High Accuracy Electronic Structure

Bryan Clark
Princeton Center for Theoretical Science (PCTS)

ES12: Wake Forest University

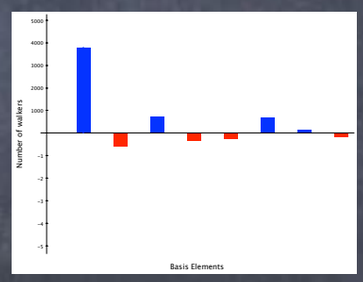
Higher Accuracy!

We have fixed computational resources. Our goal is to get electronic structure to higher accuracy.

I. Faster 'exact' methods

Improved QMC plagued by sign problems

Collaborators: Kolodrubetz



II. Better approximations

Better molecules with better wave-functions

Collaborators: Morales, McMinis, Kim, Scuseria

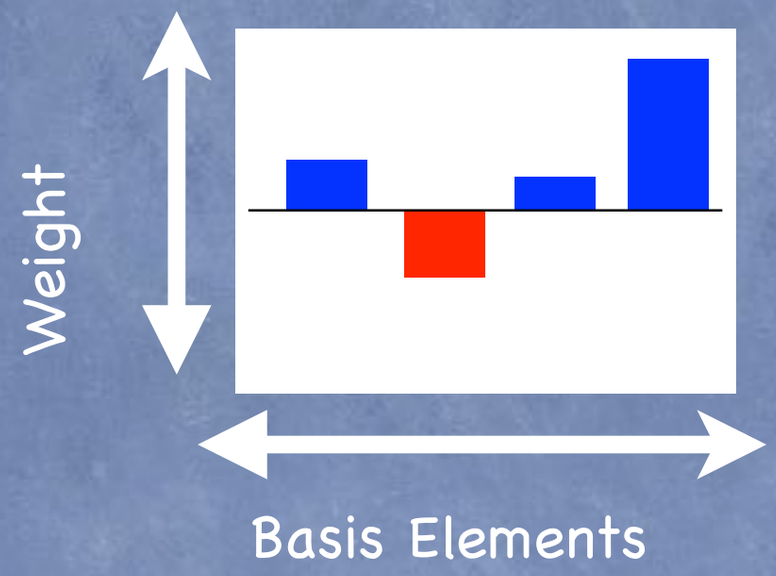
I. Faster 'exact' methods

For a given number of particles (and basis) we'd like the true answer. The fermion sign problem means this will generically be slow. We still can ask:

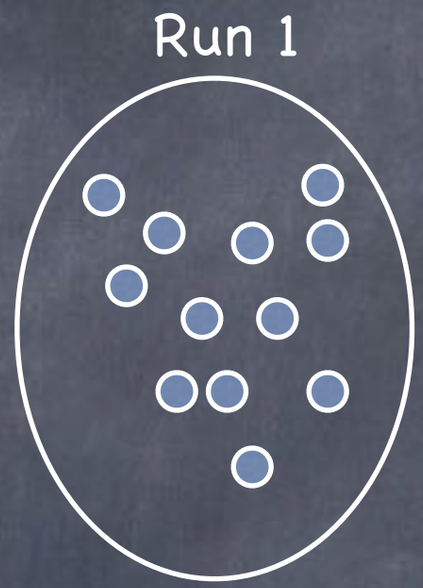
How do we most efficiently accomplish this?

* Exact diagonalization?
* Quantum Chemistry?
* QMC?
* (Improved QMC)?

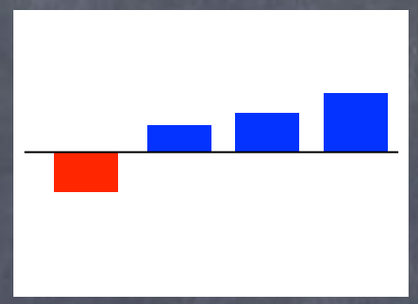
Wave-function Ψ



A snapshot of a QMC simulation gives a wave-function.

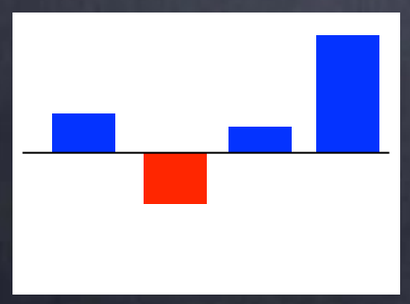


$$\Psi_{\mathrm{QMC}} = \sum_i w_i$$



The promise of QMC is if you run it many times, the sum over your wave-functions will converge to the ground state

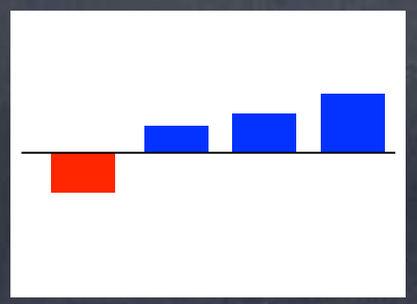
True ground state



$$(1-\tau H)^{1000}|0\rangle$$

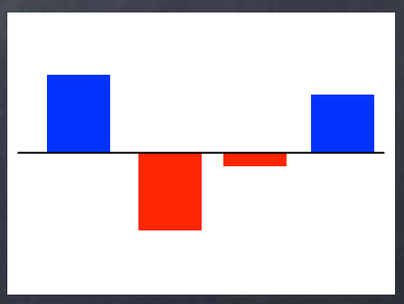
=

Run 1 (after 1000 steps)



+

Run 2 (after 1000 steps)



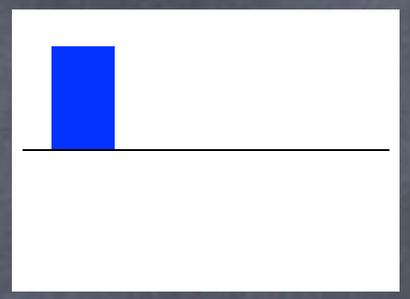
Note: This always works. A sign problem means you need exponentially many runs.

'Exact' QMC

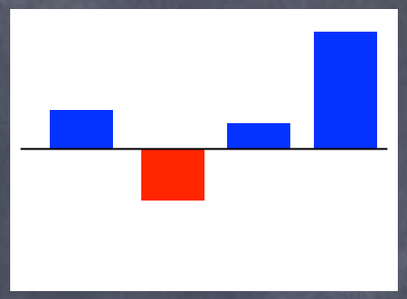
Analytically

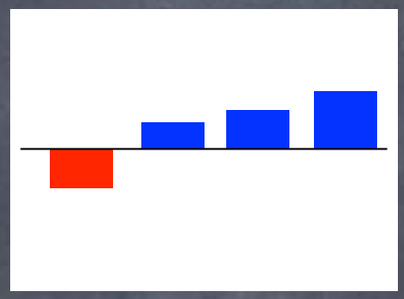
Stochastically

Ψ_T

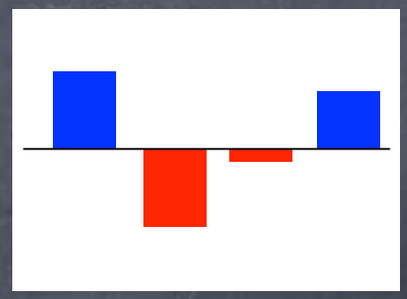


$(1-\tau H)\Psi_T$

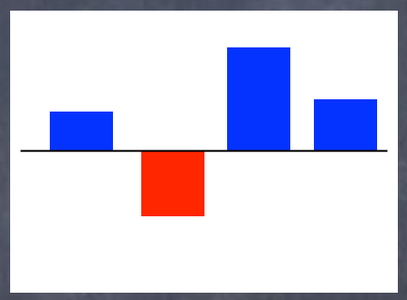




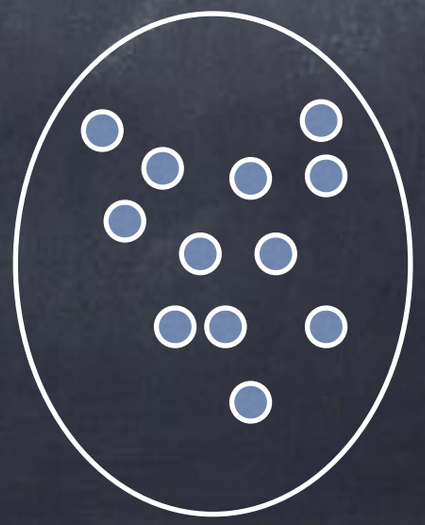
+



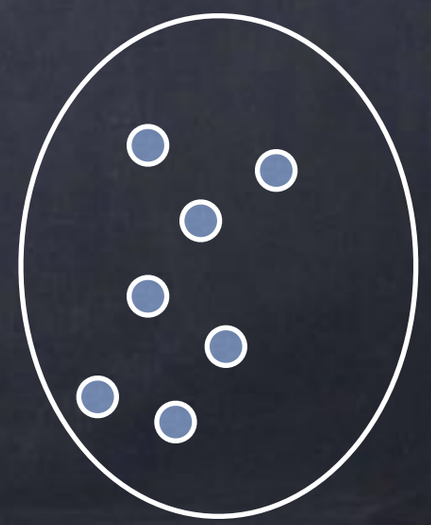
$(1-\tau H)(1-\tau H)\Psi_T$



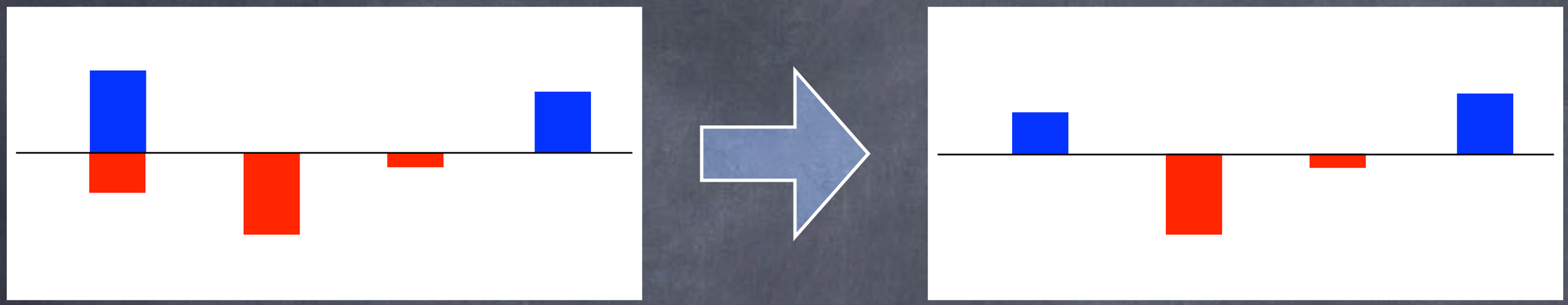
Run 1

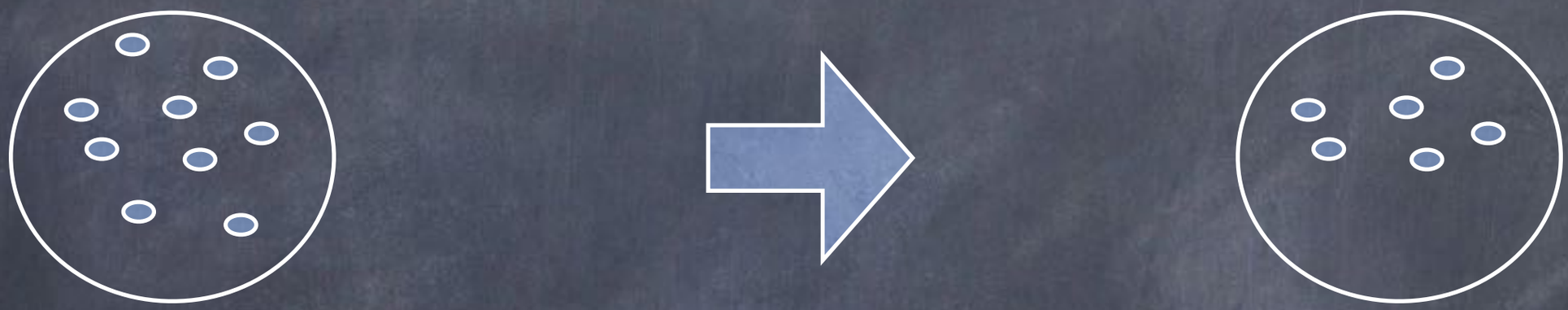


Run 2



QMC w/ Annihilation





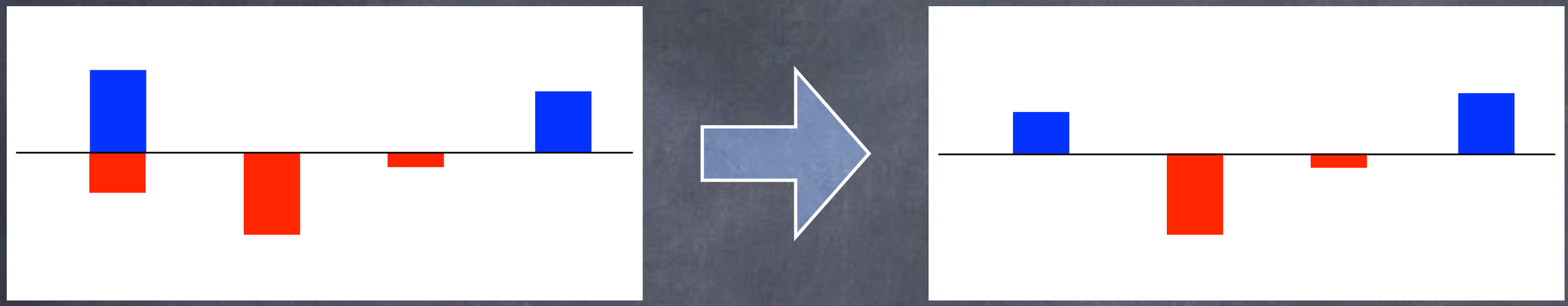
Sometimes a snapshot of the QMC wave-function during your run looks like the left. This is silly. You should remove walkers so you get the equivalent histogram at the right.

FCIQMC

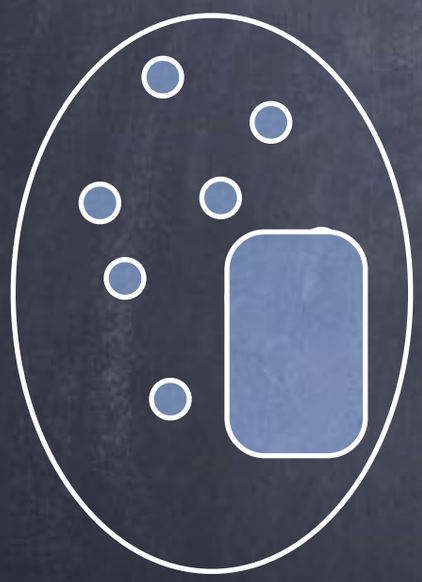
Fermion Monte Carlo

Can we do any better?

Exact QMC w/ Annihilation



Run 3



Sometimes a snapshot of the has a histogram like the left.

Sometimes a snapshot of the QMC wave-fun
your run looks like the left.

This is silly. Should remove walkers so the histogram looks like the right.

FCIQMC
Fermion Monte Carlo

Fermi-Polaron: The "hydrogen atom" of strongly correlated systems.

$$H = \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \frac{g}{V} \sum_{kpq} c^\dagger_{k+q,\uparrow} c^\dagger_{p-q,\downarrow} c_{p,\downarrow} c_{k,\uparrow}$$

$$g^{-1} = \frac{1}{8\pi a} - \frac{\Lambda}{4\pi^2}$$

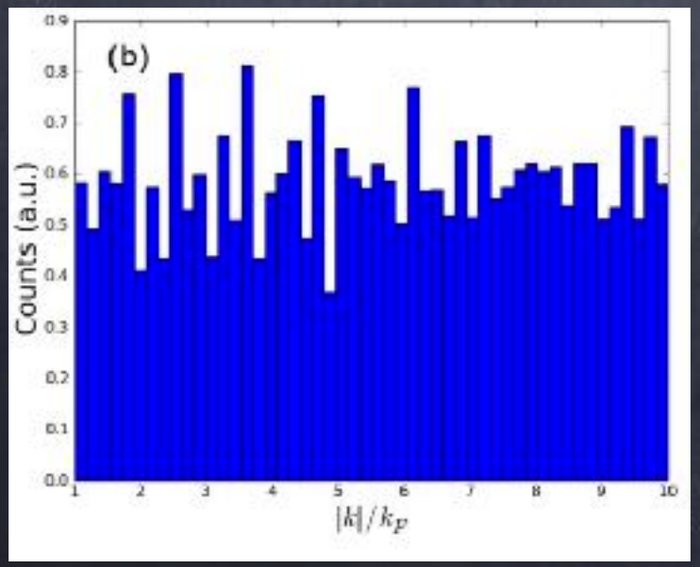
Want:

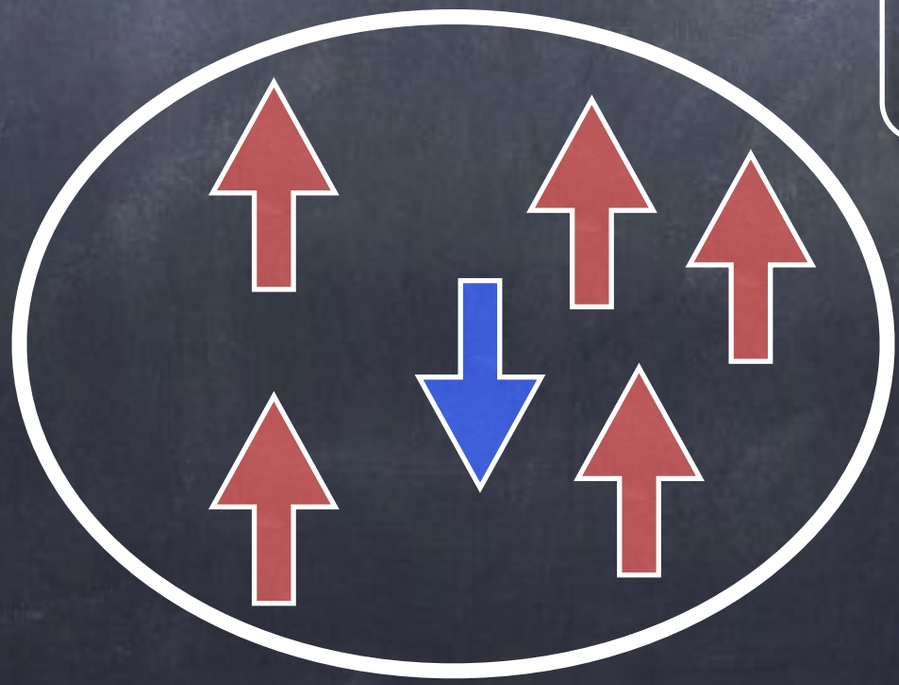
$$\Lambda \to \infty$$

$$N \to \infty$$

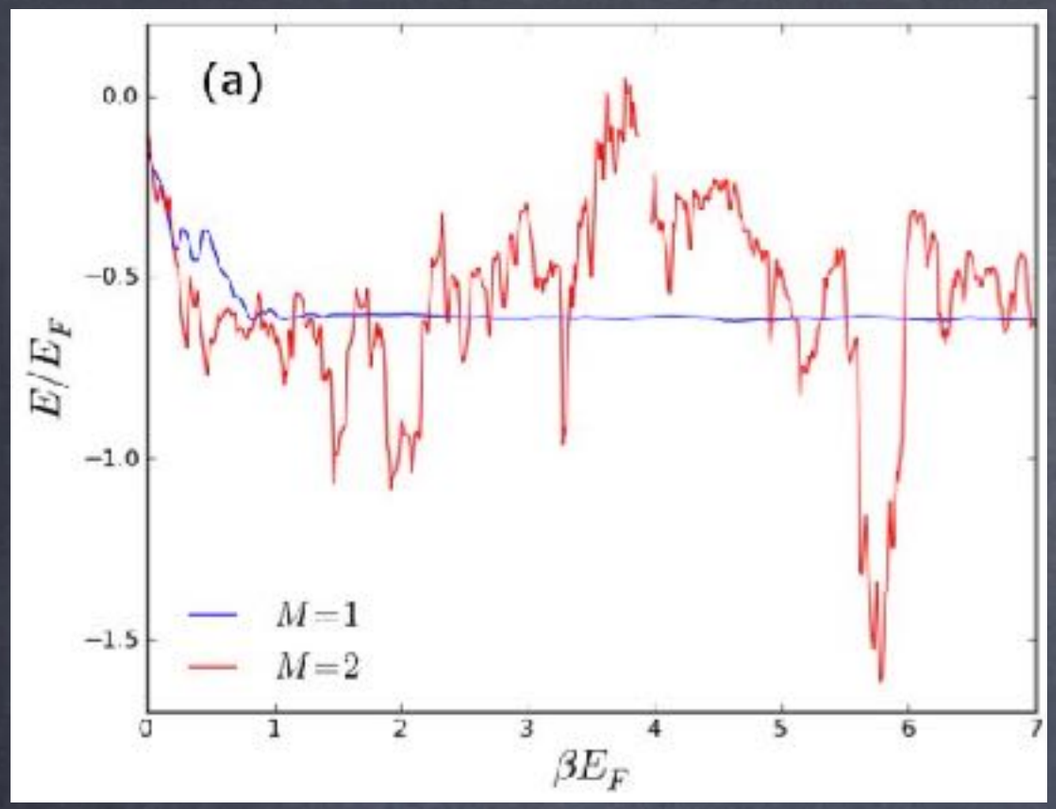
$$M \to \infty$$

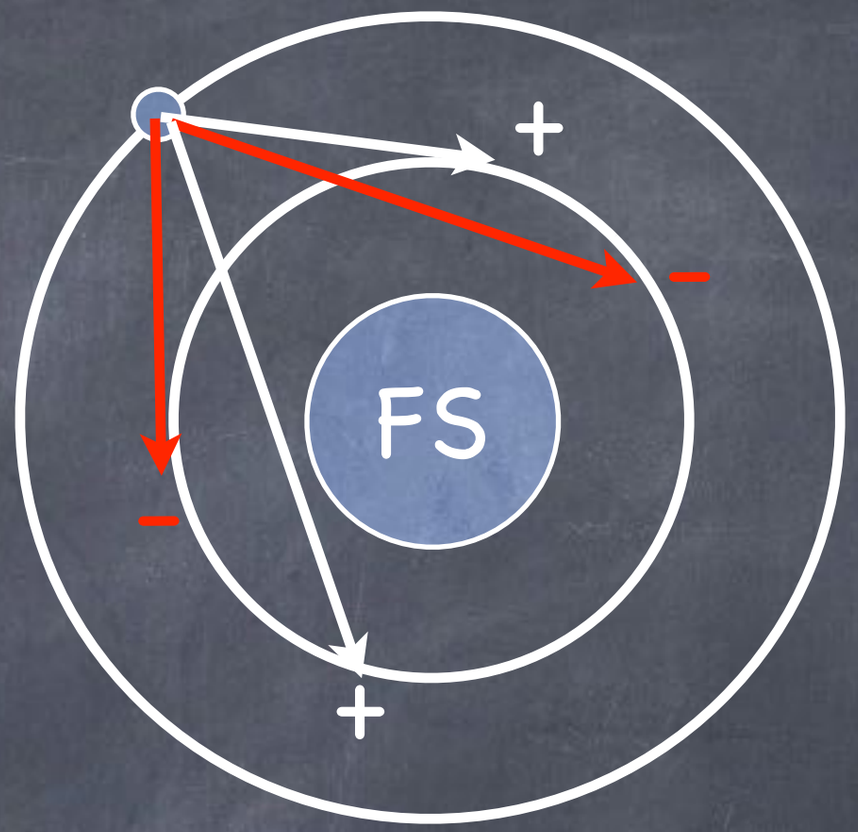
Particle-hole pairs: $|D_0\rangle \equiv |\mathrm{FS}_\uparrow, 0_\downarrow\rangle$





FCI-QMC:





Works: N=33, M=1, $\Lambda = 10, a^{-1} = 0$

Fails: N=33, M=2, $\Lambda = 10, a^{-1} = 0$

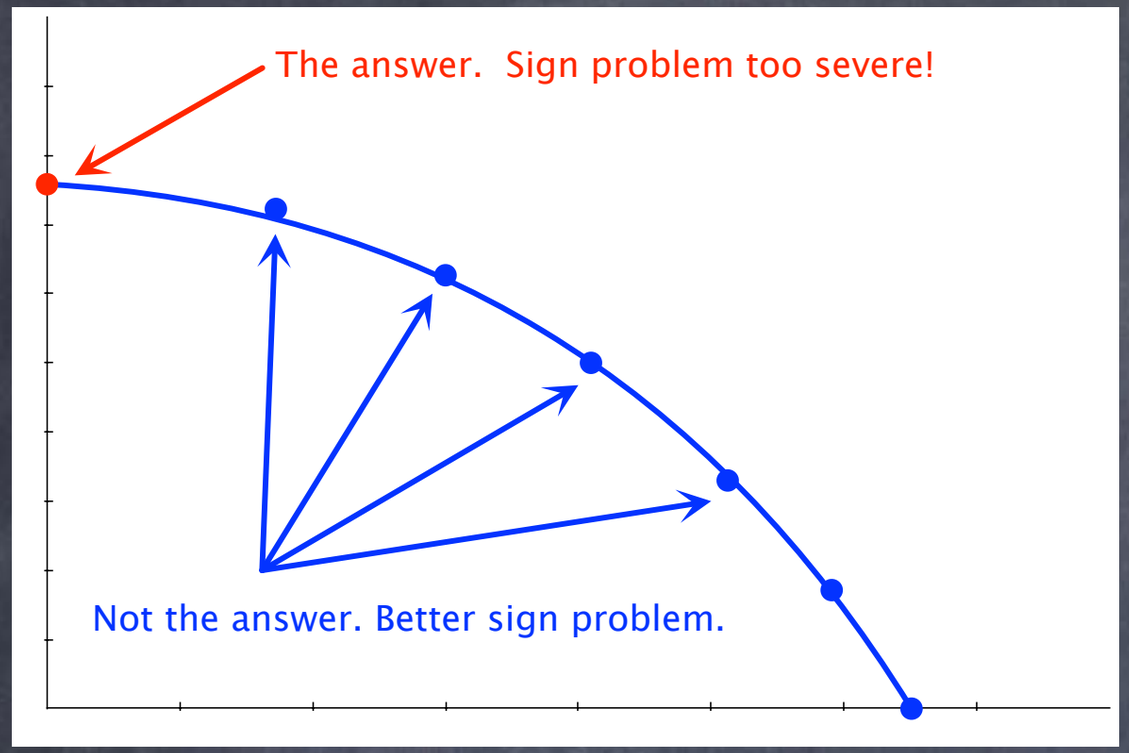
Fails: N=33, M=1, $\Lambda = 10, a^{-1} > 0$

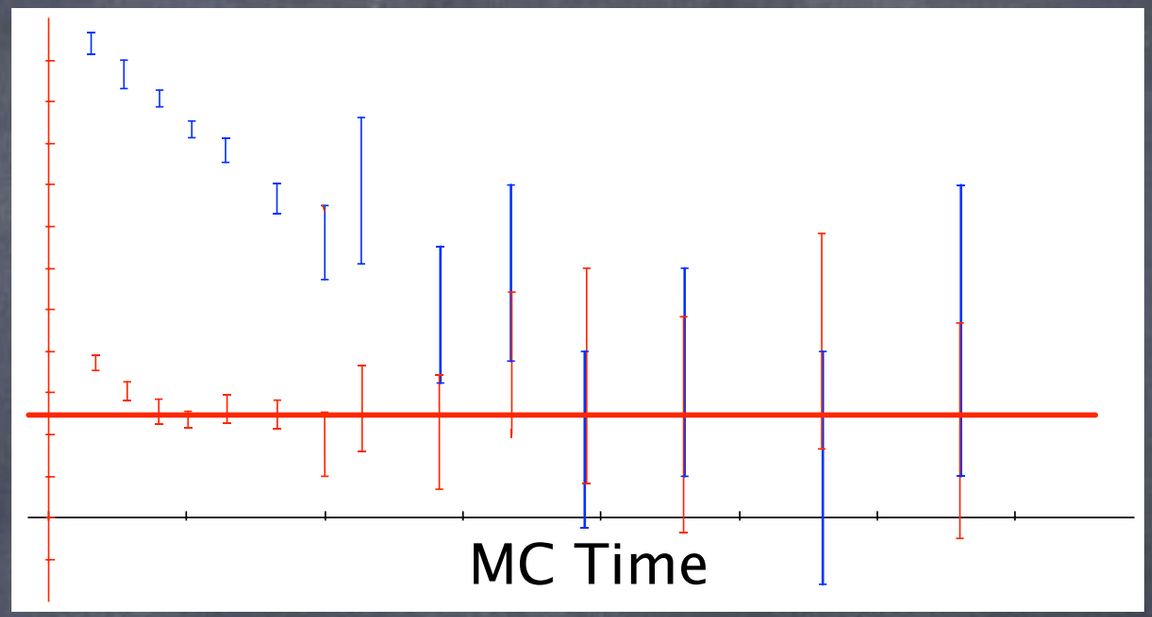
Sign problem too hard!

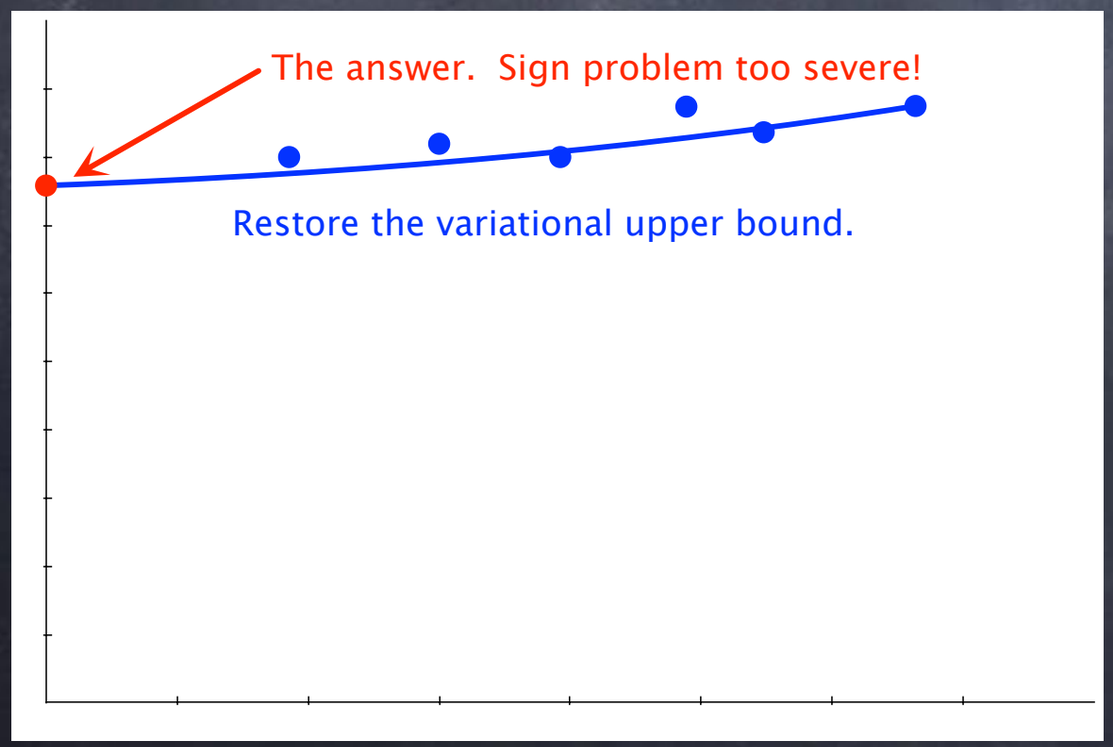
Why hard:

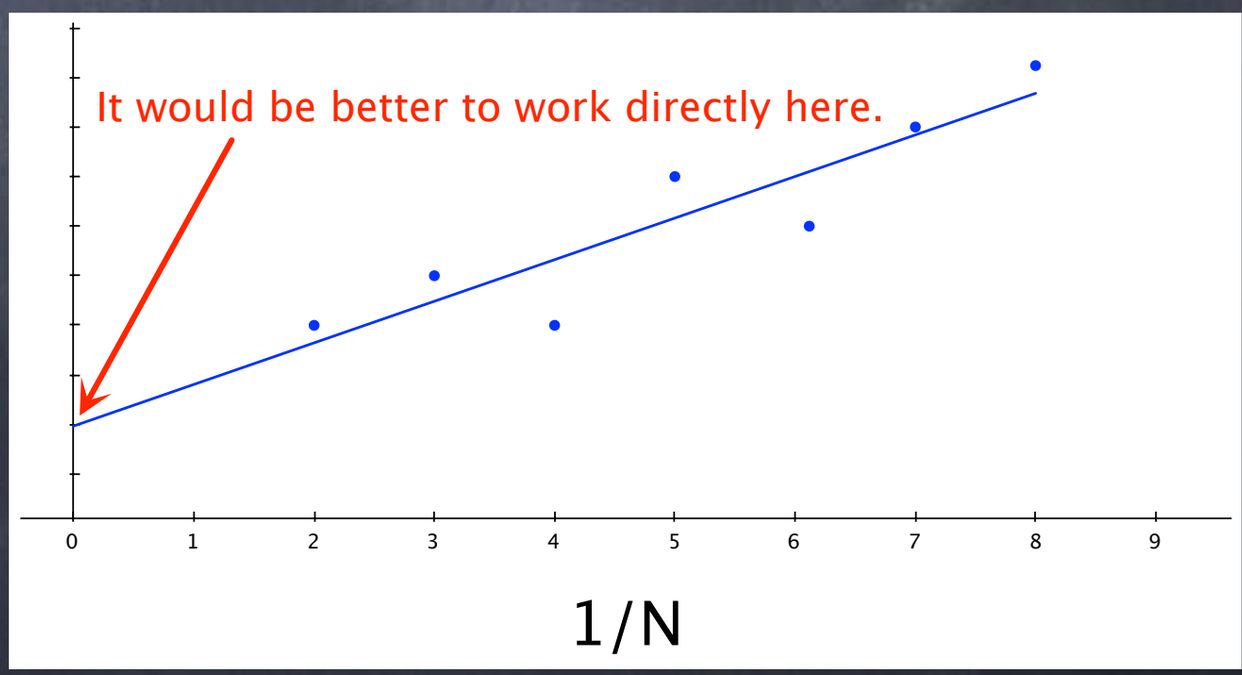
- All determinants important
- Random Signs

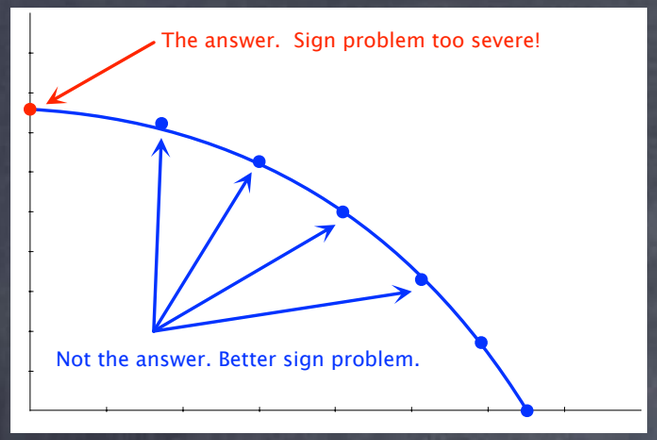
Partial Node FCIQMC

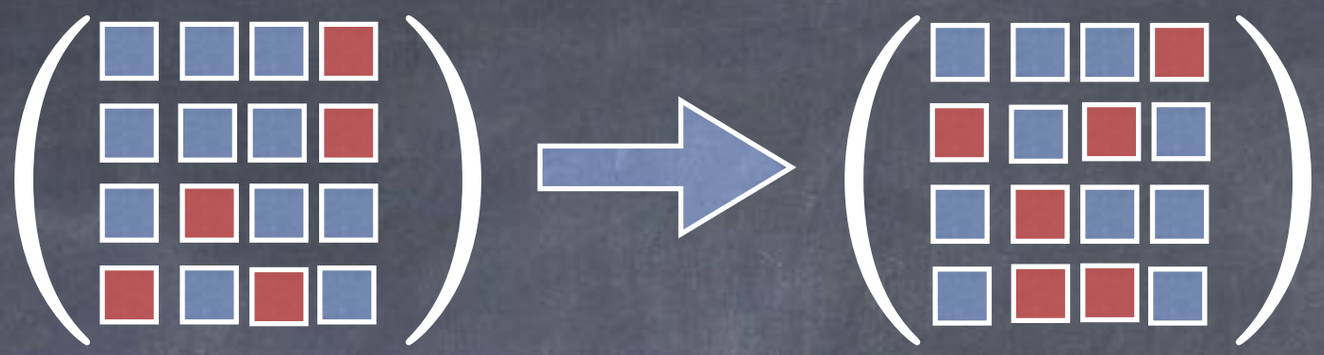












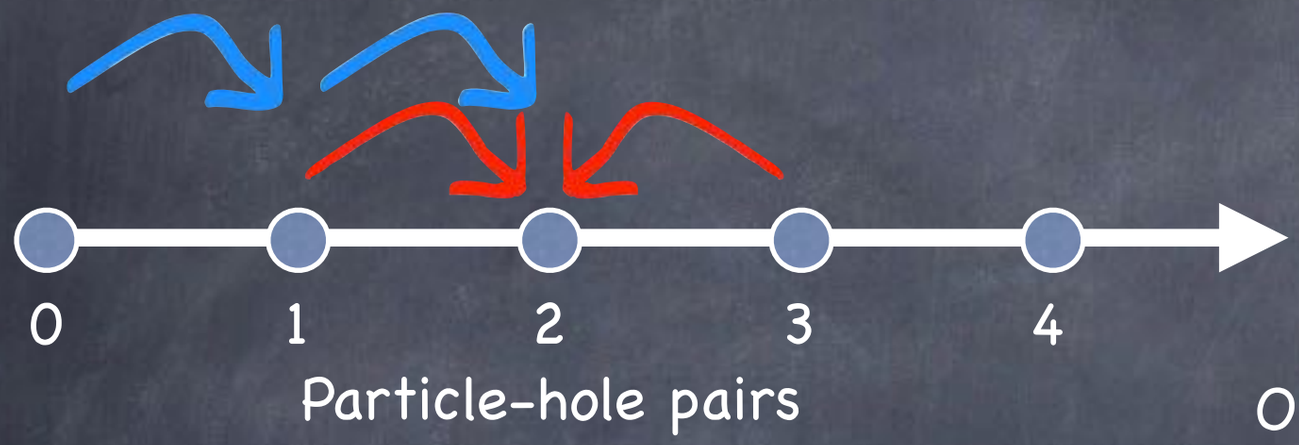
$$\langle R|(1-\tau H)|R'\rangle \longrightarrow \langle R|(1-\tau H)|R'\rangle \frac{\Psi_T(R)}{\Psi_T(R')}$$

Extrapolate to the right answer.

Equivalent to removing QMC walkers which step on the wrong signed determinant

Does this actually work?

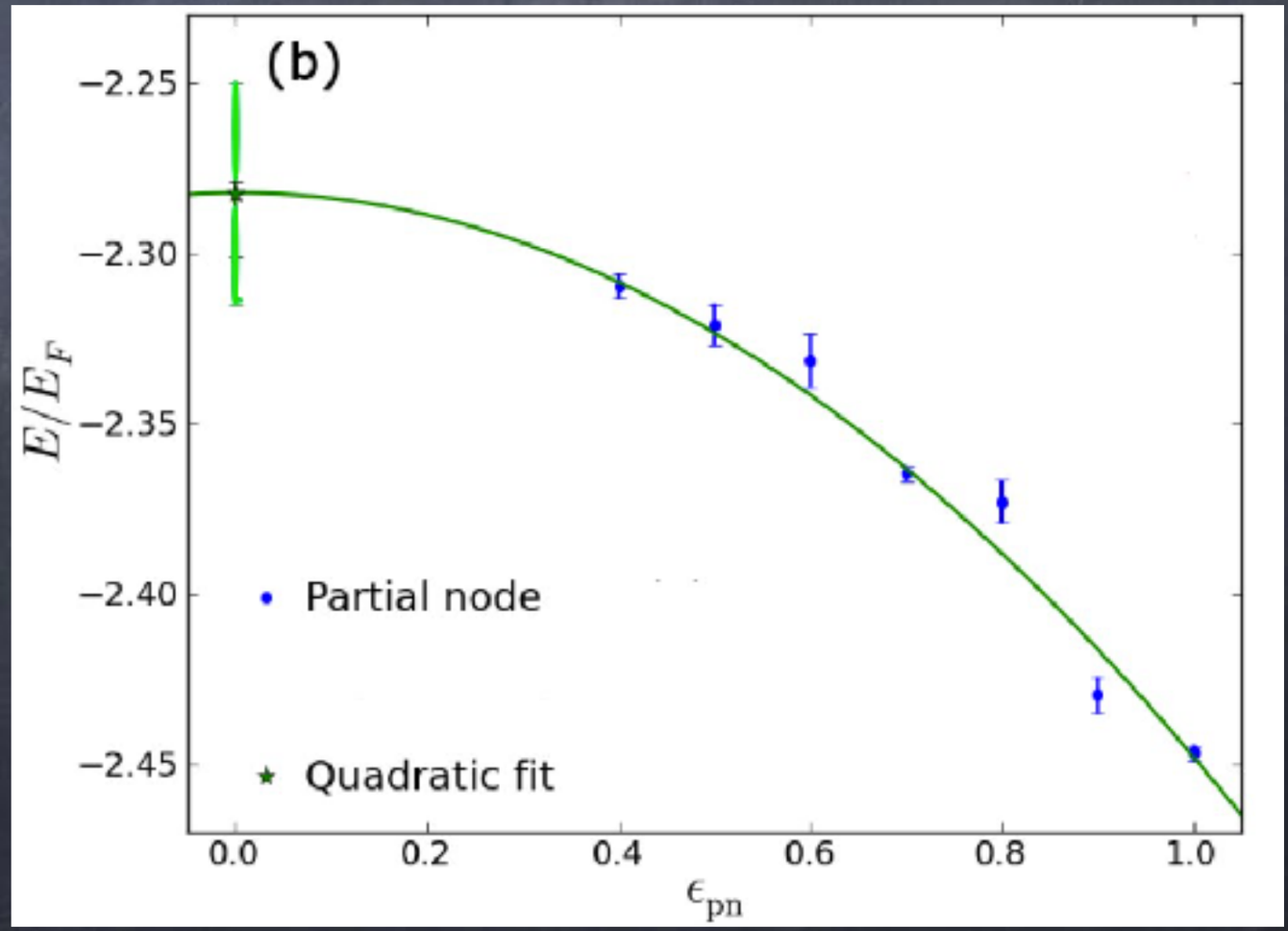
Schrodinger Eqn: $$\langle D|\Psi_0\rangle = -\frac{1}{\langle D|\hat{T}|D\rangle - E_0}\sum_{D'}\langle D|V|D'\rangle\langle D'|\Psi_0\rangle$$



2 PH pair depends on 1 and 3 PH pair

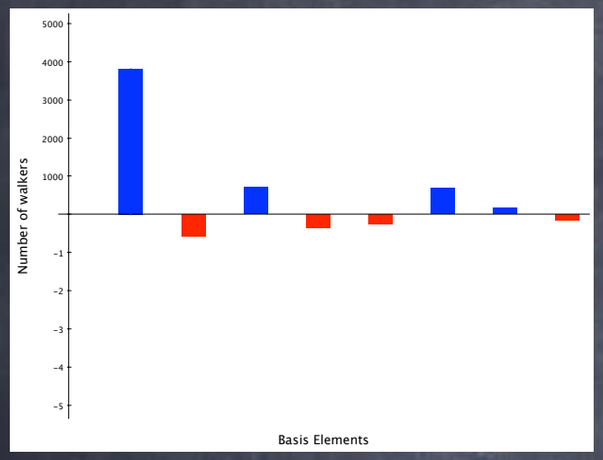
Only use smaller PH pairs for your trial w.f

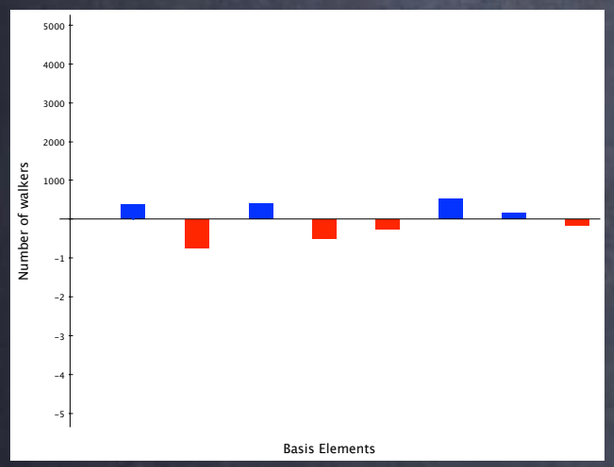
Extrapolating to the true answer works!

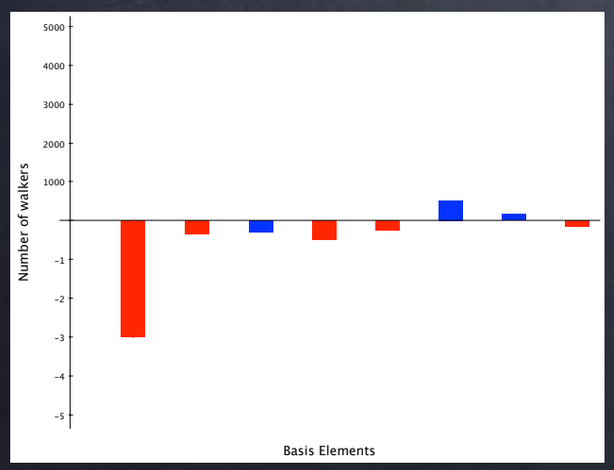


Partial Node: Is it useful?

Sign problem exponential in beta



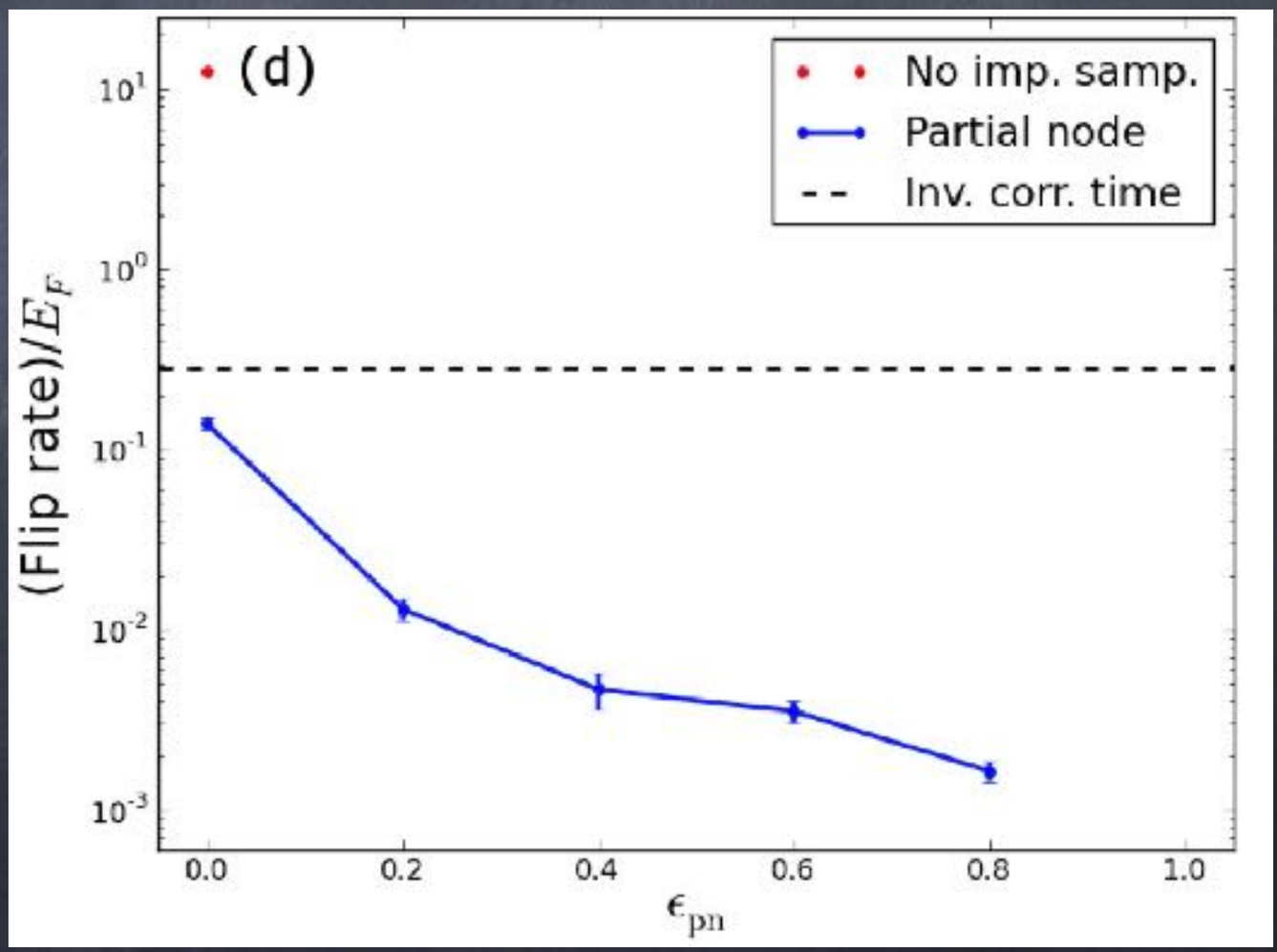




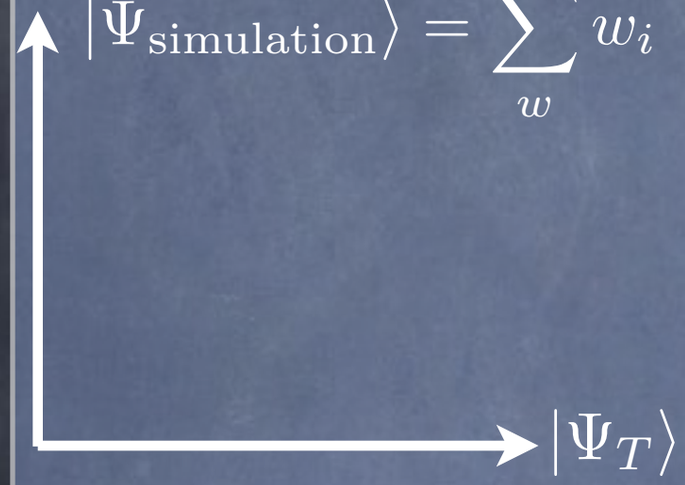
Characteristic flip rate

Beta required for

$$\exp[-\beta H]|\Psi_T\rangle = |\Psi_0\rangle$$



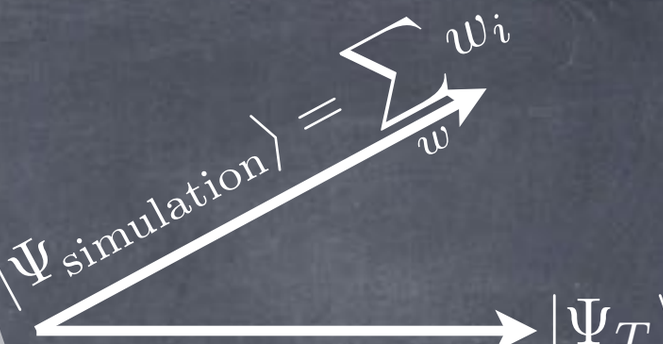
A better extrapolation?



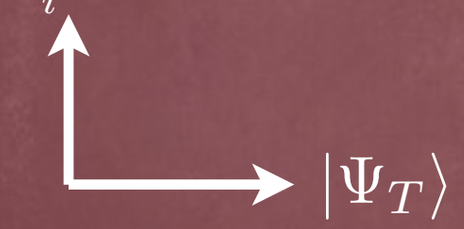
If $|\Psi_T\rangle$ is correct, then you should restart the simulation here.

If $|\Psi_T\rangle$ is slightly wrong, then restarting the simulation is still small error.

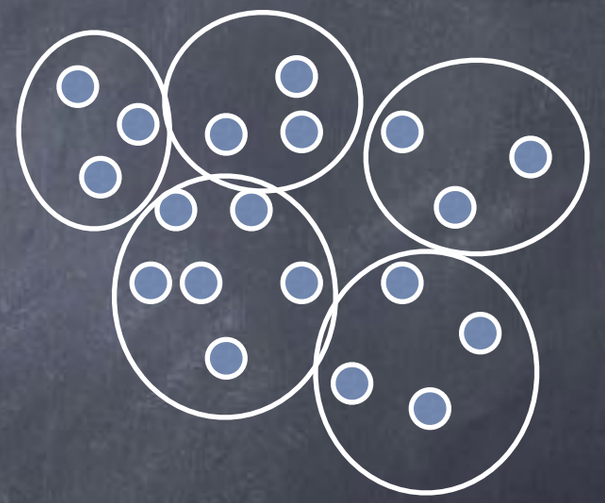
Almost no bias. Almost no help for the sign problem.



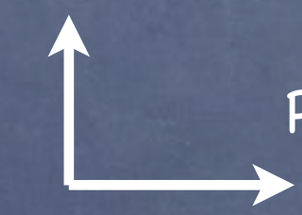
Remove when $\sum_i |w_i\rangle$ goes to 0 (approximate by sign change)



Small discretization bias; small sign problem



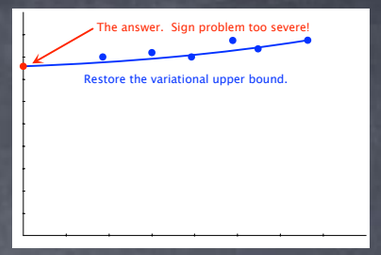
Remove when $\langle \Psi_T | w_i \rangle$ goes to 0 (approximate by sign change)



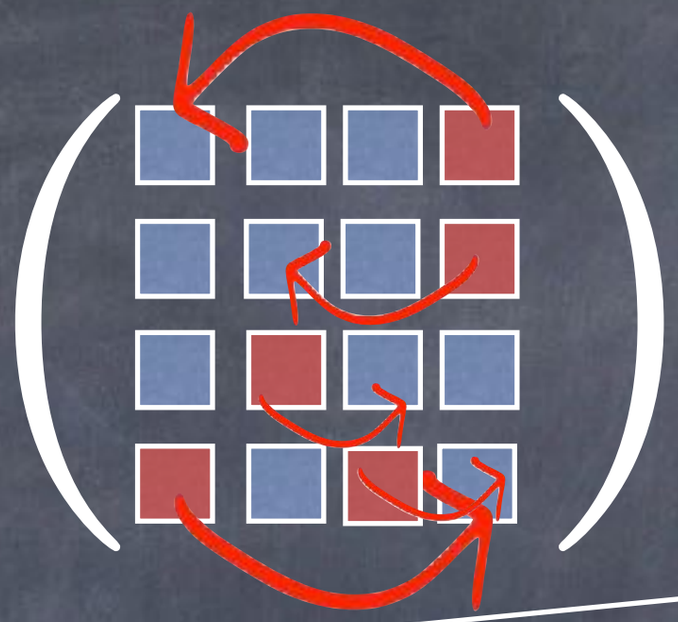
Large discretization bias. No sign problem.

Reduces to removing the bad signs.

Restore the variational upper bound.



$$1 - \tau H_{is} =$$



Partial node: ■ set to 0

Fixed node: ■ set to 0 and dump to diagonal.

Hard in momentum basis: 10^6 "bad" terms per row

$$U_{\rm diag}[D] = 1 - \tau\langle D|H_{is}|D\rangle - \tau\Delta K \qquad \Delta K = \sum_{D'\in{\rm bad}} \langle D'|H_{is}|D\rangle$$

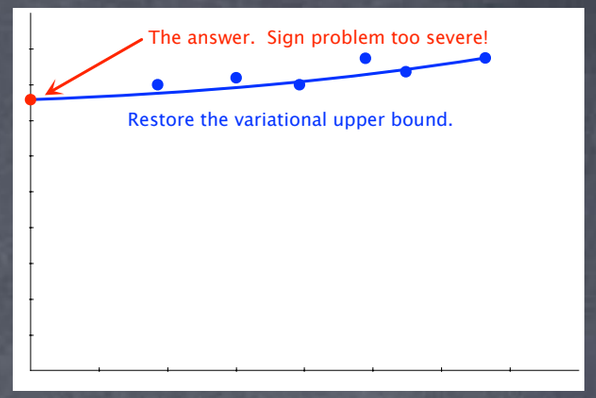
Stochastic Diagonal Dumping

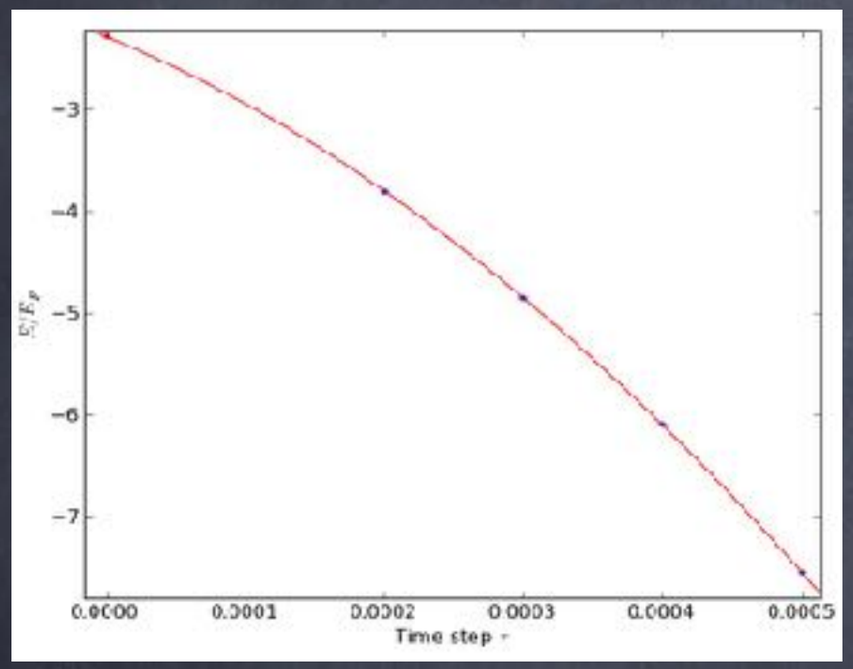
- Pick D′ according to P(D′|D)
- Let $\Delta K = \langle D'|H_{is}|D\rangle / P(D'|D)$ if $\langle D'|H_{is}|D\rangle$ is bad

Formally correct, but 'bad' if $U_{\rm diag} \ll -1$

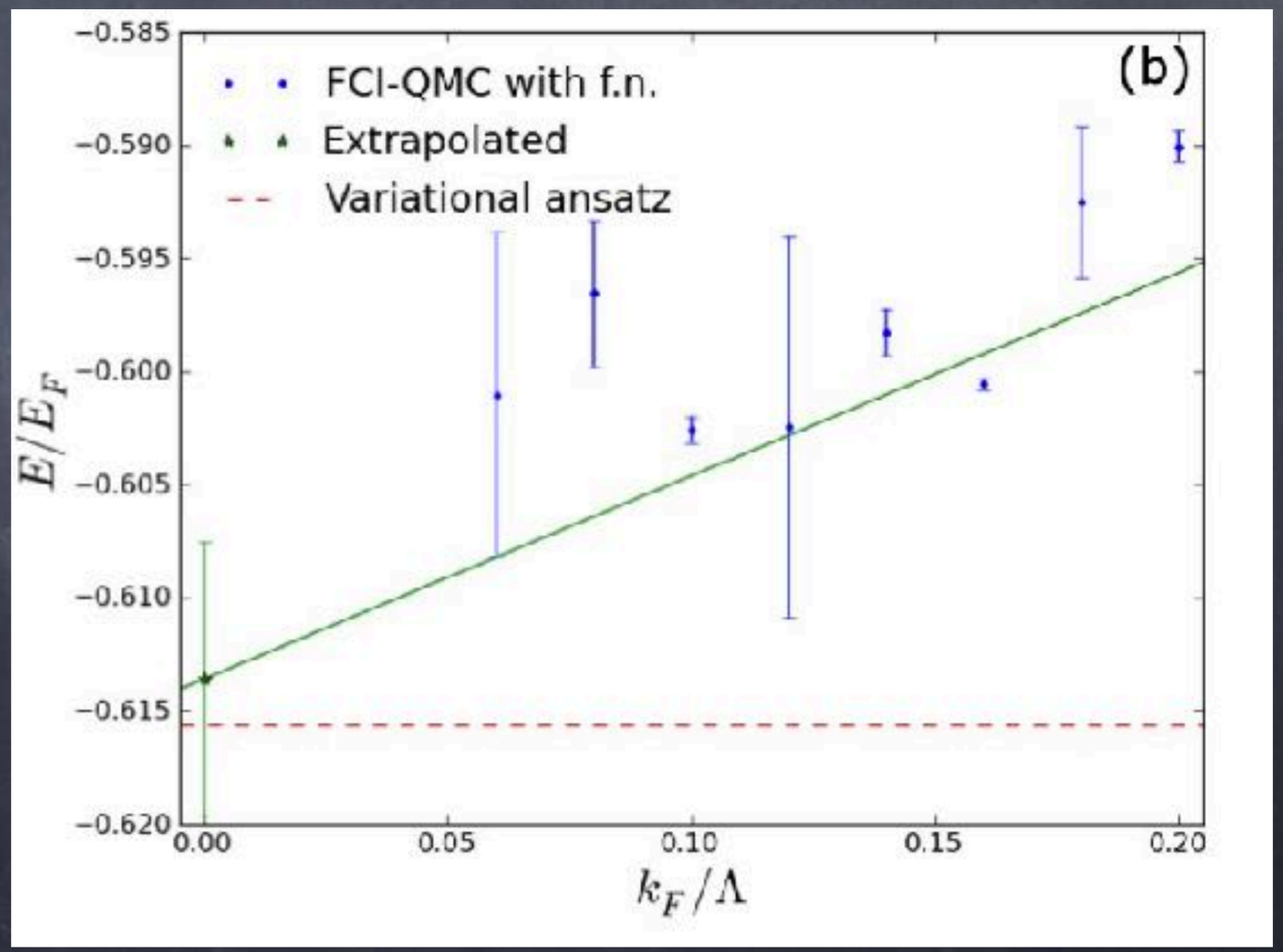
Restore the variational upper bound. by adding a time step error.

$$1 - \tau\langle D|H_{is}|D\rangle - \tau\Delta K \approx e^{-\tau(\langle D|H_{is}|D\rangle - \Delta K)}$$



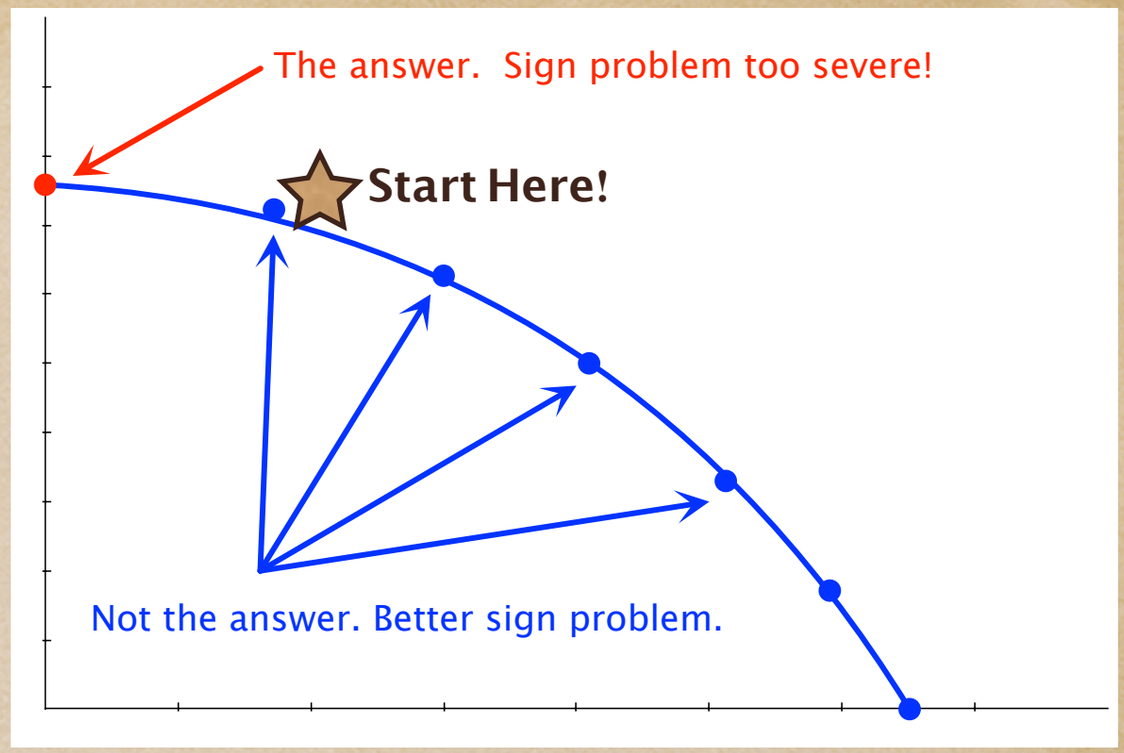


Variational Upper Bound!

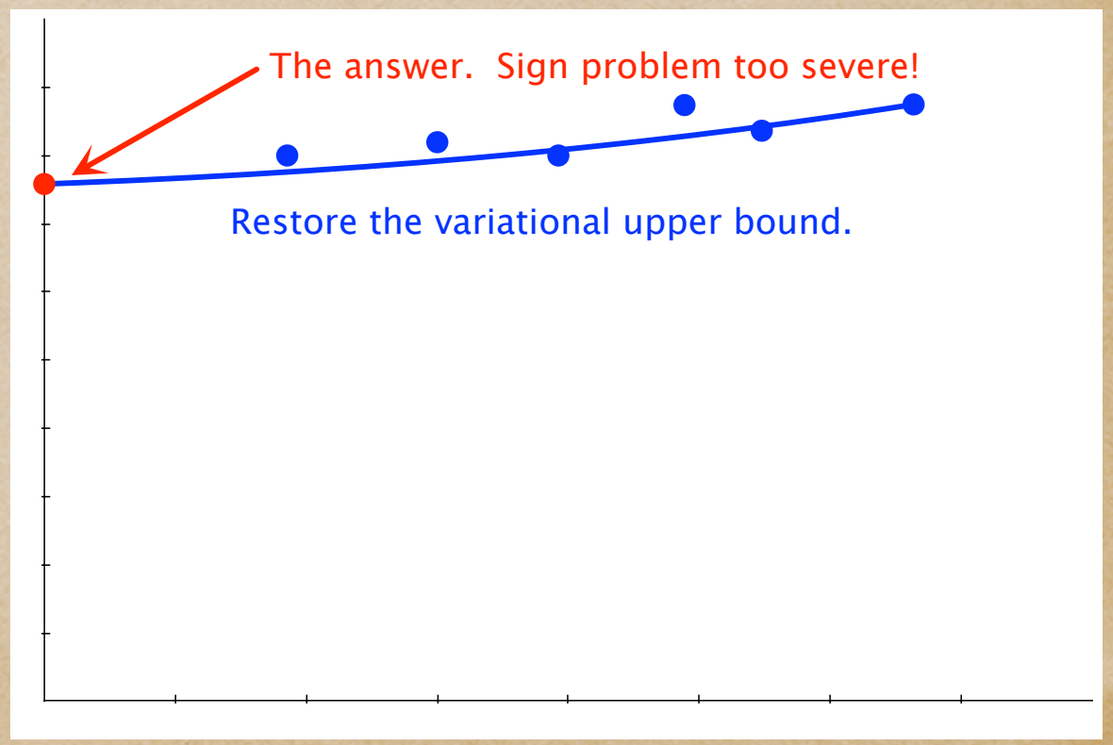


The story so far ...

Approach the exact answer either variationally (or not)



Next: Get to the right answer by starting close.

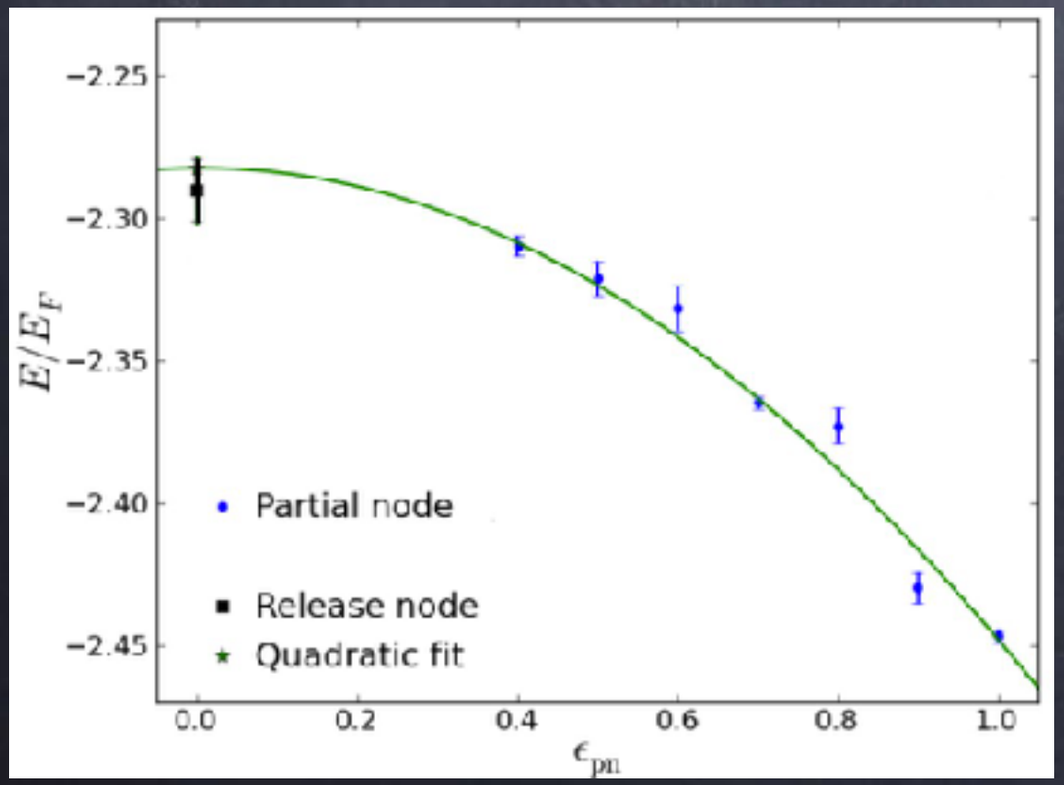


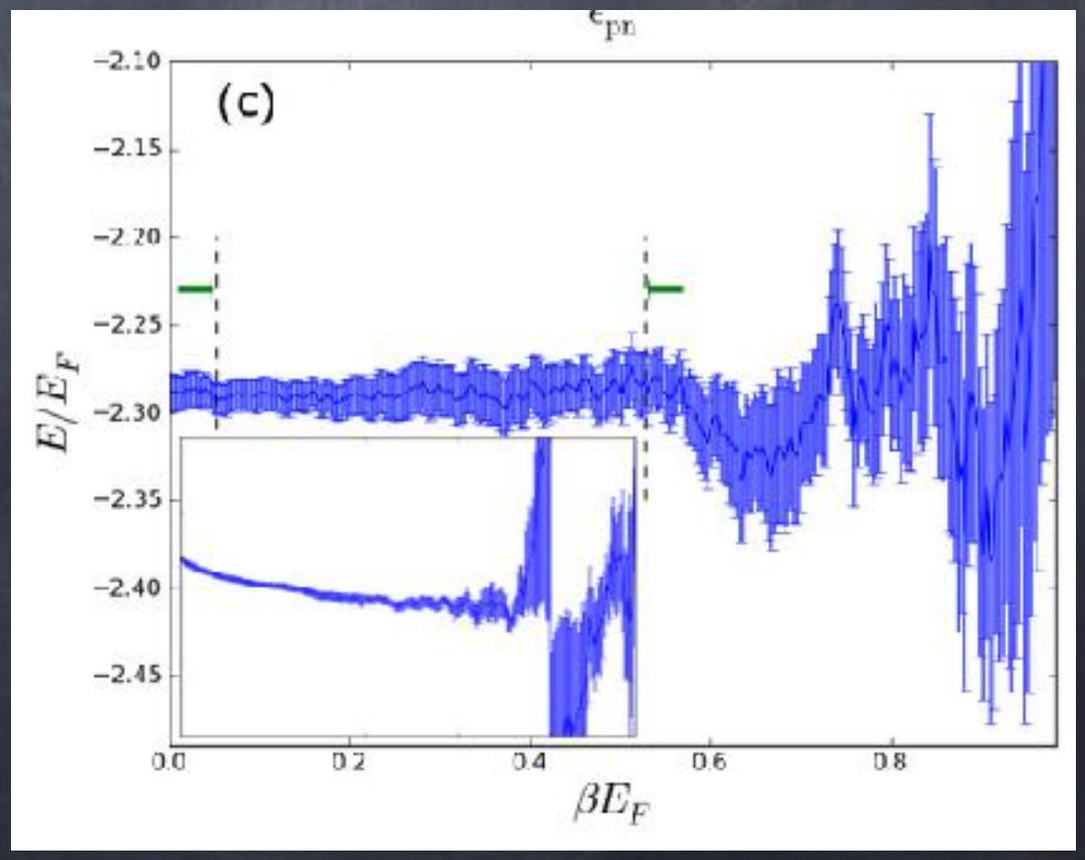
Release Node

Better trial functions = smaller beta needed

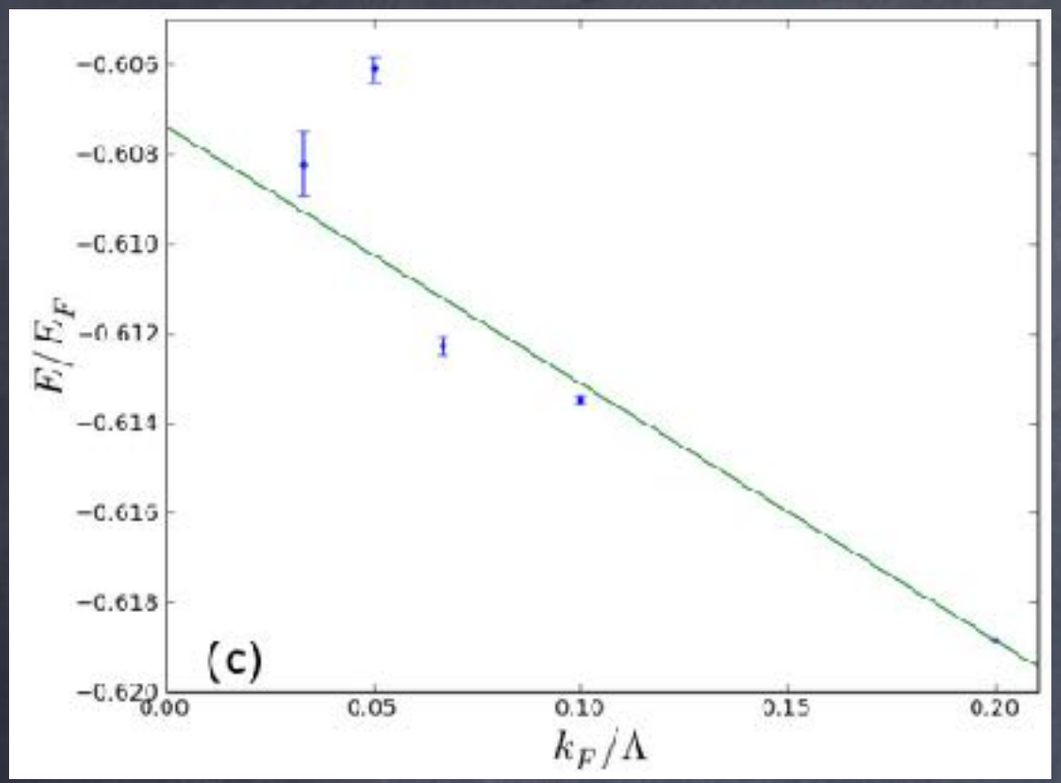
Use implicit trial function!

- Start: partial node walkers
- Propaqate each for
- Measure β





For condensed systems: ∞ basis, ∞ ptcl number

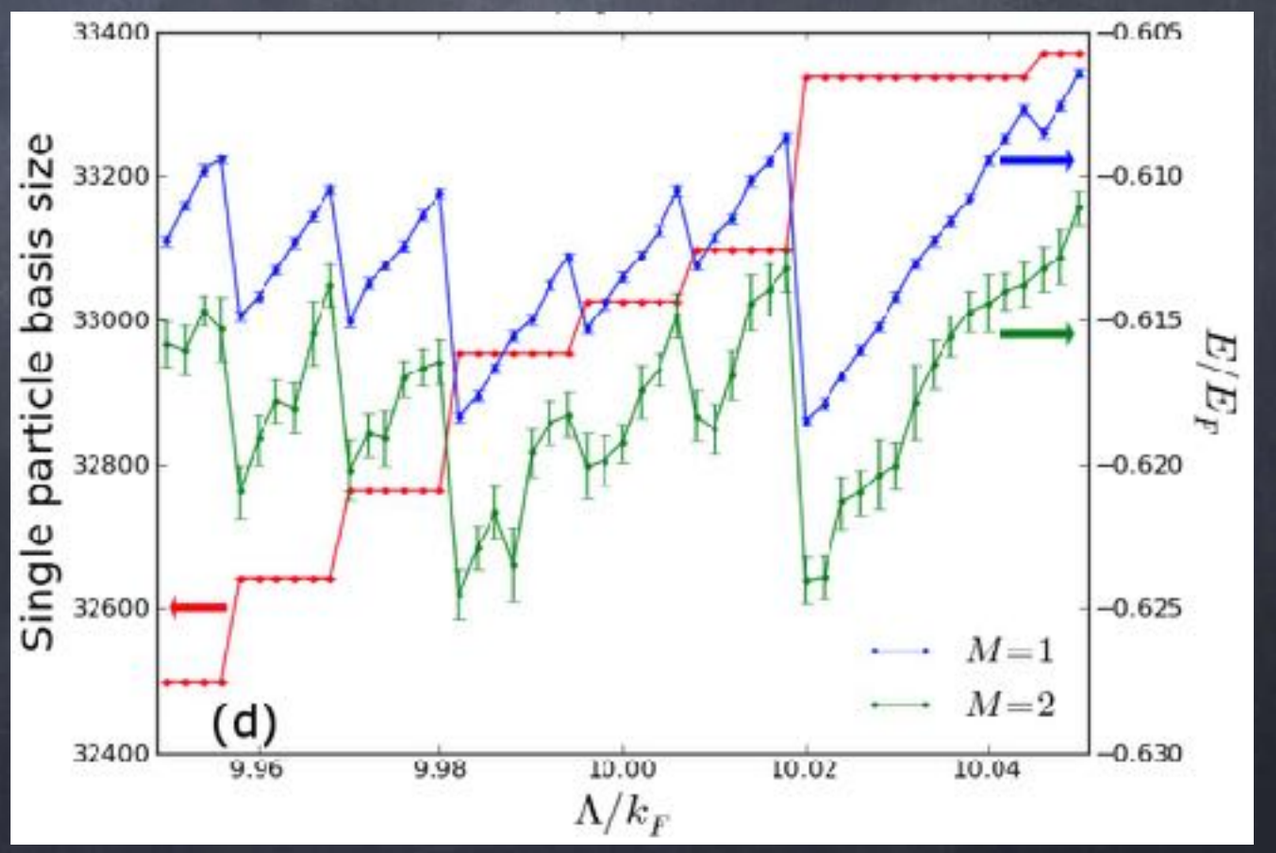


Why is this extrapolation so bad?

$$\Lambda \to \infty$$

This is because N=33 and not infinite N.

How do we get to the thermodynamic limit?



An infinite number of bits is hard :(

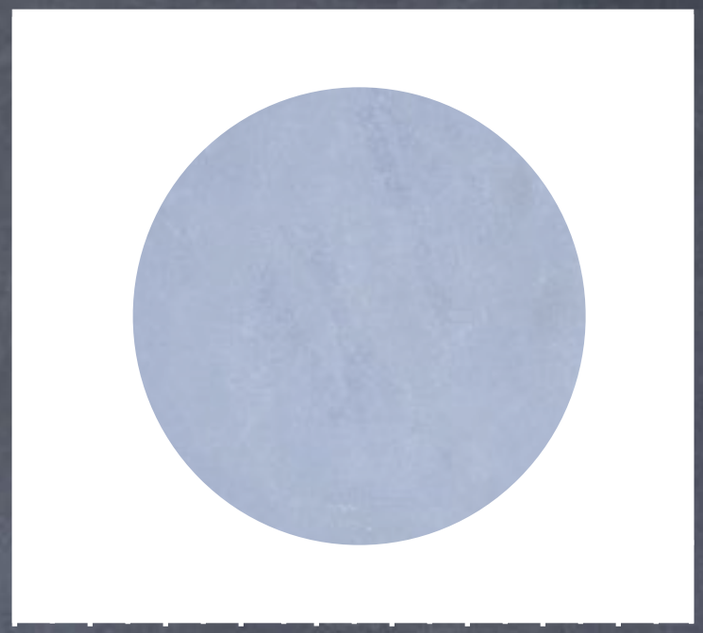
Represent:

$$|FS\rangle$$

$$|FS\rangle - |q_i\rangle + |k_i\rangle$$

$$|FS\rangle - |q_i\rangle - |q_j\rangle + |k_i\rangle + |k_j\rangle$$

$k_i \in$

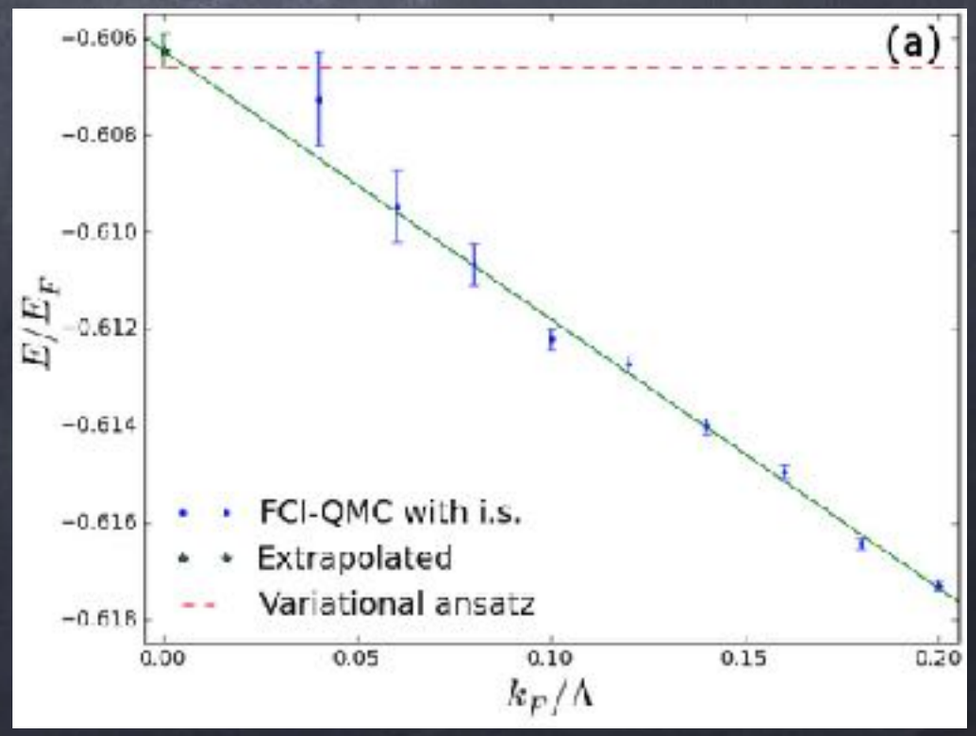


List holes, list excitations. $M = 2$

QMC in the thermodynamic limit!

2 concerns

- Sign problem
  - Annihilation only on D0
- $(1 - \tau H)$ need spectra bounded
  - "Continuous Time" possible
  - Finite M gives this.



II. Better Approximations

Many wave-functions

- Slater-Jastrow
- Correlated-Product States
- AGP
- Backflow
- Valence Bond

A good wave-function is ...

- fast to evaluate
- captures physics
- improvable

Multislater-Jastrow: $\Psi(R) = e^{-J} \sum_k \alpha_k \det M_k$

Jastrow makes each determinant more powerful then quantum chemistry.

We've developed a fast algorithm to evaluate!

$O(n^2 + n_s n + n_e)$

n : number of particles

n_s : number of single excitations

n_e : number of excitations

$$M_0 = \begin{pmatrix} \phi_1(r_i) \\ \phi_2(r_i) \\ \phi_3(r_i) \\ \phi_4(r_i) \end{pmatrix}$$

Frozen core

$$\begin{matrix} \phi_5(r_i) \\ \phi_6(r_i) \\ \phi_7(r_i) \\ \phi_8(r_i) \end{matrix}$$

m

Ratios

$$[1 + e_k^T M^{-1}(\phi_5 - \phi_4)]$$

$$[1 + e_k^T M^{-1}(\phi_6 - \phi_4)]$$

$$[1 + e_k^T M^{-1}(\phi_7 - \phi_5)]$$

$$[1 + e_k^T M^{-1}(\phi_3 - \phi_8)]$$

$$[1 + e_k^T M^{-1}(\phi_4 - \phi_8)]$$

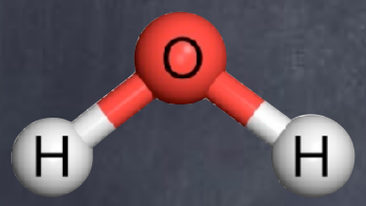
Lots of redundancy!

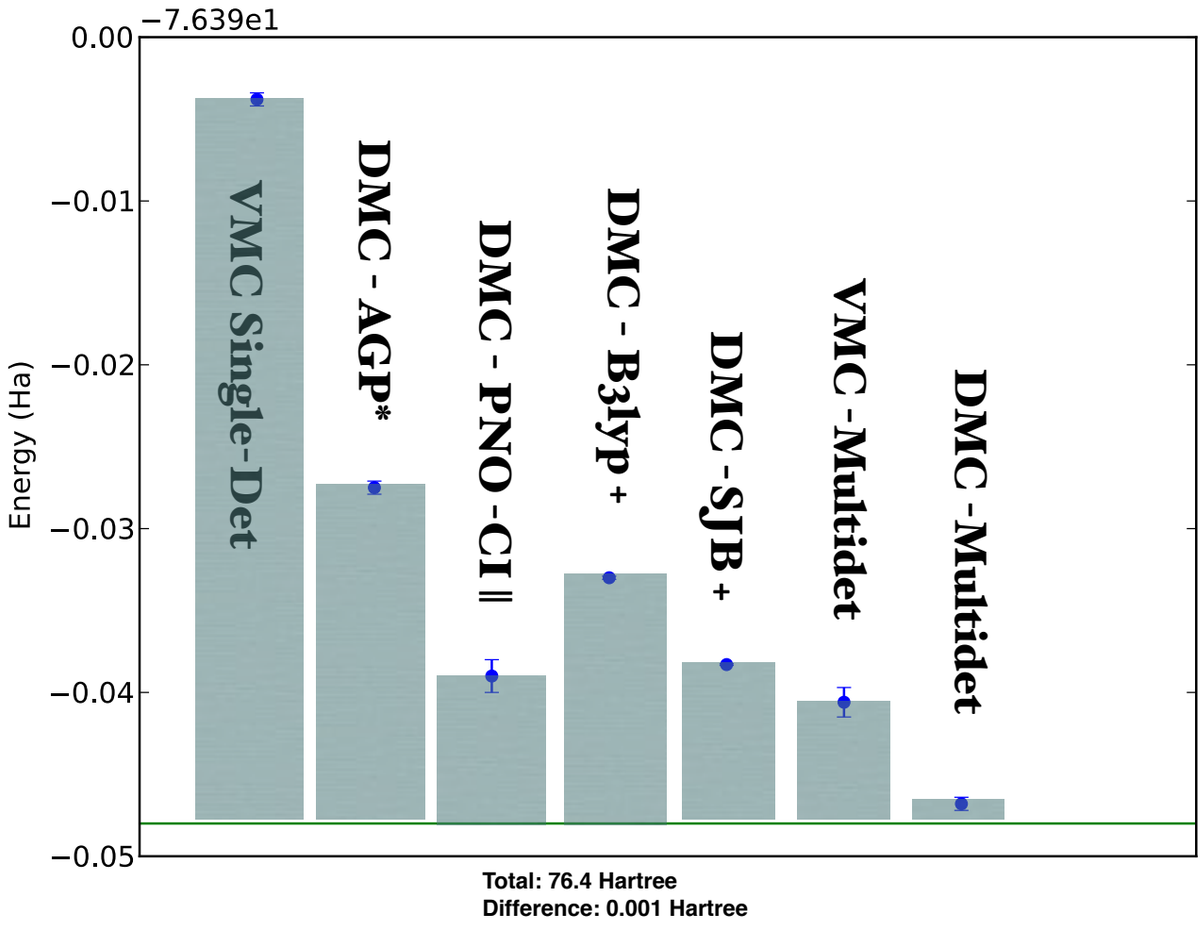
1. Build a table:

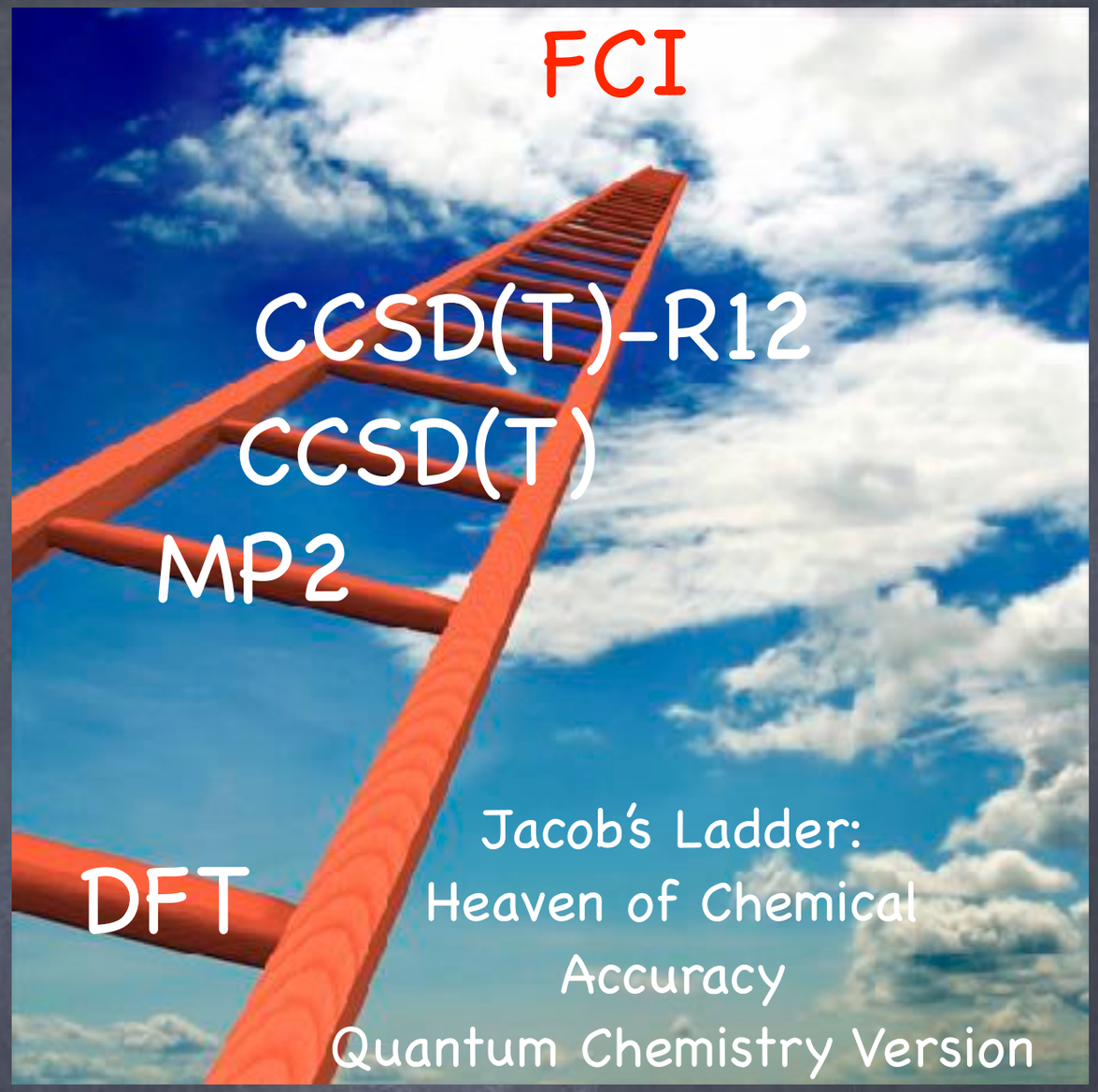
$M_2^{-1} \cdot \phi_5$	$M_3^{-1} \cdot \phi_5$	$M_4^{-1} \cdot \phi_5$
$M_2^{-1} \cdot \phi_6$	$M_3^{-1} \cdot \phi_6$	$M_4^{-1} \cdot \phi_6$
$M_2^{-1} \cdot \phi_7$	$M_3^{-1} \cdot \phi_7$	$M_4^{-1} \cdot \phi_7$
$M_2^{-1} \cdot \phi_8$	$M_3^{-1} \cdot \phi_8$	$M_4^{-1} \cdot \phi_8$

2. Read off ratios

How well does Multi-Slater Jastrow do?







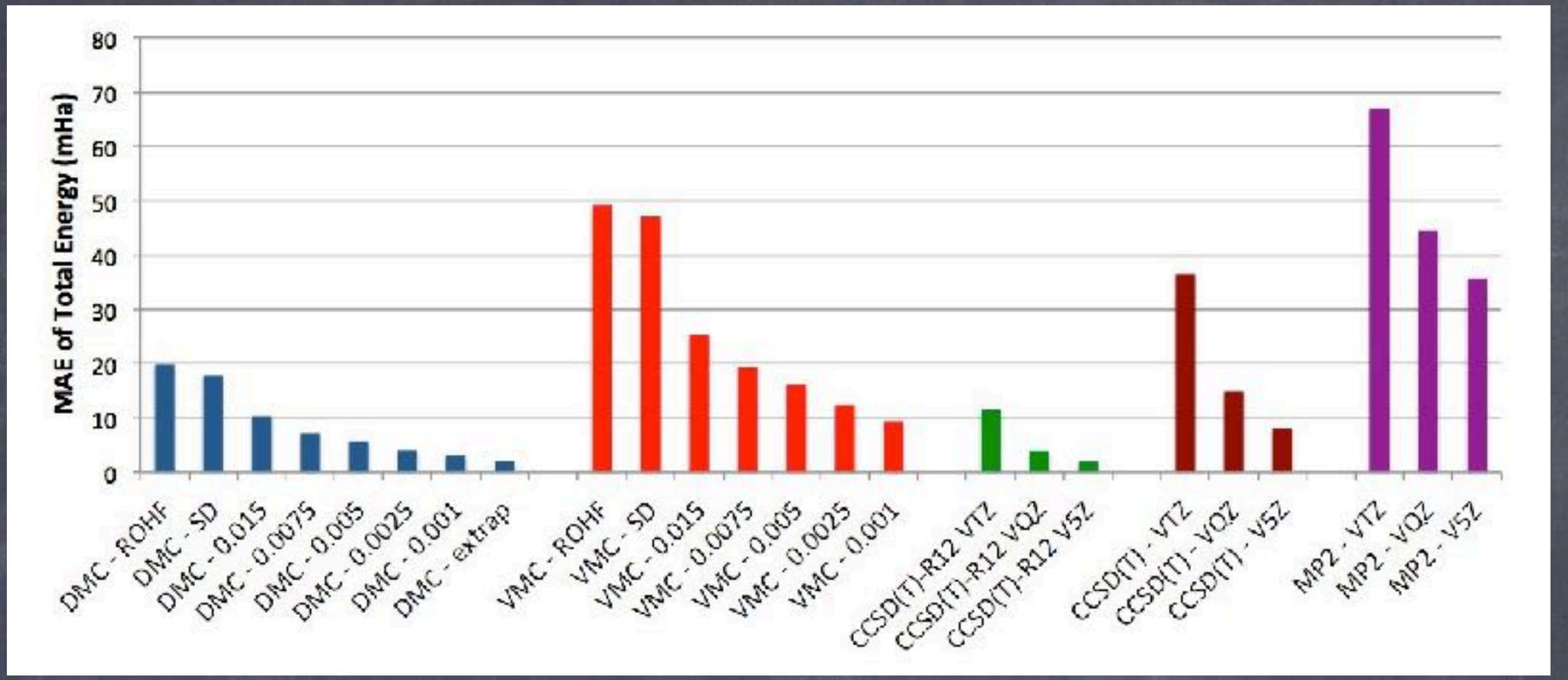
Best QMC by far

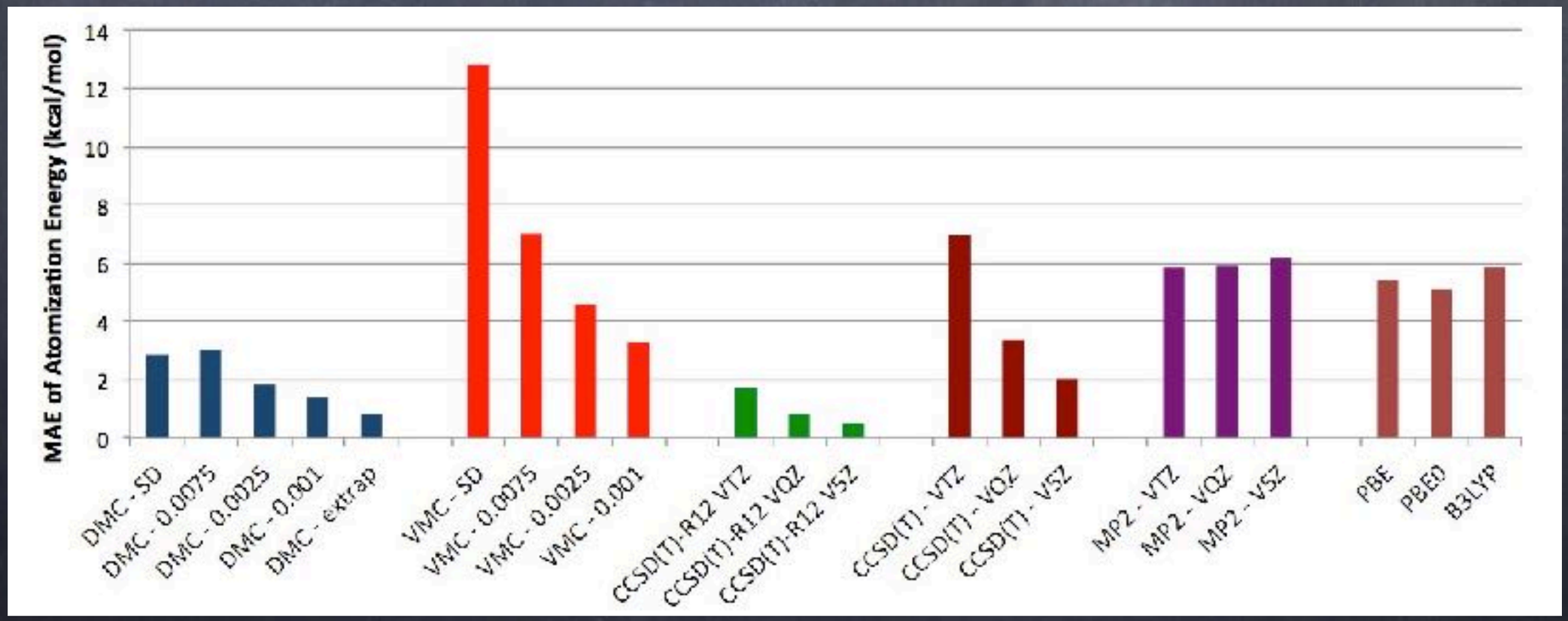
* M. Casula, C. Attaccalite, and S. Sorella, The Journal of chemical physics 121, 7110 (2004).

\+ I. G. Gurtubay and N. R. J., The Journal of chemical physics 127, 124306 (2007).

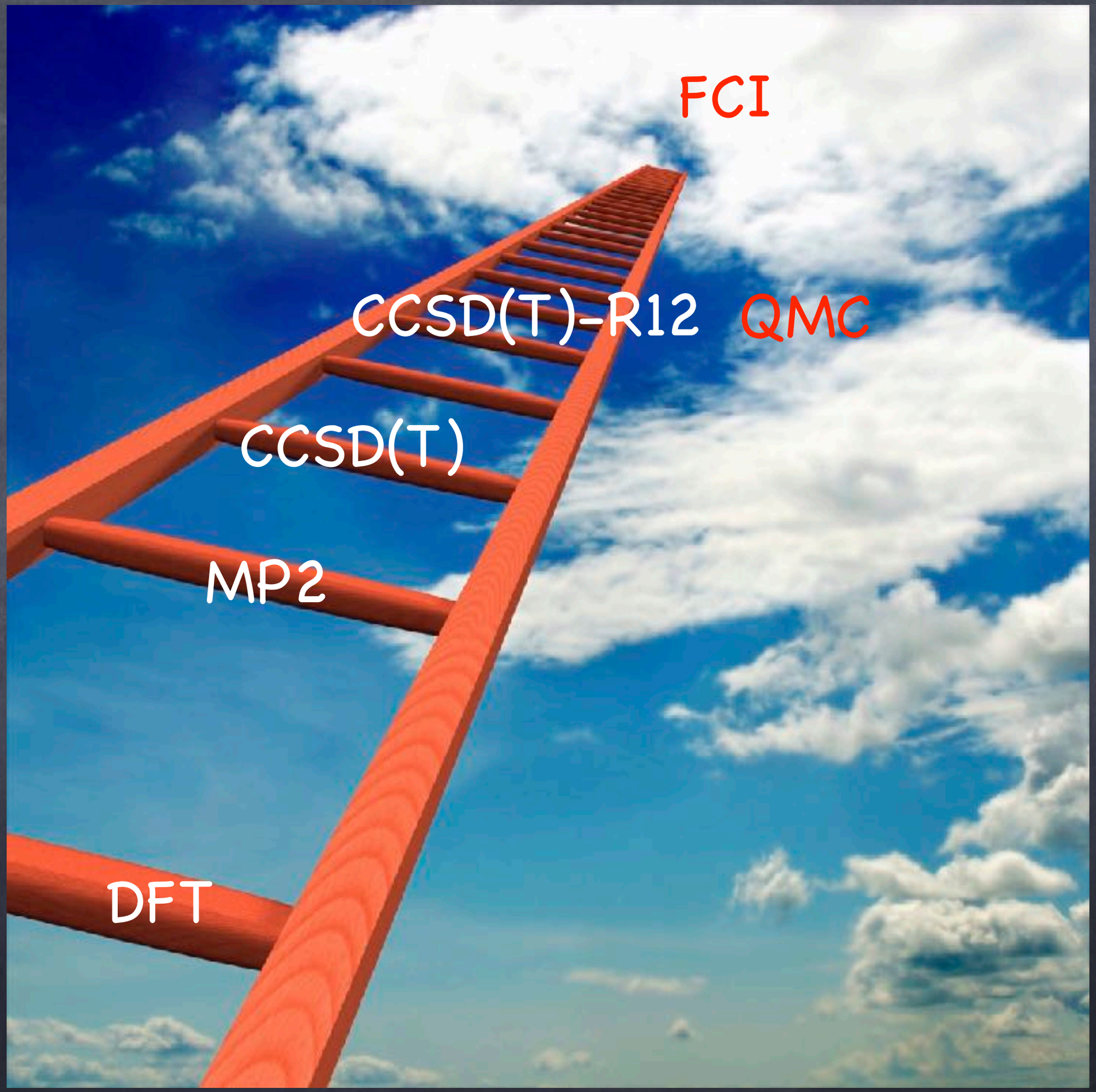
|| A. Luchow and R. F. Fink, The Journal of chemical physics 113, 8457 (2000).

G2 set


MAE of Total Energy (mHa)
80
70
60
50
40
30
20
10
0
DMC - ROHF
DMC - SD
DMC - 0.015
DMC - 0.0075
DMC - 0.005
DMC - 0.0025
DMC - 0.001
DMC - extrap
VMC - ROHF
VMC - SD
VMC - 0.015
VMC - 0.0075
VMC - 0.005
VMC - 0.0025
VMC - 0.001
CCSD(T)-R12 VTZ
CCSD(T)-R12 VQZ
CCSD(T)-R12 V5Z
CCSD(T) - VTZ
CCSD(T) - VQZ
CCSD(T) - V5Z
MP2 - VTZ
MP2 - VQZ
MP2 - V5Z


MAE of Atomization Energy (kcal/mol)
14
12
10
8
6
4
2
0
DMC - SD
DMC - 0.0075
DMC - 0.0025
DMC - 0.001
DMC - extrap
VMC - SD
VMC - 0.0075
VMC - 0.0025
VMC - 0.001
CCSD(T)-R12 VTZ
CCSD(T)-R12 VQZ
CCSD(T)-R12 V5Z
CCSD(T) - VTZ
CCSD(T) - VQZ
CCSD(T) - V5Z
MP2 - VTZ
MP2 - VQZ
MP2 - V5Z
PBE
PBE0
B3LYP

- Systematic, albeit with slow convergence.

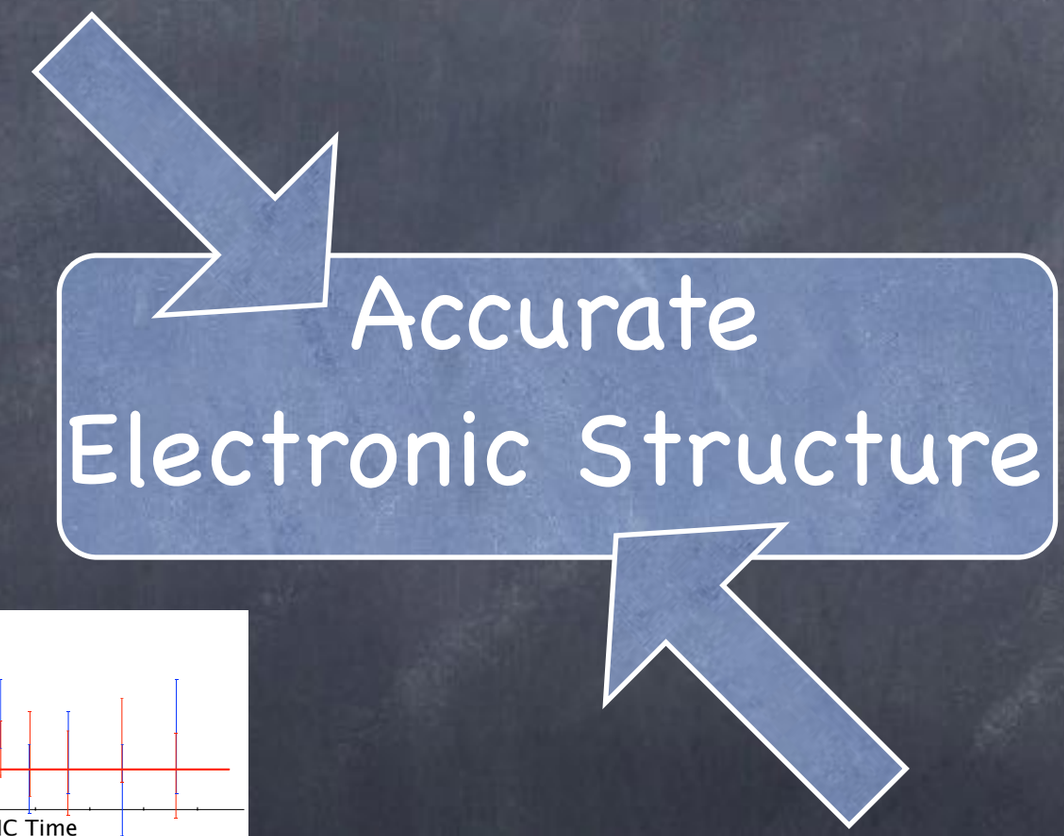

FCI
CCSD(T)-R12
QMC
CCSD(T)
MP2
DFT

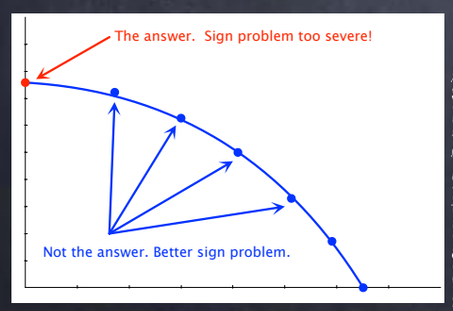
Conclusions

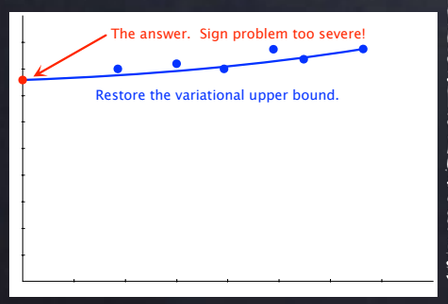
Q: How do we get to accurate electronic structure?

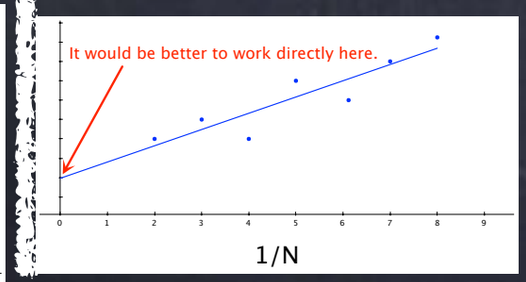
A:

Better Wave-functions









Systematically approach the exact answer.