Auxiliary-field QMC for quantum chemistry: recent progress and open issues

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Outline

- Introduction
  - Orbital-based QMC --- identical ***H*** as in quantum chemistry
  - Random walks in Slater determinant space
    - Any 1-electron basis [planewaves, gaussian type orbitals (GTO), ..]
    - Overall phase constraint on SD: a new way to deal with the sign problem
    - Code naturally builds on top of standard DFT, scales as N^3-N^4
- Applications: molecules, bond breaking, solids, ...
- Recent algorithmic developments:
  - Resolution of the identity (RI) --> larger basis sets with GTO

Collaborators:

- Wirawan Purwanto
- Shiwei Zhang
- Eric Walter

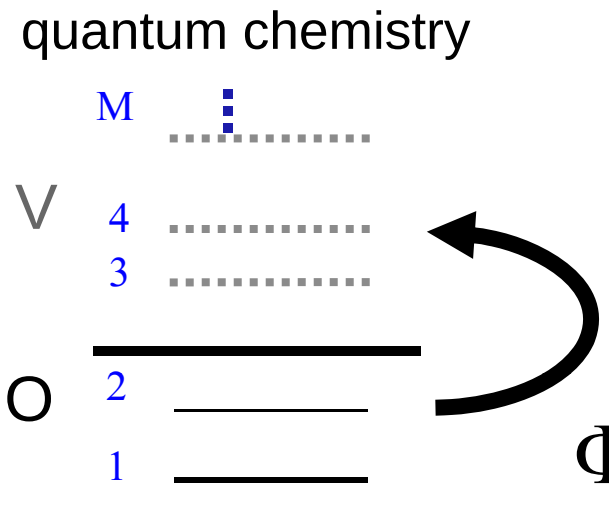
Support:

- DOE (ThChem, petascale endstation), NSF, ONR

Some references:

- Zhang & Krakauer, PRL ’03
- Al-Saidi e*t. al*., PRB ’06; JCP, ’06; JCP ’07
- Kwee *et. al*., PRL ‘08
- Purwanto *et. al*., JCP ’08; JCP ’09; PRB ’09
- Chang & Zhang, PRL ’10

Quantum chemistry

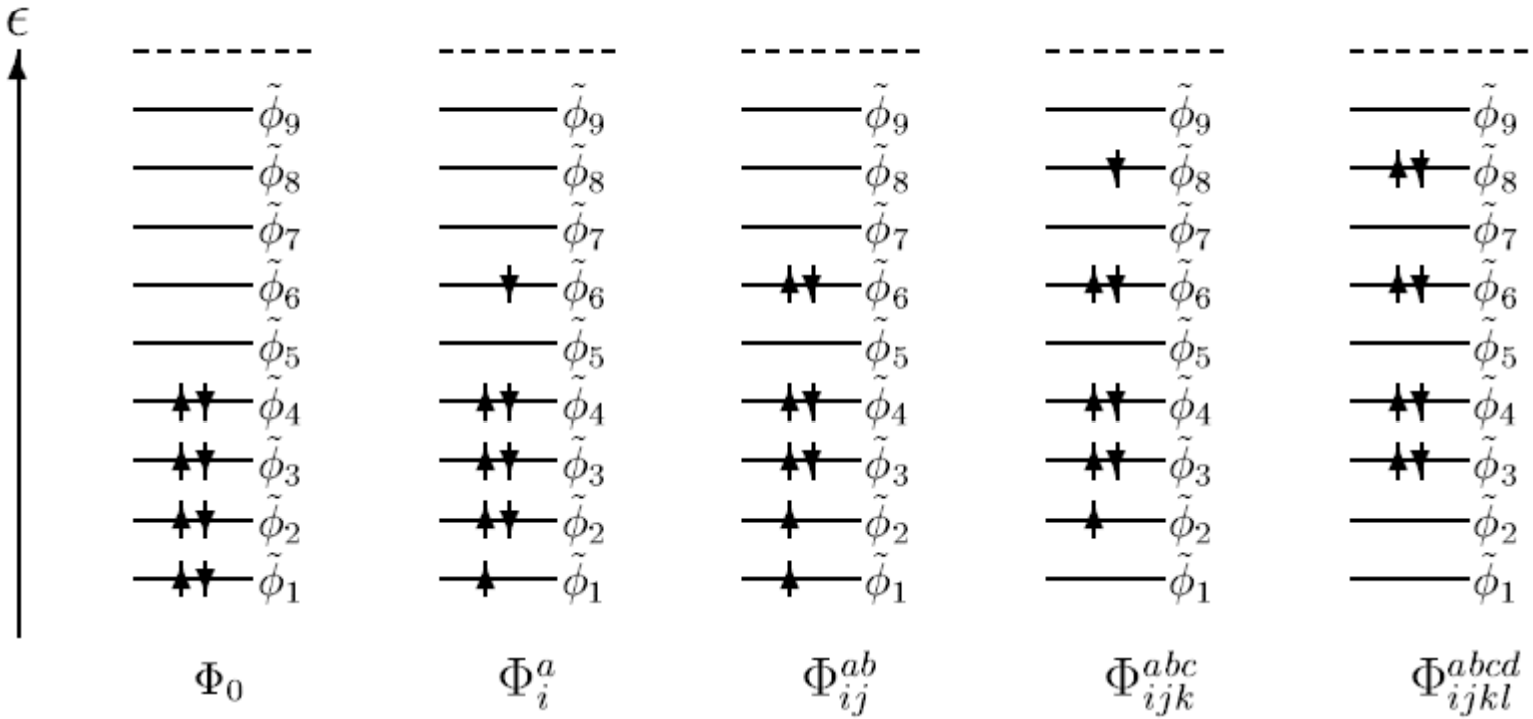


HF *N-electron* reference state: Slater determinant of *N* occupied orbitals.

$$\Phi_0 = A\left[\tilde{\phi}_1(x_1)\tilde{\phi}_2(x_2)\cdots\tilde{\phi}_N(x_N)\right]$$

The full many-body wave function is spanned by all possible Slater determinants, which can be formed from the *M* occupied and virtual HF orbitals, where *M* is the size of the 1-particle basis.

QM chem - e.g. *single* reference, *orthogonal* det's



HF **singly doubly triply quadruply**

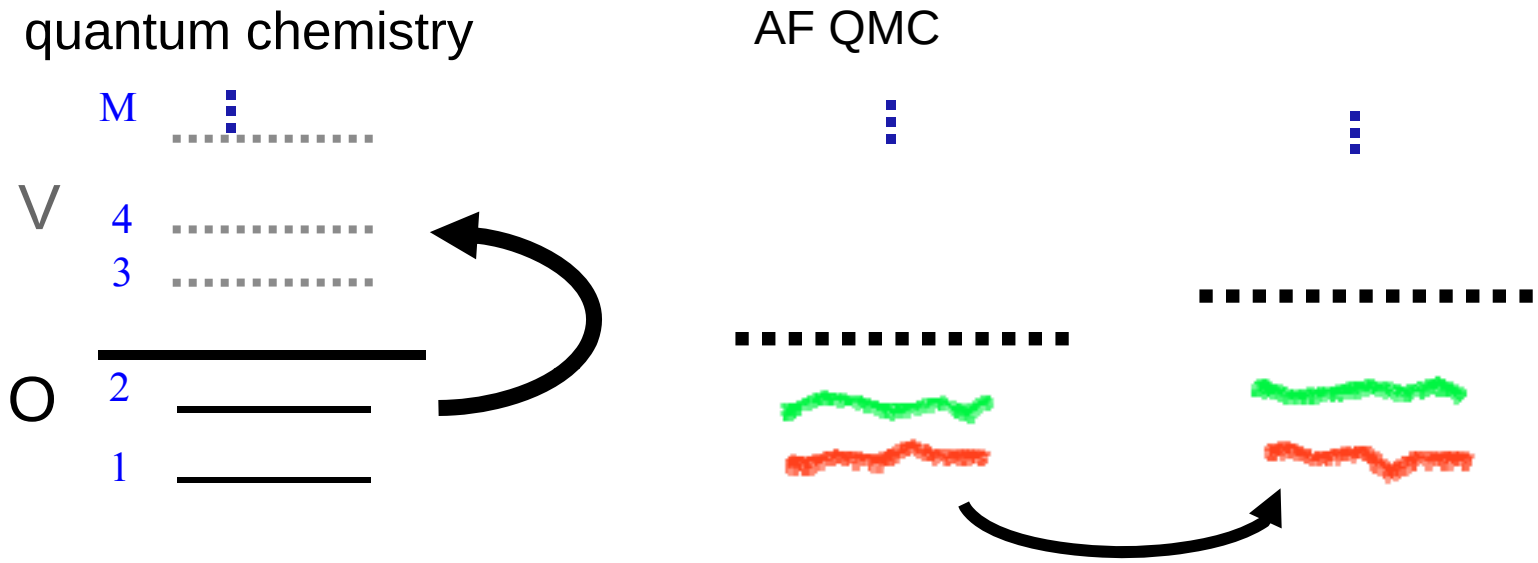
excited determinants

$$\Psi = \Phi_0 + \sum_{ia} c_i^a \Phi_i^a + \sum_{ijab} c_{ij}^{ab} \Phi_{ij}^{ab} + \cdots$$

***orthogonal* determinants**

Overview - how does auxiliary-field QMC work?

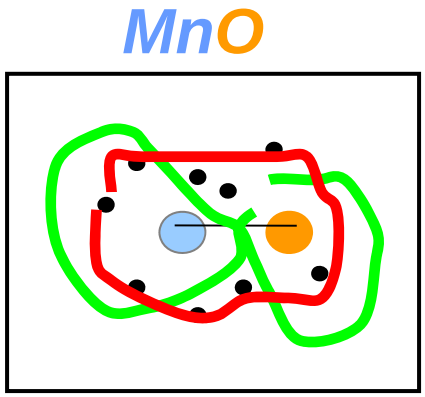
Random walks of *non-orthogonal* Slater determinants



A single random walker in AFQMC is a Slater determinant: $\Phi_0 = A\left[\phi_1(x_1)\phi_2(x_2)\cdots\phi_N(x_N)\right]$

- AFQMC is naturally ***multi***-reference: ***not*** the HF orbitals
- any orbital that can be expressed in the basis:

$$\phi_j(x) = \sum_{i=1}^{M} \alpha_{ji} G_i(x)$$



DMC: $\left(x_1, x_2, \cdots, x_N\right)$

AF QMC: basic formalism

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 functions

(textbooks: $M = \infty$)

QM chemistry: $M \propto N$

Recall

$$H = H_1 + H_2 = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i) + \sum_{i<j}^{N} V_{\text{int}}(|\mathbf{r}_i - \mathbf{r}_j|)$$

next →

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M : basis size

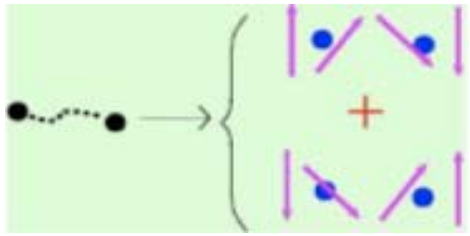
$\hat{H}_2 \to -\sum \hat{v}^2$ with $\hat{v}$ = 1-body

Hubbard-Strotonivich transf.

DFT: $\hat{H}_2 \to \sum_i f_c(n_i)\hat{n}_i$

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

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



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

next →

Auxiliary-field 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)

- Potential for real materials well recognized

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

- However,
  - sign problem for “simple” interactions (Hubbard)
  - phase problem for realistic interaction
- Our reformulation gives a way to control the problem by an approximation to have a N^3 or N^4 scaling algorithm

AF QMC - schematic implementation

Random walks in Slater determinant space:

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

$\Downarrow$ 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.

$$|\phi^{(0)}\rangle \rightarrow |\phi^{(1)}(\sigma)\rangle \rightarrow |\phi\rangle \quad \Leftarrow \textbf{Slater det.}$$

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

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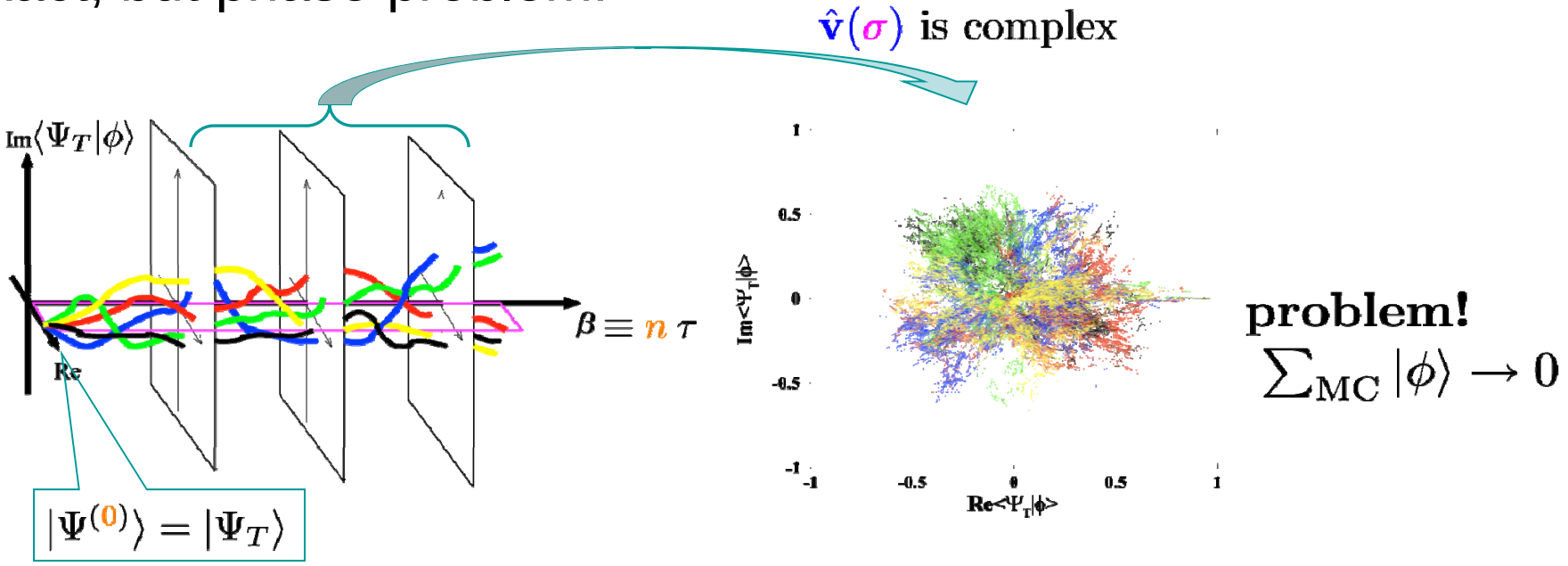
Exact, but phase problem:



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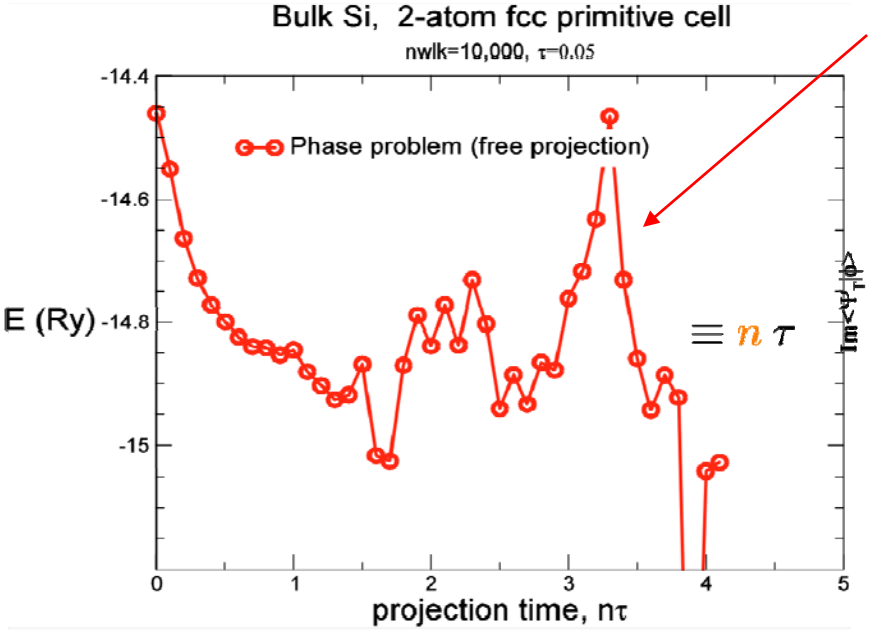
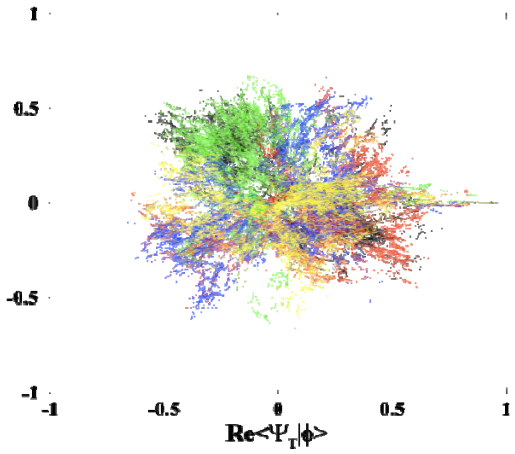
Exact, but phase problem:

Exponential noise





problem!

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

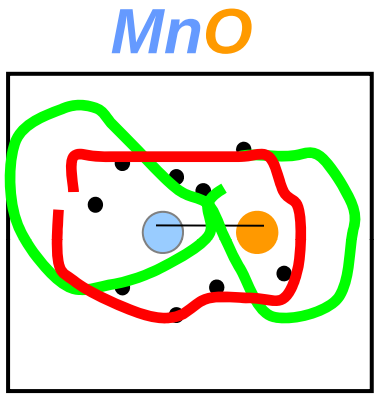
The sign problem

Sign/phase problem is due to -- $\Phi_0 = A\left[\phi_1(x_1)\phi_2(x_2)\cdots\phi_N(x_N)\right]$

"superexchange":

$$\Phi_0 = A\left[\phi_1(x_1)\phi_2(x_2)\cdots\phi_N(x_N)\right]$$

Slater det. - antisymmetric



Reasonable to expect that problem is reduced, since tendency for global collapse to bosonic state is removed

To eliminate sign problem:

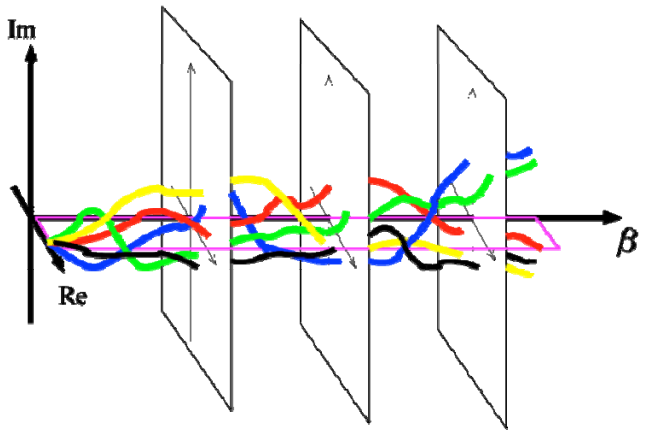
Use $\langle \Psi_T | \Psi \rangle = 0$ to determine if **"superexchange"** has occurred

The sign problem and the constraint

- The constraint is exact when $\mathrm{sgn}[\langle \Psi_T | \Psi \rangle] = \mathrm{sgn}[\langle \Psi_{GS} | \Psi \rangle]$
  - similar to fixed-node in DMC, but the global sign of a $\Psi\rangle$ (fermionic) is less demanding than that of *R* (bosonic)
- "Mixed estimate" of total energy not an upper bound
- The method is exact if $\langle \Psi_T | \Psi \rangle$ is always non-negative

Controlling the phase problem

Sketch of approximate **solution**:



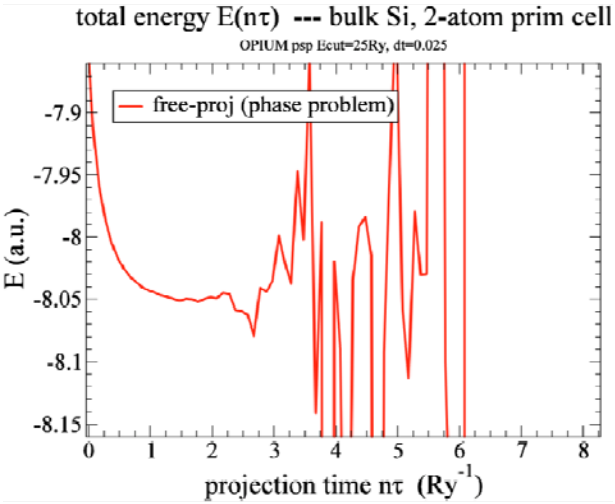
- Modify propagator by "gauge transformation':
  phase → degeneracy (use trial wf)
- Project **to one overall phase**:
  break "rotational invariance"

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

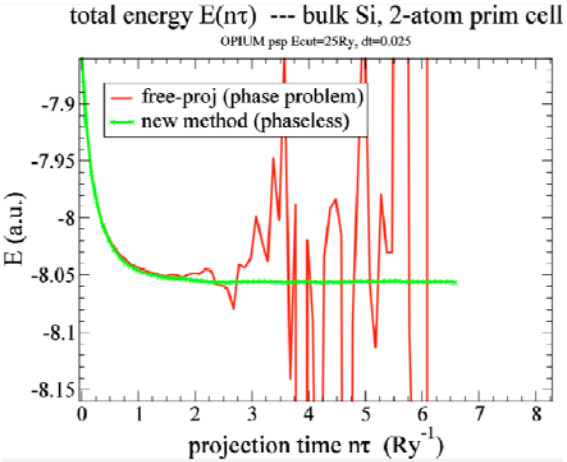
- subtle, but key, difference from: real $\langle \Psi_T | \phi \rangle$

(Fahy & Hamann; Zhang, Carlson, Gubernatis)

Before:

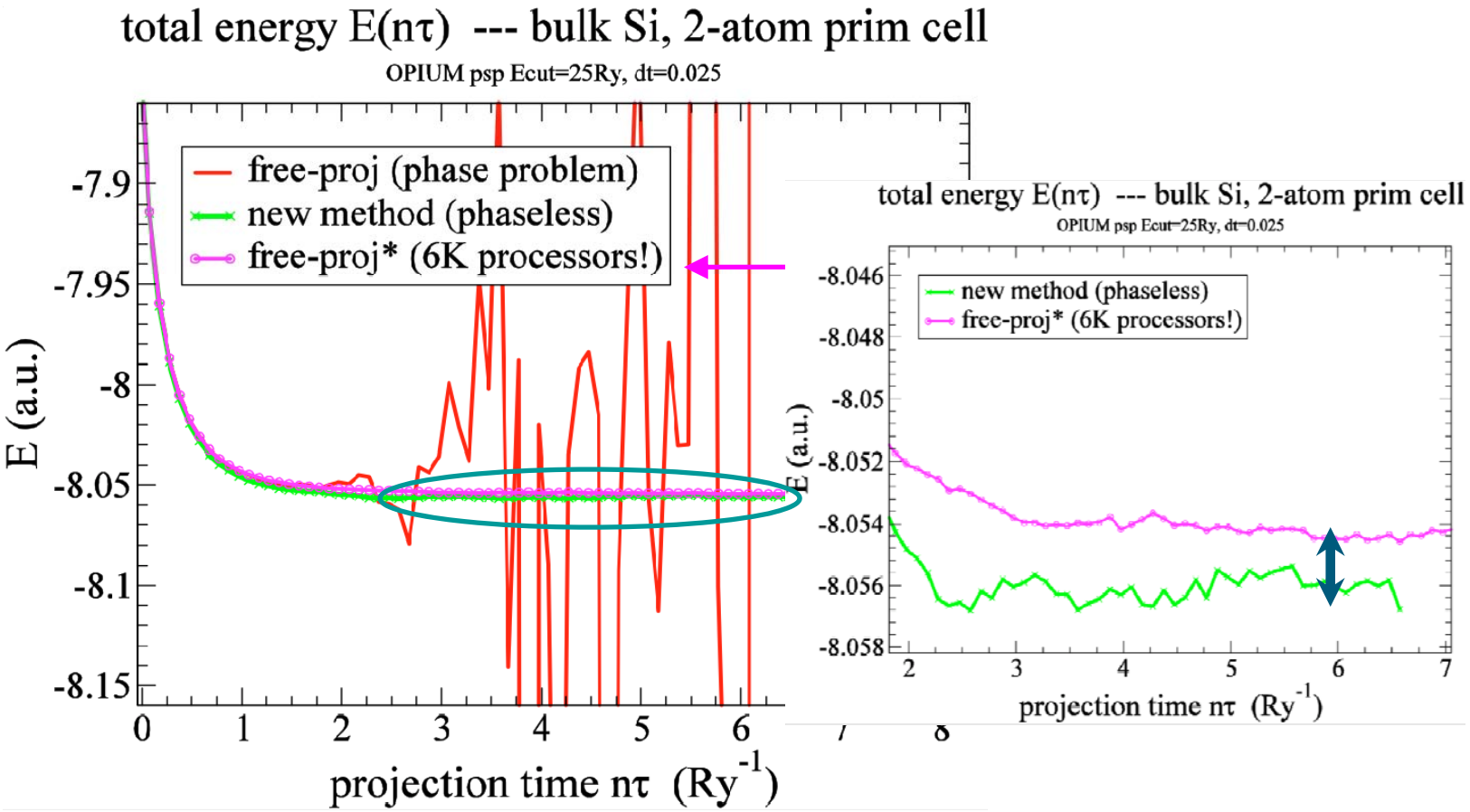


After:



Controlling the phase problem

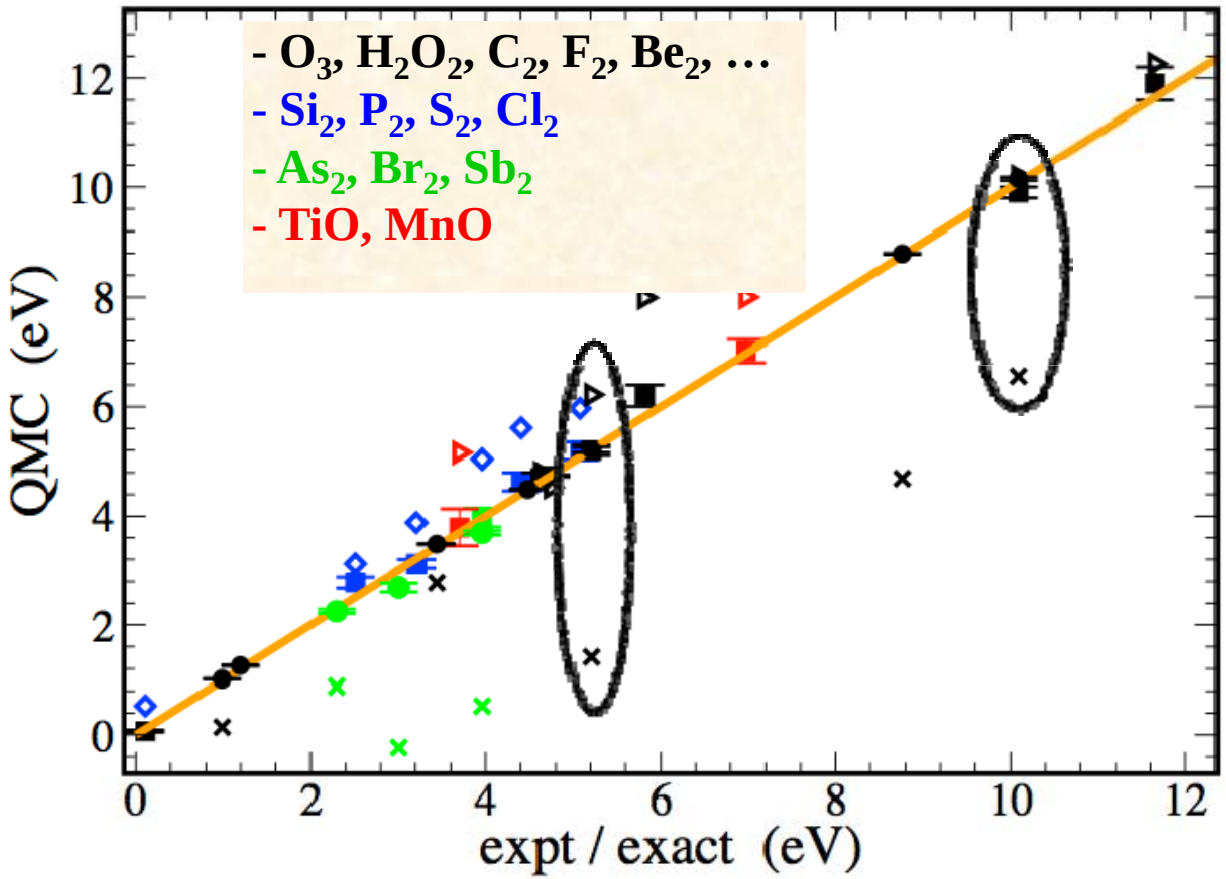
Quantify the approximation?



Error in total E < 0.3mH/atom

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

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 independent of trial wf details

MnO solid in antiferromagnetic II phase:

	Evar	*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=21.96 A^3

QMC insensitive to details of the trial wave function

Spin restriction (R vs U type of trial wfs) does have effect:

e.g., water molecule:

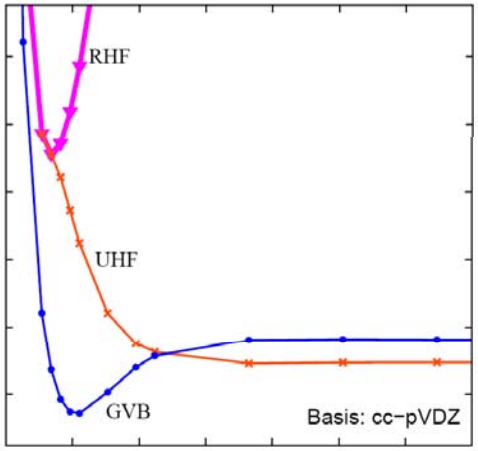
Bond length	RHF	UHF	CCSD(T)	FCI	QMC/RHF	QMC/UHF
STO-6G						
$1.5R_e$	−75.440 432	−75.502 069		−75.600 039	−75.5768(3)	−75.5965(6)
$2R_e$	−75.141 587	−75.464 541		−75.486 528	−75.3557(3)	−75.4880(3)

no upper bound!

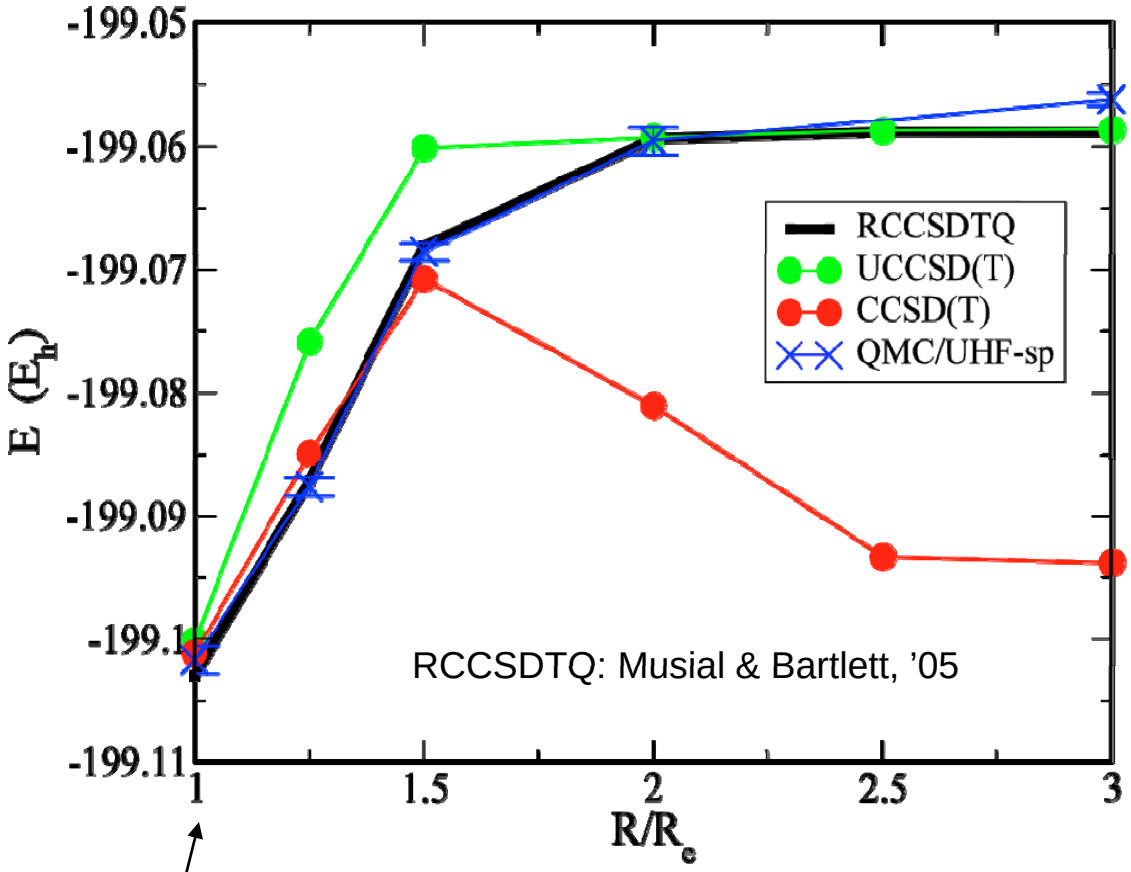
F_2 bond breaking

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)



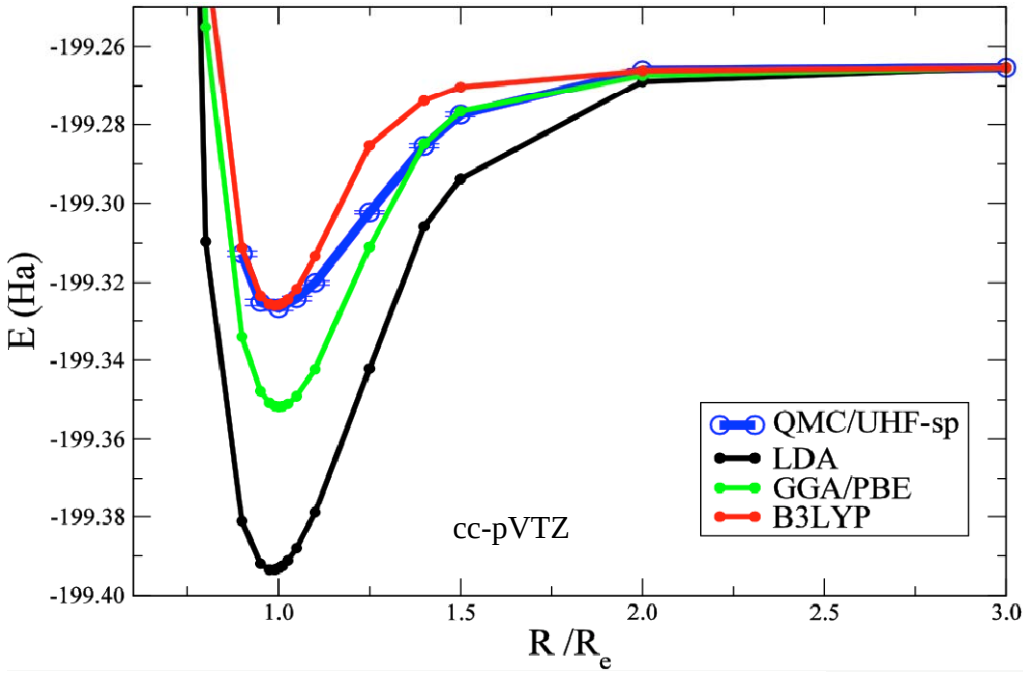
Equilibrium → **Dissoc. limit**

"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			

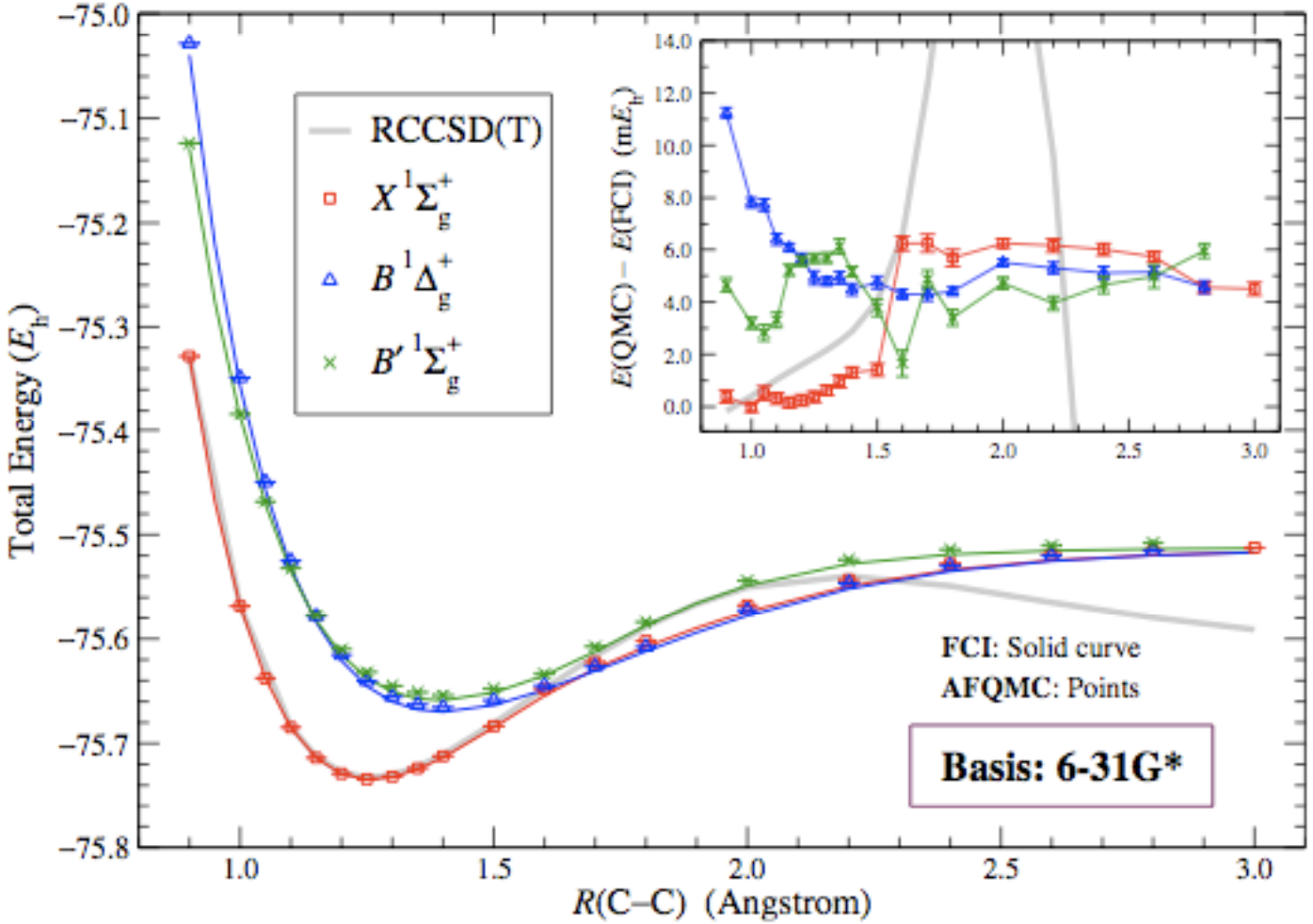
Purwanto et. al., JCP, '08

Excited states

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

Excited states

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



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

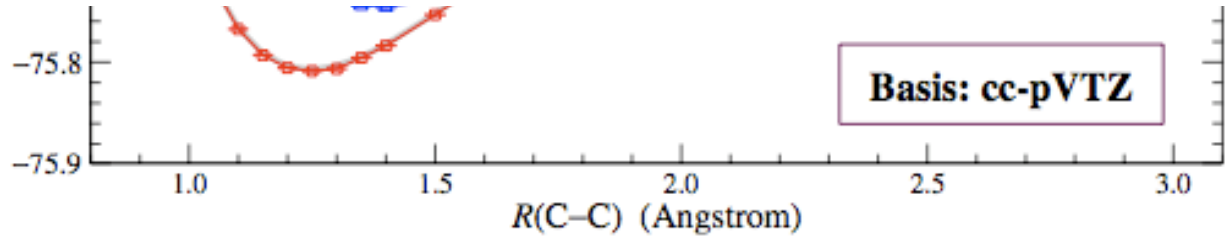
Excited states

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.



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

Larger basis size with GTOs

- computational scaling of phaseless AF QMC

basis	**start-up**	**propagating**
planewave/psp	~0	$N^2 M \log(M)$
GTO	M^6 (brute force)	M^3 & M^4 (energy calc)

- We've implemented a modified Cholesky to remove M^6

Table: Comparison of diagonalization vs. modified Cholesky method. *M* is the basis size. Times are reported in seconds. Calculations were done on an AMD workstation with 8-core OpenMP parallelism.

M	Time (diagonalization)	Time (mod-Cholesky)	J_{max}
101	3608	11	592
155	33649	66	1044
180	67194	108	1247
216	---	112	1480
344	---	1066	2255

M^6 bottleneck? - AFQMC with GTO basis:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{\mu\nu}^{M} T_{\mu\nu} c_\mu^\dagger c_\nu + \sum_{\alpha\beta\mu\nu}^{M} V_{\alpha\beta\mu\nu} c_\alpha^\dagger c_\mu^\dagger c_\beta c_\nu$$

Hubbard-Stratonivich transformation requires:

$$\hat{H}_2 = \sum_\lambda \hat{v}_\lambda^2 \quad \hat{v}_\lambda = \text{ 1-body}$$

Brute force solution - diagonalize M^2 x M^2 matrix:

$$V_{\alpha\beta\mu\nu} = V_{\{\alpha\beta\},\{\mu\nu\}}$$

*

Avoid bottleneck: resolution of identity (RI)

2-body Coulomb: $(\mu\nu|\lambda\sigma) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1) r_{12}^{-1} \chi_\lambda(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2)$

RI: $\boxed{r_{12}^{-1} = \sum_n^{\infty} \phi_n(\mathbf{r}_1)\phi_n(\mathbf{r}_2)}$

e.g., PW's: $\frac{1}{2\Omega}\sum_{\mathbf{Q}\neq\mathbf{0}} \frac{4\pi}{Q^2}\hat{\rho}^\dagger(\mathbf{Q})\hat{\rho}(\mathbf{Q})$

O(8*M*)

I) density fitting:

pre-defined

auxiliary basis

$$|\mu\nu) \approx |\widetilde{\mu\nu}) = \sum_P C_{\mu\nu}^P |P) \qquad P << M^2$$

$$(\mu\nu|\lambda\sigma) \approx \sum_{PQ} C_{\mu\nu}^P (P|Q) C_{\lambda\sigma}^Q$$

II) modified Cholesky*:

accuracy controlled by one parameter - unbiased

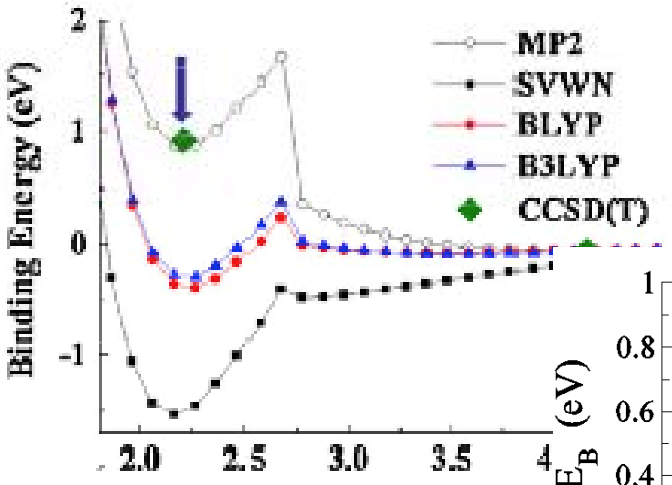
$$(\mu\nu\,|\,\lambda\alpha) \approx \sum_{j=1}^{J} L_{\mu\nu}^{(j)} L_{\lambda\alpha}^{(j)} \qquad J << M^2$$

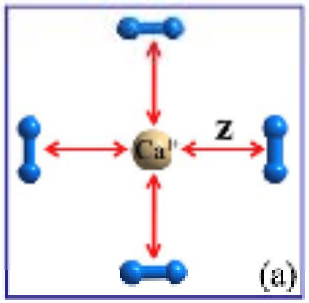
* Beebe NHF, Linderberg J (1977) Int J Quantum Chem 12:683

Test: model H-storage problem

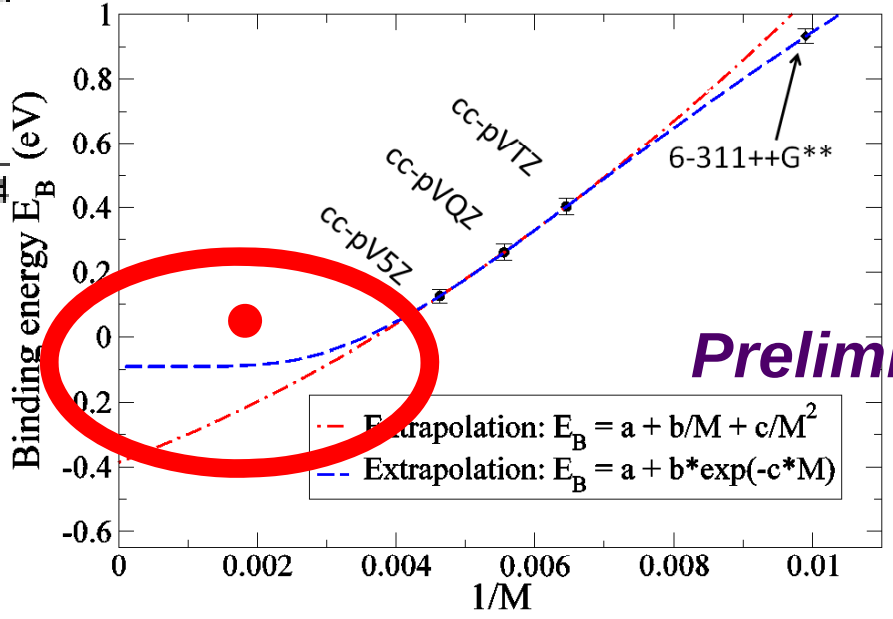
- Model system of Ca^{1+} / 4H2
  Possible high-density H storage by dispersed alkaline-earth metals?

6-311+G**





Finite Basis set error?



Preliminary

Can now do with modified Cholesky

next →

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 F_2)
  - Further improvement:
    better constraining wf; back propagation; release; ....
- Favorable computational scaling ~ O(M^3-M^4)
  - reduce prefactor: (remove M^4?)
    GTO tricks; better basis; resolution of the identity (modified Cholesky example); .....
  - natural hierarchy in auxiliary-fields, localization, ...

Summary

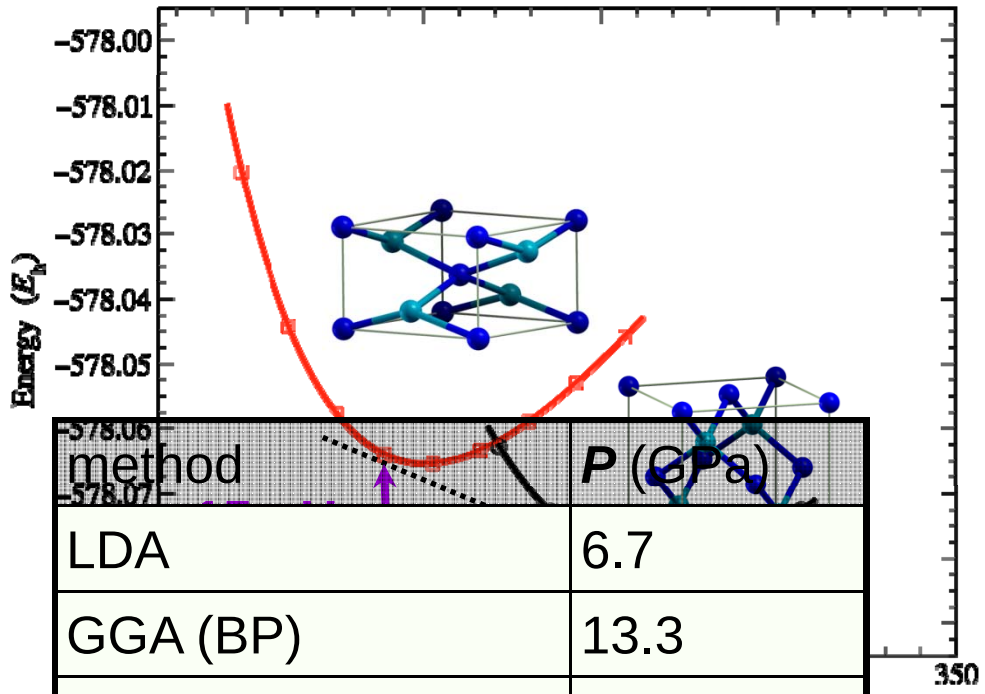
- AF QMC : random walks in mean-field space
  - Orbital-based, non-perturbative, many-body method
  - Approximate: (exact without constraint -- FCI-like)
    - QMC's only source of error reduced --> making QMC more a "blackbox", for more problems
    - encouraging accuracy and robustness
- Applications & benchmarks
  - comparable to CCSD(T) around equilibrium geometry
  - better for stronger correlations, e.g. bond-breaking in molecules
- Modified Cholesky for GTOs
- Various opportunities to import techniques from QC
- A new wf-based method which can directly use much of the existing machinery from DFT/HF:

  --- **superposition** of **independent-particle calculations**

Thank you!

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