

FCIQMC: A practical perspective I

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MOLSSI QMC summerschool,
Pittsburgh, USA, July 2019
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FCIQMC I Plan (c. 2010)

- Second Quantization
- Philosophy and motivation for FCIQMC
- Propagator and algorithm
- Sign problem and results

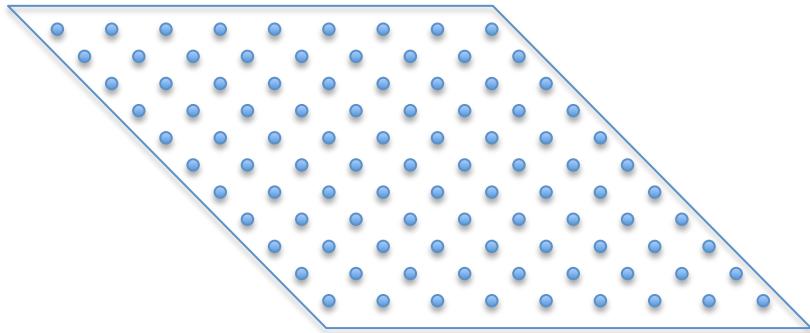
FCIQMC II Plan

- Second quantization in practice
- Hamiltonian matrix element evaluation
- Random excitation generation
- Initiator approximation
- Successes, Failures and the future...

Second quantization

DMC samples this:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

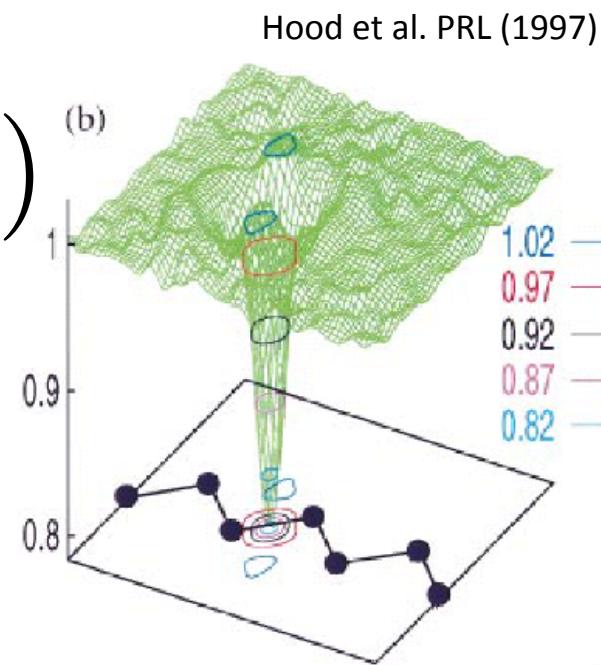


Define amplitudes
only at grid-points (c.f. LR-DMC)

Instead of labeling N electrons, label m grid-points.

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$

Wave function amplitudes as tensor

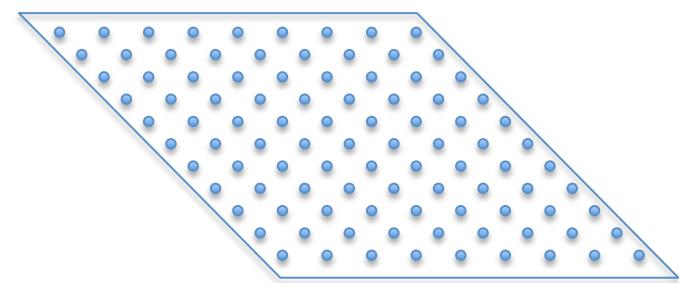


Four possible states:

$$|q_i\rangle = \{| \cdot \rangle_i, |\uparrow\rangle_i, |\downarrow\rangle_i, |\uparrow\downarrow\rangle_i\}$$

Second quantization

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$



Wfn is now defined by finite number of basis states: 4^m

Exact solution only in limit of infinite grid resolution

First quantized Hamiltonian (explicit electrons):

$$\hat{H} = \sum_i -\frac{1}{2} \nabla_i^2 + v_{ext}(r_i) + \sum_{i < j} \frac{1}{r_{ij}} + E_{NN}$$

Commutation of SQ operators enforces antisymmetry

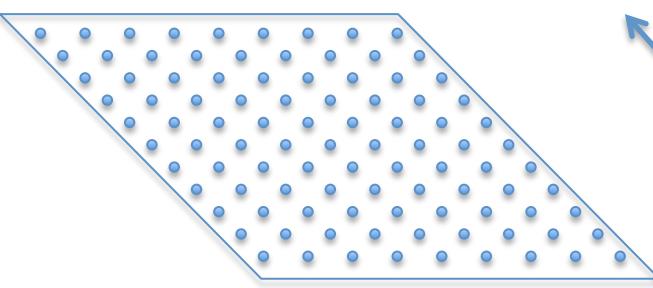
Second quantized Hamiltonian (explicit basis functions):

$$\hat{H} = \sum_{ij} h_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} c_i^\dagger c_j^\dagger c_l c_k + E_{NN}$$

$h_{ij} = \langle \phi(\mathbf{r})_i | -\frac{1}{2} \nabla^2 + v_{ext}(r_i) | \phi(\mathbf{r})_j \rangle$

Coulomb interaction encoded into coefficients

Second quantization

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$


Wfn is now defined by finite number of basis states: 4^m

Exact solution only in limit of infinite grid resolution

Linear superposition of quantum fluctuations:

$$\frac{1}{\sqrt{2}} |\text{cat sitting}\rangle + \frac{1}{\sqrt{2}} |\text{cat jumping}\rangle$$

We conclude that traditional wavefunction methods, ... are generally limited to a small number of electrons, $N < O(10)$.

Kohn (Nobel Address, 1999)



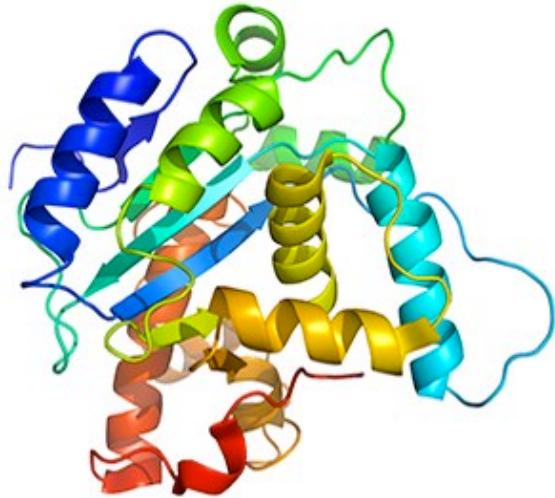
[The Schrodinger equation] cannot be solved accurately when the number of particles exceeds about 10. No computer existing or that will ever exist can break this barrier because it is a catastrophe of dimension

Pines and Laughlin (PNAS 2000)

Second quantization

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$

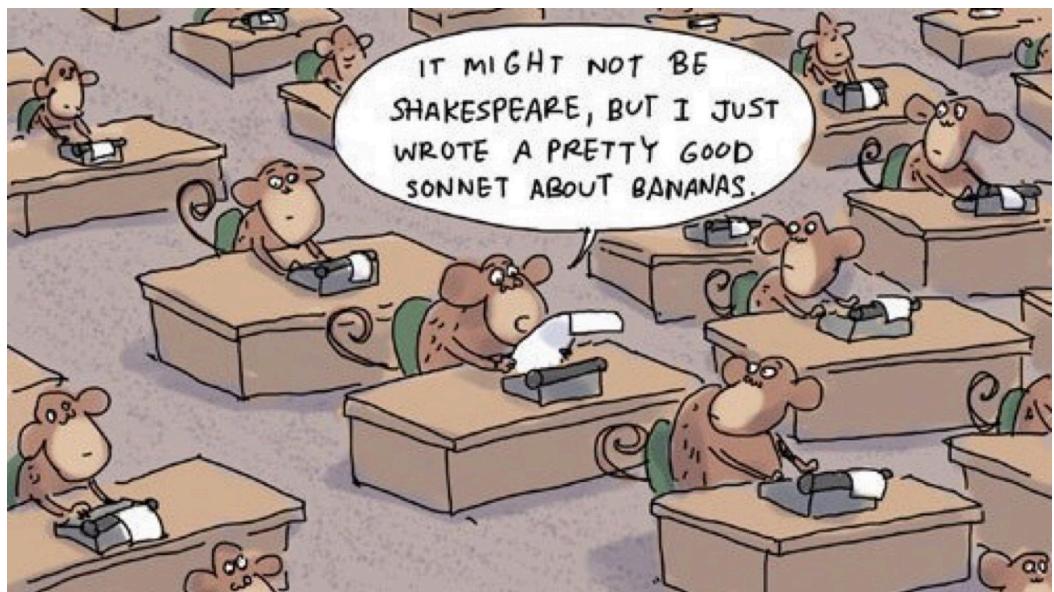
Phase space of proteins $\sim 20^{500} \sim 10^{650}$



Redundancy in space – Neutral mutations

Bias towards low-complexity

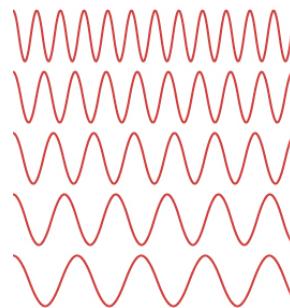
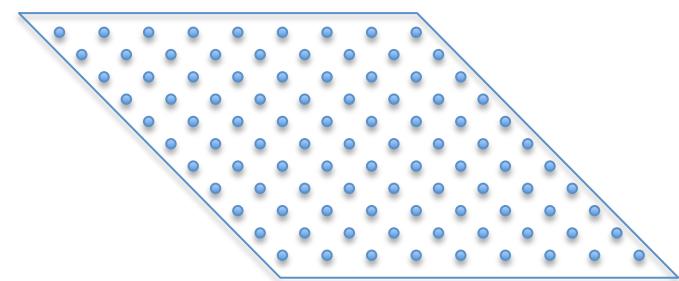
However, we **can** make progress with wave functions
Nature is **not** monkeys at keyboards...



We know that there are many physical principles with constrain the complexity of wfns

Second quantization

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$



Plane waves



Atomic orbitals

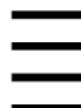
Antisymmetry
'built in'

(not explicit)

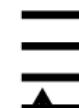
$$|\Psi_{HF}\rangle$$

Reference determinant

'Orbitals' which diagonalize one-electron operator



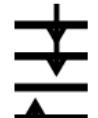
HF



S



D



T



T



T



T



T

$$c_i^a |\Psi_i^a\rangle$$

$$c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle$$

$$c_{ijk}^{abc} |\Psi_{ijk}^{abc}\rangle$$

Excited determinants

Second quantization

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$

2) We can well parameterize the wave function coefficients for many systems with polynomial number of parameters:

Coupled cluster, Slater-Jastrow, RVB,...: Low-body expansion

$$\Psi = e^{U(x)} |\psi_0\rangle \quad |CC\rangle = e^T |\psi_0\rangle \quad \Psi = P_G \left(\sum_{r < r'} f_{r-r'} (a_{r\uparrow}^\dagger a_{r'\downarrow}^\dagger + a_{r'\uparrow}^\dagger a_{r\downarrow}^\dagger) \right) |0\rangle$$

Tensor networks: Local entanglement

$$|\Psi(q_1, q_2, q_3 \dots q_N)\rangle = \sum_{i,j,k,l} C(q_1, i) C(q_2, i, j) C(q_3, j, k) \dots C(q_N, l) |q_1 q_2 q_3 \dots q_N\rangle$$

Second quantization

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$

3) In certain representations, for certain systems, the amplitudes can be very **sparse**



$$|\Psi\rangle = \sum_{\mathbf{i}}^{N_{FCI}} C_{\mathbf{i}} |D_{\mathbf{i}}\rangle \sim \sum_{\mathbf{i}}^{N_D \ll N_{FCI}} \tilde{C}_{\mathbf{i}} |D_{\mathbf{i}}\rangle$$

CISD is generally very accurate (just double excitations) $\sim 80\text{-}90\%$ correlation

SCI is generally exceptionally accurate [Malrieu, Pulay, Evangelista, Umrigar, Sharma,...]

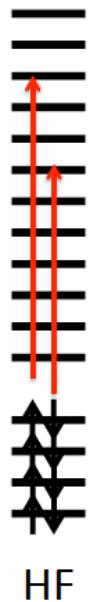
HF

Size extensivity difficult with truncated CI

Second quantization

$$|\psi\rangle = \sum_{q_1 q_2 q_3 \dots q_m} C^{q_1 q_2 q_3 \dots q_m} |q_1 q_2 q_3 \dots q_m\rangle$$

4) High-dimensional phase spaces can (sometimes) be efficiently sampled with QMC



$$|\Psi\rangle = \sum_{\mathbf{i}}^{N_{FCI}} C_{\mathbf{i}} |D_{\mathbf{i}}\rangle \sim \left\langle \sum_{\mathbf{i}(\beta)}^{N_D \ll N_{FCI}} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle \right\rangle_{\beta}$$

Motivation for **FCIQMC*** (2nd quantized projector Monte Carlo)

- Unitary freedom
- Sparsity of amplitudes
- Monte Carlo sampling



- No imposition of nodal surface
- Basis set incompleteness (E diffs)
- No constraint on wfn form (sys. imp.)
- (Much) more expensive than DMC

*Booth, Thom, Alavi, JCP 2009. Building on / recasting old ideas. [Umrigar, Ten-no, Faulkes, ...]

FCIQMC

$$|\Psi\rangle = \sum_{\mathbf{i}}^{N_{FCI}} C_{\mathbf{i}} |D_{\mathbf{i}}\rangle$$

$$\left\langle \sum_{\mathbf{i}(\beta)}^{N_D \ll N_{FCI}} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle \right\rangle_{\beta}$$

Instantaneous, coarse-grained
'snapshot' of wfn

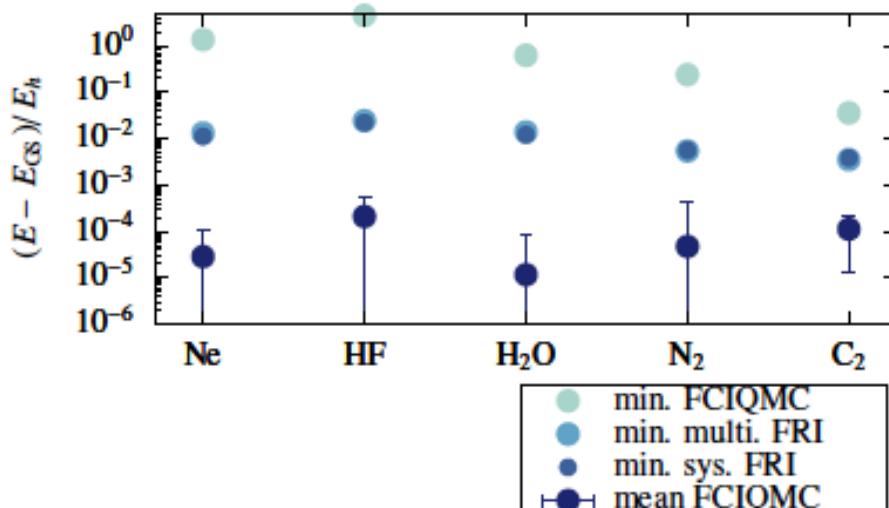
Dynamic set of dets.

Average over
sampling iterations

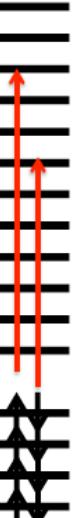
Condition on amplitude sampling:

$$\langle \tilde{C}_{\mathbf{i}}(\beta) \rangle_{\beta} \approx C_{\mathbf{i}}$$

Is any single snapshot any good?



FCIQMC


$$|\Psi\rangle = \sum_{\mathbf{i}}^{N_{FCI}} C_{\mathbf{i}} |D_{\mathbf{i}}\rangle \sim \left\langle \sum_{\mathbf{i}(\beta)}^{N_D \ll N_{FCI}} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle \right\rangle_{\beta}$$

HF

Condition on amplitude sampling: $\langle \tilde{C}_{\mathbf{i}}(\beta) \rangle_{\beta} \approx C_{\mathbf{i}}$

Clearly, we don't want to explicitly average the amplitudes, but only **expectation values**

$$E = \langle E(\tilde{C}_{\mathbf{i}}(\beta)) \rangle_{\beta}$$

Wave function compression

$$|\Psi\rangle = \sum_{\mathbf{i}}^{N_{FCI}} C_{\mathbf{i}} |D_{\mathbf{i}}\rangle \sim \left\langle \sum_{\mathbf{i}(\beta)}^{N_D \ll N_{FCI}} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle \right\rangle_{\beta}$$

Given the exact wfn, how would we stochastically compress it?

Initial FCIQMC: Let all coefficients have integer weight...

Ex.

$$\begin{aligned} \tilde{C}_{\mathbf{i}}(\beta) = 3.4 &\rightarrow 3 \text{ with prob. } p = (1 - 0.4) \\ &\rightarrow 4 \text{ with prob. } p = 0.4 \end{aligned}$$

If rounded to zero, remove from simulation (only store ‘occupied’ determinants)

Resolution of the wavefunction controlled by normalization of number of **walkers**

(signed) unit amplitude of wave function



Wave function compression

$$|\Psi\rangle = \sum_{\mathbf{i}}^{N_{FCI}} C_{\mathbf{i}} |D_{\mathbf{i}}\rangle \sim \left\langle \sum_{\mathbf{i}(\beta)}^{N_D \ll N_{FCI}} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle \right\rangle_{\beta}$$

Given the exact wfn, how would we stochastically compress it?

Umrigar: Why let 1 be minimum weight?

Ex. $\chi = 0.2$

$$\rightarrow \chi \quad \text{with prob. } p = \frac{|\tilde{C}_{\mathbf{i}}(\beta)|}{\chi}$$

$$\tilde{C}_{\mathbf{i}}(\beta) = 0.05$$

$$\text{Round up or down?} \quad \rightarrow 0 \quad \text{with prob. } p = 1 - \frac{|\tilde{C}_{\mathbf{i}}(\beta)|}{\chi}$$

Keep the term ‘walkers’ for the absolute weight

Propagating ‘walkers’

$$|\Psi(\beta)\rangle = \sum_{\mathbf{i}}^{N_D} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle$$

We need to devise stochastic propagation, s.t. $\langle \tilde{C}_{\mathbf{i}}(\beta) \rangle_{\beta} \approx C_{\mathbf{i}}$

Imaginary-time propagation? $\lim_{\beta \rightarrow \infty} e^{-\beta H} |\phi_0\rangle \propto |\Psi_0\rangle$ assuming $\langle \phi_0 | \Psi_0 \rangle \neq 0$

$$\lim_{n \rightarrow \infty} (e^{-\tau H})^n |\phi_0\rangle \propto |\Psi_0\rangle$$



Difficult operator to work with in SQ (c.f. AFQMC)

Much simpler,
with same eigenstates:
(no trotter error)

$$\lim_{n \rightarrow \infty} (1 - \tau H)^n |\phi_0\rangle \propto |\Psi_0\rangle$$



Apply hamiltonian to wave function each iteration

Propagating ‘walkers’

$$|\Psi(\beta)\rangle = \sum_{\mathbf{i}}^{N_D} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle \quad \lim_{n \rightarrow \infty} (1 - \tau H)^n |\phi_0\rangle \propto |\Psi_0\rangle$$

What constraints are there on this propagation?

Rewrite in eigenbasis:

$$\lim_{n \rightarrow \infty} |\Psi_m\rangle (1 - \tau E_m)^n \langle \Psi_m | \phi_0 \rangle \propto |\Psi_0\rangle$$

To ensure ground-state dominates at large n:

$$E_0 = 0 \quad \tau E_{\max} < 2 \quad \langle \phi_0 | \Psi_0 \rangle \neq 0$$

Shift propagator, and ensure timestep small enough...

Propagating ‘walkers’

$$\lim_{n \rightarrow \infty} (1 - \tau(H - E_0 - S))^n |\phi_0\rangle \propto |\Psi_0\rangle$$

Lowest (HF) determinant energy Unknown correlation energy: ‘*Shift*’

Finite basis set saves us!

$$\tau < \frac{2}{E_{\max} - E_0}$$

Convergence depends exponentially on gap

Propagating ‘walkers’

$$\lim_{n \rightarrow \infty} (1 - \tau(H - E_0 - S))^n |\phi_0\rangle \propto |\Psi_0\rangle$$

Lowest (HF) determinant energy Unknown correlation energy: ‘*Shift*’

How to choose shift?

When $S = \text{corr. energy}$, then propagator is **norm-conserving**
(i.e. N_w does not change)



Dynamically update S s.t. walker number is fixed (const. comp. resources!)

$$S(\beta + A\tau) = S(\beta) - \frac{\xi}{A\tau} \ln \frac{N_w(\beta + A\tau)}{N_w(\beta)}$$

Propagating ‘walkers’

Lagrangian (variational) perspective:

$$\mathcal{L}[\Psi] = \langle \Psi | H | \Psi \rangle - \lambda (\langle \Psi | \Psi \rangle - A)$$

Gradient descent

$$\Delta C_i = -\tau \frac{\partial \mathcal{L}[\Psi]}{\partial C_i}$$

$$\Delta C_i = -\tau' \sum_j \langle D_i | H - \lambda | D_j \rangle C_j$$

Lagrangian variation controls norm ‘Shift’
Equal to energy at convergence

Other direction: Accelerated GD

Stochastic Krylov space /
Power method perspective:

$$\kappa_r(A, b) = \text{span}\{b, Ab, A^2b, \dots, A^{r-1}b\}$$



Converges to ground state as Power method
(linearly dependent).

$$\left\{ \psi, \frac{dE}{d\psi}, \frac{d^2E}{d\psi^2}, \dots \right\}$$

Other directions: Krylov projected FCIQMC
[Blunt, Alavi, Booth, PRL 2016]

Algorithm

$$|\Psi(\beta)\rangle = \sum_{\mathbf{i}}^{N_D} \tilde{C}_{\mathbf{i}}(\beta) |D_{\mathbf{i}}\rangle$$

Recast propagator as a stochastic, local Markov chain

$$\lim_{n \rightarrow \infty} (1 - \tau(H - E_0 - S))^n |\phi_0\rangle \propto |\Psi_0\rangle$$

Sparse walker snapshot

$$\Delta \tilde{C}_{\mathbf{i}} = -\tau(H_{\mathbf{ii}} - H_{00} - S)\tilde{C}_{\mathbf{i}}$$

Spawning step (do backwards)

Loop through *occupied determinants* (\mathbf{j}):

Pick a number of spawning *attempts* n_s :

For each attempt, generate \mathbf{i} , create weight as:

$$p_{\text{spawn}}(\mathbf{j} \rightarrow \mathbf{i}) = -\tau \frac{H_{\mathbf{ij}} \tilde{C}_{\mathbf{j}}}{p_{\text{gen}}(\mathbf{i}|\mathbf{j}) n_s}$$

$$-\tau \sum_{\mathbf{j} \neq \mathbf{i}} H_{\mathbf{ij}} \tilde{C}_{\mathbf{j}}$$



Potentially large sum?
Stochastically sample!

- How to ‘represent’ determinants? (Part I: Index, Part II: List of occupied orbitals)
- How to pick n_s ?
- How to pick \mathbf{j} ? (random excitation generation)
- When to stochasticize amplitudes? (TODAY: 1 round per iteration. $n_s \times n_D$ spawns)

Algorithm

Recast propagator as a stochastic, local Markov chain

$$\Delta \tilde{C}_i = -\tau(H_{ii} - H_{00} - S)\tilde{C}_i - \tau \sum_{j \neq i} H_{ij}\tilde{C}_j$$

Death step

Loop through *occupied determinants* (**i**):

Reduce (/increase) amplitude on determinant by

$$\Delta \tilde{C}_i = -\tau(H_{ii} - H_{00} - S)\tilde{C}_i(\beta)$$

- Stochastically round, or not?
- Amount of death is controlled each iteration by shift (**S**). Higher shift will lead to exponentially more walker weight.

Algorithm

Recast propagator as a stochastic, local Markov chain

$$\Delta \tilde{C}_i = -\tau(H_{ii} - H_{00} - S)\tilde{C}_i - \tau \sum_{j \neq i} H_{ij}\tilde{C}_j$$

Annihilation step

- Add spawned weight into the main walker list (may increase number of occupied determinants)
- Cancels walker weight of opposite sign
- Is this really a step? Why do we not do it as we go?
- Turns out that this is a critical step in the algorithm for breaking symmetry between signed solutions and establishing sign structure of amplitudes.

Simulation procedure

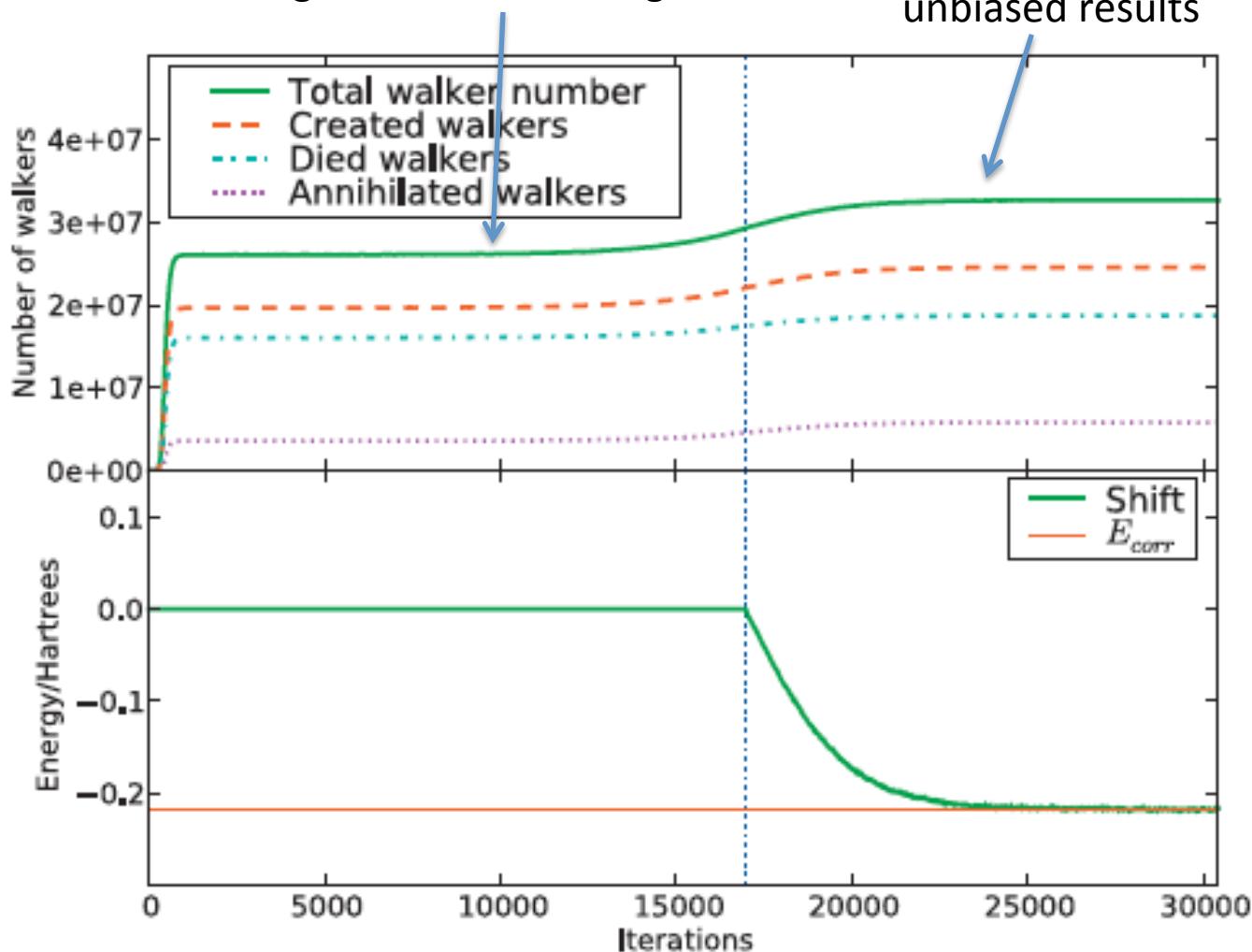
Two phases of simulation:

- **Constant shift** (grow walker population)
- **Variable shift** (stabilize walker population)

Note the natural emergence of a **plateau** phase in the growth profile

Sign coherence emerges...

Above this plateau, we get reliable, unbiased results



$\text{H}_2\text{O}, \text{VDZ}.$
 $N_{\text{FCI}}=5\text{e}8$ determinants

Energy estimator

Mixed (projected)
estimator

$$E(\beta) = \frac{\langle \Psi_T | H | \tilde{\Psi}(\beta) \rangle}{\langle \Psi_T | \tilde{\Psi}(\beta) \rangle}$$

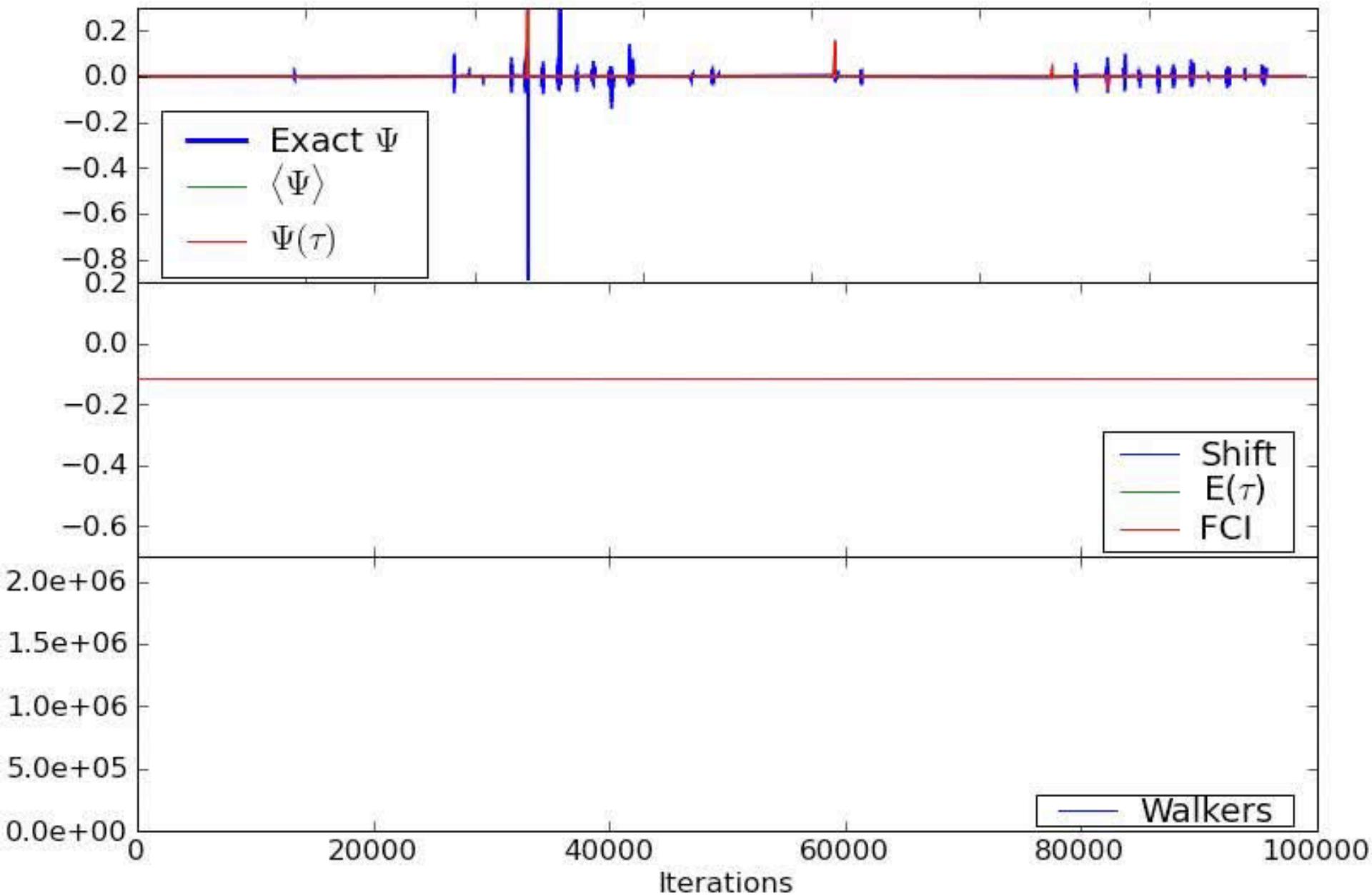
To start with, assume trial
wfn is a single (reference)
determinant (Hartree-Fock)

Numerator and
denominator
are **linear**
functions of
stochastic
variables

$$E(\beta) = \frac{\sum_{\mathbf{i} \neq \mathbf{0}}^{N_d} H_{0i} \tilde{C}_{\mathbf{i}}(\beta)}{\tilde{C}_{\mathbf{0}}(\beta)} + H_{\text{ref}}$$

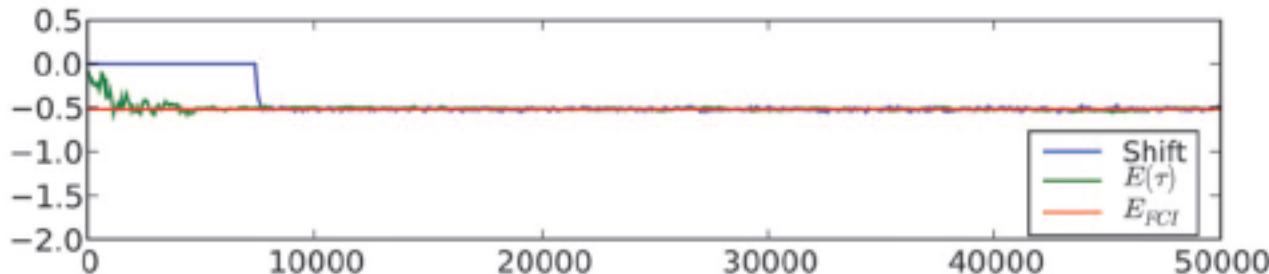
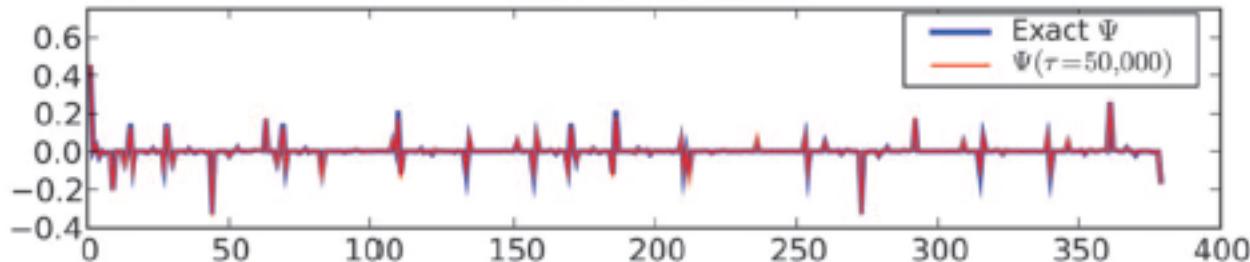
- Avoid having to average the amplitudes themselves
- Improvements can be made by choosing other trial wfns

Be_2 (cc-pVTZ). $N_{FCI} = 346,485$ determinants

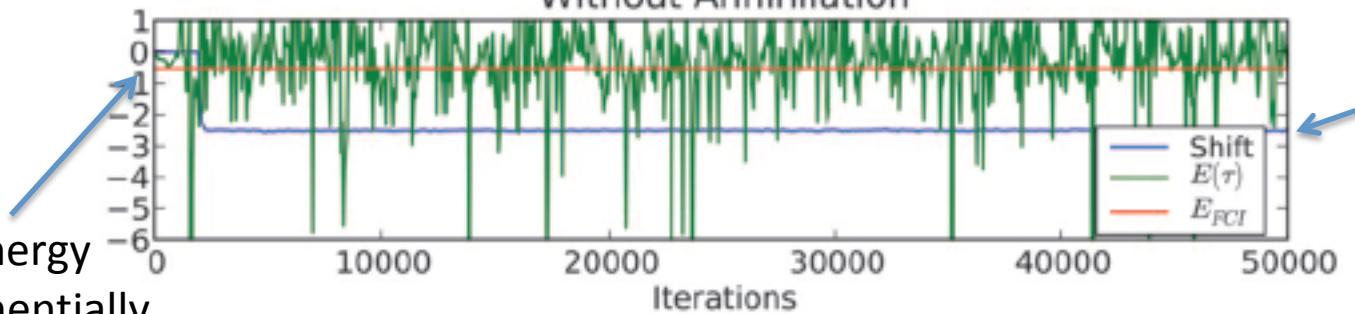


Sign problem in FCIQMC

With Annihilation



Without Annihilation



Noise in projected energy grows exponentially

Shift too low

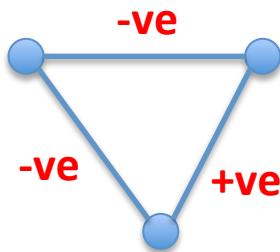
Annihilation **critical** in order to ensure correct wfn sampled
Wfn is explicitly antisymmetric, so where is the sign problem?!

Sign problem in FCIQMC

+	-	+	+
-	+	-	-
+	-	+	+
+	-	+	+

Sign structure of the columns of the propagator (hamiltonian) must be same (up to a sign) to be sign-problem-free

...or can we make every off-diagonal negative?



Cycles the hamiltonian matrix can cause problems

Burden of sign-problem shifted onto **operator** rather than ensuring antisymmetry of sampled states in 2nd quant.

Dependent on representation!

Sign problem in FCIQMC

Separate evolution of +ve
and -ve walker contributions

$$\frac{dC_{\mathbf{i}}^+}{d\beta} = \sum_{\mathbf{j}} H_{\mathbf{ij}}^+ C_{\mathbf{j}}^+ + H_{\mathbf{ij}}^- C_{\mathbf{j}}^-$$

$$\frac{dC_{\mathbf{i}}^-}{d\beta} = \sum_{\mathbf{j}} H_{\mathbf{ij}}^- C_{\mathbf{j}}^+ + H_{\mathbf{ij}}^+ C_{\mathbf{j}}^-$$

Linear equations, so can add and subtract:

Signed wfn

$$\frac{d(C_{\mathbf{i}}^+ - C_{\mathbf{i}}^-)}{d\beta} = \sum_{\mathbf{j}} (H_{\mathbf{ij}}^+ - H_{\mathbf{ij}}^-)(C_{\mathbf{j}}^+ - C_{\mathbf{j}}^-)$$

True Ham.

Desired

$$\frac{d(C_{\mathbf{i}}^+ + C_{\mathbf{i}}^-)}{d\beta} = \sum_{\mathbf{j}} (H_{\mathbf{ij}}^+ + H_{\mathbf{ij}}^-)(C_{\mathbf{j}}^+ + C_{\mathbf{j}}^-)$$

Spurious

Growth in number of walkers

Modulus of Ham

Latter dominates depending on gap between H and $|H|$

Annihilation suppresses latter, but not former

Still in general less severe sign problem than 1st quant.

TABLE III. Ne atom results in Dunning (Ref. 32) basis sets, giving correlation energies in hartrees. All electrons (10) were correlated over all excitation levels. The “exact” result is the nonrelativistic infinite-nuclear mass corrected experimental value, calculated in Ref. 40. The extrapolated result for comparison is obtained using the technique by Halkier *et al.* (Ref. 39) using the cc-pCVTZ and cc-pCVQZ correlation energies.

Basis set	Orbitals	$N_{\text{FCI}} / 10^6$	$N_c / 10^6$	$f_c / 10^{-3}$	E_{corr}
VDZ	14	0.502	0	0	0.19211(4)
CVDZ	18	9.19	0	0	0.23365(3)
AVDZ	23	142	0.248	1.7	0.21510(3)
VTZ	30	2540	0.506	0.199	0.28341(9)
CVTZ	43	116 000	2.3	0.0198	0.33628(2)
AVTZ	46	235 000	338	1.43	0.2925(4)
VQZ	55	1.51×10^6	681	0.451	0.3347(10)
CVQZ	84	119×10^6	2200	0.0185	0.3691(1)
Extrapolation					0.3930
Exact					0.3905

- **No trial wavefunction. No fixed node error.** Nodal surface *emergent* property
- Many systems can be sampled with far fewer walkers than basis configurations

FCIQMC Part I Summary (circa 2010)

Projector QMC in 2nd quant, in basis of Slater determinants

DMC	FCIQMC
Infinite, continuous coordinate space	Finite, (exponentially large) basis of Slater determinants in arbitrary basis
Severe FSP	Less severe FSP
Fixed node	Walker annihilation (cancellation)
Weak basis set dependence	Strong basis set dependence
Exact if nodes exact	Exact in limit of large walker numbers
Low poly cost	'Weak' exponential cost
Generally needs pseudopotentials	Frozen core simple

Part I Exercises

Skeleton code in github repository

- `fciqmcmc_partI.py`
- `system.py`
- `Full_Ham_6H.npy`
- `Full_Ham_8H.npy`

Skeleton code to modify

Code to store info, and compute energy

Full Hamiltonian in Slater determinant Basis.

Read the notes, try to understand the code, and ask for help when stuck!

Don't look at the solutions folder until you've really had a go!

FCIQMC: A practical perspective II

George Booth

MOLSSI QMC summerschool,
Pittsburgh, USA, July 2019
King's College London

FCIQMC I Plan (c. 2010)

- Second Quantization
- Philosophy and motivation for FCIQMC
- Propagator and algorithm
- Sign problem and results

FCIQMC II Plan

- Second quantization in practice
- Hamiltonian matrix element evaluation
- Random excitation generation
- Initiator approximation
- Successes, Failures and the future...

Exponentially scaling algorithm from Part I:

- Full hamiltonian enumeration and storage
- Excitation generation

$$p_{\text{spawn}}(\mathbf{j} \rightarrow \mathbf{i}) = -\tau \frac{H_{\mathbf{ij}} \tilde{C}_{\mathbf{j}}}{p_{\text{gen}}(\mathbf{i}|\mathbf{j}) n_s}$$

Need to generate excitations and Hamiltonian matrix elements ‘on-the-fly’...

$$\hat{H} = \sum_{ij} h_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} c_i^\dagger c_j^\dagger c_l c_k + E_{NN}$$

```
&FCI NORB= 8,NELEC= 8,MS2=0,  
ORBSYM=1,1,1,1,1,1,1,1,  
ISYM=1,  
&END  
0.368526296719686    1    1    1    1  
0.3648910464500734    1    1    2    2  
0.3648910464500733    1    1    3    3  
0.3653021751781265    1    1    4    4  
5.547894088575589e-10   1    1    5    4  
0.3653021751781329    1    1    5    5
```

What is the expectation value of this operator between any two Slater determinants...?

“FCIDUMP”

Slater-Condon rules

$$\hat{H} = \sum_{ij} h_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} c_i^\dagger c_j^\dagger c_l c_k + E_{NN}$$

Only up to **two**-spin orbitals can change in the basis states. H matrix is exp. sparse...

Double-electron substitution: $p \rightarrow a$ and $q \rightarrow b$

$$H_{\mathbf{ij}} = \langle pq | ab \rangle - \langle pq | ba \rangle$$

Single-electron substitution: $p \rightarrow a$

$$H_{\mathbf{ij}} = h_{pa} + \sum_q^N \langle pq | aq \rangle - \langle pq | qa \rangle$$

Slater-Condon rules

$$\hat{H} = \sum_{ij} h_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} c_i^\dagger c_j^\dagger c_l c_k + E_{NN}$$

Only up to **two**-spin orbitals can change in the basis states. H matrix is exp. sparse...

Diagonal matrix elements:

$$|D_i\rangle = |D_j\rangle$$

$$H_{ii} = E_{NN} + \sum_p^N h_{pp} + \sum_p^N \sum_{q>p}^N \langle pq | pq \rangle - \langle pq | qp \rangle$$

Hang on a sec...

$$\hat{H} = \sum_{ij} h_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} c_i^\dagger c_j^\dagger c_l c_k + E_{NN}$$

Only up to **two**-spin orbitals can change in the basis states. H matrix is exp. sparse...

Double-electron substitution: $p \rightarrow a$ and $q \rightarrow b$

$$H_{ij} = \langle pq | ab \rangle - \langle pq | ba \rangle$$

What about... $p \rightarrow b$ and $q \rightarrow a$

Consistent ordering of basis functions and commutation!

Parity of excitation

'Excited' determinants must be *consistently* ordered.

What is the number of permutations required to order SQ string...?

$$c_a^\dagger c_k |ijkl\rangle = c_a^\dagger c_k c_i^\dagger c_j^\dagger c_k^\dagger c_l^\dagger | \rangle$$

More practical approach:

$$|ijal\rangle$$

$(-1)^P$ multiplies the result of the SC rules, and results in matrix elements invariant to order of electron excited.

How should we store a programmatic representation of the determinant?

Excitation generation

What about excitation generation?

$$p_{\text{spawn}}(\mathbf{j} \rightarrow \mathbf{i}) = -\tau \frac{H_{ij}\tilde{C}_j}{p_{\text{gen}}(\mathbf{i}|\mathbf{j})n_s}$$

Pick unoccupied (virtual)



$$c_a^\dagger c_k |ijkl\rangle$$



Pick occupied

Double excits: pick two (different) occupied, and two (different) virtuals.

Apply sequentially, and work out permutation as you go...

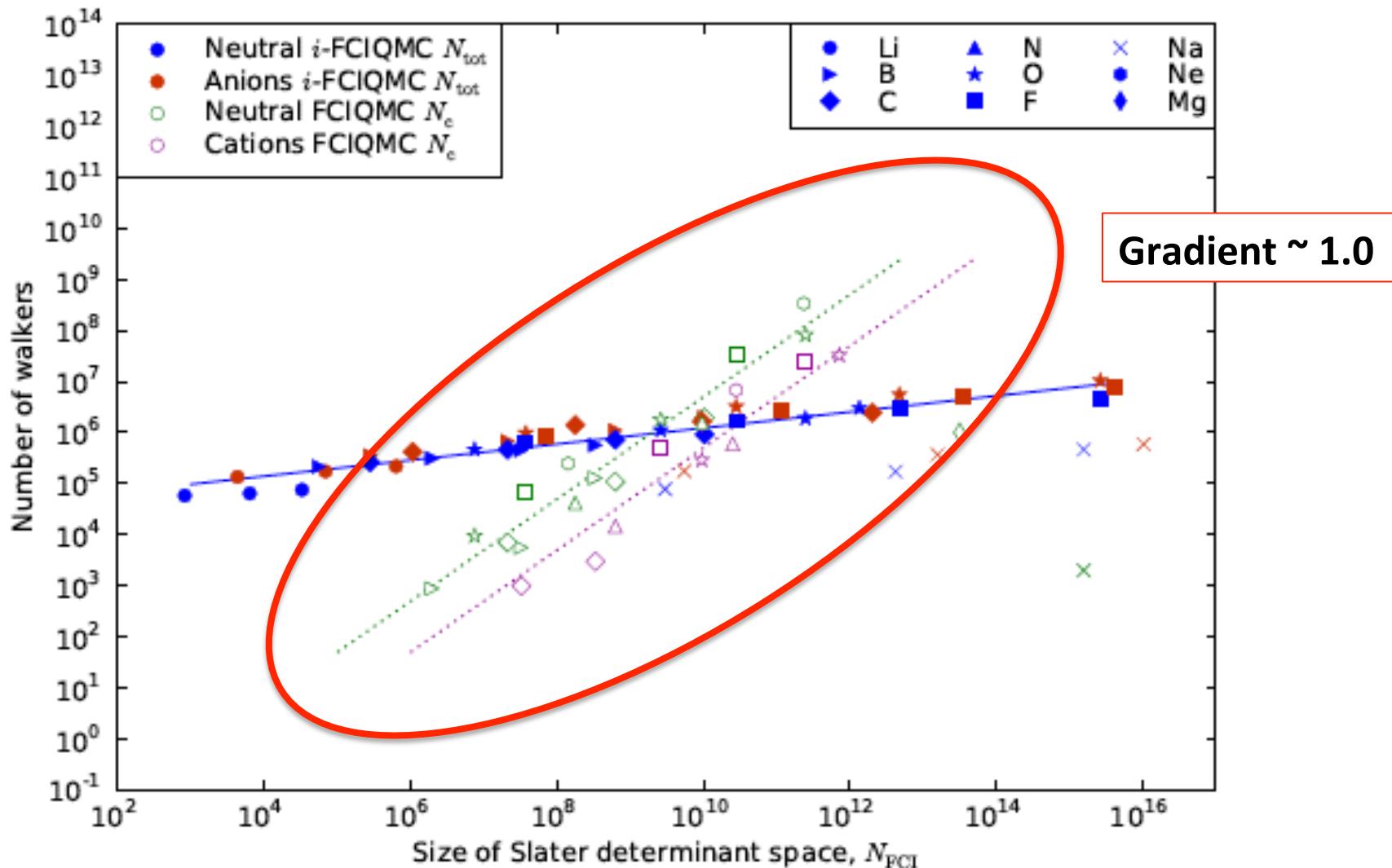
How can we test the algorithm...?

What is the optimal algorithm...?

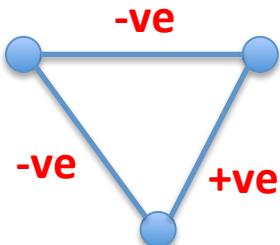
Anatomy of a calculation

1. Define basis and geometry [Gaussian, LMTO, PW...]
2. Mean-field calculation (HF or DFT) [Not essential, but almost always done]
3. Build 2nd quantized hamiltonian in orthogonal basis
[What is the best basis: Canonical, local natural, bootstrapped, symmetries...?]
4. Read in hamiltonian integrals, and ‘run’ FCIQMC
[NECI, HANDE,...]

Scaling of FCIQMC



Initiator approximation



Difficulty is in simultaneously determining ***coherent relative sign-structure*** of occupied determinants

Constrain growth of new determinants by ensuring ‘parent’ determinants have well-established sign-coherence



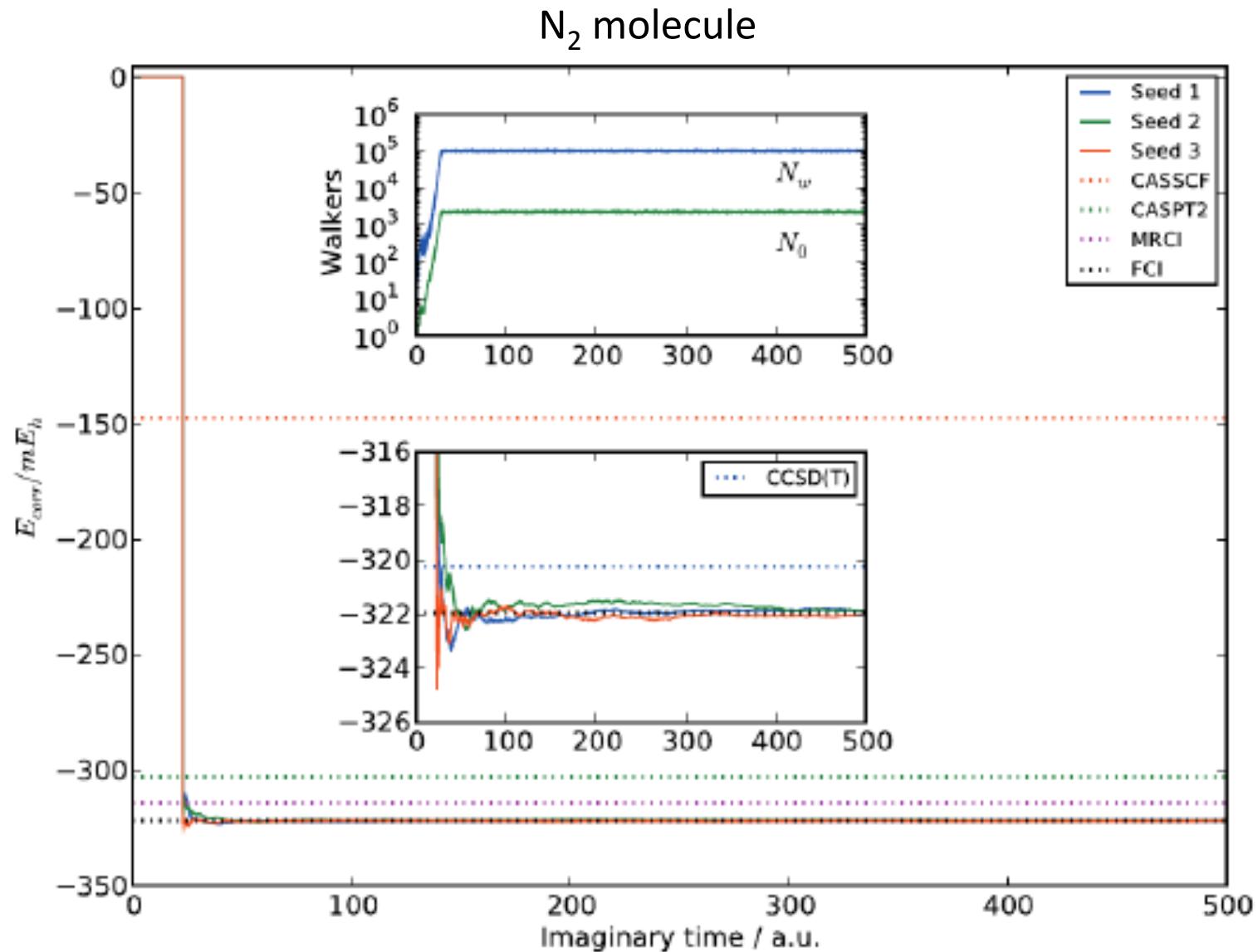
New rule: Spawning attempts to **unoccupied** determinants only allowed by *initiators*

Use amplitude on determinant as proxy for sign-coherence with neighbours

$$n_i > n_a \Rightarrow |D_i\rangle \in \{\text{initiators}\}$$
$$n_i \leq n_a \Rightarrow |D_i\rangle \in \{\text{non-initiators}\}$$

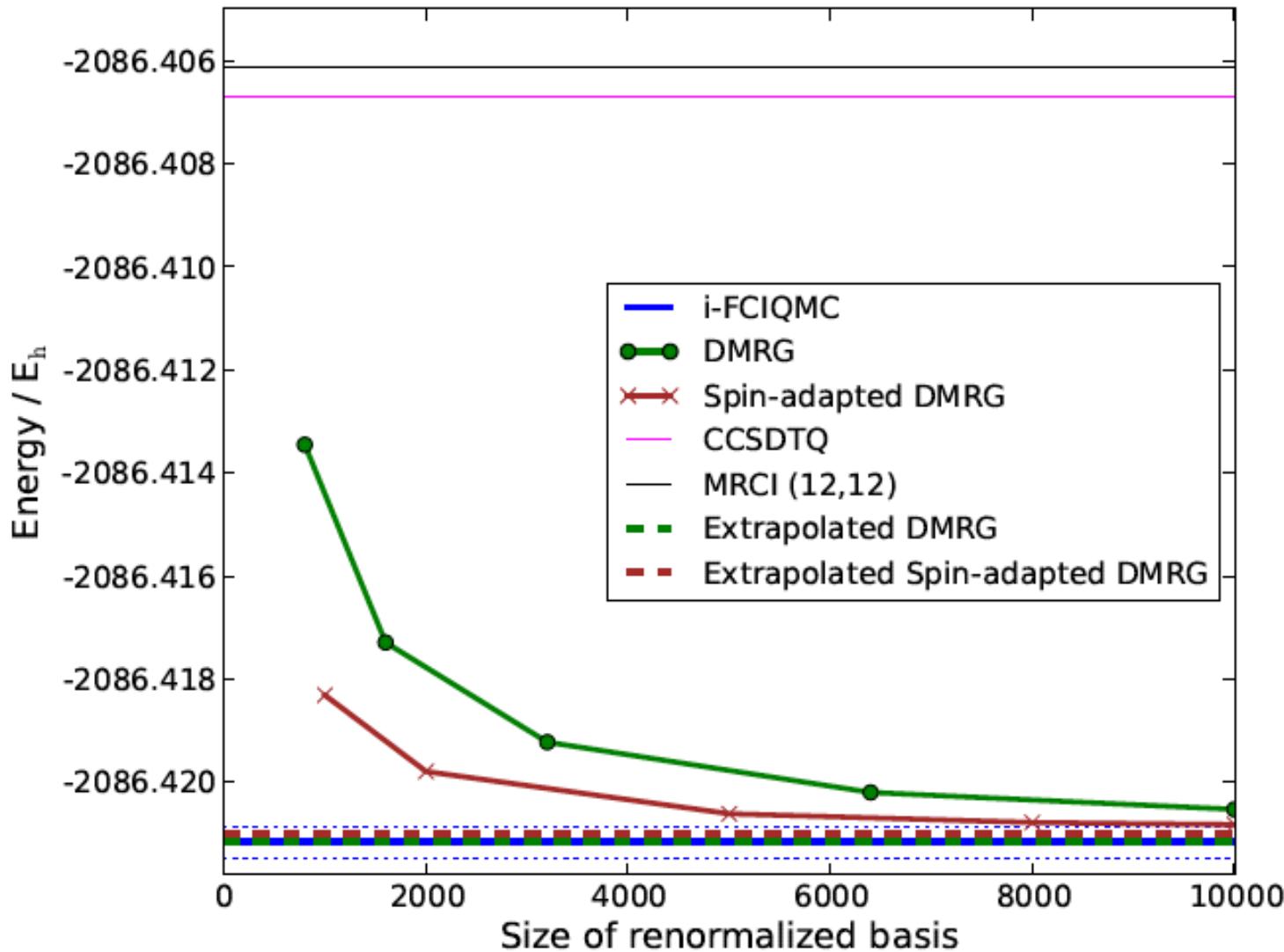
- Dynamic truncation of Hilbert space
- Noise propagation (esp. around loops) reduced
- Spawnings which couldn’t annihilate reduced, boosting annihilation relative to growth of walkers
- Plateau removed. Stable simulation.
- **Rapidly and systematically improvable to exactness as number of walkers increase (or $n_a \rightarrow 0$).**

Initiator approximation

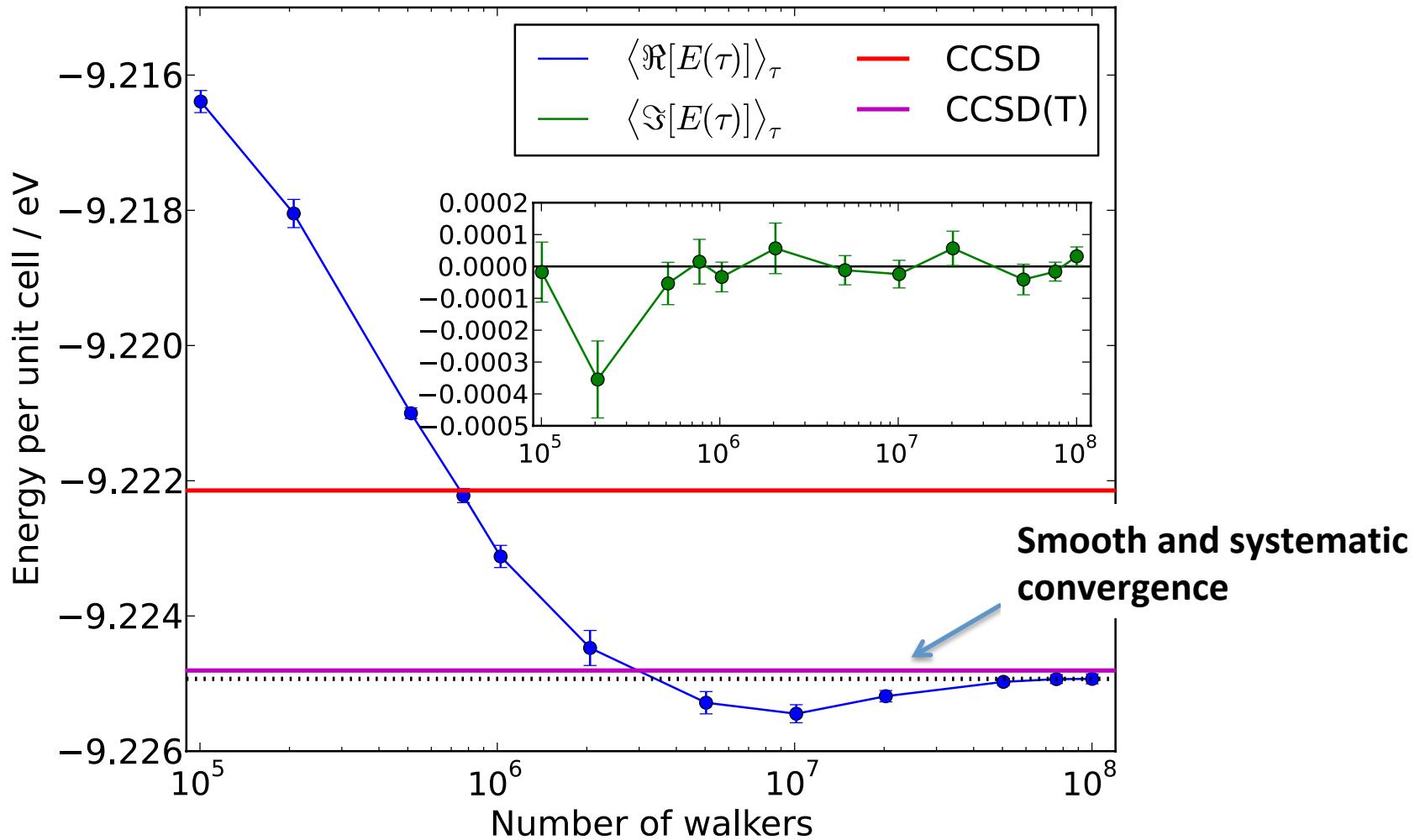


Initiator approximation

Chromium
Dimer, svp basis

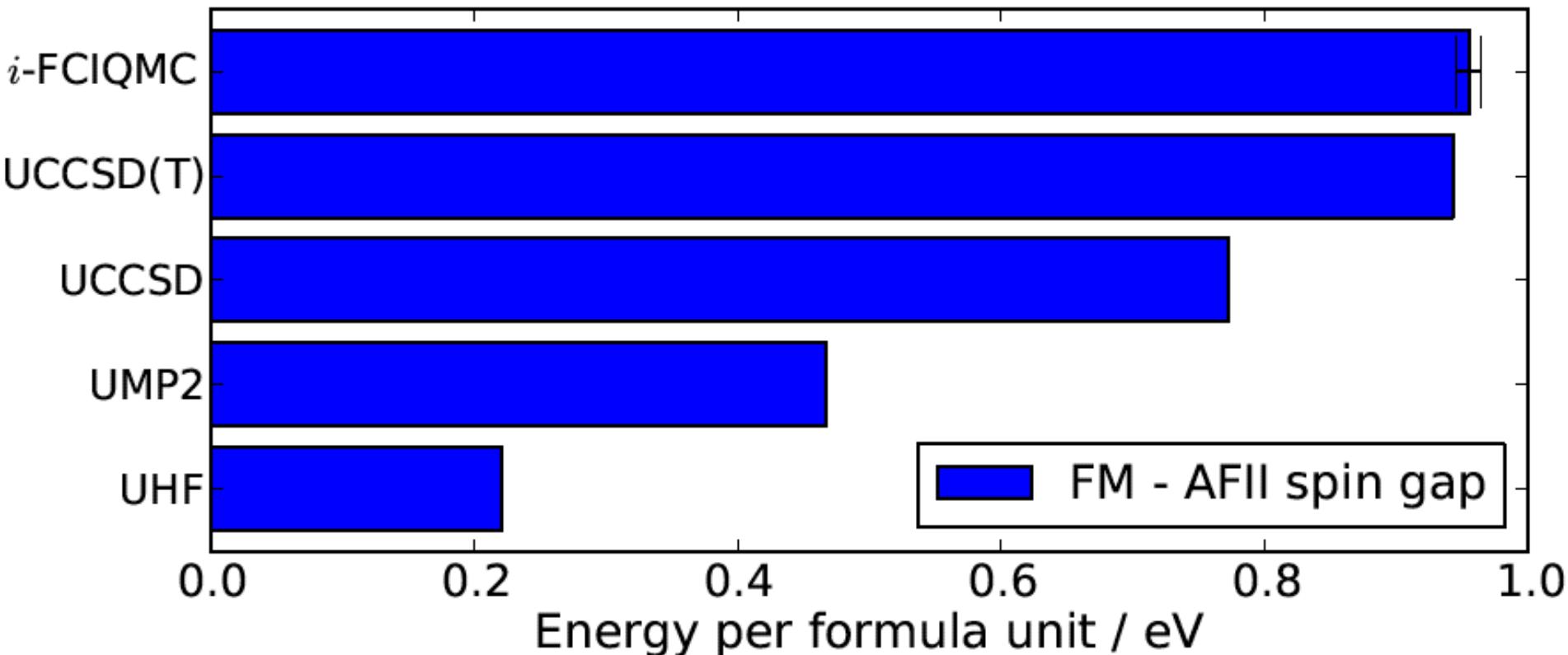


Into the solid state...?



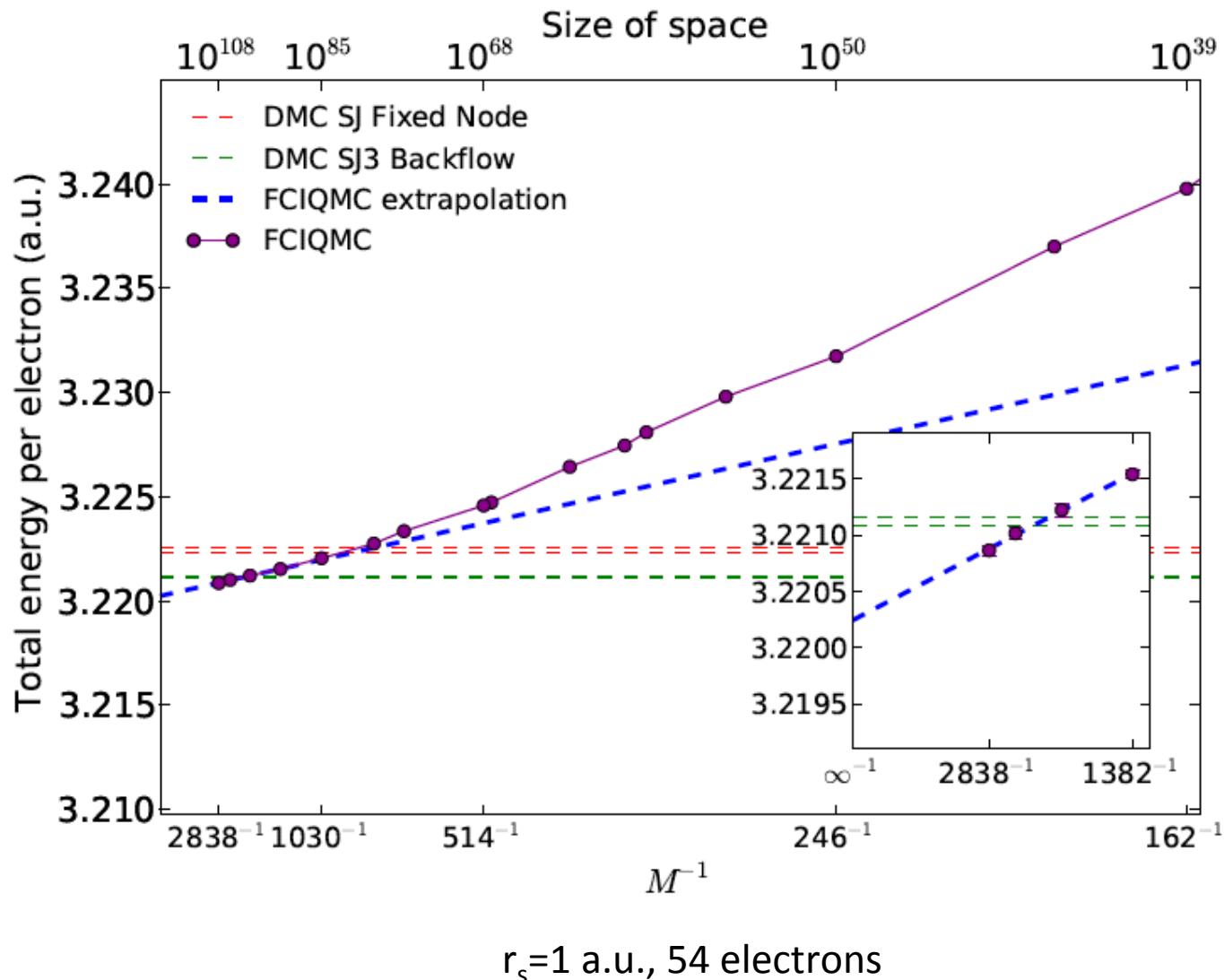
Exact solution to the Schrodinger equation
3x3x3 unit cell (10³¹ determinants)

Nickel Oxide

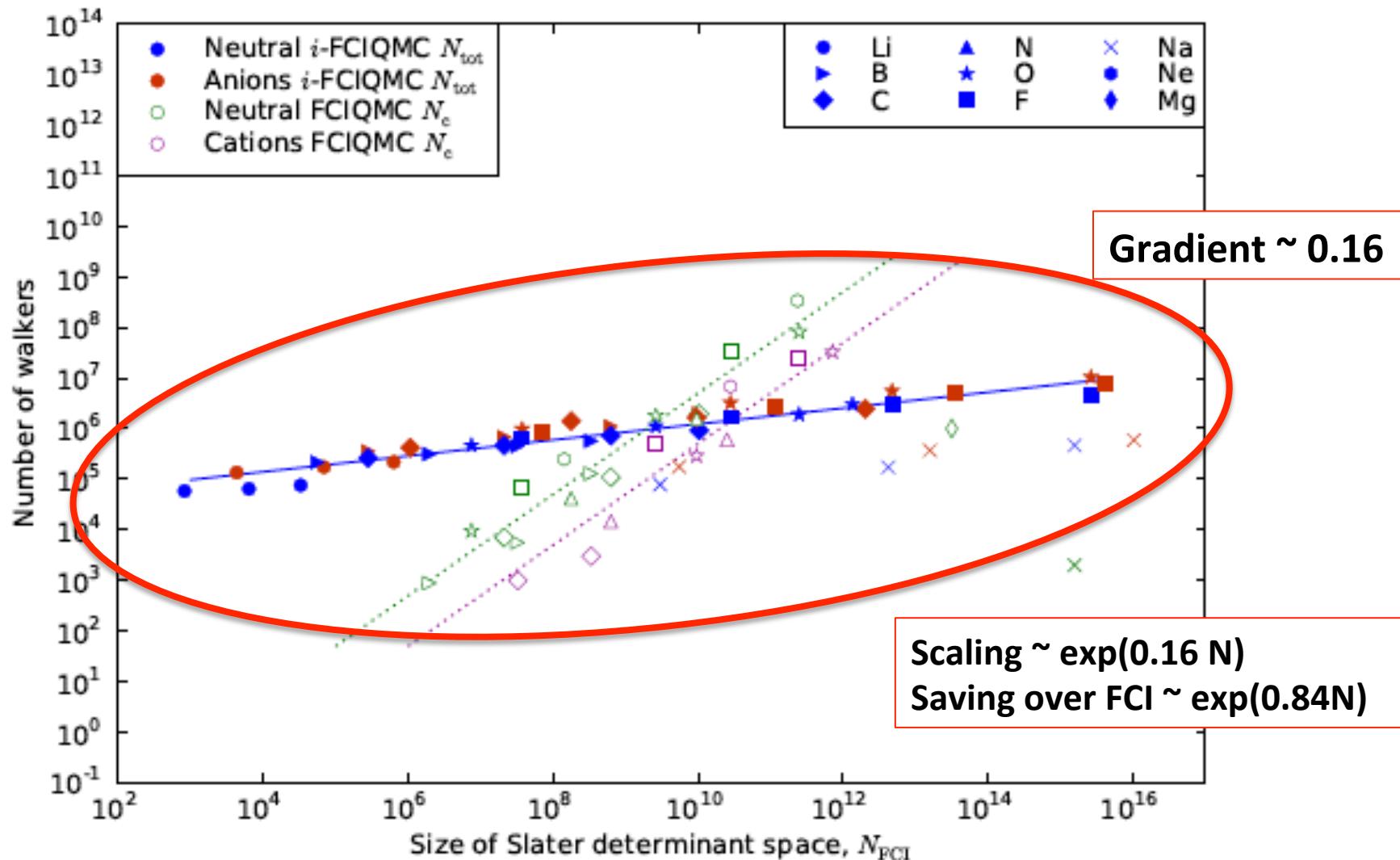


- Unrestricted reference
- Two formula units
- 32 electrons in 38 UHF bands

Uniform electron gas



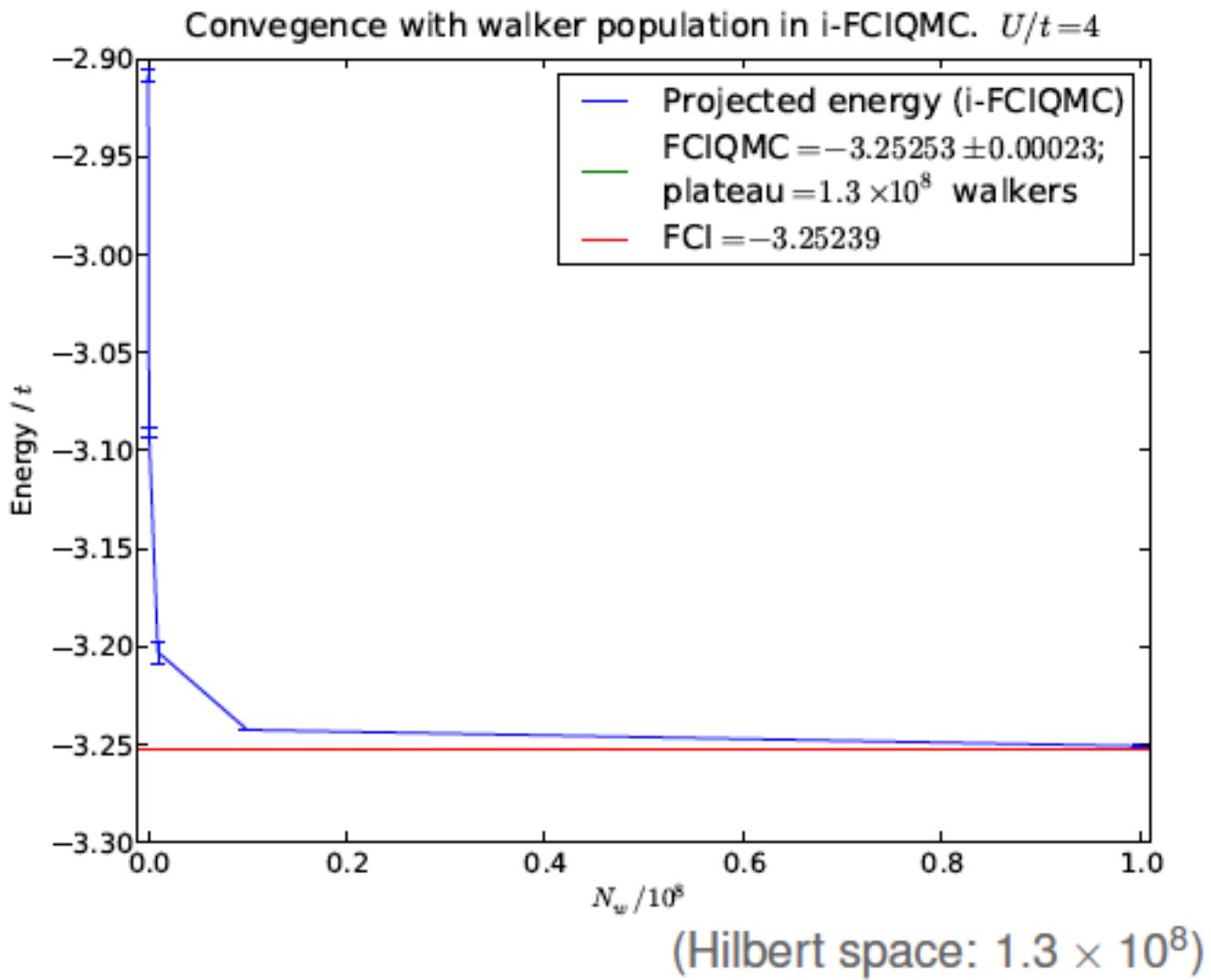
Scaling of FCIQMC



Failures...

2D hubbard
model, $U=4t$
18-sites

Efficiency is still
very dependent
on ***sparsity*** of
solution

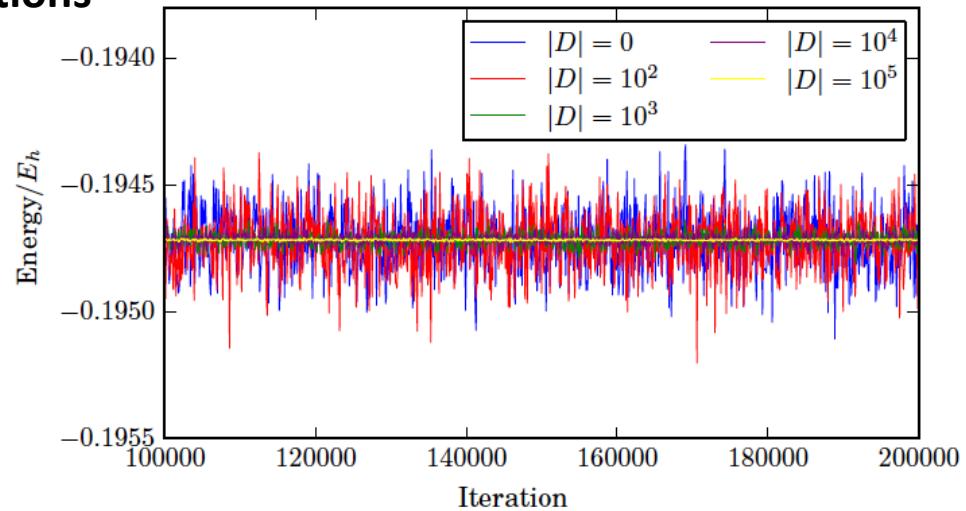


Newer technical improvements

Semi-stochastic & trial wave functions

[Umrigar et. al., PRL, 2014]

$$E_{proj} = \frac{\langle D_0 | H | \Psi \rangle}{\langle D_0 | \Psi \rangle}$$

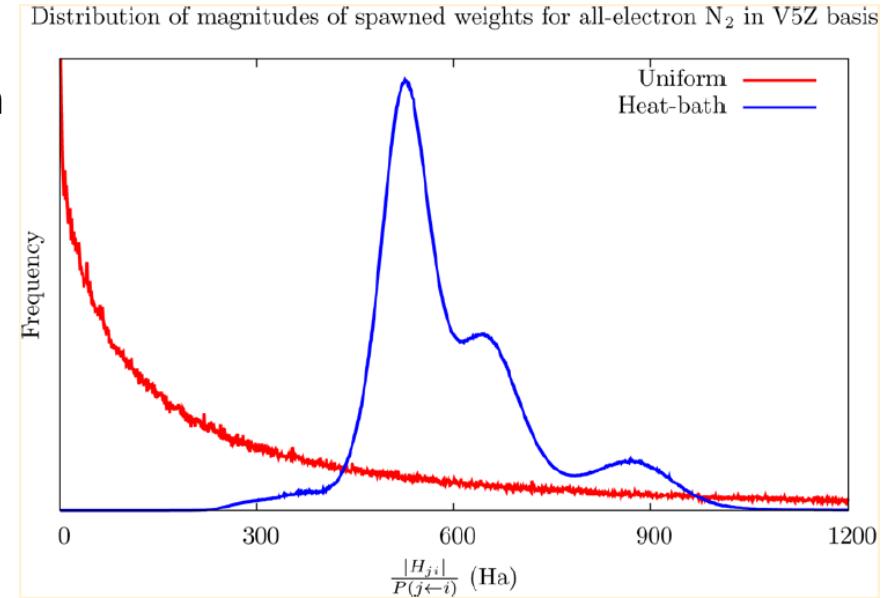


“Importance sampled” excitation generation

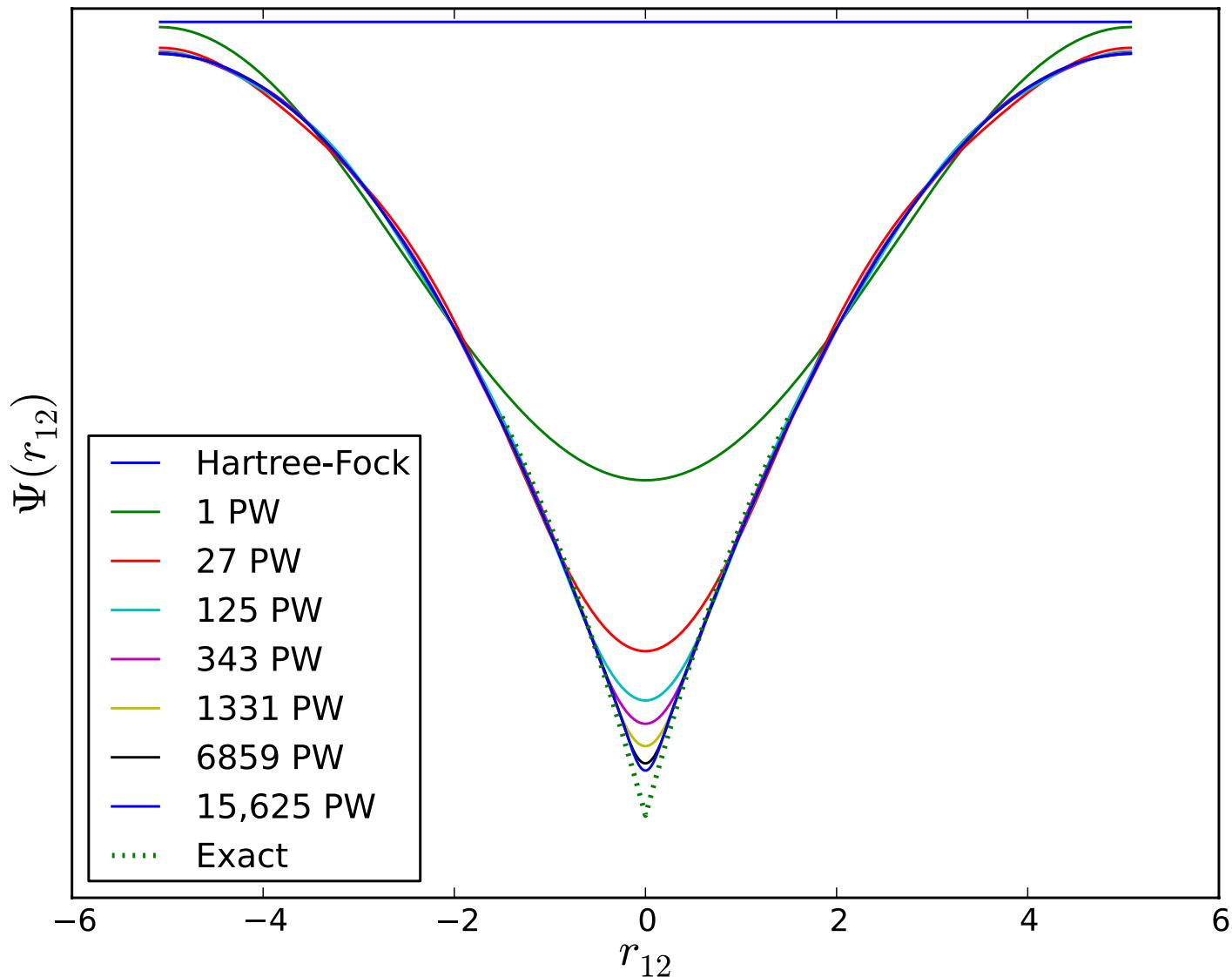
Umrigar et. al. JCTC 2016: Heat Bath

Booth, Smart, Alavi (Thom): Cauchy-Schwarz

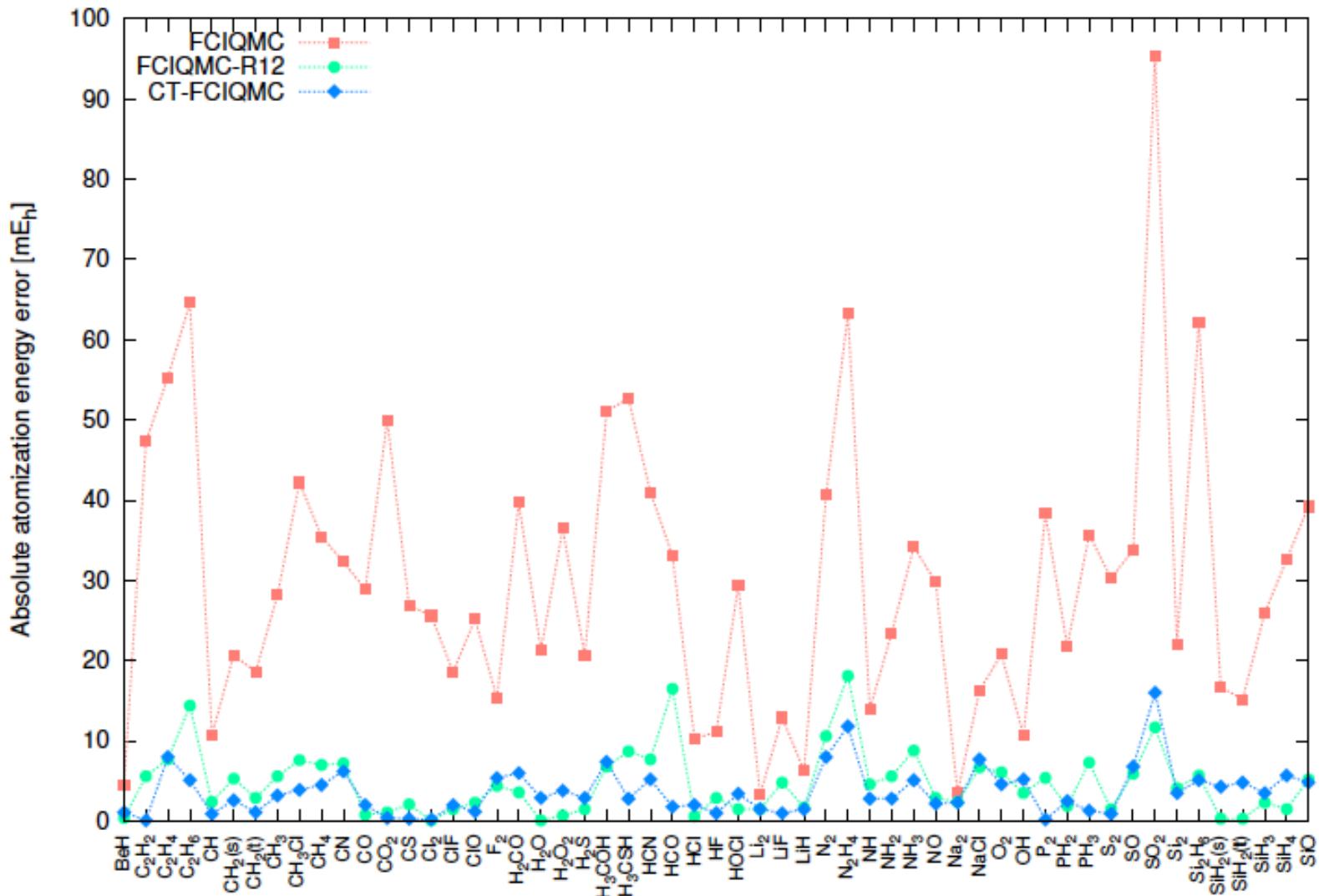
$$p_{\text{spawn}}(\mathbf{j} \rightarrow \mathbf{i}) = -\tau \frac{H_{ij} \tilde{C}_j}{p_{\text{gen}}(\mathbf{i}|\mathbf{j}) n_s}$$



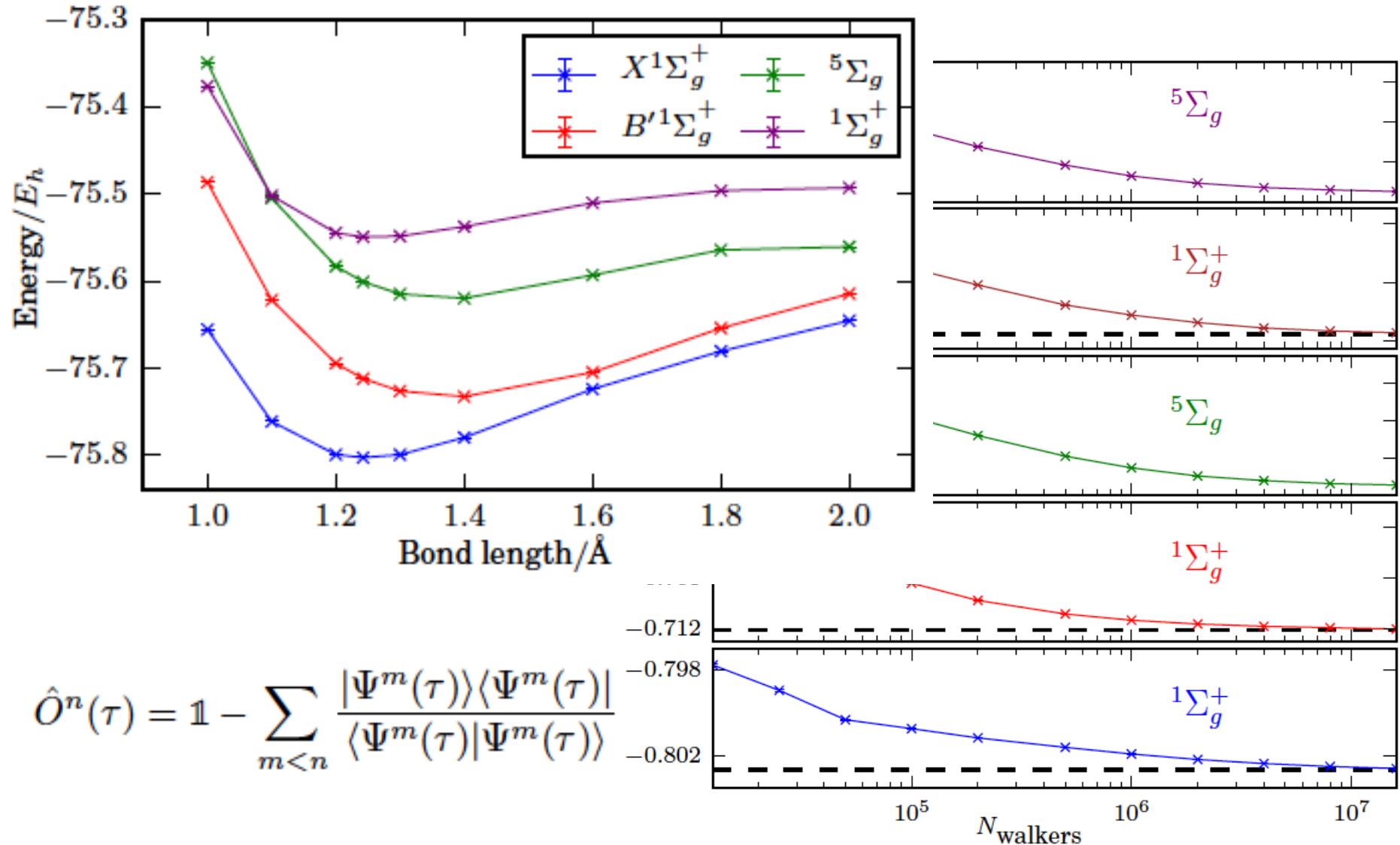
‘Explicit’ correlation



'Explicit' correlation



Excited States



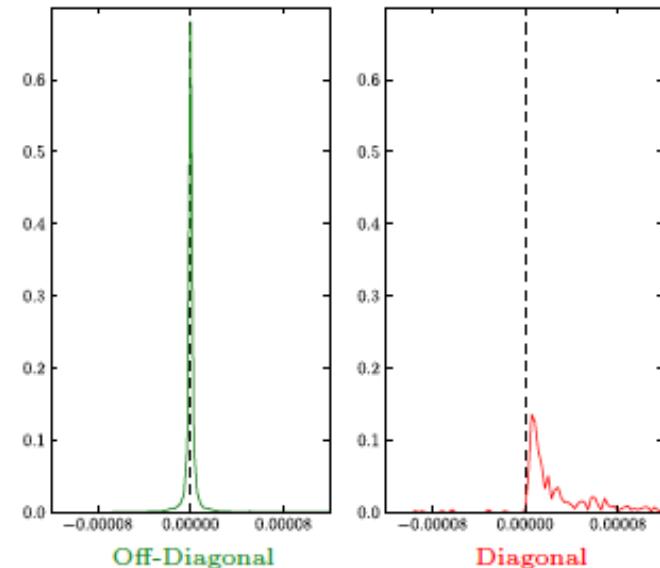
Pure expectation values

$$\langle \hat{A} \rangle = \text{Tr} (\rho \mathbf{A})$$

$$\begin{aligned}\Gamma_{pqrs} &= \left\langle \Psi \left| \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \right| \Psi \right\rangle \quad \text{Sampled stochastically with spawning} \\ &= \sum_{\mathbf{i}\mathbf{j}} C_{\mathbf{i}} C_{\mathbf{j}} \left\langle D_{\mathbf{i}} \left| \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \right| D_{\mathbf{j}} \right\rangle\end{aligned}$$

$$\begin{aligned}\langle N_{\mathbf{i}}(\tau) \rangle_\tau \langle N_{\mathbf{j}}(\tau) \rangle_\tau &= \langle N_{\mathbf{i}}(\tau) N_{\mathbf{j}}(\tau) \rangle_\tau - \sigma(N_{\mathbf{i}}(\tau), N_{\mathbf{j}}(\tau)) \\ &\approx \langle N_{\mathbf{i}}(\tau) N_{\mathbf{j}}(\tau) \rangle_\tau,\end{aligned}$$

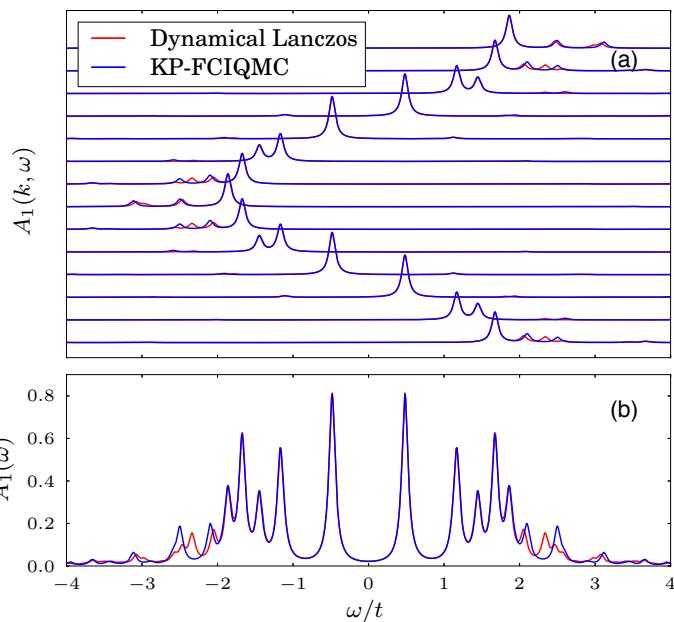
Use two independent replicas:
covariance is now removed!



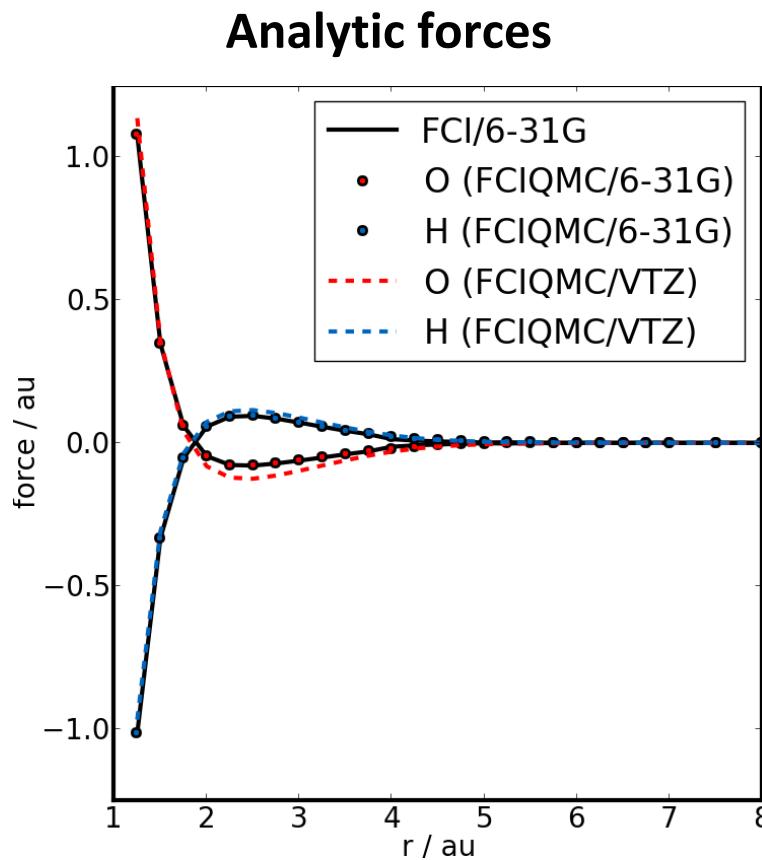
Pure expectation values

	μ_z / ea_0
HF	-0.0915
MRCI	0.0973
CCSD	0.0996
CCSDT	0.0931
CCSDTQ	0.0906
CCSDTQP	0.0905
<i>i</i> -FCIQMC	0.09045(3)

Dipole moment of CO

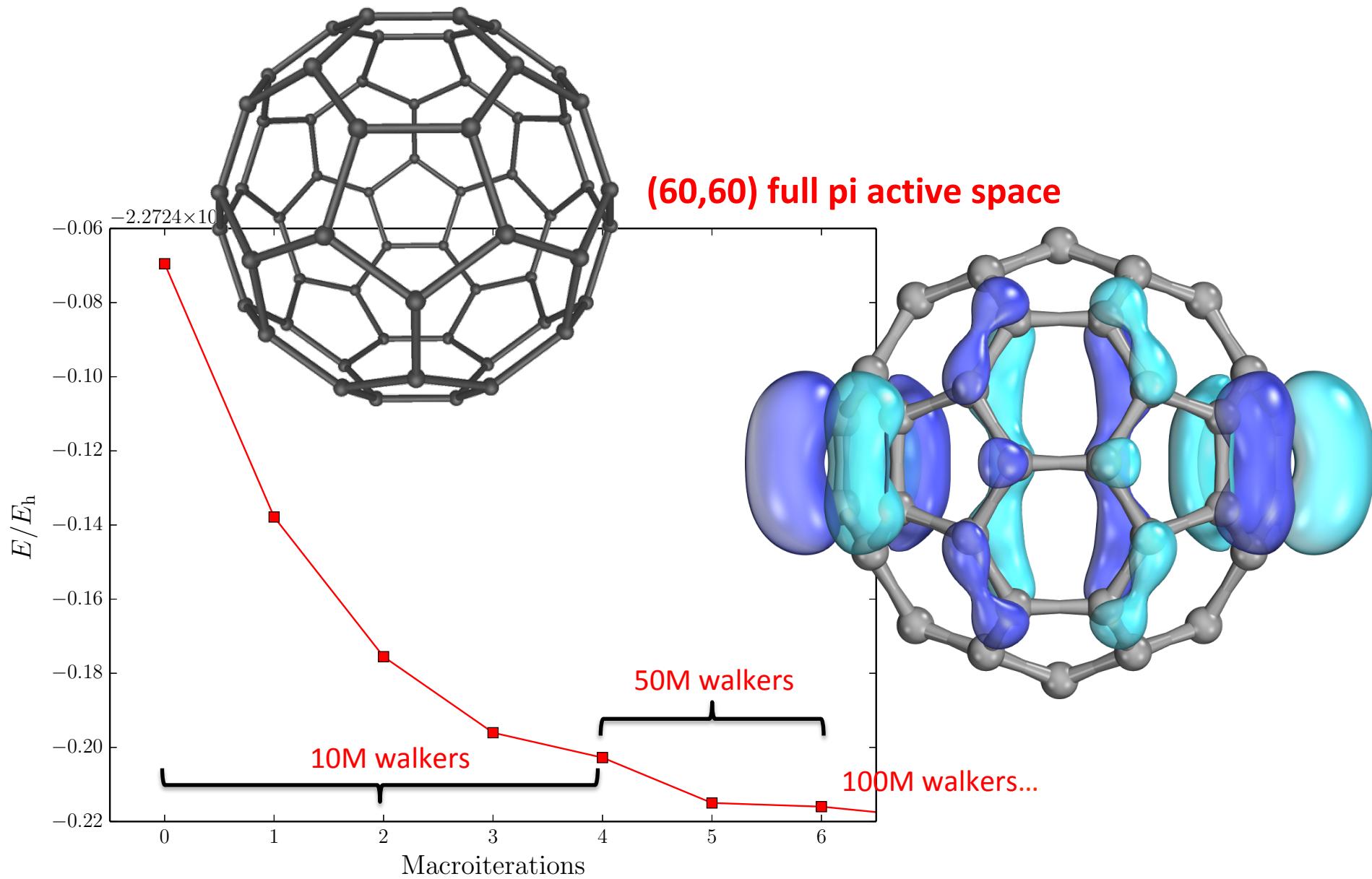


Response and spectra



Analytic forces

“Active space” embedding



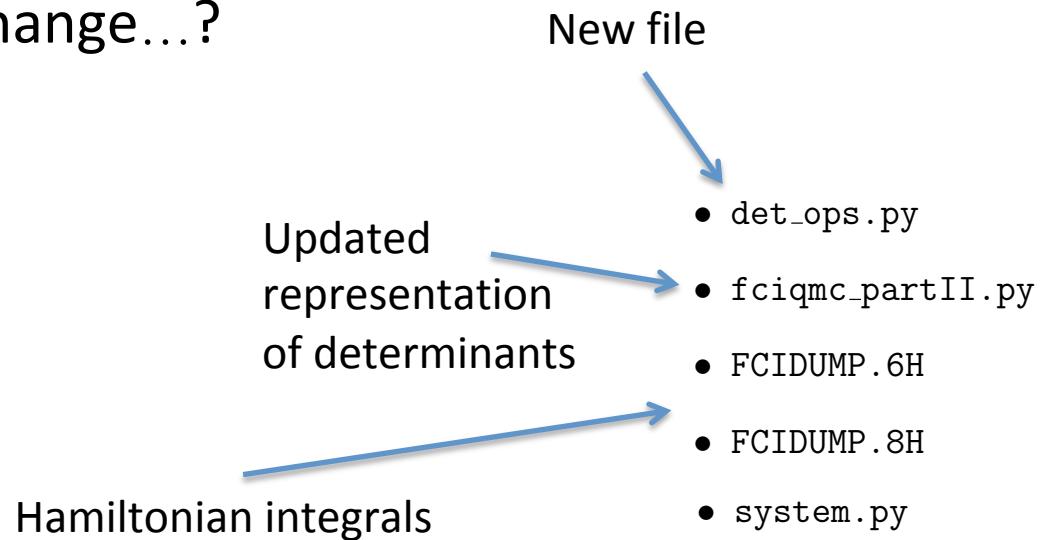
Prospects and future

- High accuracy, relatively small systems... (improve scope)
- Crossover ideas (VMC, SCI, Stochastic QC, Initiator...?)
- “Part” of the solution (Multiscale approach, CAS, impurity models)
- Other approximations and space for creative ideas...

Hands on session II

- Change your FCIQMC code to implement on-the-fly sampling of Hamiltonian
- Random excitation generation
- Initiator approximation
- How do your results change...?

$$\langle pq | rs \rangle = \text{self.h2}[p, r, q, s]$$



Scaling of FCIQMC

