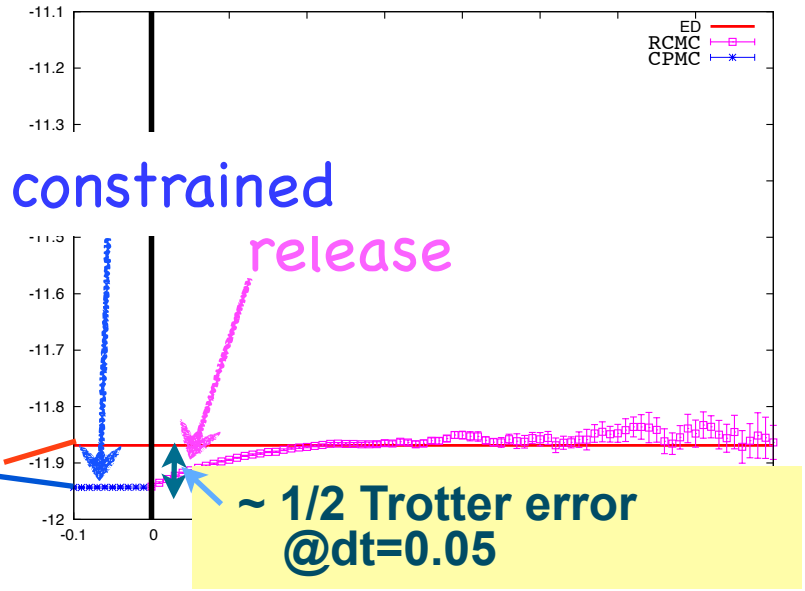
but in Slater determinant space --> different behavior

next →

Controlling the sign/phase problem

4x4, n=0.875, U/t=8





constrained

release

~ 1/2 Trotter error @dt=0.05

Can release constraint

Shi & SZ (PRB, 2013)

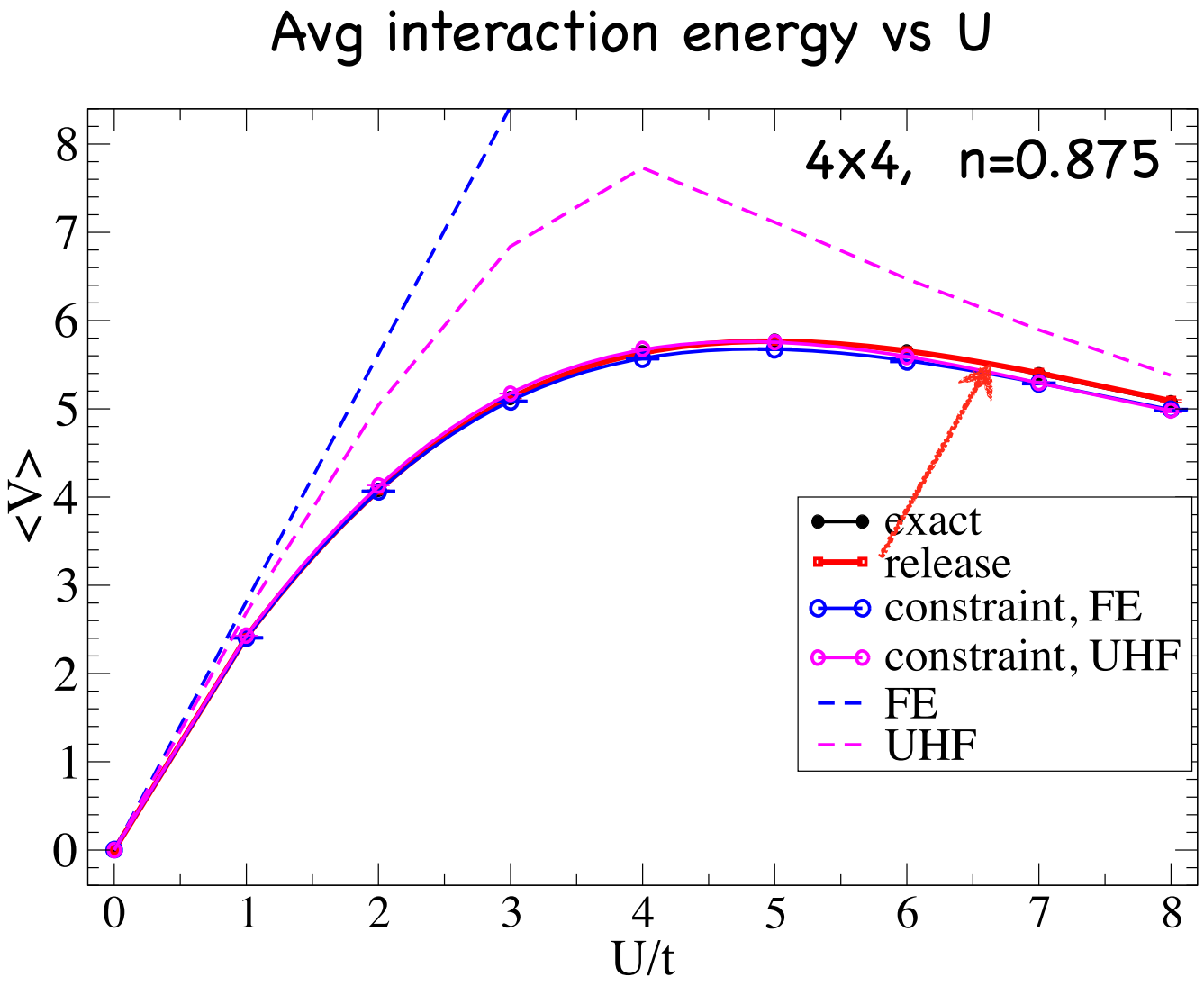
- Free-projection is exact, but exponential scaling
- Constraining the paths to remove contamination
- N^3 scaling, approximate -- high accuracy
- Constraint release: a systematically improvable approach with more computational cost

(also Ceperley; Sorella)

Controlling the sign/phase problem: accuracy

<V> = U*(double occupancy)

- Recovers from incorrect physics of constraint
- Insensitive to choices of constraining wf

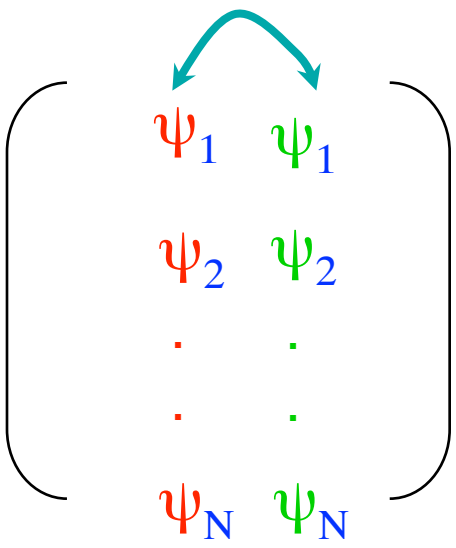


Shi & SZ (unpublished, 2013)

The phase problem

Sign/phase problem is due to --

"superexchange":



Many-body: $\hat{H}_2 = -\sum_\gamma \hat{v}_\gamma^2$

$$e^{v^2} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\sigma^2} e^{2\sigma v} d\sigma$$

Slater det. - antisymmetric

To eliminate sign problem:

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

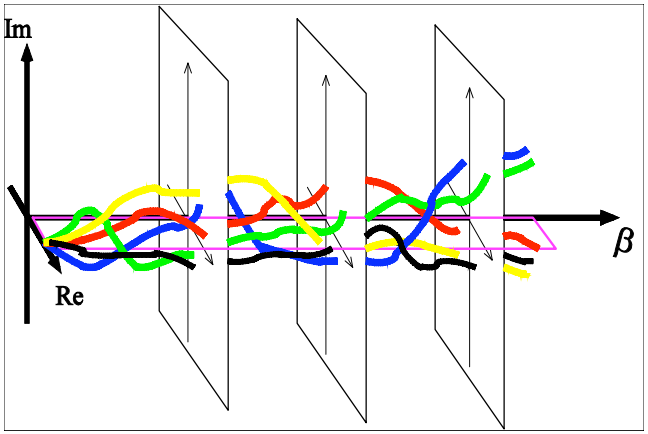
To eliminate phase problem:

Generalize above with gauge transform --> "phaseless constraint"

SZ & Krakauer, '03; Chang & SZ, '10

Controlling the phase problem

Sketch of approximate **solution**:



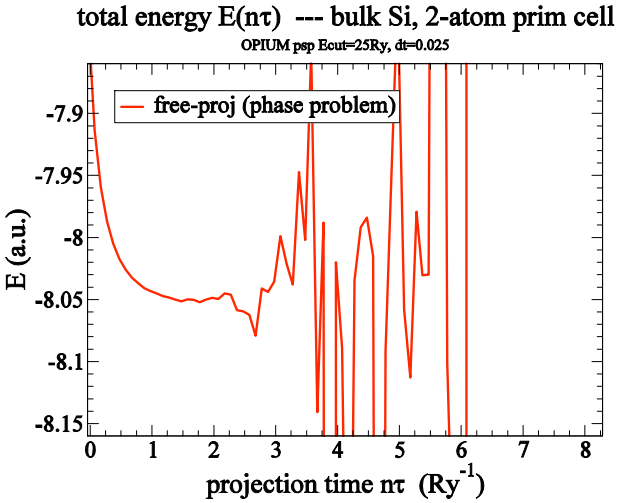
- Modify propagator by "gauge transformation': phase → degeneracy (use trial wf)
- Project **to one overall phase**: break "rotational invariance"

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

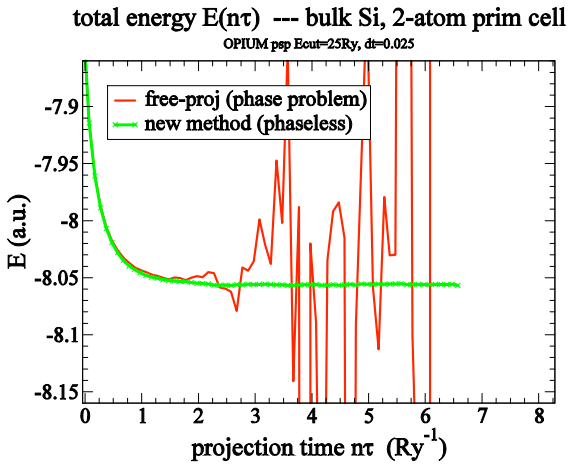
- subtle, but key, difference from: real$\langle \Psi_T | \phi \rangle$ 0

(Fahy & Hamann; Zhang, Carlson, Gubernatis)

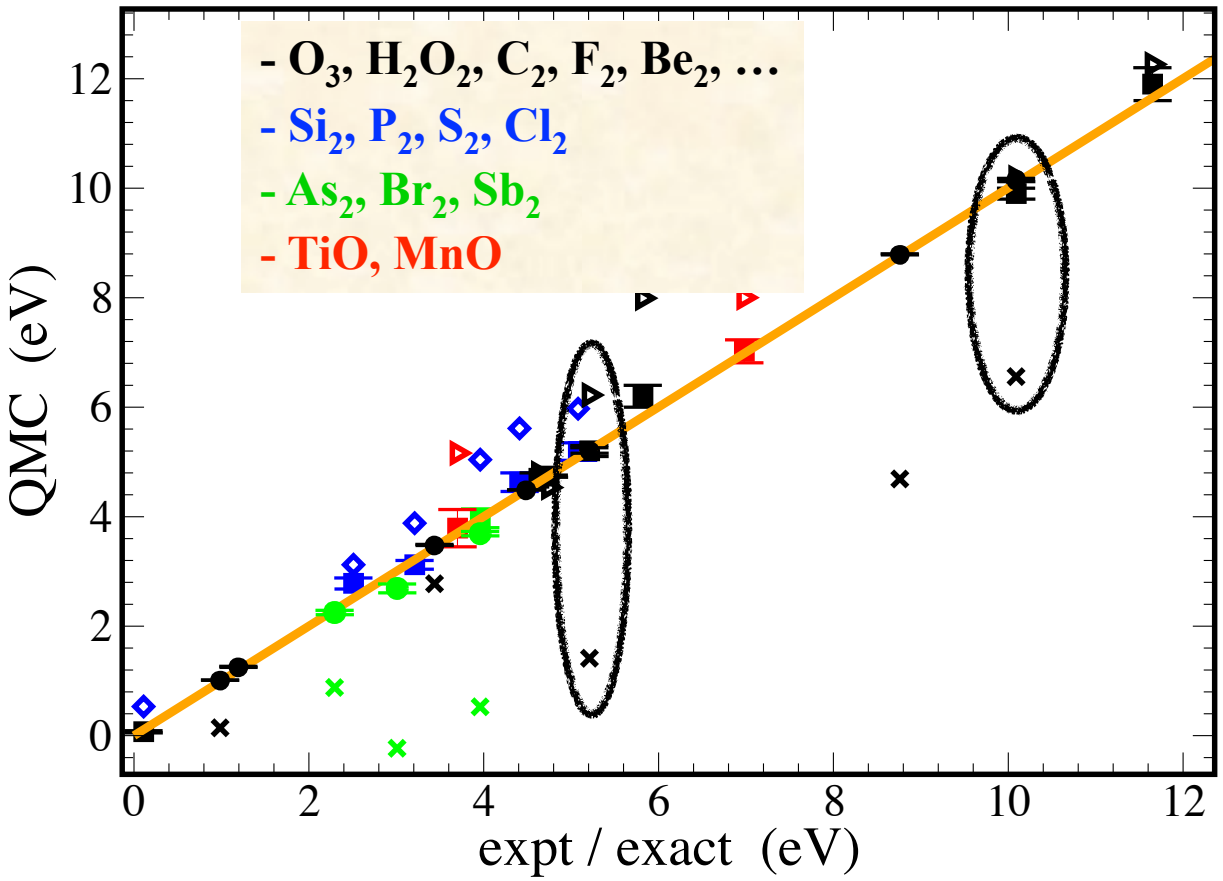
Before:



After:



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

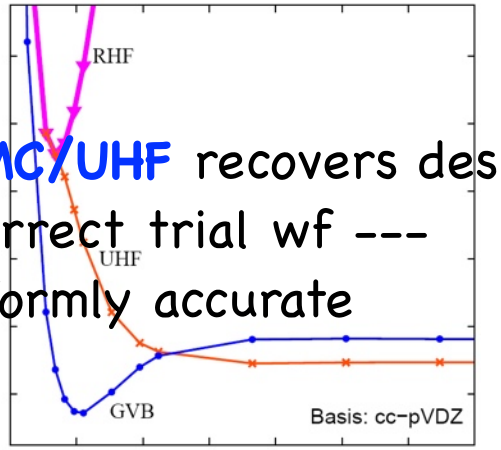
LDA: triangle

GGA: diamond

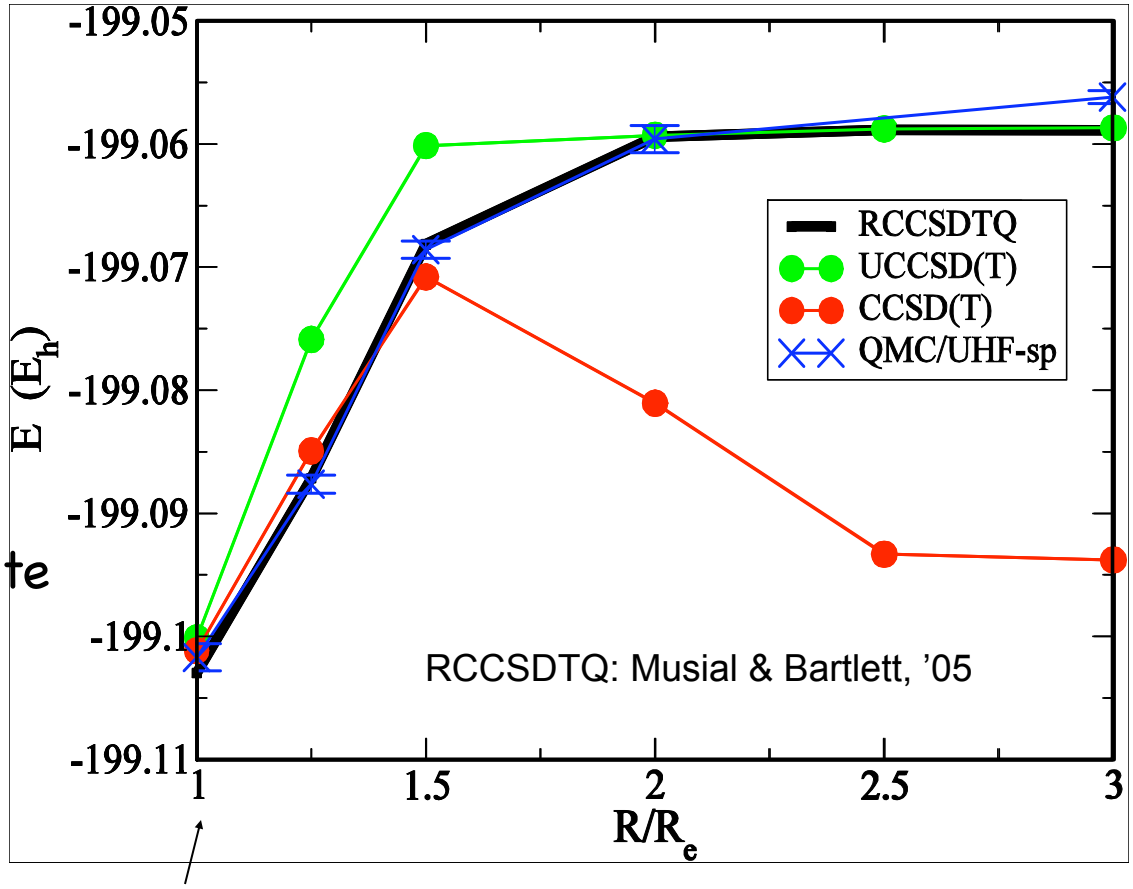
F_2 bond breaking

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



Equilibrium → **Dissoc. limit**

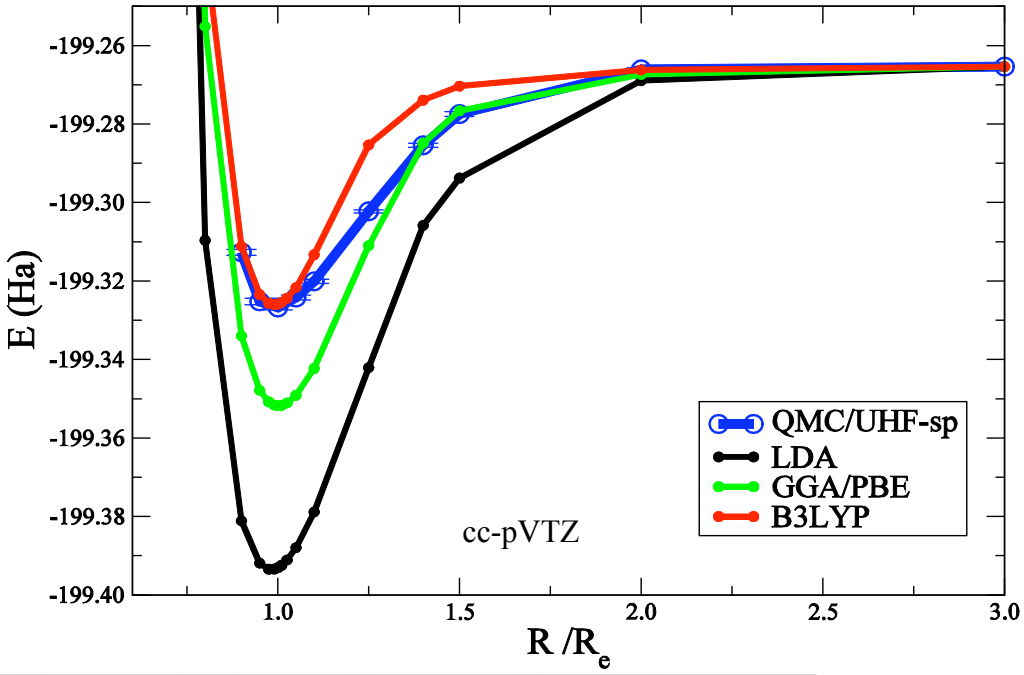
"bonding" *"insulating"*

(removes spin contamination)

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:

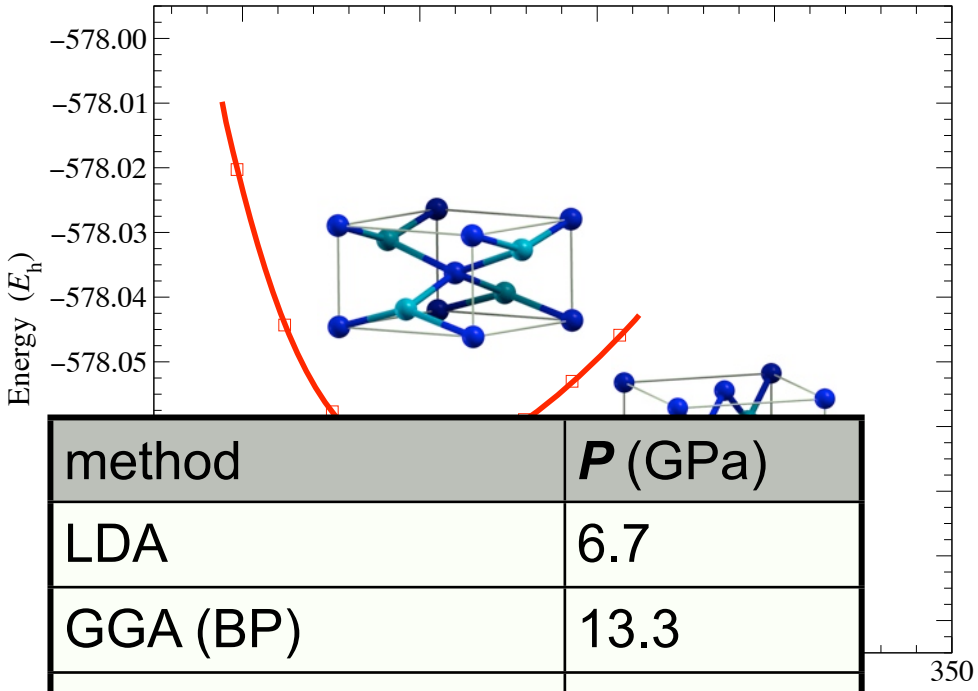


	Expt[a]	AFQMC	RCCSD(T)	UCCSD(T)	LSDA	GGA/PBE	B3LYP
Basis: cc-pVQZ							
r_e (Å)	1.4131(8)	1.411(2)	1.4108	1.3946	1.3856	1.4136	1.3944
ω_0 (cm^{-1})	916.64	912(11)	929	1036	1062	997	1109
D_e (eV)[b]	1.693(5)	1.77(1)	–	1.567	3.473	2.321	1.634
D_e (eV)[c]	1.693(5)	1.70(1)	1.594	1.569			

Purwanto et. al., JCP, '08

Periodic Solids

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



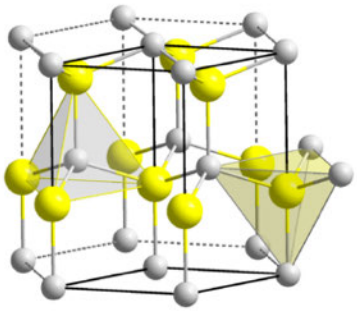
method	***P*** (GPa)
LDA	6.7
GGA (BP)	13.3
GGA (PW91)	10.9
GGA (PBE)	~8.9
DMC (*Alfe et al '04*)	16.5(5)
AFQMC	**12.6(3)**
experiment	**10.3-12.5**

- 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

Purwanto et. al., PRB, '09

Excited states in solids

- Method can be generalized to excited states, by an additional orthogonalization step of the excited orbitals in each walker with virtual orbitals



- ZnO: LEDs, laser diodes

  band gap challenge:

  - GW: recent debates
  - hybrid: choice of functionals? predictive?

- **AFQMC**: uses GGA trial wf; high-quality small-core pseudopotential; finite-size correction

Fundamental gap in ZnO (wurtzite)

method	***Band gap*** (eV)
GGA	0.77
LDA+*U*	1.0
Hybrid functionals	3.3; 2.9
GW	3.4, 3.6, 2.56
AFQMC	**3.26(16)**
experiment	**3.30, 3.44, 3.57**

Ma, SZ, Krakauer, NJP (2013)

Superconductivity: cold atomic gases

- 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 →

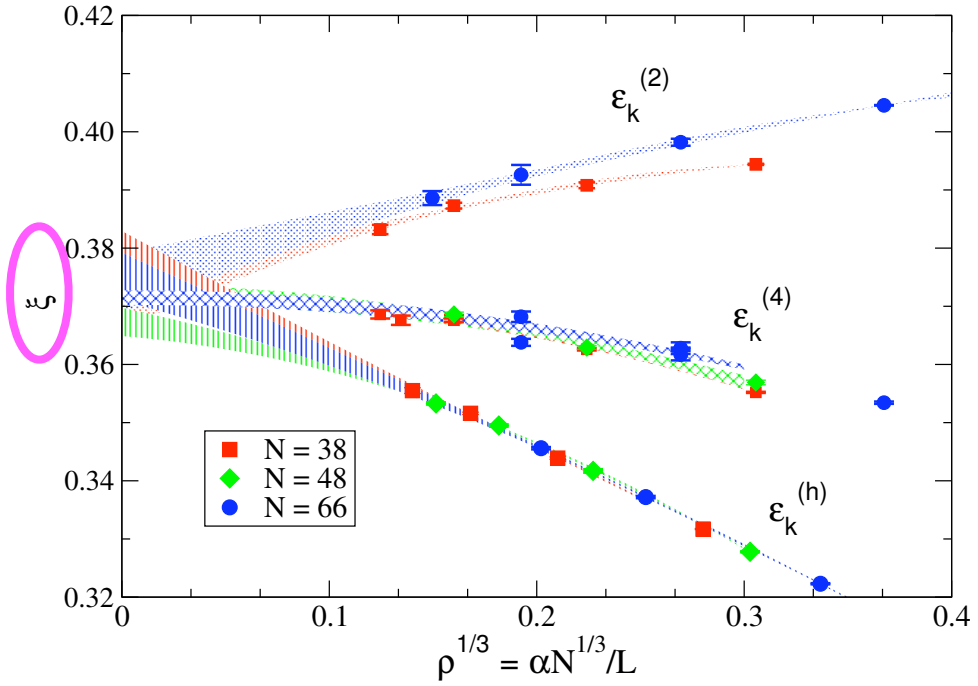
Superconductivity: cold atomic gases

- In this case, no sign problem in AFQMC. Trial wf is projected BCS (AGP)

$$\text{Need } \langle \Psi_{\rm AGP} | c_i^\dagger c_j | \phi \rangle \text{ and } \langle \Psi_{\rm AGP} | c_i^\dagger c_j | \phi \rangle$$

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

same scaling as single Slater determinant



Exact result:

$$\xi = 0.372(5)$$

MIT expt (Zwierlein group):

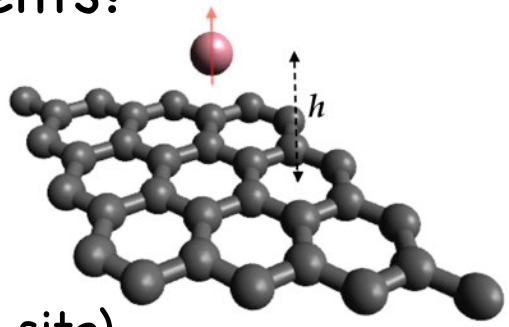
$$0.376(5)$$

arXiv:1110.3309

next →

Magnetism: Co adsorption on graphene

- Spintronics applications of graphene --- adsorb transition metal atoms to induce local moments?
- Conflicting theoretical results:
  - ✦ GGA: min is Co low-spin, h~1.5
  - ✦ B3LYP: high-spin, h~1.8
  - ✦ GGA+U: high-spin, h ~ 1.9 (but global min is top site)



- AFQMC benchmark study in Co/benzene:
  - ✦ Gaussian basis sets as in quantum chem
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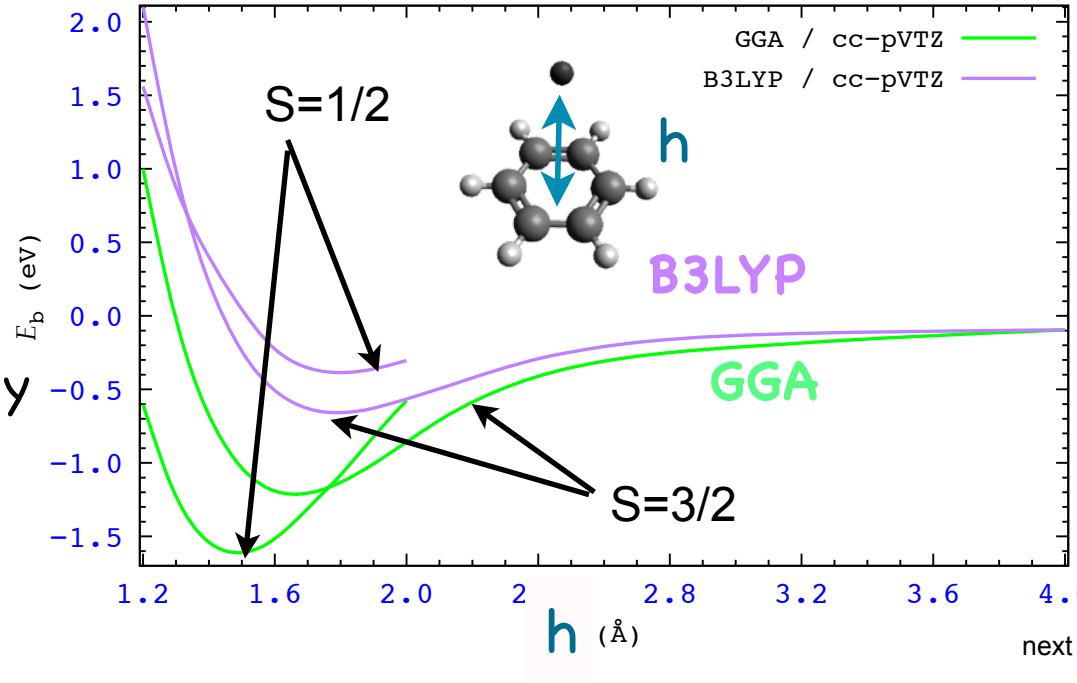


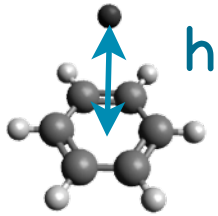
Y. Virgus et al, PRB(R), '12

next →

Co adsorption on graphene

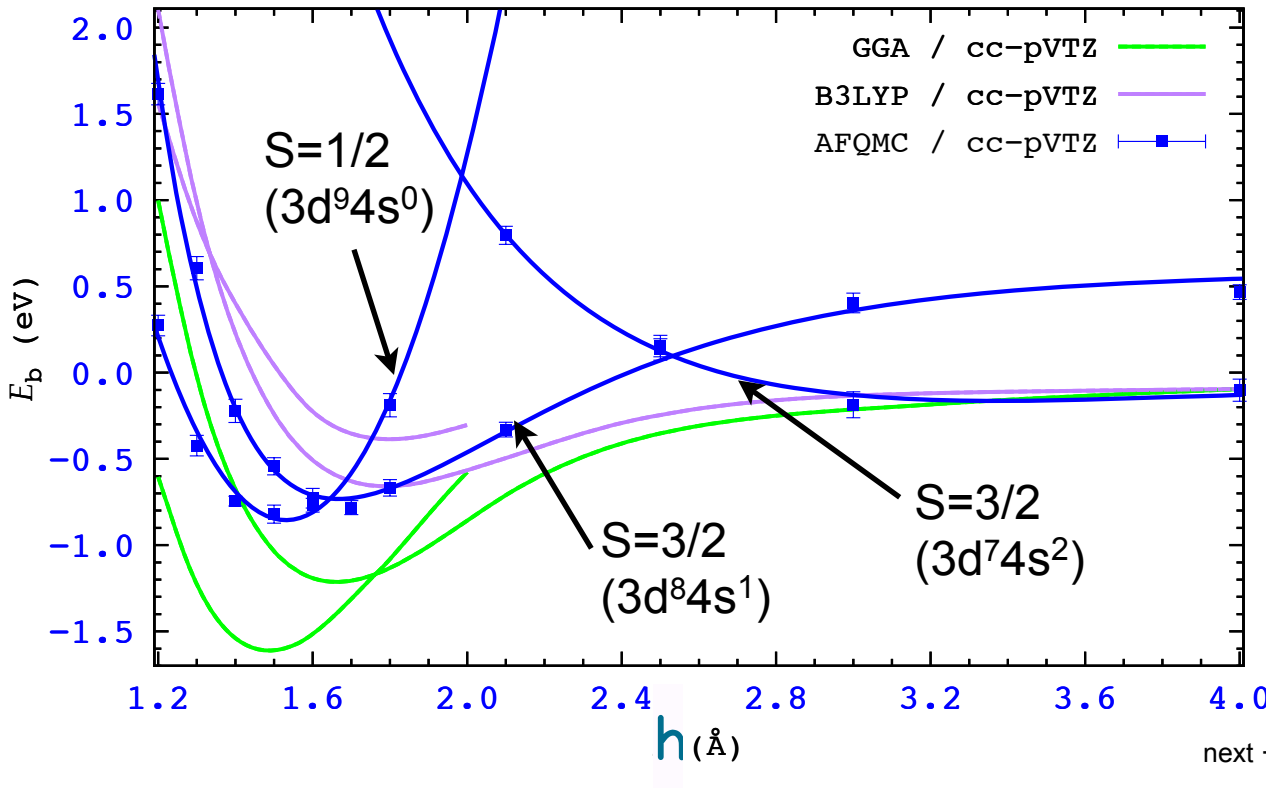
- Co on benzene --- what are the states and what is the binding energy as a function of h?

  - **AFQMC**:
    spin: high -> high -> low h~1.5 (min)



  - DFT incorrect dissociation limit (vdW problem)

  - Neither is correct, but GGA better than B3LYP here

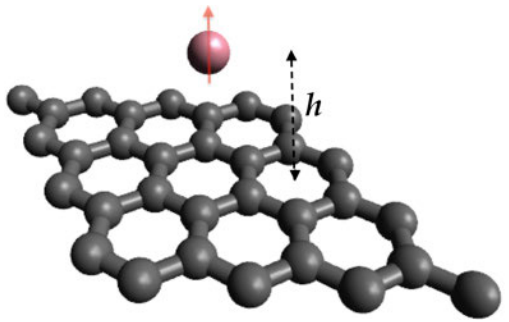


Y. Virgus et al

next →

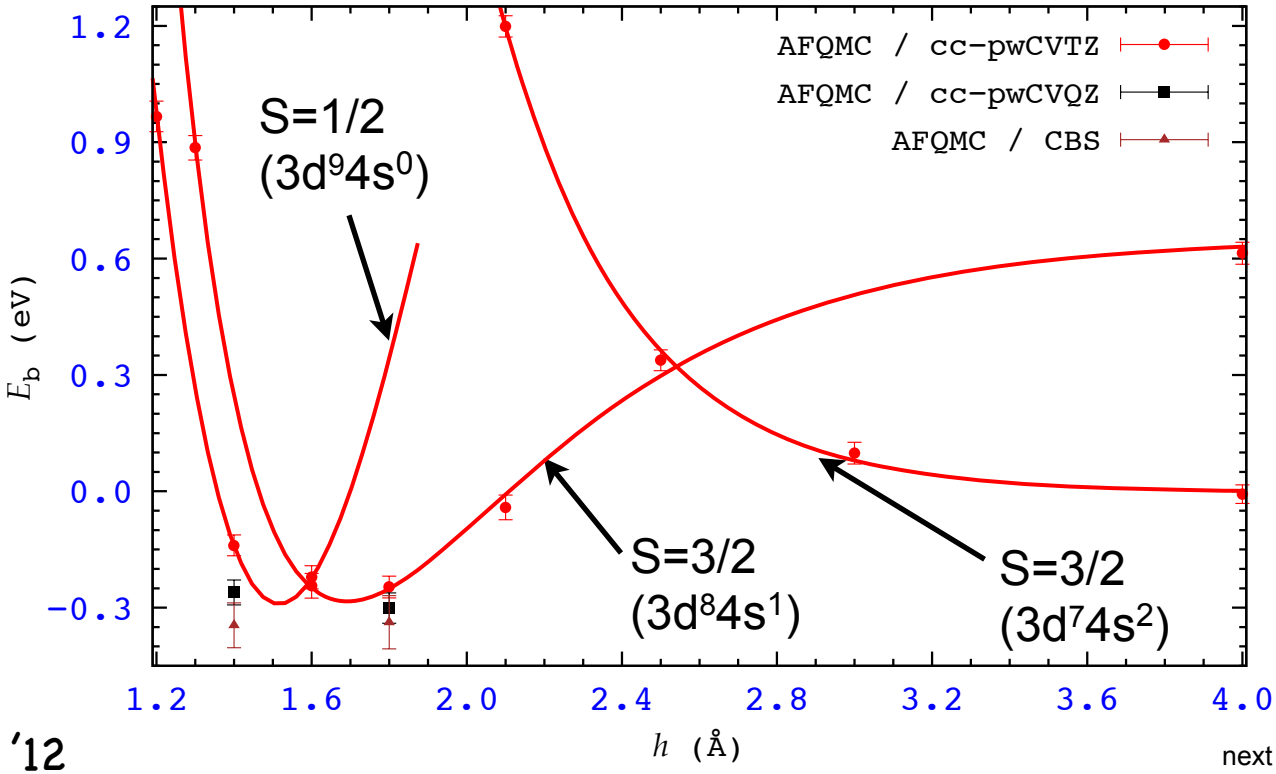
Co adsorption on graphene

- What are the states and what is the binding energy as a function of h? (STM?)



  - ✦ Embedding ONIOM correction (W/ GGA or B3LYP)
  - ✦ Nominal spin: high -> high -> low h~1.5 (min)

  - ✦ double well feature
  - ✦ comparable binding energies, small barrier



Y. Virgus et al, PRB(R) '12

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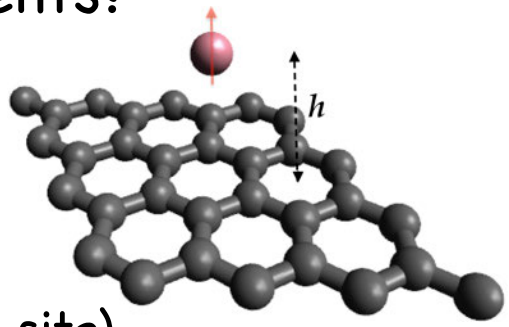

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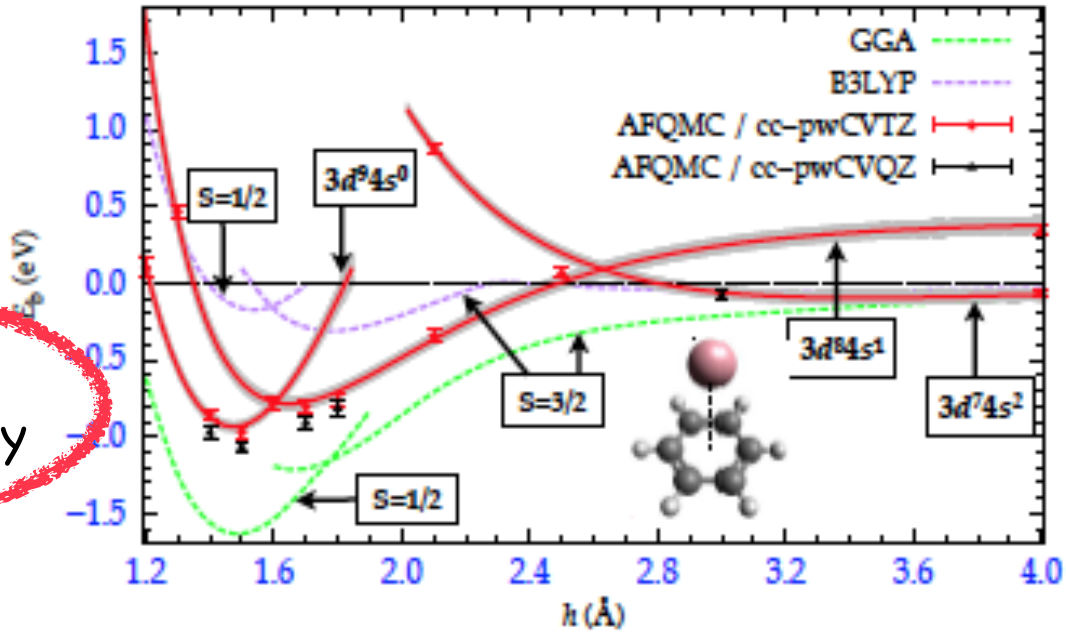


Binding energy of Co/C_6H_6 as a function of height h

Y. Virgus et al, PRB(R), '12; unpublished

next →

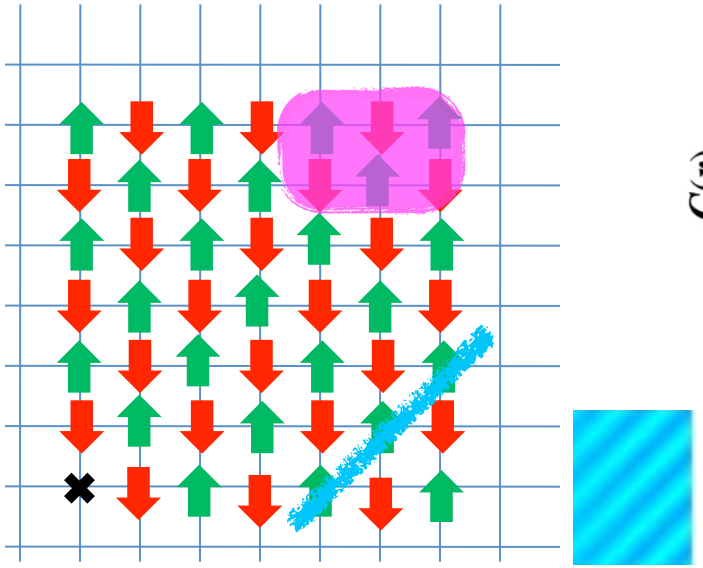
Magnetic properties in the 2D Hubbard model

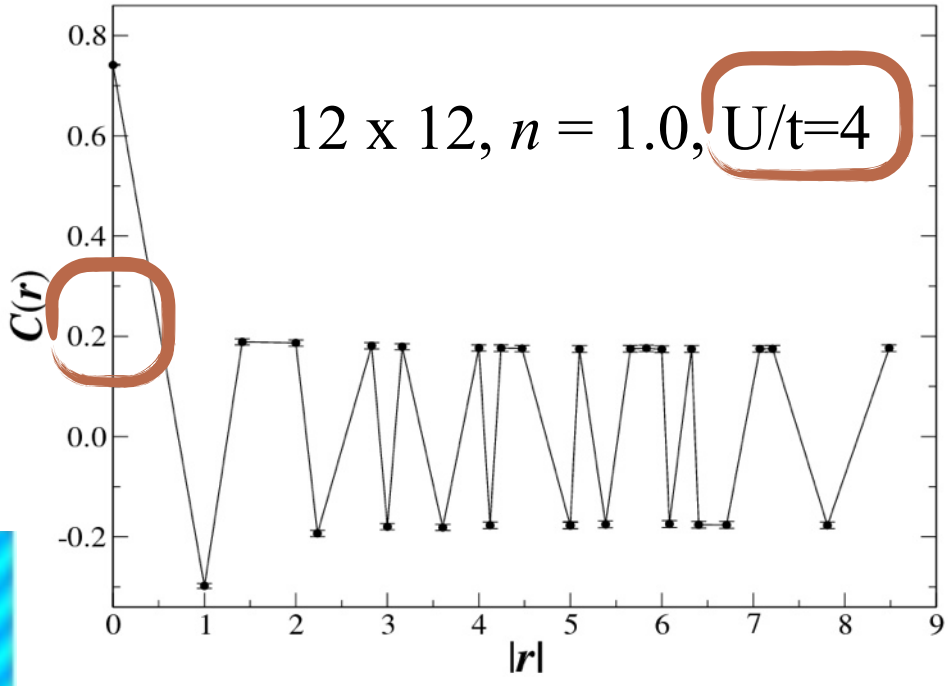
- Model for CuO plane in cuprates?
- Half-filling: antiferromagnetic (AF) order

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

AF correlation:

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





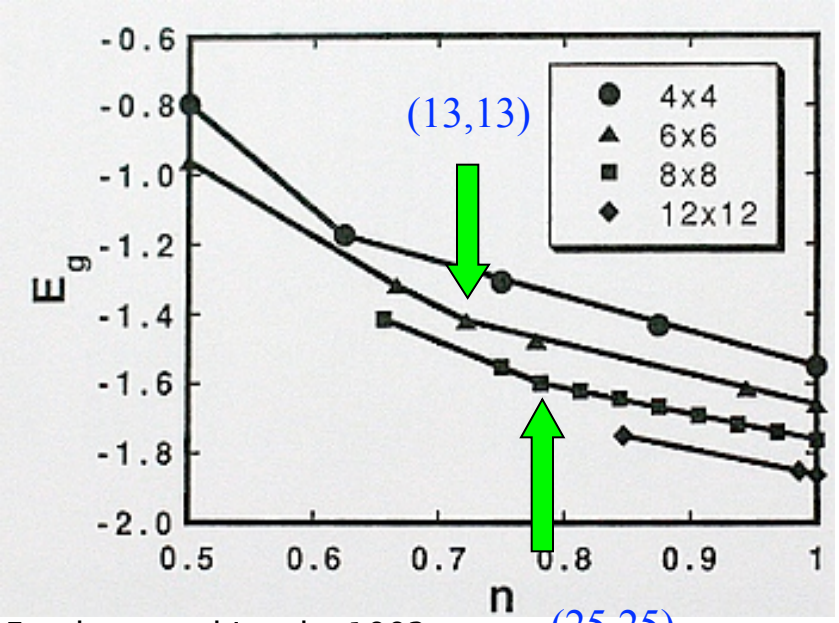
What happens to the AF order upon doping?

next →

Challenges for many-body calculations

AFM? Phase separation? Stripes?

- Large body of numerical work --- Conflicting results
  - GFMC (Cosentiri et al.; Sorella et al.)
  - GFMC in t-J (Hellberg & Manousakis, 1997, 2000)
  - DMRG w/ open BC (White, ...)
  - DMFT (Zitler et al. 2002)
  - DCA (Macridin, Jarrell et al. 2006)
  - Variational Cluster (Aichhorn et al. 2007)
  - many others ....



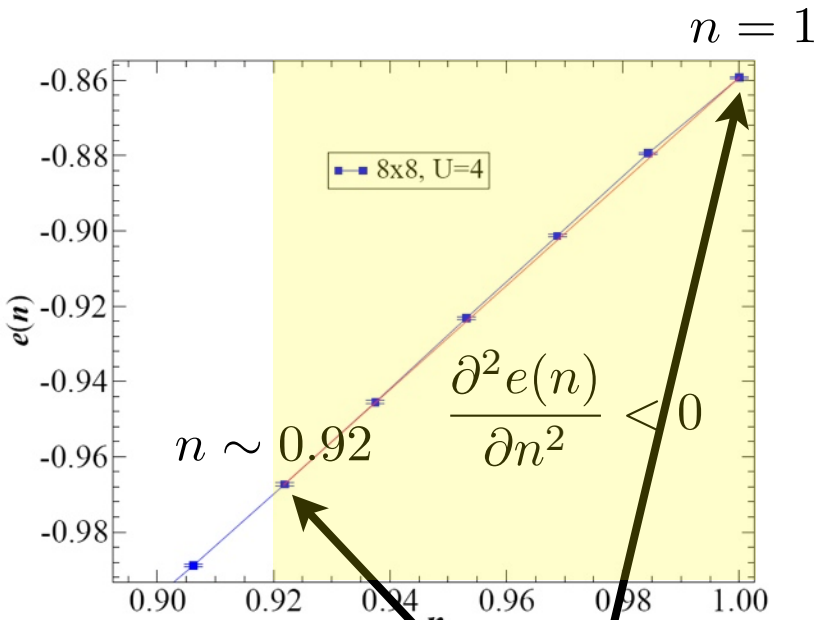
Furukawa and Imada, 1992

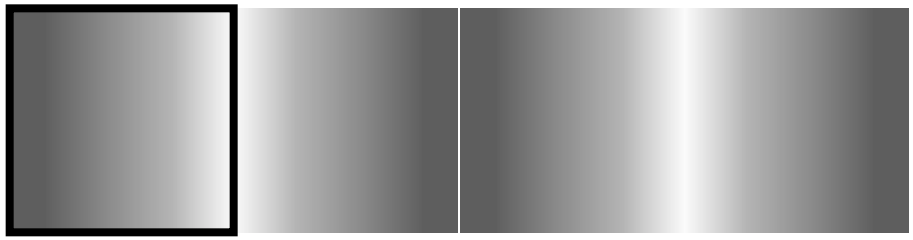
- Challenges:
  - Many competing orders with tiny energy differences: high accuracy
  - Reaching the thermodynamic limit reliably

    sensitivity to both finite-size and shell effects (numerical derivative!)

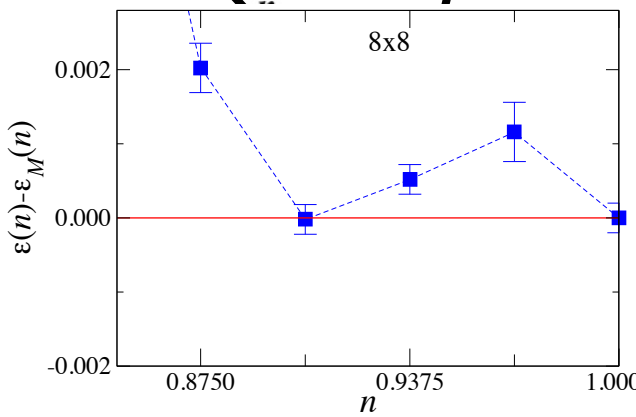
Equation of state -- 2D Hubbard model

- Free-electron trial w.f.
- Twisted average boundary condition (Zhong & Ceperley, '01)
  20 ~ 300 random twists
- Different lattice sizes
  in good agreement
  for n < 0.9
- "Unstable" region is found
  on 8x8, 12x12, 16x16





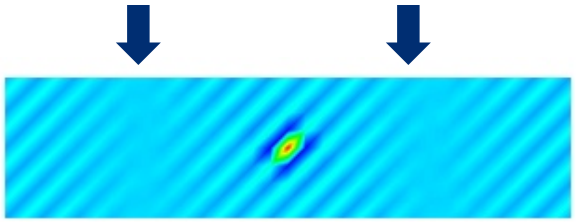
frustrated long wavelength mode ?



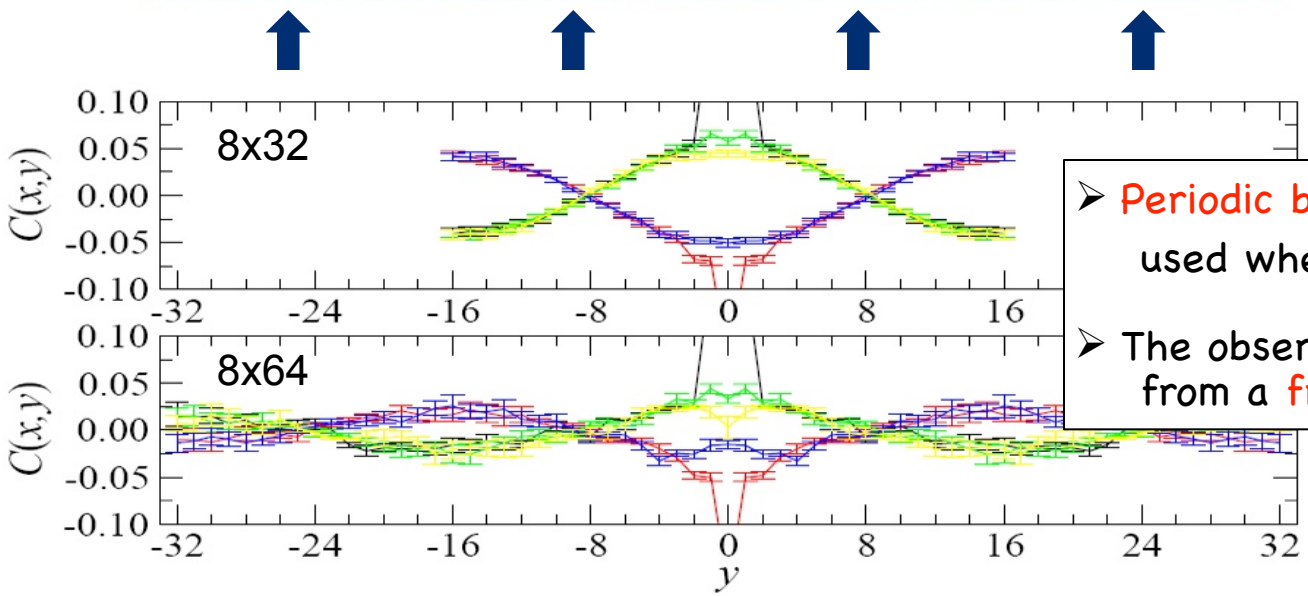
Spin-spin correlation

- Use rectangular lattices to probe correlation length L > 16
- Up to 8x128 supercell (dimension of CI space: 10^600 ! vs. 'DFT' 1k x 1k)
- Detect spatial structures using correlation functions

8x32
n = 0.9375



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

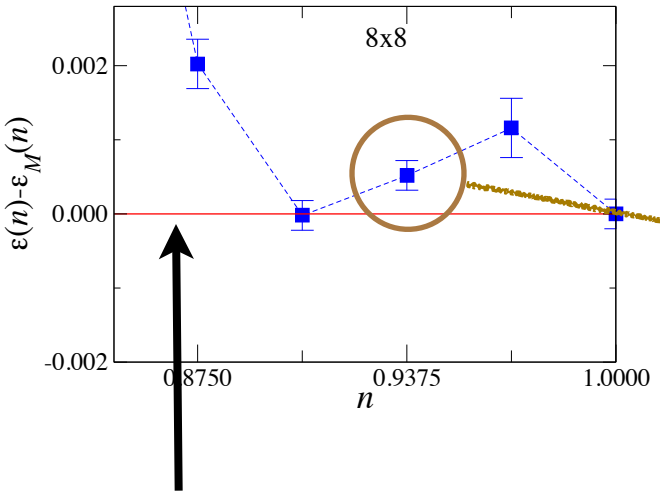


- Periodic boundary condition is used when calculating C(**r**)
- The observed structure emerges from a free electron trial state

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

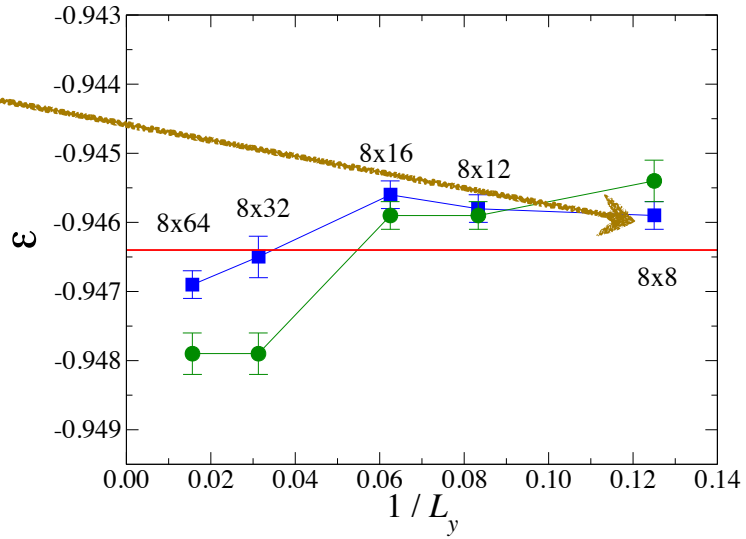
Equation of state, again

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



Maxwell construction

Rectangular supercells, increasing Ly



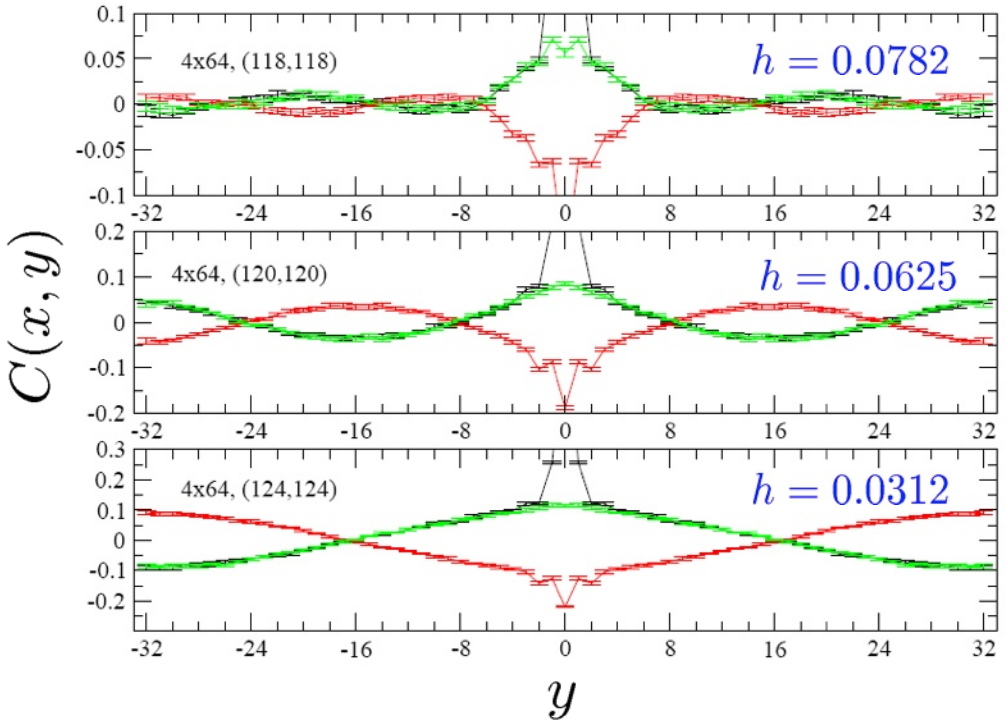
- Instability is from frustration of SDW due to finite size
- At n = 0.9375, need L>~32 to detect SDW state

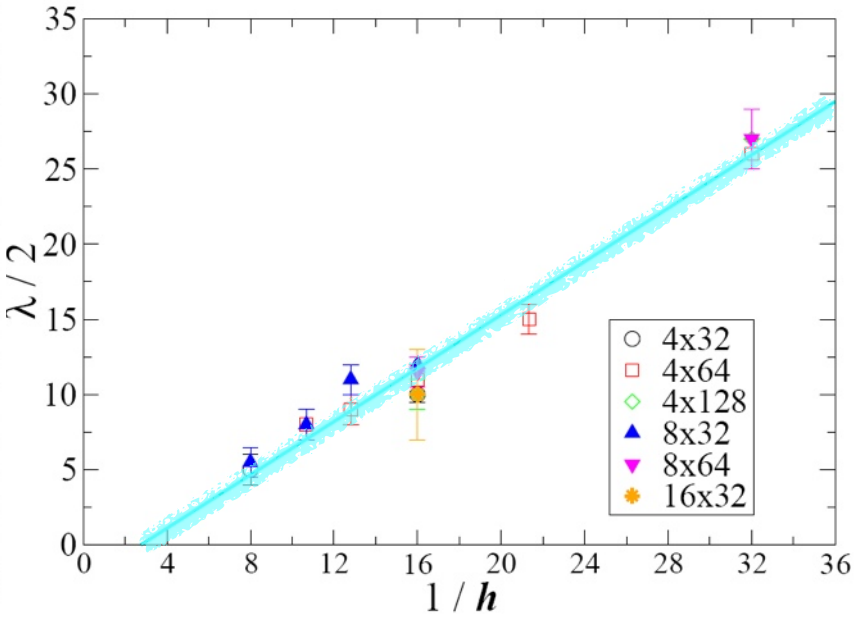
  (Previous calculations: Ly~12, with large shell effects)

Wavelength versus doping

Doping h = (1-n) dependence

4x64, U/t = 4.0





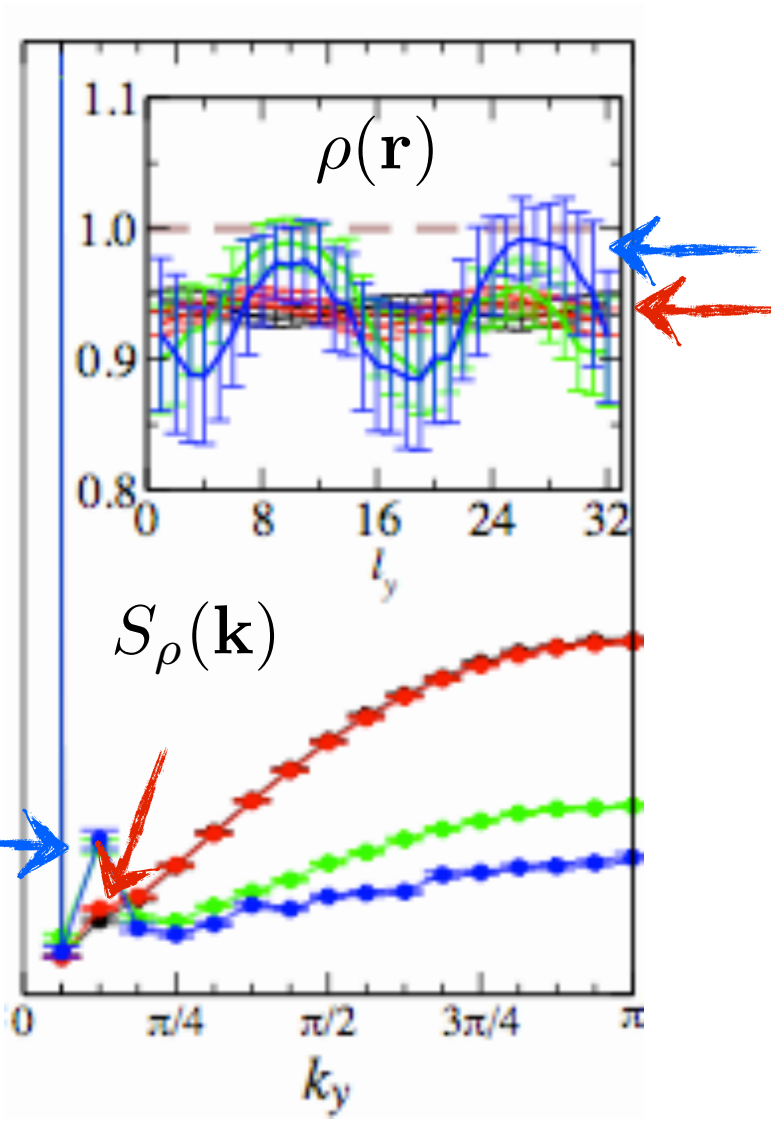
- Wavelength decreases with doping; as does the amplitude
- SDW terminates at finite doping (~0.15), enters paramagnetic state
- Wavelength appears $\propto 1/h$

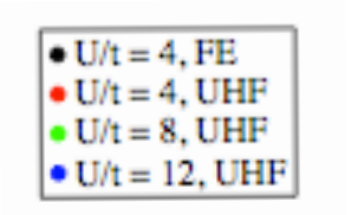
C.-C. Chang & SZ, PRL,'10

Dependence on U

Smectic state - connection and difference to 'stripe phase':

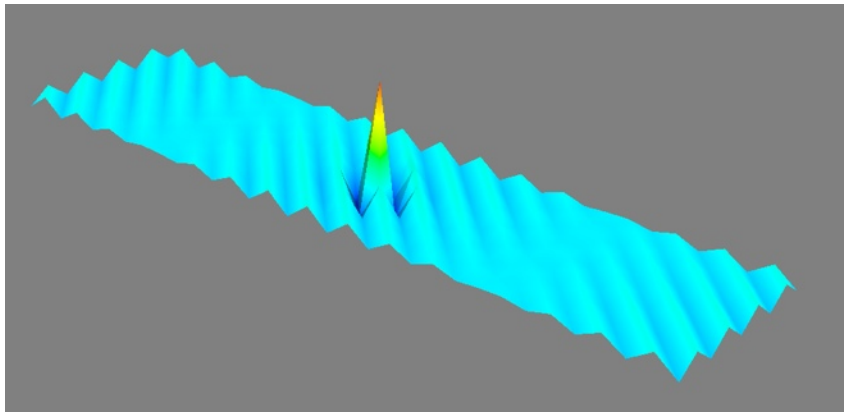
- At U/t=4, charge is uniform:
  - No peak in charge struc. factor
  - holes fluid-like (de-localized)
- At U/t=8-12, CDW develops:
  - Peak in structure factor
  - Clumps of density=1, separated by dips (SDW nodes)
  - Consistent with DMRG results at large U/t (White et al, '03, '05)
  - holes Wigner-like (localized)





Summary

- Computational framework for correlated electronic systems (equilibrium)
  - ✦ Both materials specific and model Hamiltonians
  - ✦ Much development still to be done, but a blueprint for systematic calculations
- Exact calculation of Bertch parameter in BCS-BEC crossover
- Co adsorption on graphene: double-well high-low spin states
- Magnetic phases in 2D Hubbard:
  - ✦ AF SDW, long wavelength modulation
  - ✦ Wavelength $\propto 1/h$
  - ✦ SDW amplitude decreases with doping, vanishes at n~0.85(5)
  - ✦ Holes "liquid like"



- Quantum simulations provide a 'new' tool for studying quantum matter:
  - ✦ The algorithms have reached a turning point
  - ✦ Need you! Many opportunities for breakthroughs