A stochastic independent-electron approach to correlated systems

Shiwei Zhang
College of William & Mary, USA

Outline

- Why a new QMC approach?
- The phaseless auxiliary-field QMC
  - Both electronic structure (PW or localized) and model calculations
  - Potential for improved accuracy and robustness
- Molecules and solids near equilibrium geometry
- Bond breaking: stronger correlations
- Phase separation in the Hubbard model

Collaborators:

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

Support:

- ARO, NSF, DOE petascale QMC-endstation, DOE-cmsn

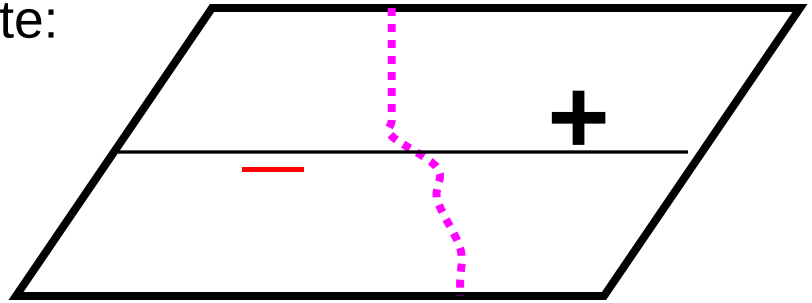
Some references: (http://physics.wm.edu/~shiwei)

- Zhang & Krakauer, PRL, '03
- Al-Saidi e*t. al*., PRB, '06; JCP, '06; JCP, '06; JCP, '07
- Suewattana *et. al*., PRB, '07
- Kwee *et. al*., PRL, '08
- Purwanto *et. al*., JCP, '08
- Chang & Zhang, arXiv:0805.4831

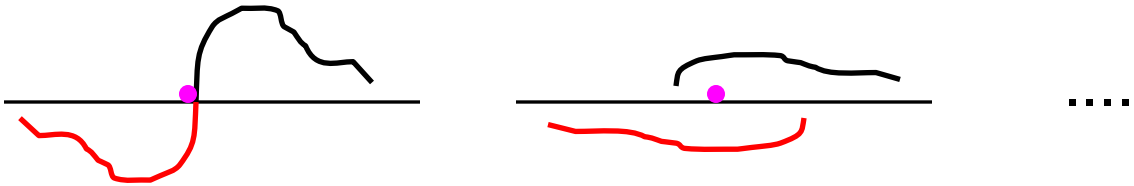
Introduction: why auxiliary-field methods?

Recall sign problem:

1 particle -- first excited state:



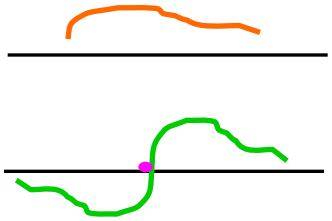
In QMC, we need **+** and **–** walkers to cancel



2 fermions -- ground state: same problem

Fermion 1:

Fermion 2:



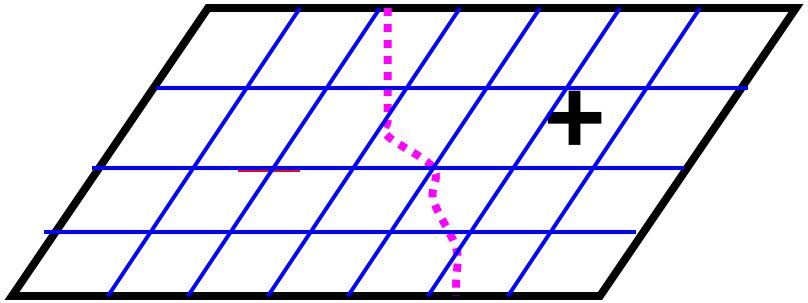
Sign problem – a fight against

global bosonic state

Why auxiliary-field methods?

Recall sign problem:

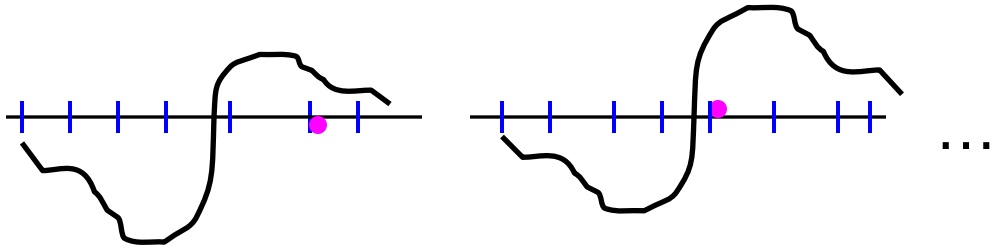
1 particle, first excited state:



Solid state or quantum chemistry?

➔ **basis**

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



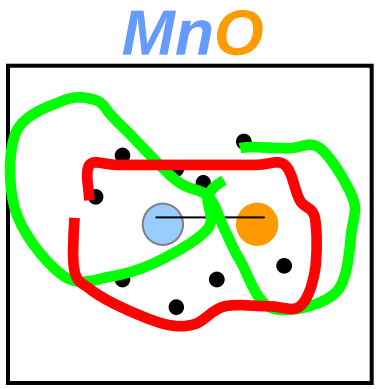
Explicit --- matrix * vec

No sign problem

Why auxiliary-field methods?

Reduce sign problem:

many ***free*** fermions:



Solid state or quantum chemistry:

➔ **basis**

$$e^{-\tau H}\begin{pmatrix} \psi_1 & \psi_1 & \\ \psi_2 & \psi_2 & \\ . & . & \cdots \\ . & . & \\ \psi_N & \psi_N & \end{pmatrix}$$

Matrix * matrix

Still no sign problem

(orthogonalize)

Slater det. - antisymmetric

Now ***turn on*** interaction. Can we use these as walkers ?

Summary: basic formalism of AF methods

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

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

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

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

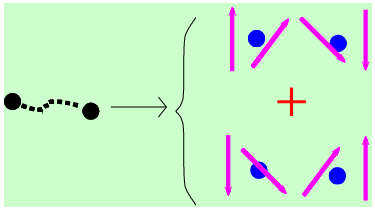
$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i,j}^{M} T_{ij} c_i^\dagger c_j + \sum_{i,j,k,l}^{M} V_{ijlk} c_i^\dagger c_j^\dagger c_k c_l$$

M : basis size

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

Hubbard-Strotonivich transf.

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



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

next →

AF methods: some background

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

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

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

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

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

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

- Reformulate ---

New AF QMC approach

Random walks in Slater determinant space:

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

SZ, Carlson, Gubernatis

SZ, Krakauer

H-S transformation

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

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

Schematically:

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

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

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

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

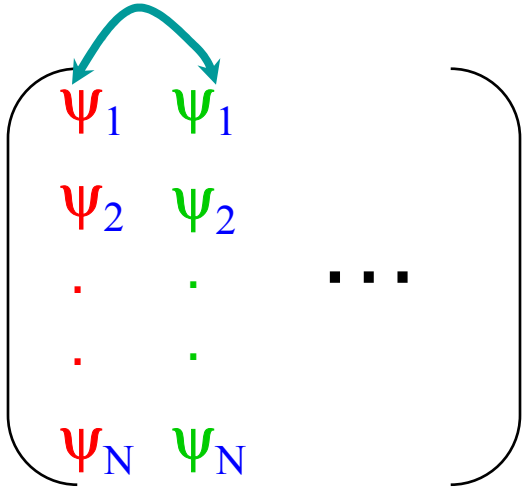
Exact so far

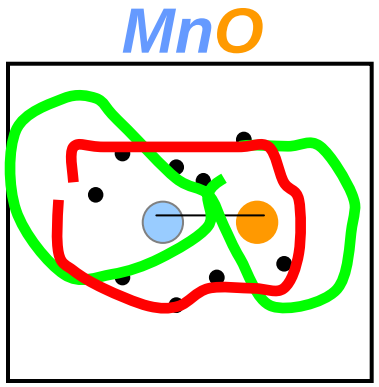
next →

New approach

Sign/phase problem is due to --

“superexchange”:





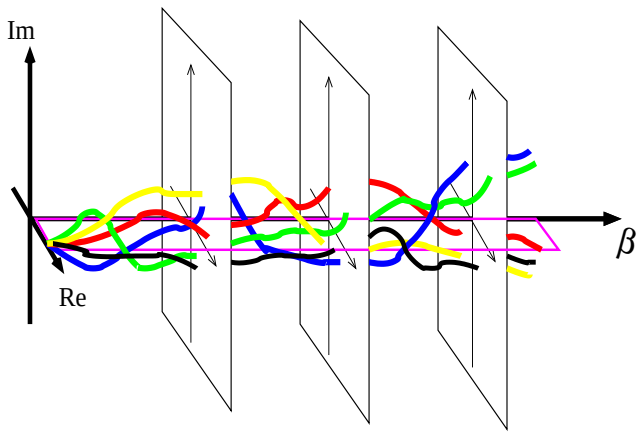
Slater det. - antisymmetric

Reasonable to expect it’s reduced, since

tendency for global collapse to bosonic state is removed

Controlling the phase problem

Sketch of approximate **solution**:



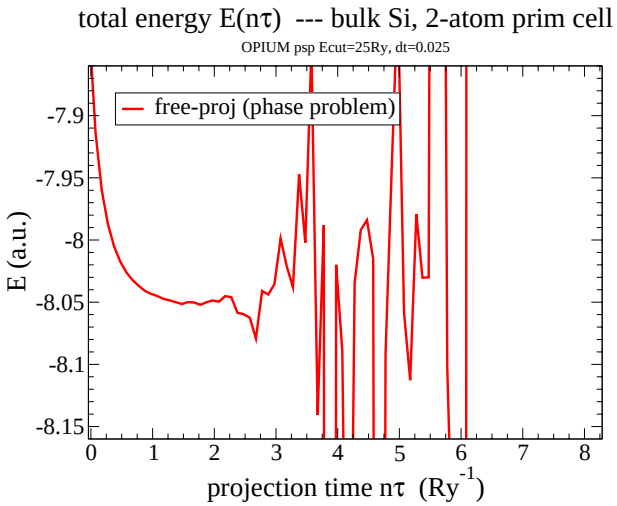
- Modify propagator by "gauge transformation': phase → degeneracy (use trial wf)
- Project **to one overall phase**: break "rotational invariance"

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

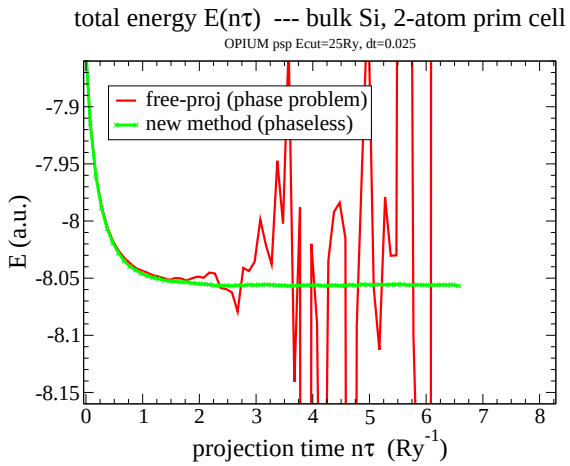
- subtle, but key, difference from: real$\langle \Psi_T | \phi \rangle > 0$

(Fahy & Hamann; Zhang, Carlson, Gubernatis)

Before:

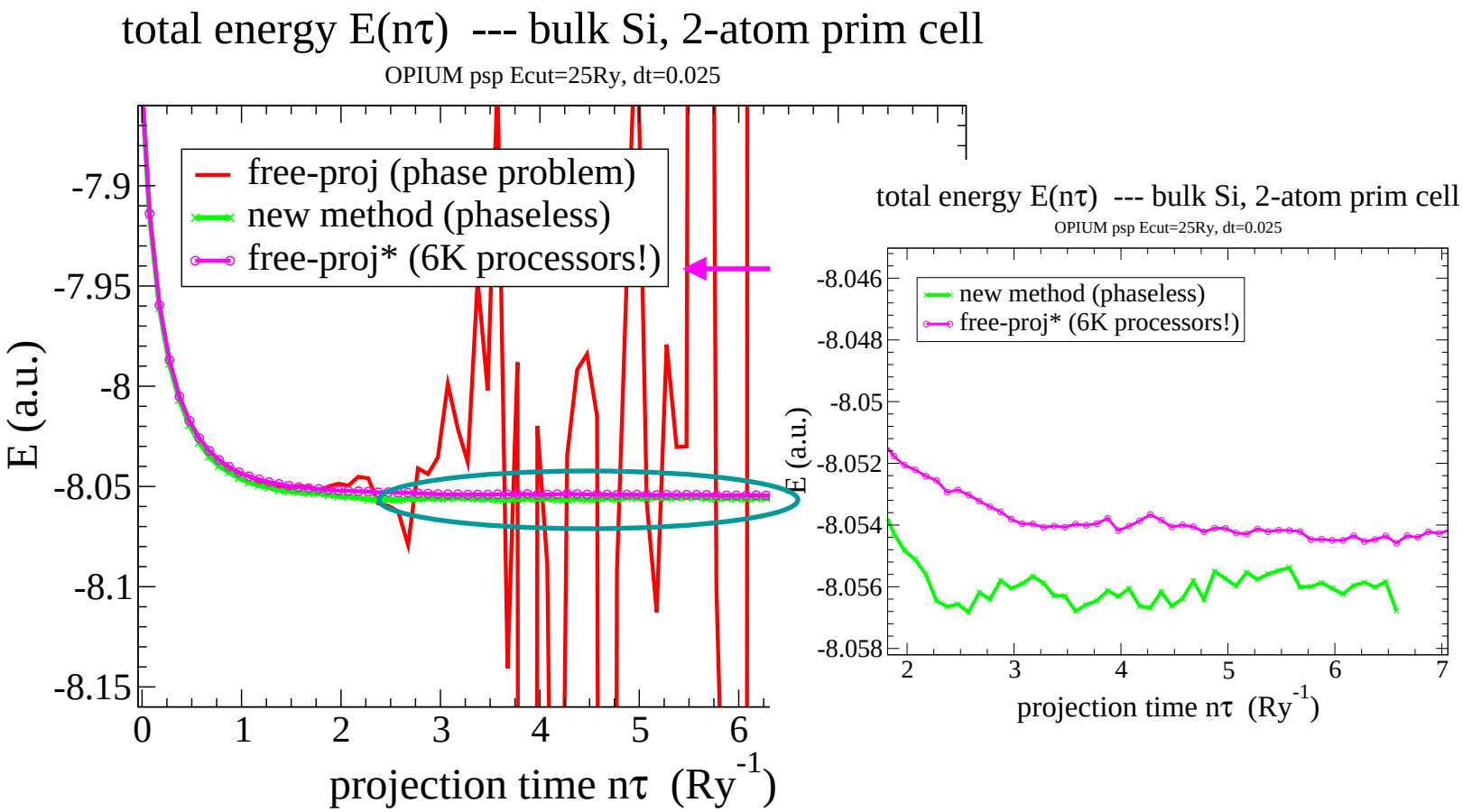


After:



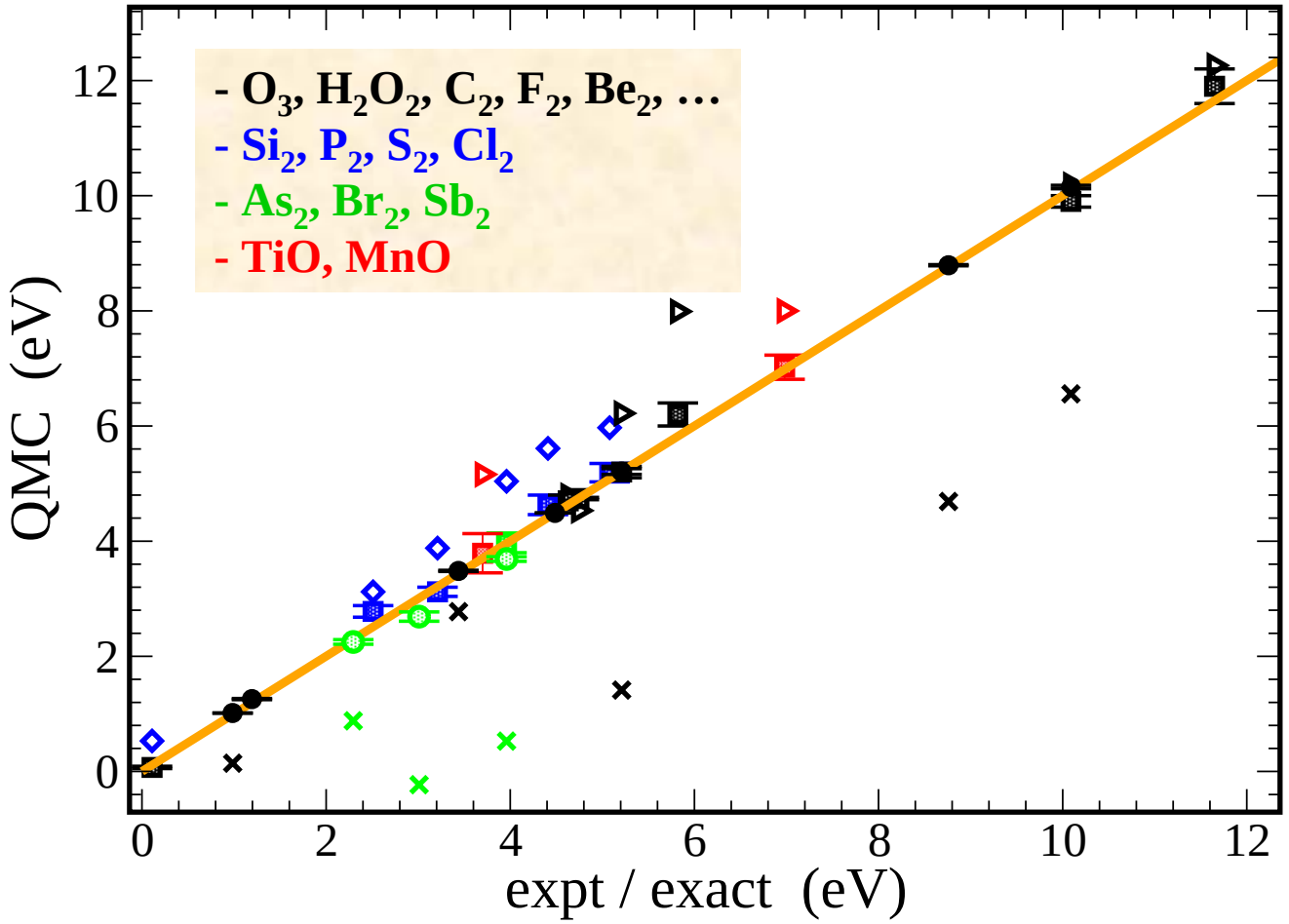
Controlling the phase problem

Quantify the approximation?



Error in total E < 1mH

Application: molecular binding energies



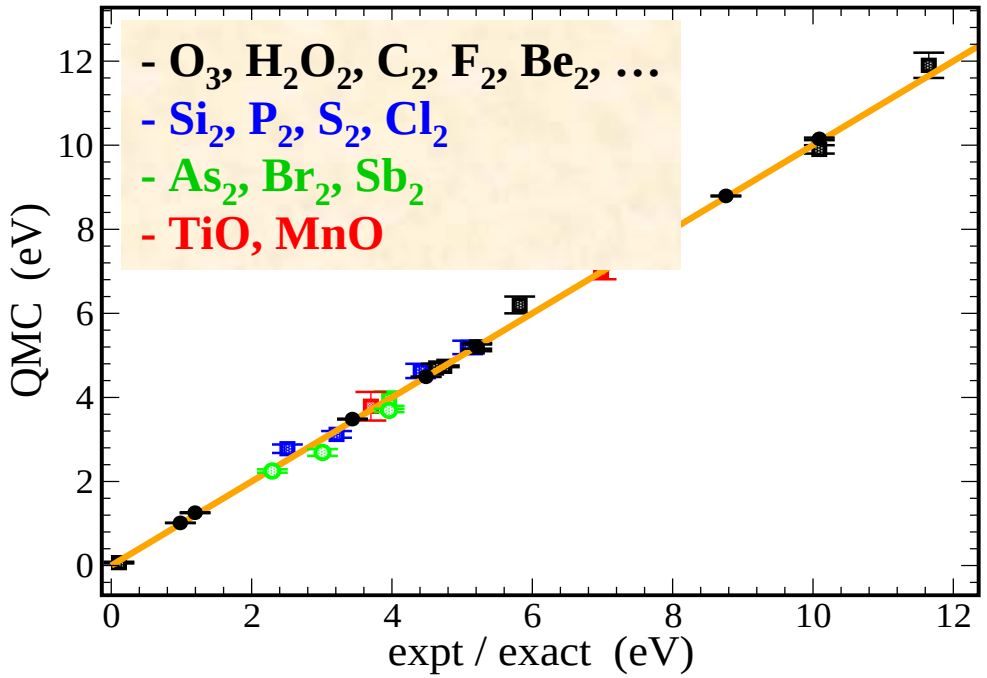
3 types of calc's:

- **PW +psp:** □
- **Gaussian/AE:** ●
- **Gaussian/sc-ECP:** ○

N_{val} up to ~ 60

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

Molecular binding energies



3 types of calc's:

- **PW +psp:** □
- **Gaussian/AE:** ●
- **Gaussian/sc-ECP:** ○

N_{val} up to ~ 60

- ~ 100 systems (also IP, EA, a_B, ω): eq. geom., moderate correlation
- Error < a few mHa (0.1 eV)
- Accuracy ~ CCSD(T) (gold standard in chemistry, but N^7)

- QMC: linear superposition of 'LDA solutions' in random fields

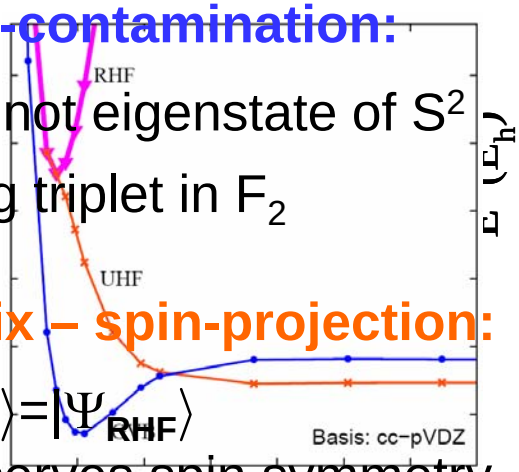
scaling to petascale ~ scaling LDA to O(100) processors

F_2 bond breaking

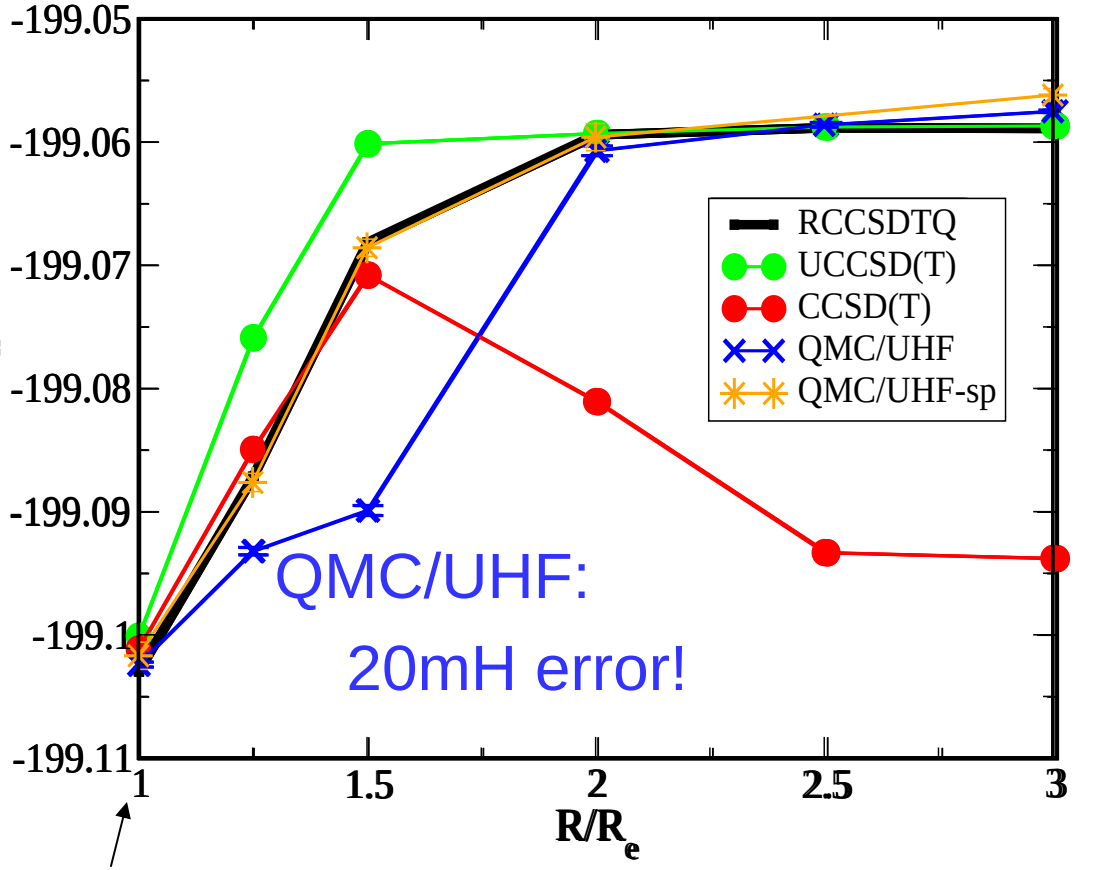
Mimics increasing correlation effects:

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

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



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



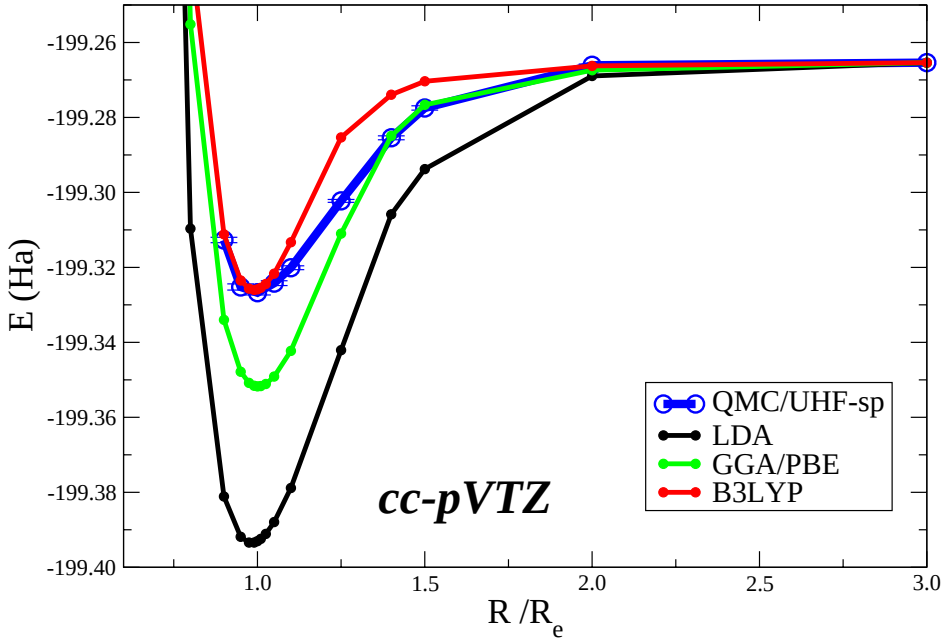
Equilibrium → **Dissoc. limit**

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

F_2 bond breaking --- larger basis

- LDA and **GGA/PBE** well-depths too deep
- **B3LYP** well-depth excellent, but "shoulder" too steep
- Compare with expt
  --- 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

Large extended systems

Cohesive energies: (eV/atom)

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

- plane-wave + pseudopotential calculations
- DMC -- Needs *et al* (Cambridge group)
- Na:
  - metal: k-point integration in many-body QMC
  - new finite-size correction scheme

Kwee, et al, PRL, '08

Application: 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 2-D lattice

- near-neighbor hopping
- on-site repulsion

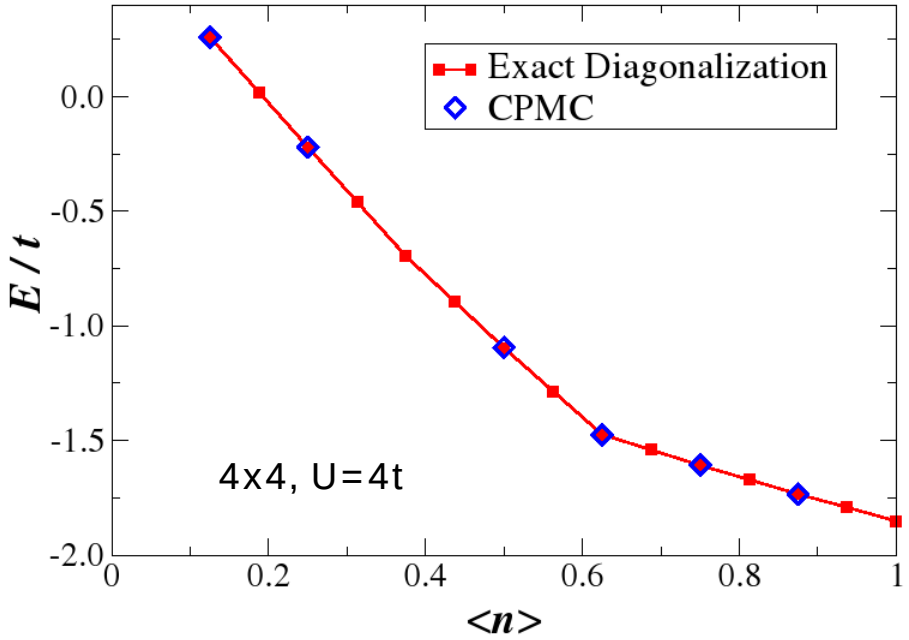
Size $N = L \times L$

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

- Renewed interest from experimental opportunities:
  - optical lattice emulators
- Long-standing questions: (conflicting numerical results)
  - model for high-Tc?
  - phase separation? (Expt: spatial inhomog. in cuprates?)

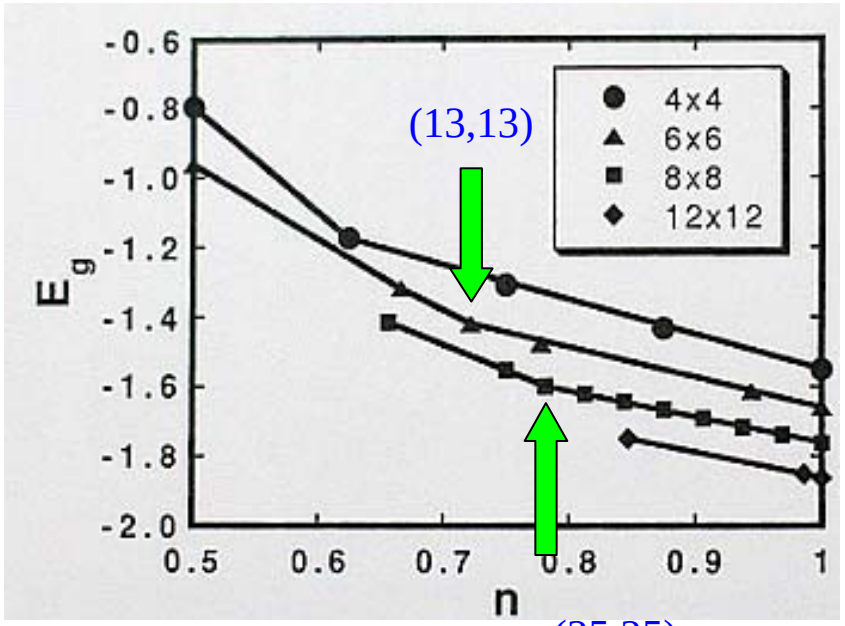
Chang & Zhang, arXiv:0805.4831

Hubbard model: equation of state



Exact diagonalization: Dagotto et.al. 1992

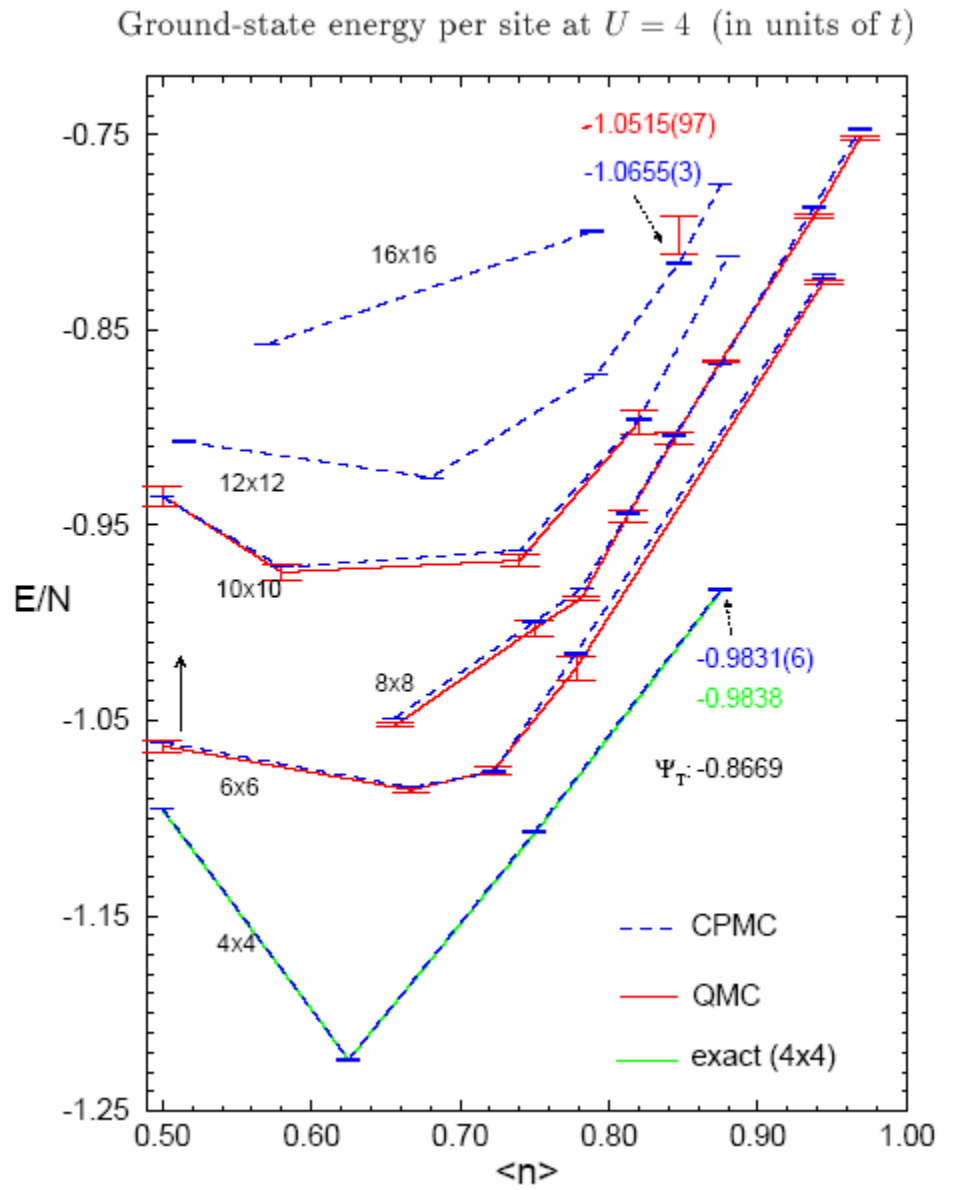
CPMC: Zhang et.al., 1997

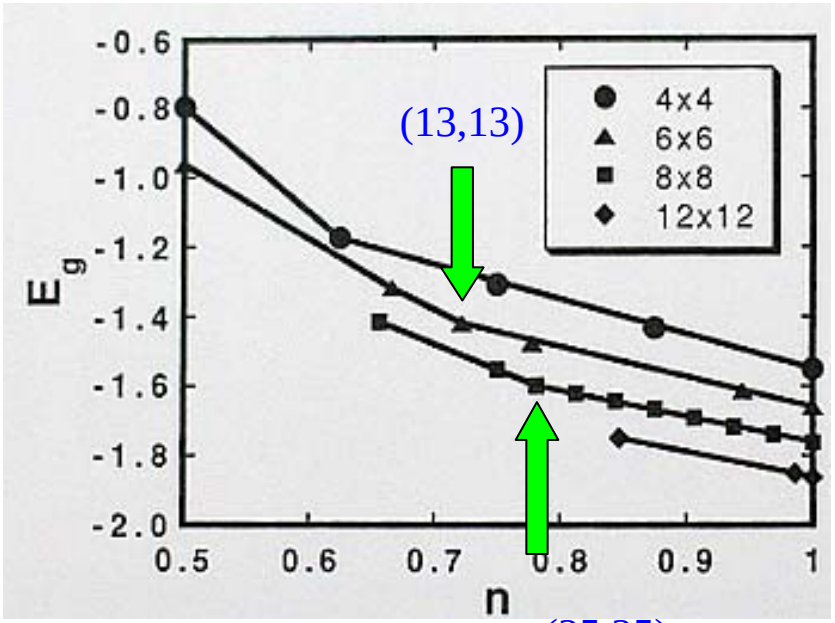


Furukawa and Imada, 1992

- Constrained-path auxiliary field QMC (CPMC) is accurate.
- There are kinks at closed-shell fillings => large shell effects.

Hubbard model: equation of state



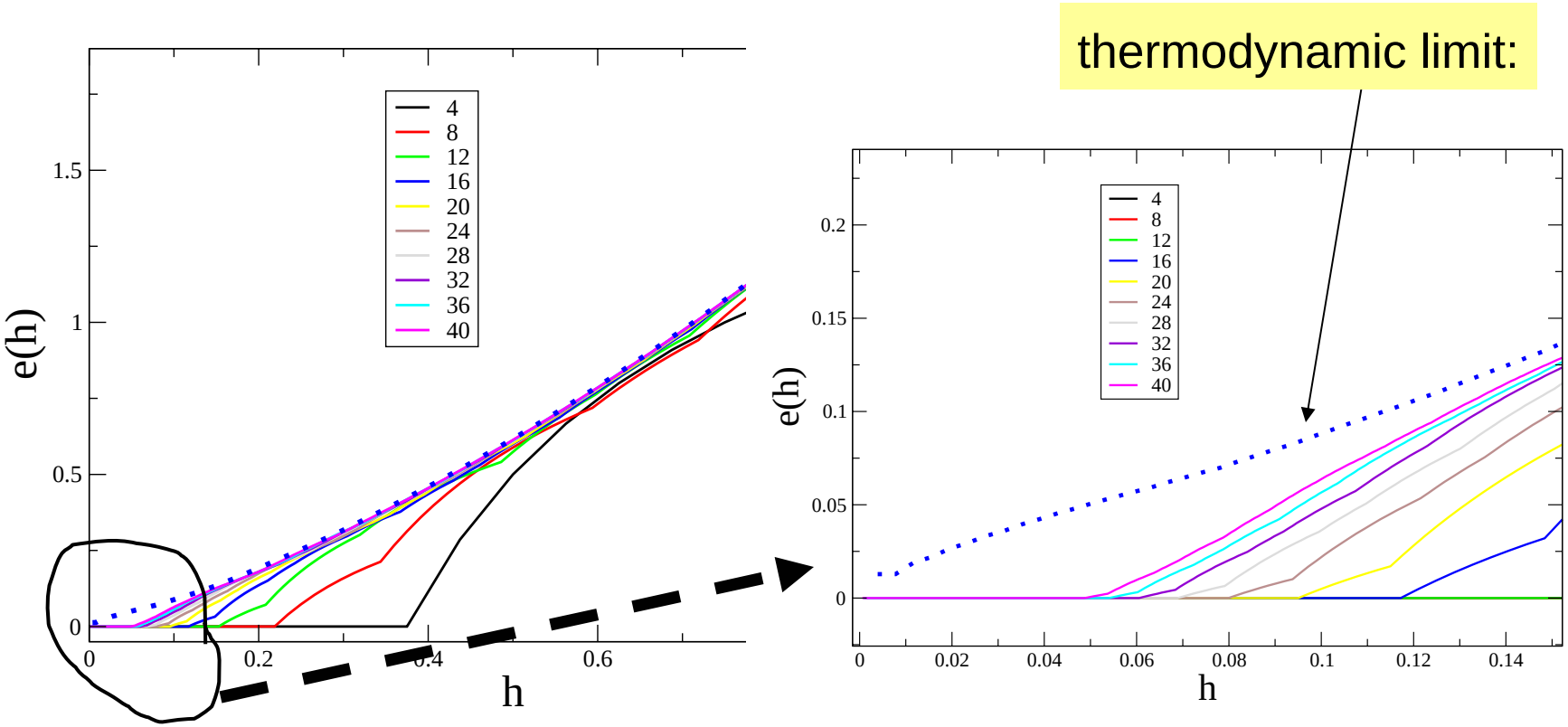


Furukawa and Imada, 1992

(25,25)

CPMC data

Hubbard model: persistent shell effects



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

e(h) fast Fourier Maxwell construction

h=1-n: doping

Twist averaged boundary conditions (TABC)

- TABC widely used in band structure methods; recently in QMC (Lin, Zhong & Ceperley)

- Hubbard:
  - A phase when electron goes around the lattice:

$$\Psi(x+L) = e^{i\theta_x}\Psi(x)$$

  - Modifies kinetic energy:

$$H = \sum_{i,\sigma}\left(-te^{i\theta_x/L}c^{\dagger}_{i+1\sigma}c_{i\sigma} - te^{-i\theta_x/L}c^{\dagger}_{i-1\sigma}c_{i\sigma}\right) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$

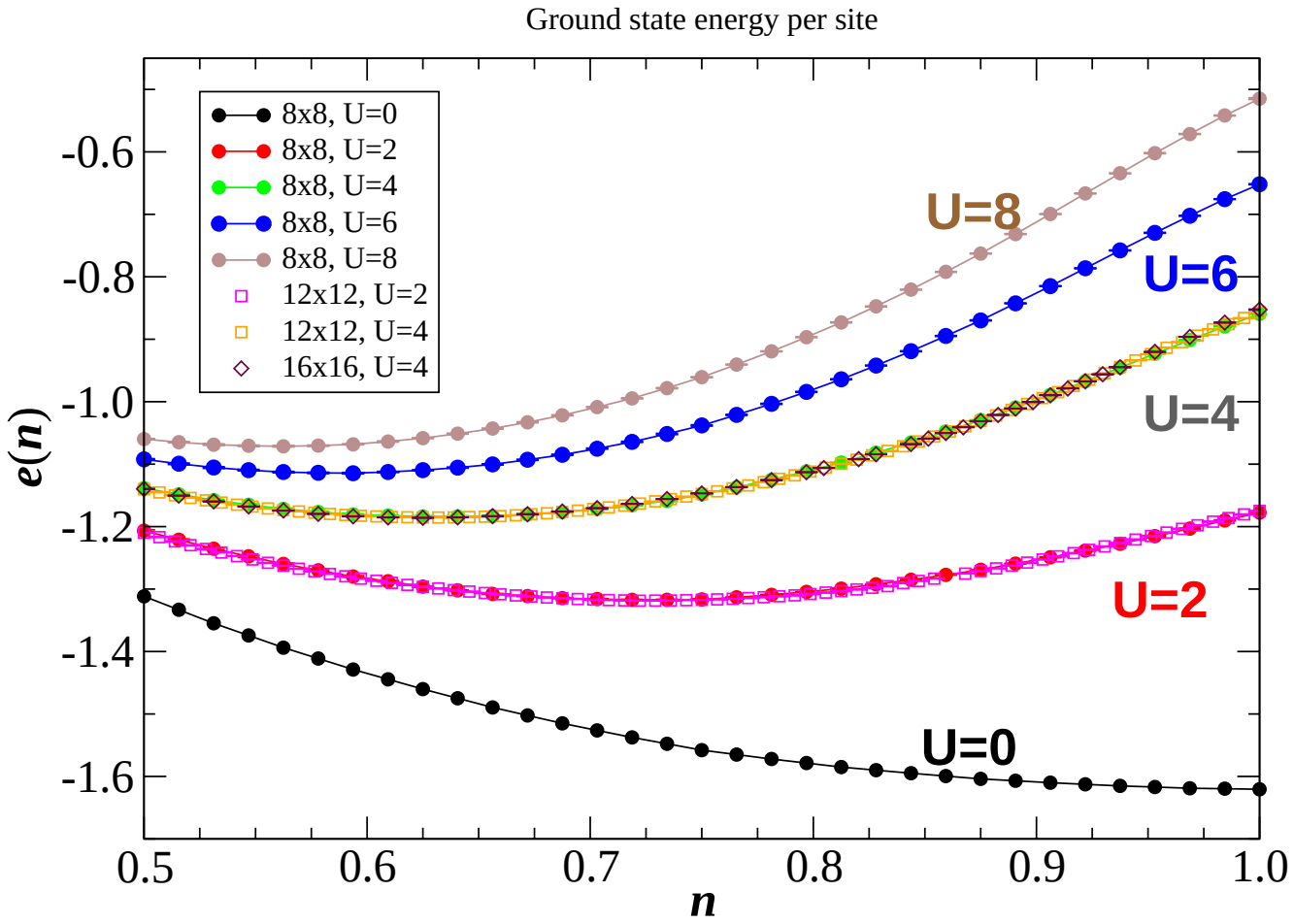
- Breaks degeneracy in free-particle spectrum. But introduces phase problem

  → use the new method

  example of “downfolded hamilt”

Hubbard model: equation of state

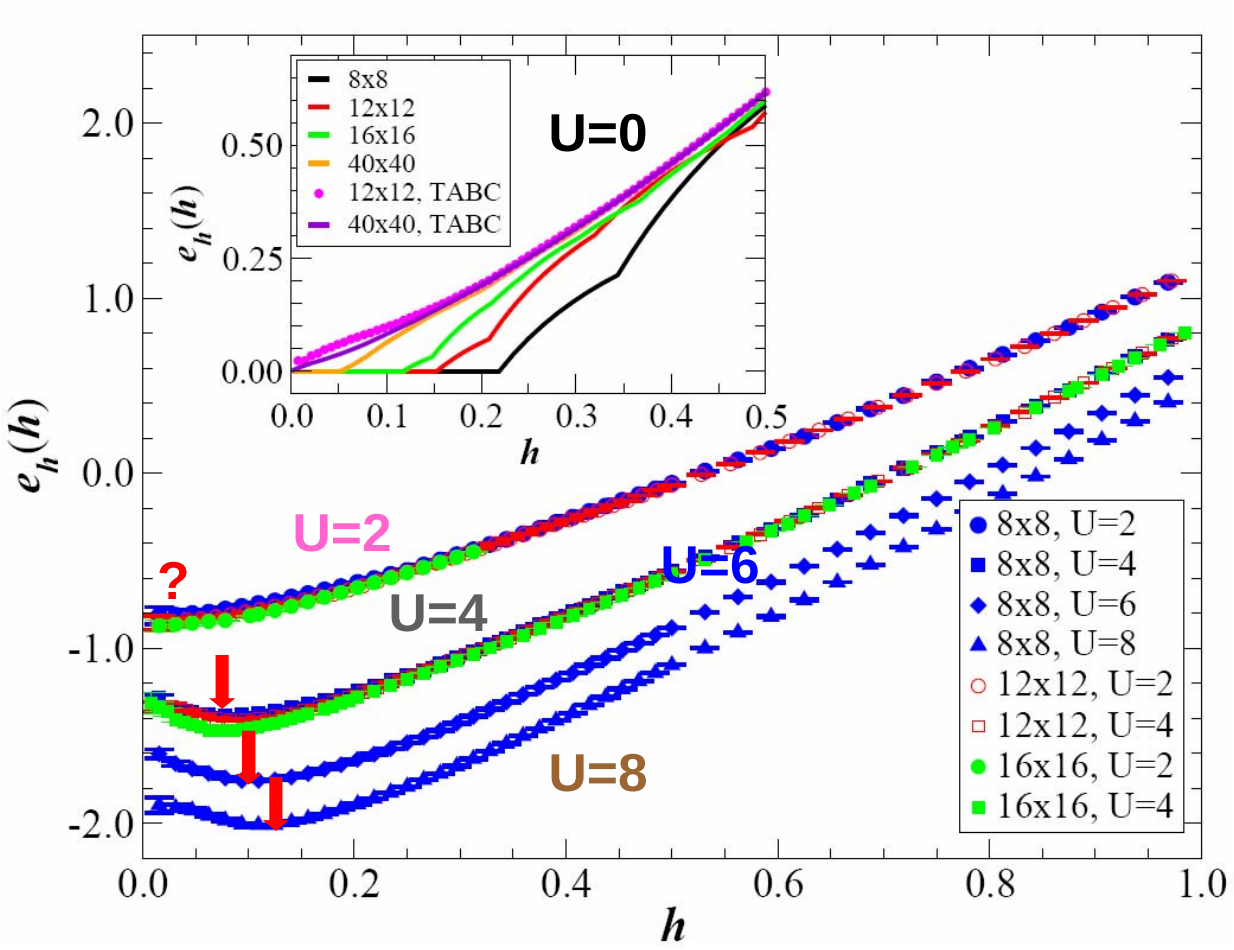
Phaseless AF QMC with TABC:



-
- Convergence to thermodynamic limit achieved

Hubbard model: phase separation

Phaseless AF QMC with TABC:



- **Minimum** in $e_h(h)$ at doping h ~ 0.1
- Appears to shift (larger) as U increases

$|\Psi_T\rangle$ has no min (U=0 wf)

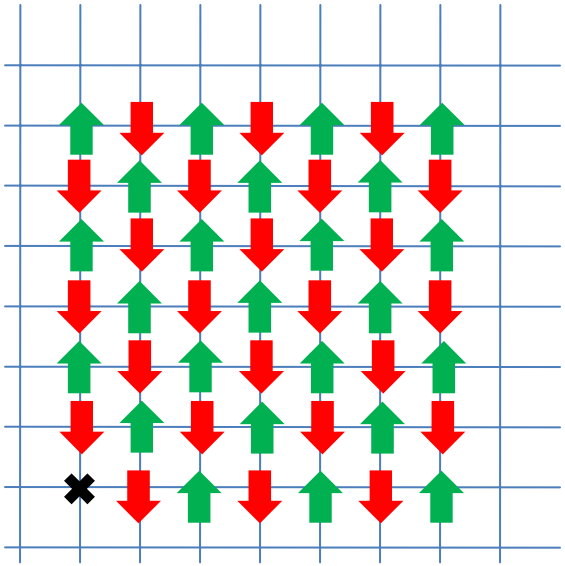
Relation: phase separation & antiferromagnetism

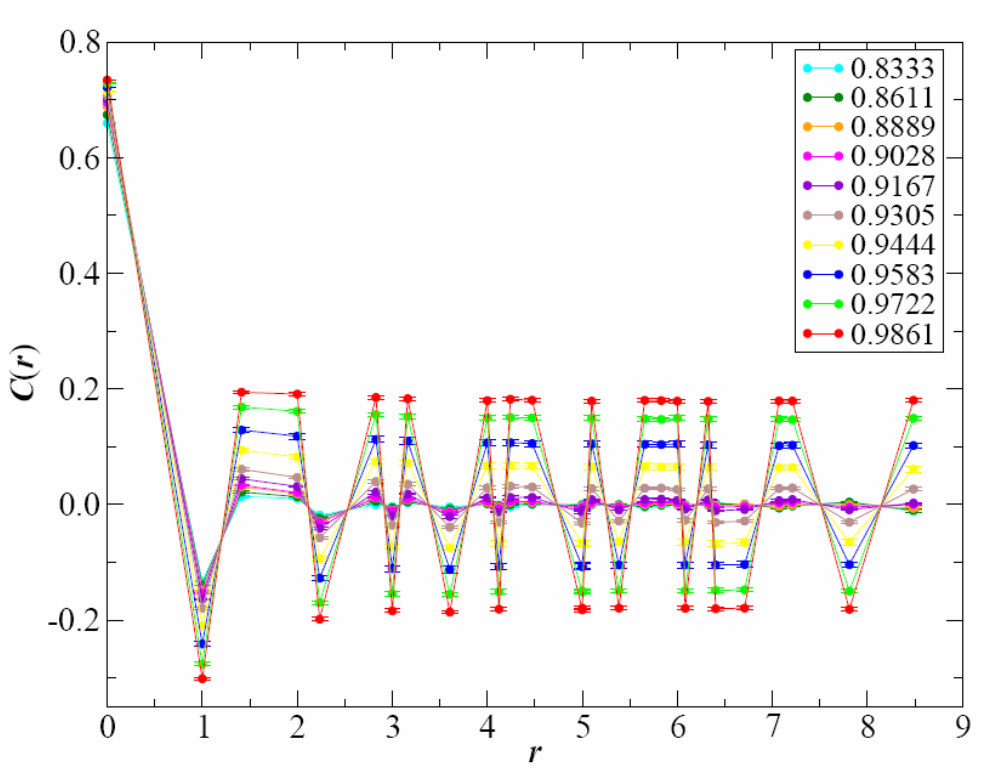
- Half-filling: antiferromagnetic (AF)

  (Furukawa & Imada 1991, Tang & Hirsch 1983, and many more…)

Calculate AF correlation as density increases (→ half-filling)

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

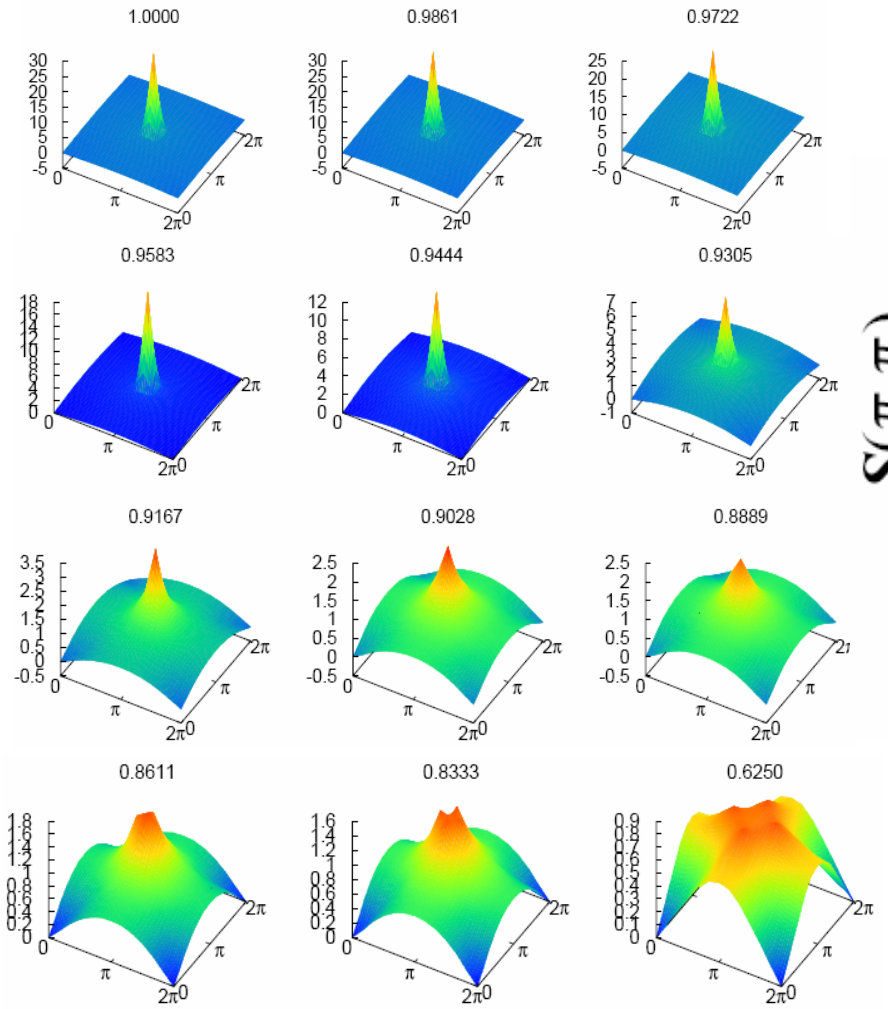




Recall $|\Psi_T\rangle$ has no AF order (U=0 wf for all)

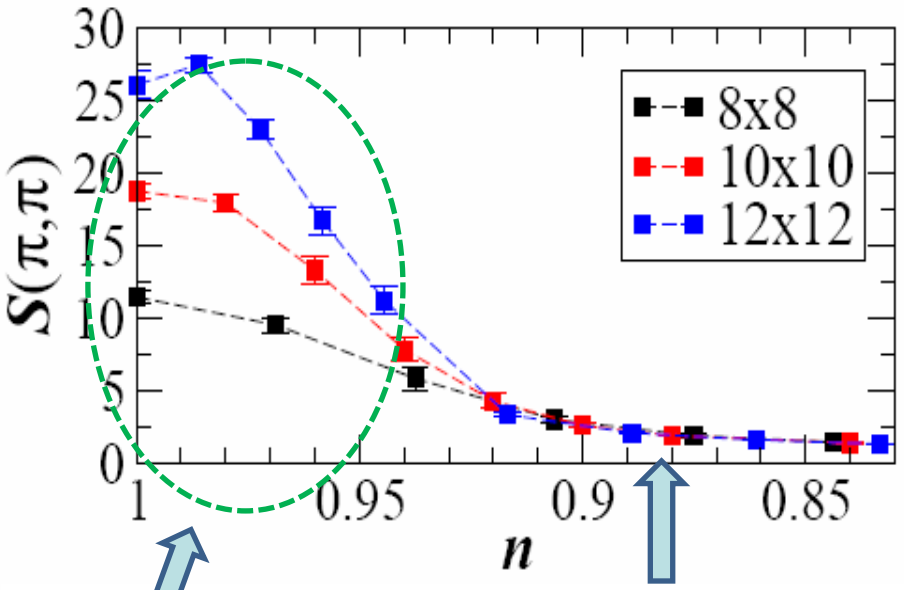
Relation: phase separation & antiferromagnetism

Spin structure factor:



$$S(\mathbf{q}) = \sum_{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} C(\mathbf{r})$$

peak at (π, π) if AF order



Long-range AF correlation $\propto$ system size

short-range correlation, indep of system size

Summary

- AF QMC : random walks in mean-field space
  - Potentially a method to systematically go beyond LDA while using much of its machinery

    --- **superposition** of **independent-particle calculations**
  - Approximate, but accuracy appears systematic
- Applications & benchmarks (~100 systems)
  - *s*-, *p*-, and *d*-electron atoms, molecules, and bulk
  - Bond-breaking in molecules – increased correlation
  - Phase separation in 2-D repulsive Hubbard model:
    - upon doping, two spatial regions: n=1 & n=n_c (~0.9)
    - causes loss of long-range AF order at n_c