QMC for Strongly Correlated Systems

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Strongly Correlated Systems: Columbia University

Better Approximations

Understand the sign problem?

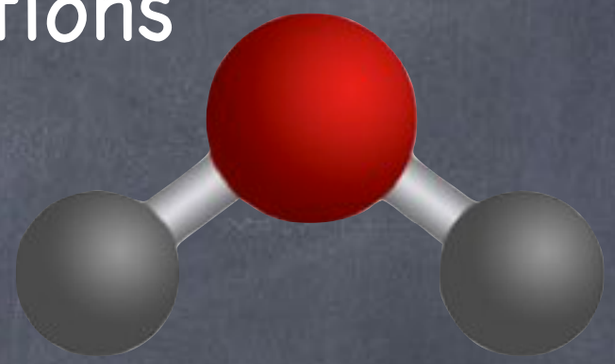
Molecules, Hubbard Model, Spin Liquids, etc.

Faster Exact Methods

Three "Examples"

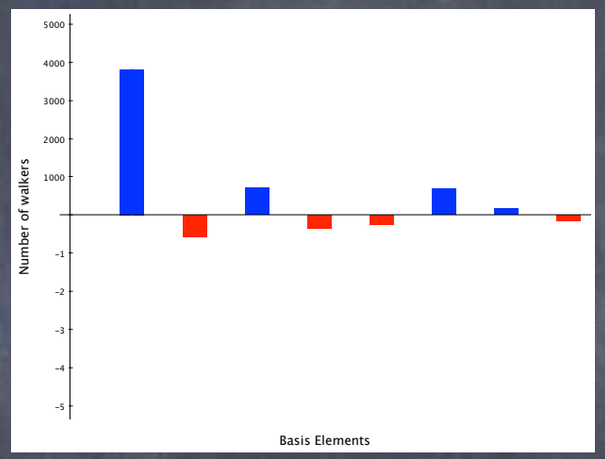
- Better molecules with better wave-functions

  Collaborators: Morales, McMinis, Kim, Scuseria

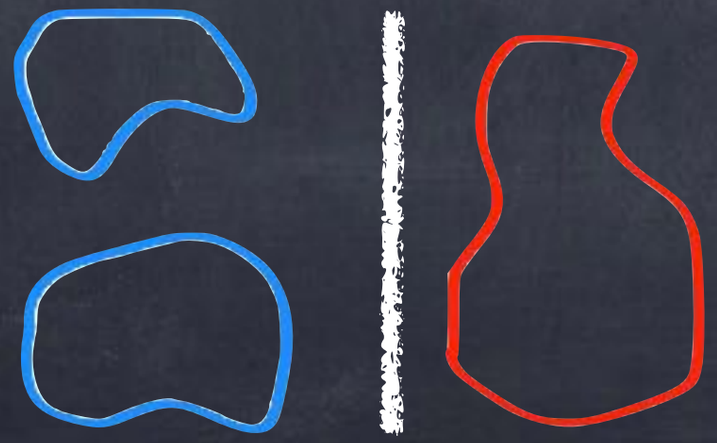


- Improved FCI-QMC

  Collaborators: Kolodrubetz



- Sign problems in Path Integrals



Story 1:
Molecules
with
Better Wavefunctions

Wavefunctions

- Slater-Jastrow, MPS, TPS, Geminals, CPS, PBC, etc.
- Better variational ansatz give better approximate answers for strongly correlated systems.
- A useful wavefunction is one we can write down compactly and evaluate quickly.
- 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

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

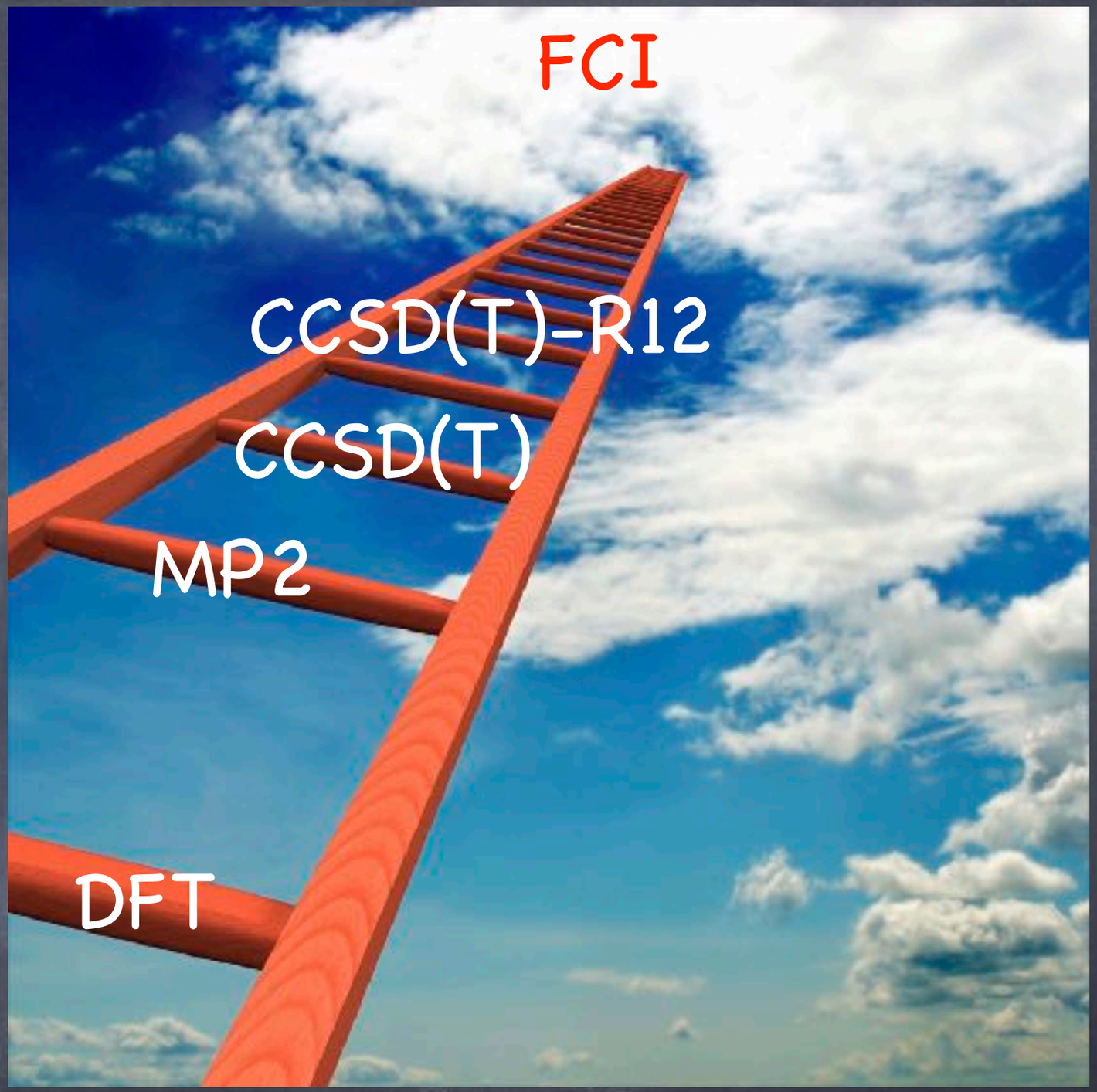
Frozen core

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

m

How well does Multi-Slater Jastrow do?

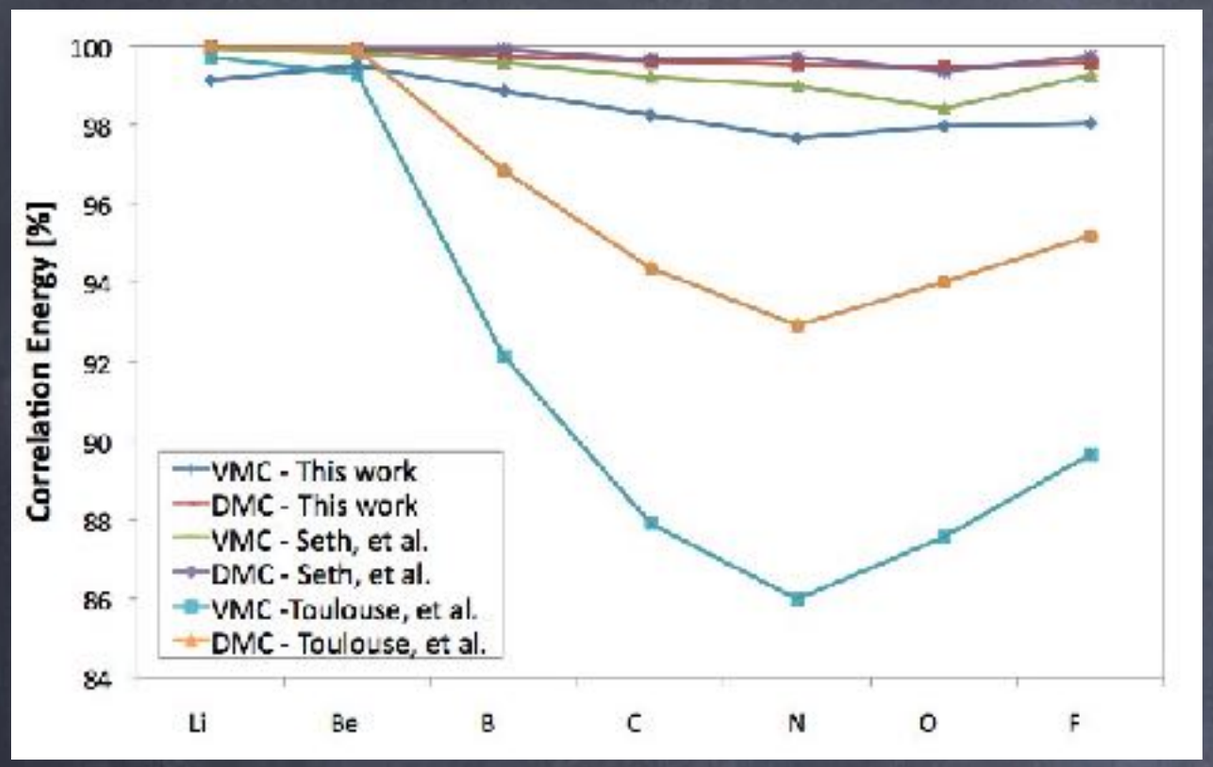
- Atoms
- Dimers
- G1 Set

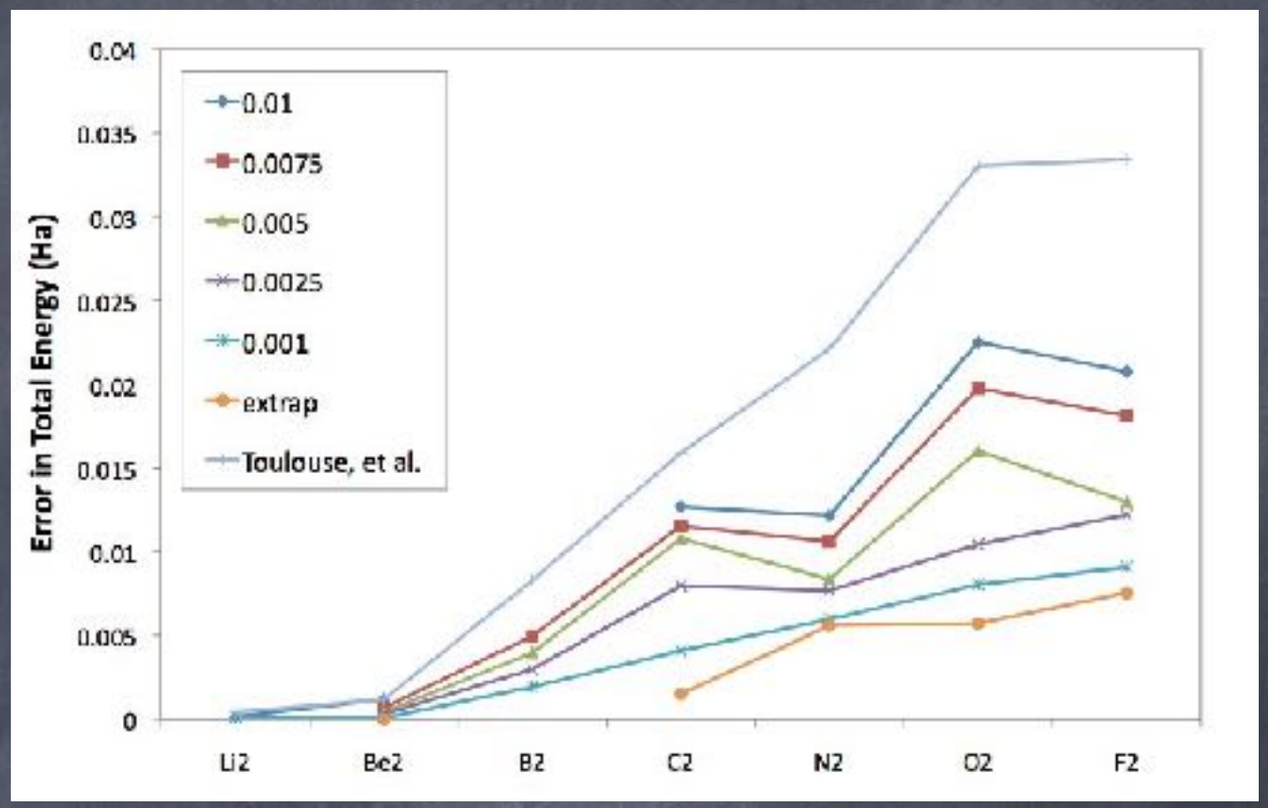


Jacob's Ladder: Heaven of Chemical Accuracy
Quantum Chemistry Version

Atoms and Dimers

DMC: All > 99% correlation energy



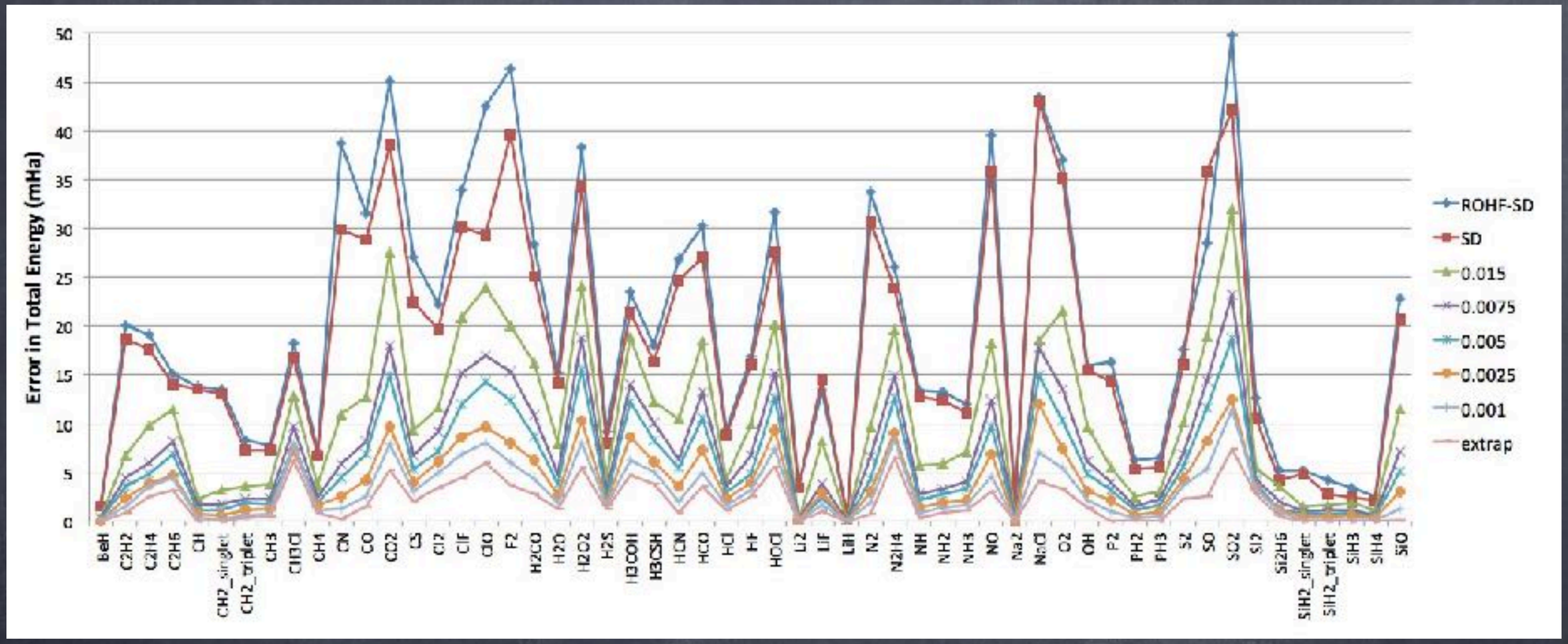


All electron calculations

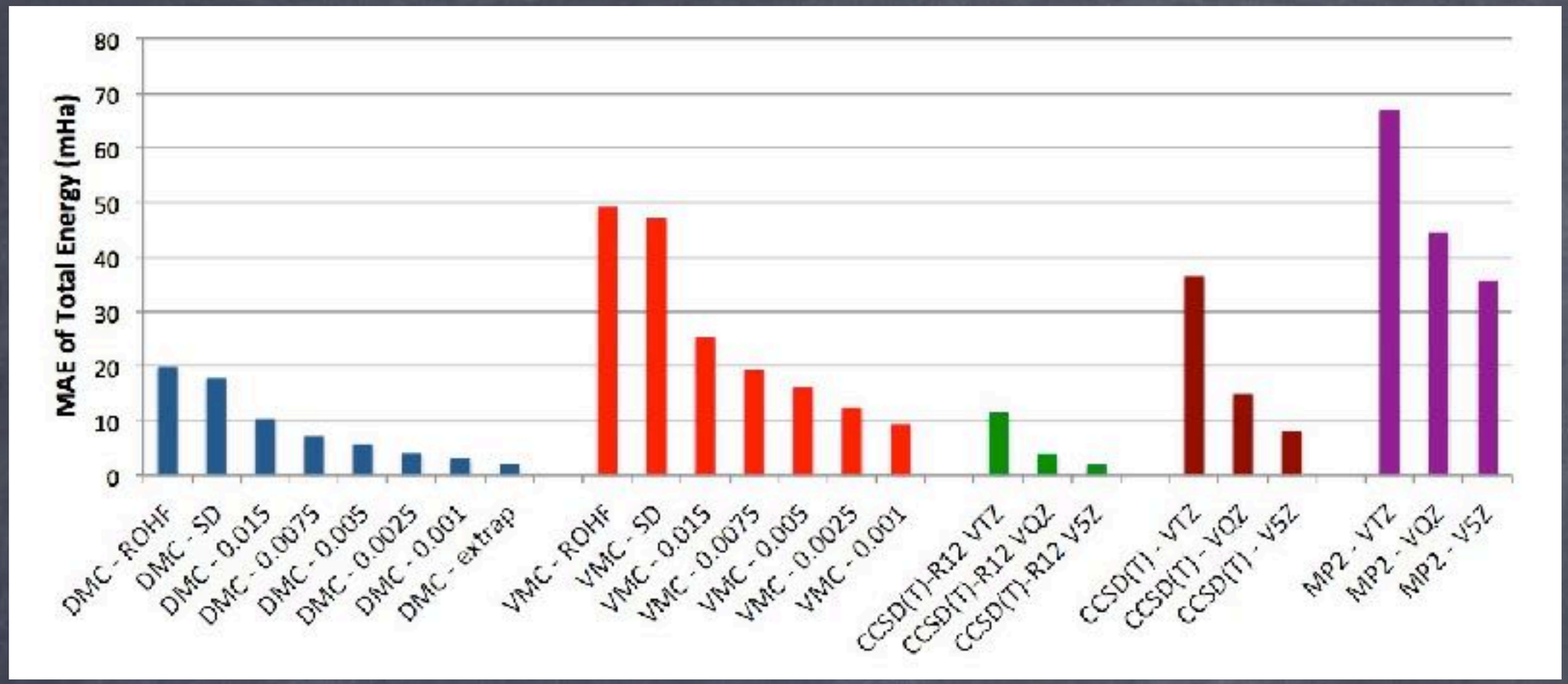
Determinants from SOCI

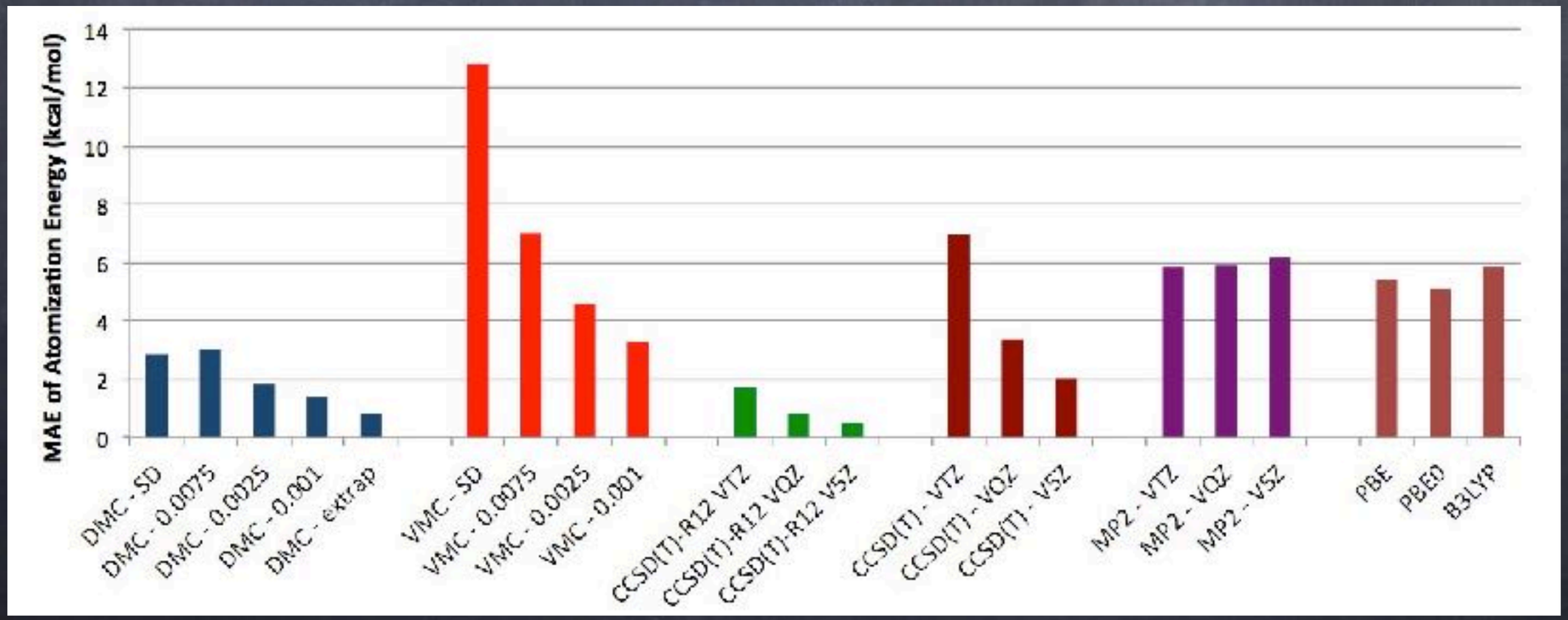
Active Space: All electrons in 10 orbitals + 40 orbitals in virtual space.

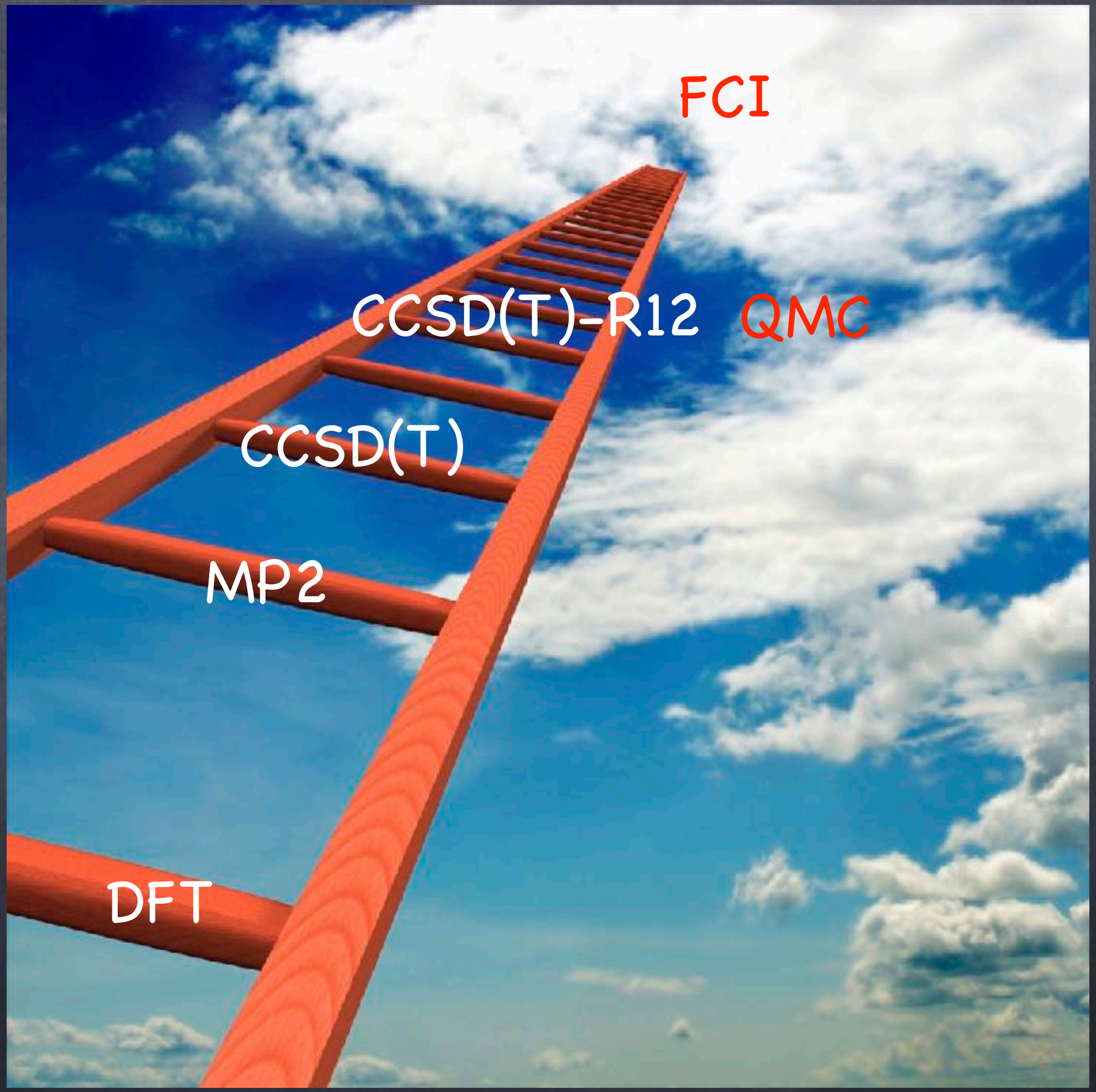
The G1 Set



Burkatzi-Filippi-Dolg-Dolg pseudopotentials
Typical geometries
MP2 Natural Orbitals
Determinants from CISDTQ

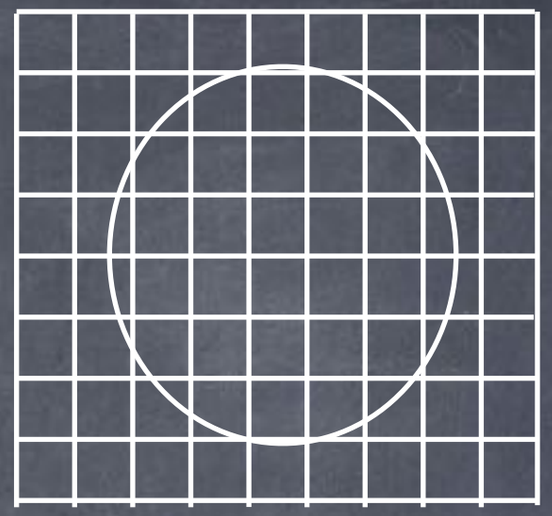

MAE of Total Energy (mHa)
80
70
60
50
40
30
20
10
0
DMC - ROHF
DMC - SD
DMC - 0.015
DMC - 0.0075
DMC - 0.005
DMC - 0.0025
DMC - 0.001
DMC - extrap
VMC - ROHF
VMC - SD
VMC - 0.015
VMC - 0.0075
VMC - 0.005
VMC - 0.0025
VMC - 0.001
CCSD(T)-R12 VTZ
CCSD(T)-R12 VQZ
CCSD(T)-R12 V5Z
CCSD(T) - VTZ
CCSD(T) -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


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

Story 2: FCI-QMC

FCI-QMC



Typical QMC

$$\Psi_0 = (1 - \tau H)^N \Psi_T$$

Basis: $\{R_i\}$

First Quantized

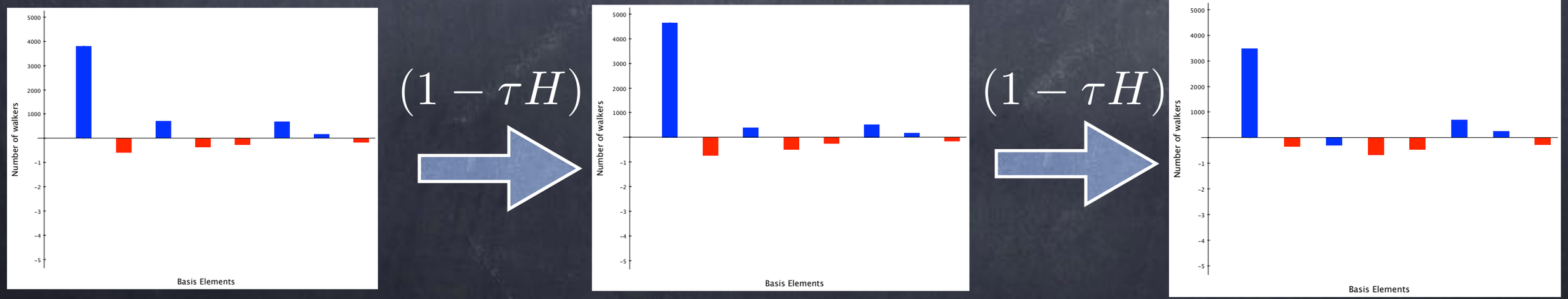
FCI-QMC

$$\Psi_0 = (1 - \tau H)^N \Psi_T$$

Basis: $\{k_i\}$

Second Quantized

Annihilation



Booth, Alavi, et. al

FCI-QMC

D0	D1	D2	D3	D4	D5	D6	D7	D8	D9
				3					

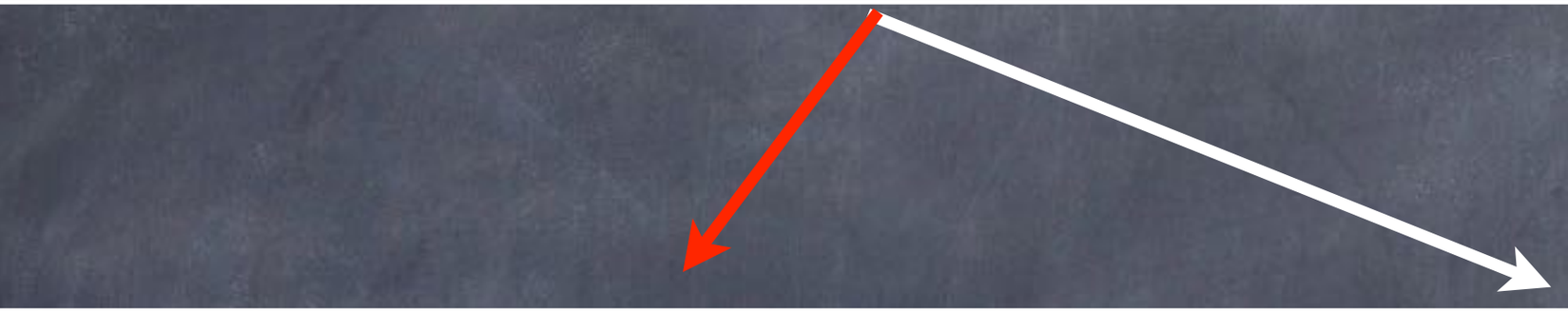
			-2	3			1		

		-1	-2 1	3		1 -1	1		

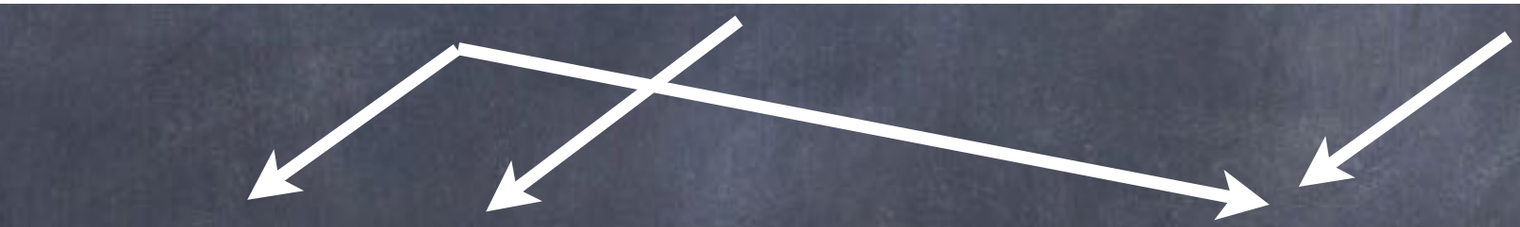
	-1	-1	-2 1	3	2	1 -1	1 -1		

FCI-QMC

D0	D1	D2	D3	D4	D5	D6	D7	D8	D9
				3					



			-2	3			1		

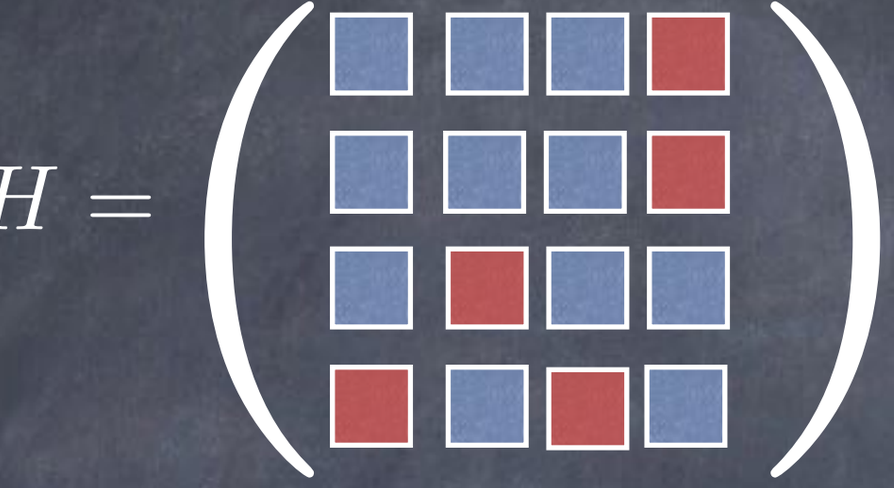


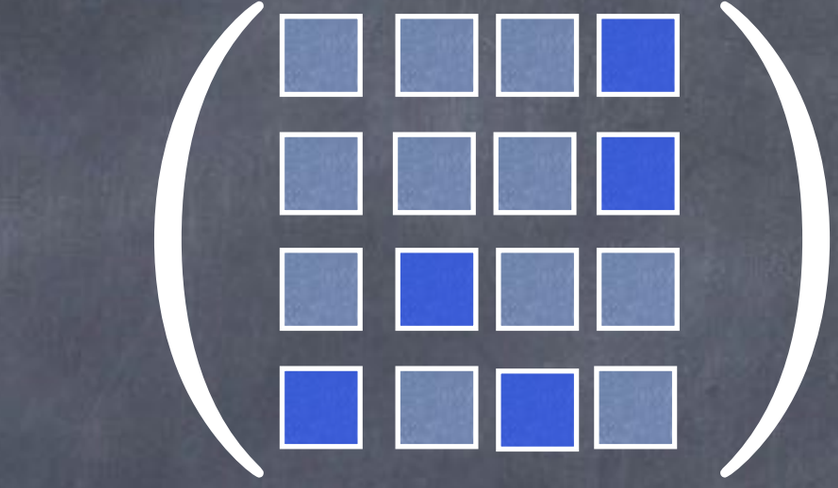
		-1	-1	3		0	1		

	-1	-1	-2 1	4		0	1		

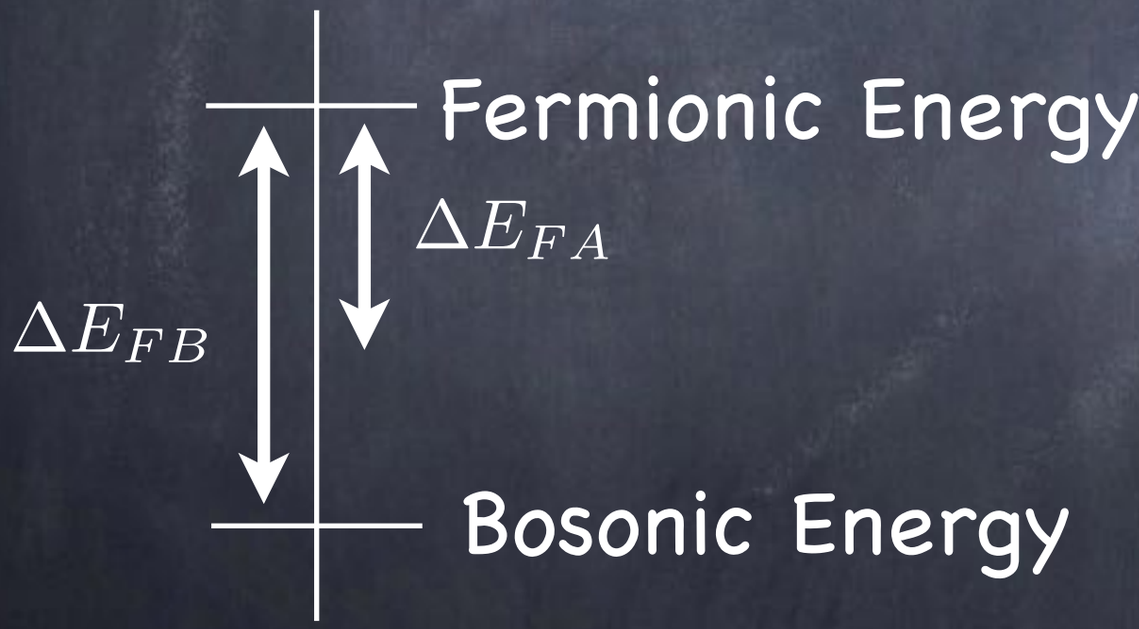
Sign Problem

$$1 - \tau H = \left(\text{Fermionic} \right) - \left(\text{'Bosonic'} \right)$$





$$E_F \quad - \quad E_B \quad = \Delta E_{FB}$$



Sign Problem:

No annihilation: $e^{\beta \Delta_{FB}}$

Some annihilation: $e^{\beta \Delta_{FA}}$

Sign problem a bit better but hard to compete with fixed node!

Can we do better?

Polaron:

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

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

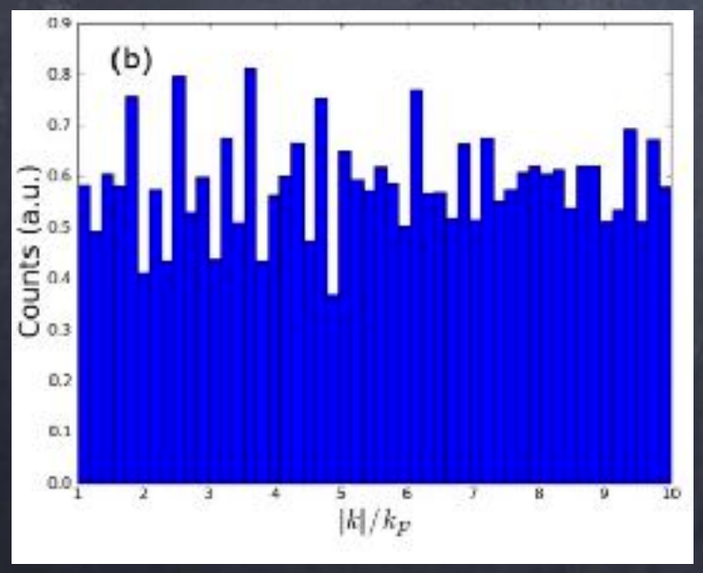
Want:

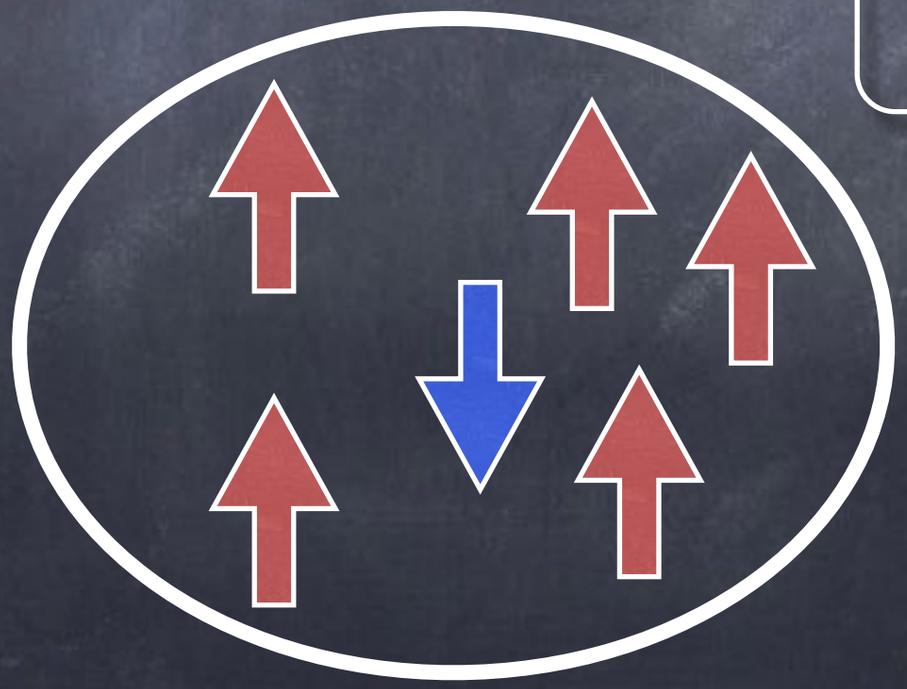
$$\Lambda \to \infty$$

$$N \to \infty$$

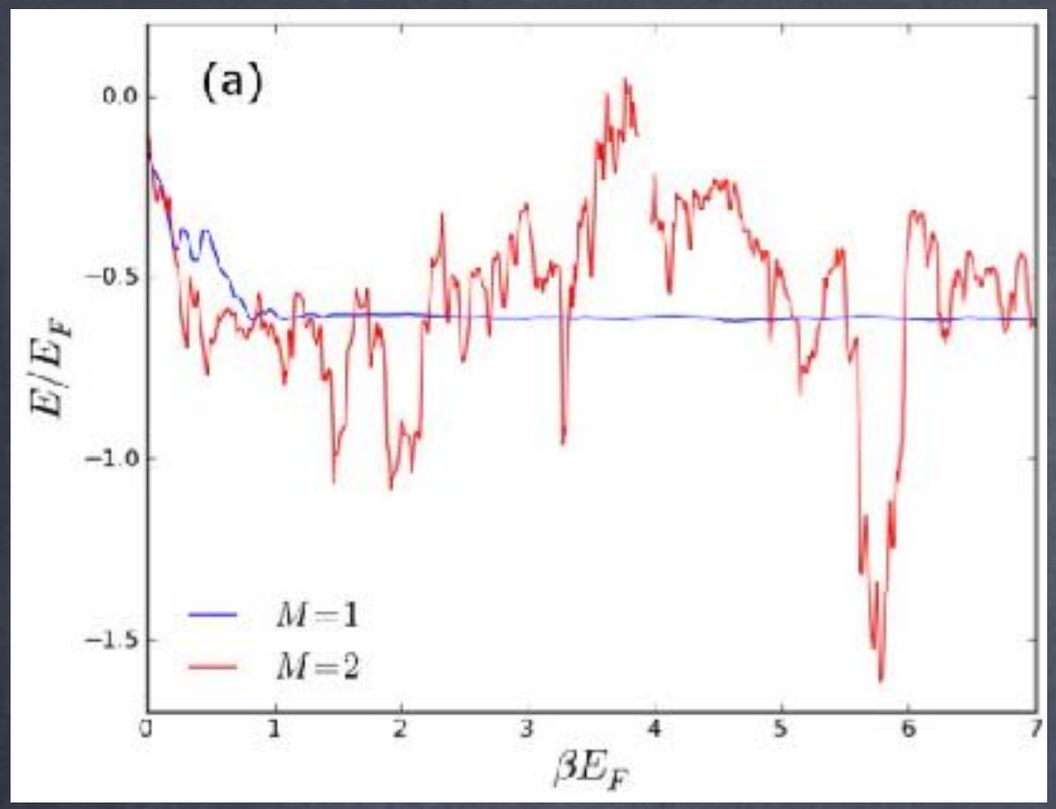
$$M \to \infty$$

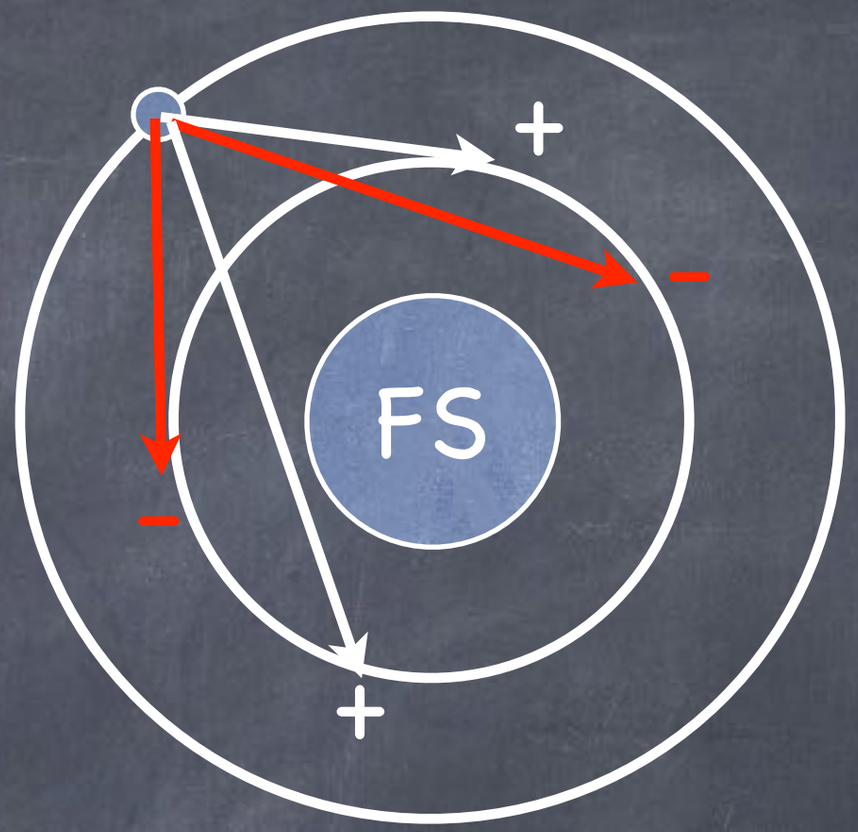
Particle-hole pairs: $|D_0\rangle \equiv |\mathrm{FS}_\uparrow, 0_\downarrow\rangle$





FCI-QMC:





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

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

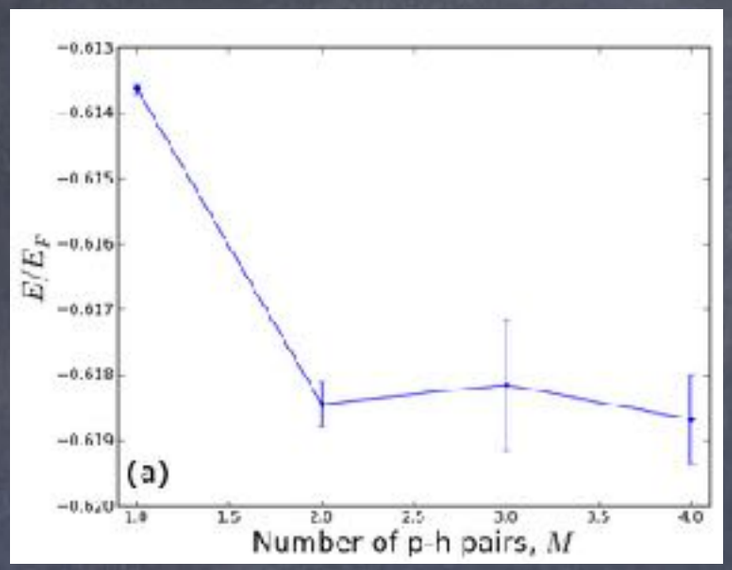
Fails: N=33, M=1, $\Lambda = 10, a^{-1} > 0$

Why hard:

- All determinants important
- Random Signs

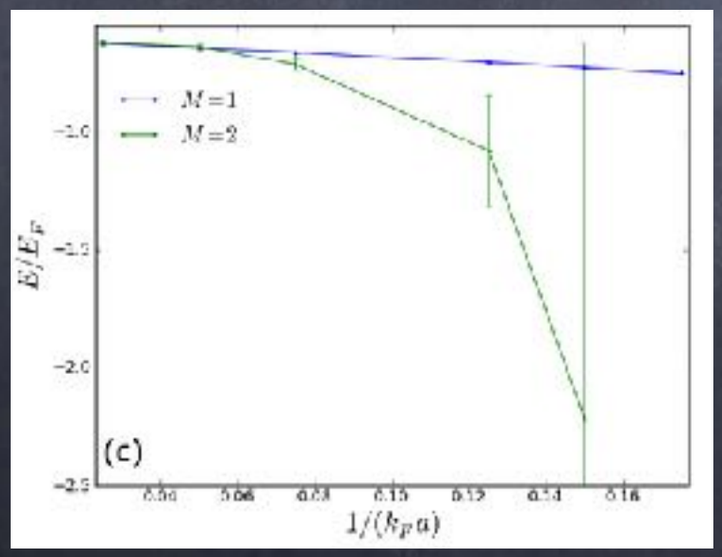
Importance Sampling:

$$\langle D'|H_{is}|D\rangle = \langle D'|H|D\rangle \frac{\langle \Psi_T|D'\rangle}{\langle \Psi_T|D\rangle}$$



Helps at unitarity, but we are still stuck beyond that!

At Unitarity



Want to be at 1/a=0.9

Past Unitarity

$N = 33, \Lambda = 20$

Choosing the wave function

Build it recursively from the Fermi Sea!

Partial Node

Set the sign-positive terms of H_{is} to 0.

$$\langle D'|H_{is}|D\rangle \quad \begin{pmatrix} 2 & 7r & -4 \\ 7r & 6 & r \\ -4 & r & 3 \end{pmatrix}$$

r=0: Easy to simulate; wrong answer

Extrapolate to r=1 from r<1!

- Similar in spirit to ivec
- Advantages: Ate right answer

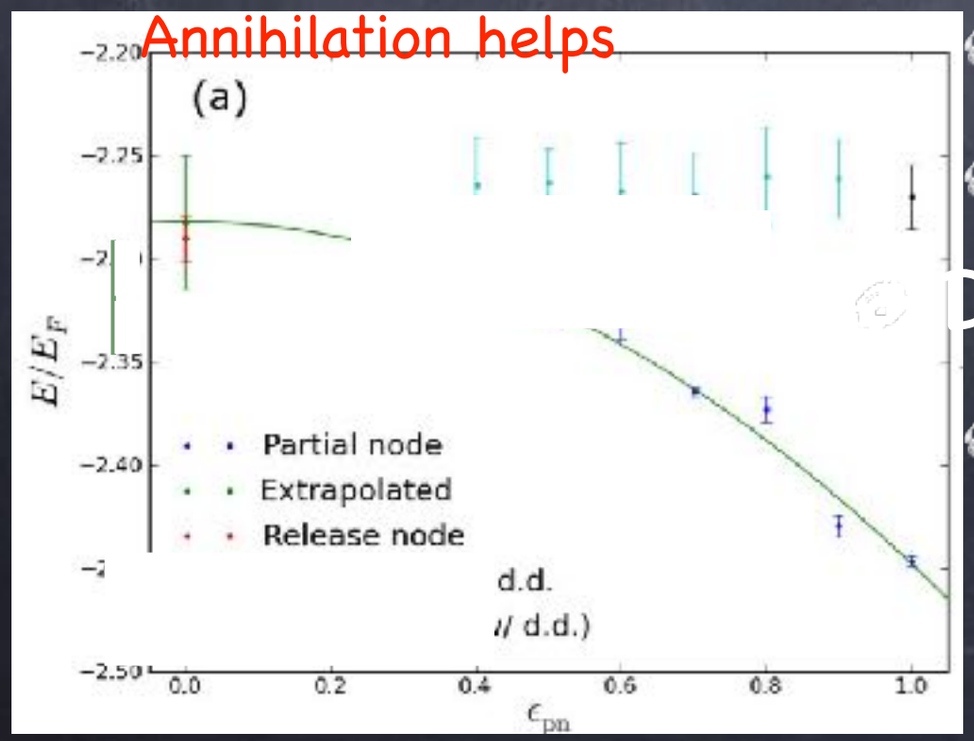
r=1: Hard to simulate; right answer

- Can put in physics! $r \equiv (1-\epsilon)$
- Can control bad sign problems.
- Markovian

Disadvantages:

- could push in wrong direction.

Annihilation helps



(d)

No imp. samp.

Partial node

Inv. corr. time

10^1

10^0

10^{-1}

10^{-2}

10^{-3}

(Flip rate)$/E_F$

0.0

0.2

0.4

0.6

0.8

1.0

ϵ_{pr}

Release Node

Better trial functions = smaller beta needed

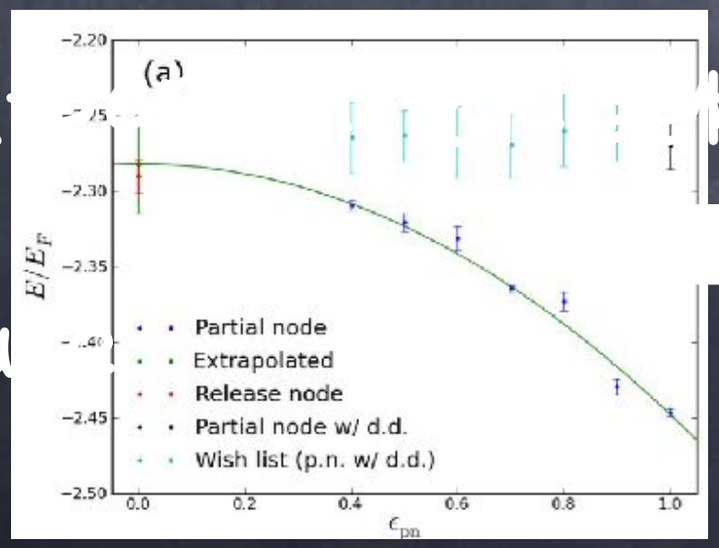
$$\exp[-\beta H]|\Psi_T\rangle$$

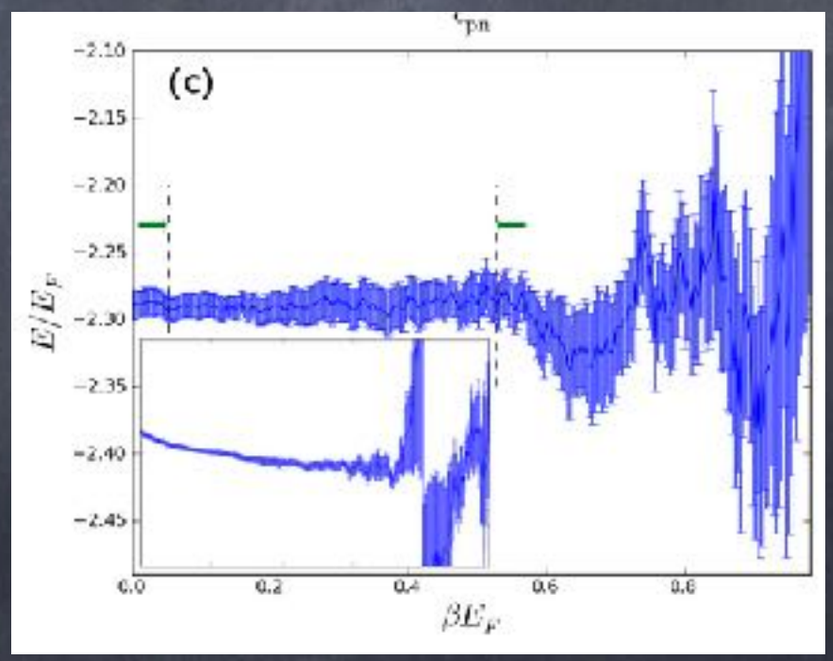
$$\exp[-\beta H][\alpha_0|\Psi_0\rangle + \alpha_1|\Psi_1\rangle + \alpha_2|\Psi_2\rangle]$$

$$\alpha_0 \exp[-\beta E_0]|\Psi_0\rangle + \alpha_1 \exp[-\beta E_1]|\Psi_1\rangle + \alpha_2 \exp[-\beta E_2]|\Psi_2\rangle$$

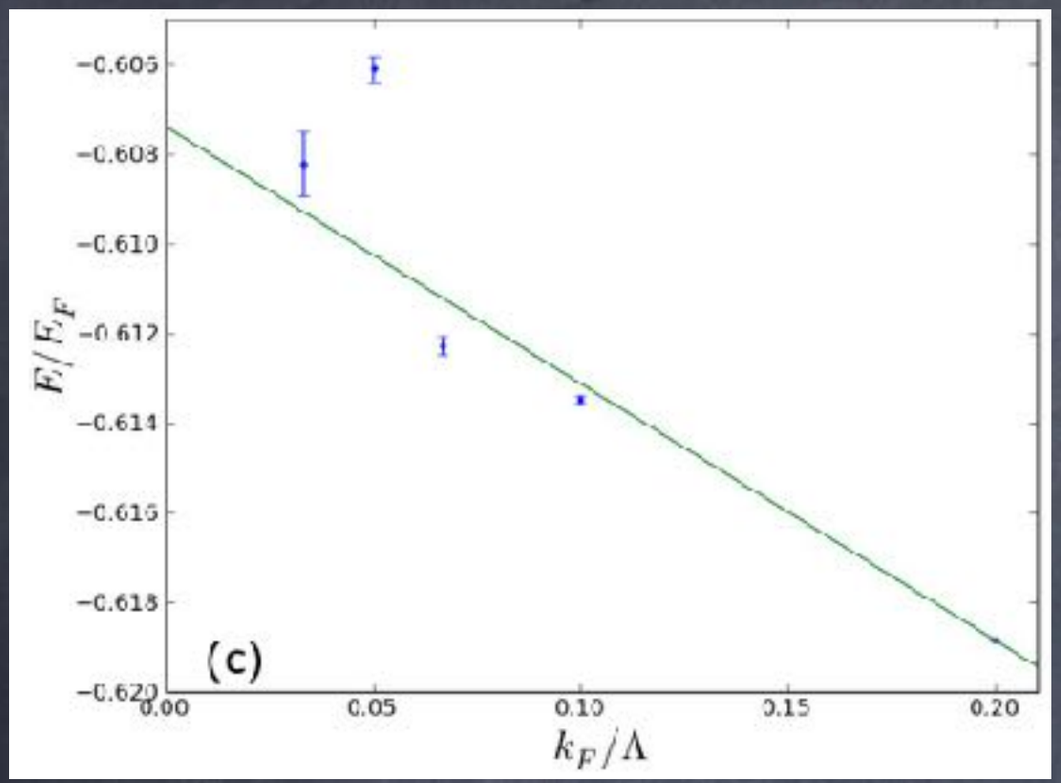
Use g.s. of $H_{is}[r = 0.4]$ for the trial w.f

- Propagate walkers
- Measure





Extrapolating

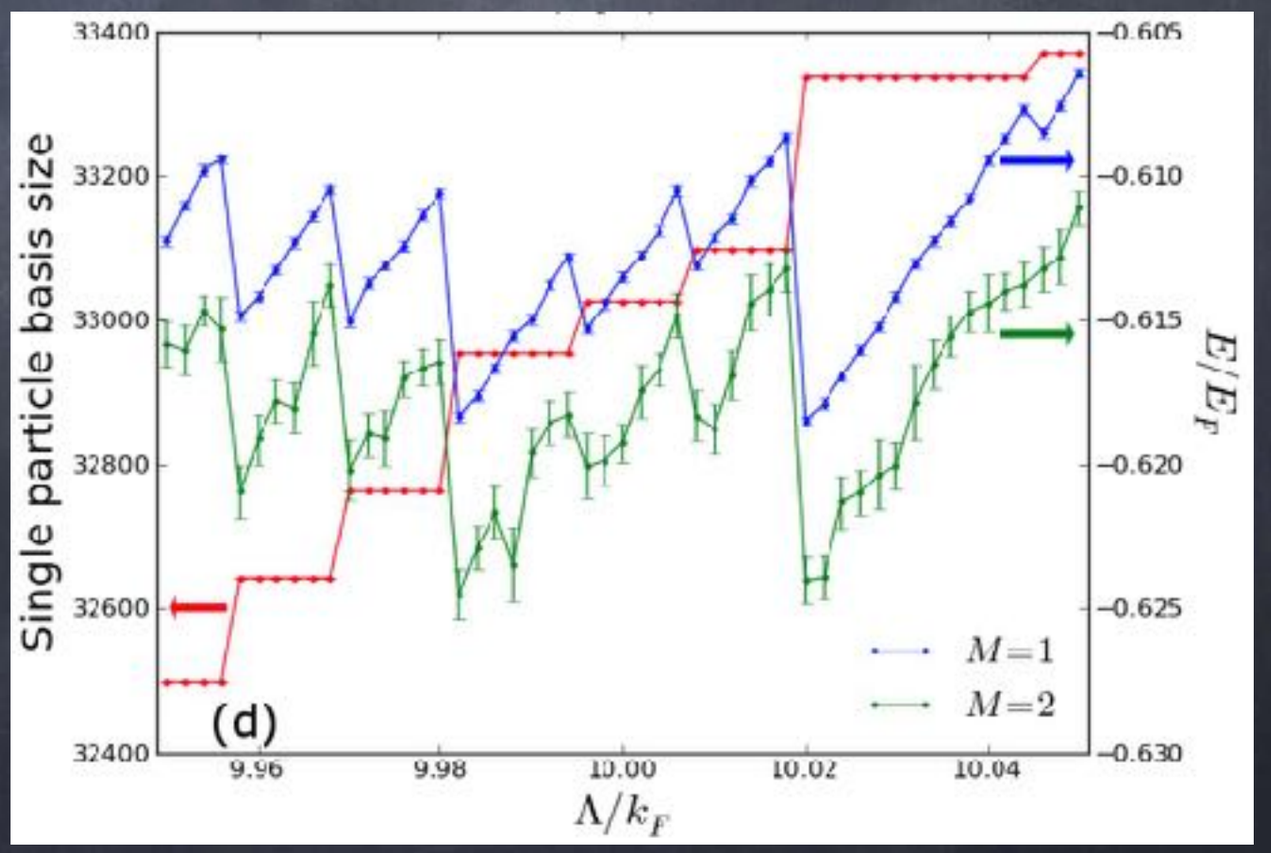


Why is this extrapolation so bad?

$$\Lambda \to \infty$$

This is because N=33 and not infinite N.

How do we get to the thermodynamic limit?



An infinite number of bi

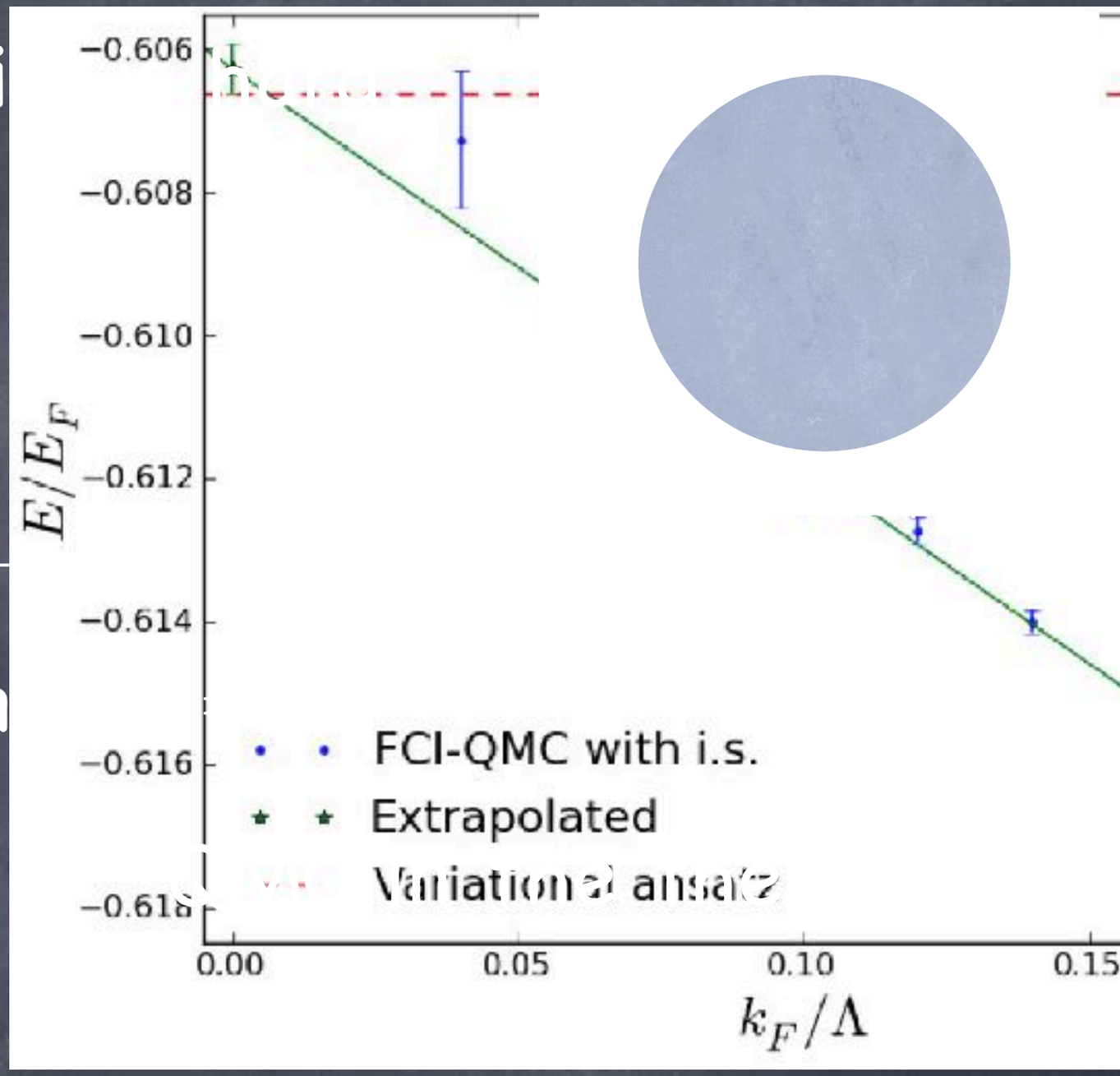
Represent:

$$|FS\rangle$$

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

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

List holes, list excitation

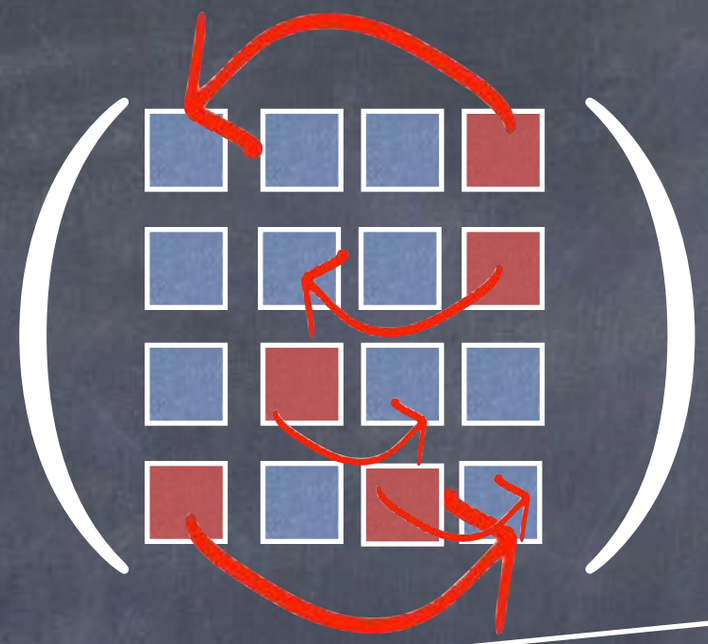


2 concerns

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

Fixed node

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



Partial node: ■ set to 0

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

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

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

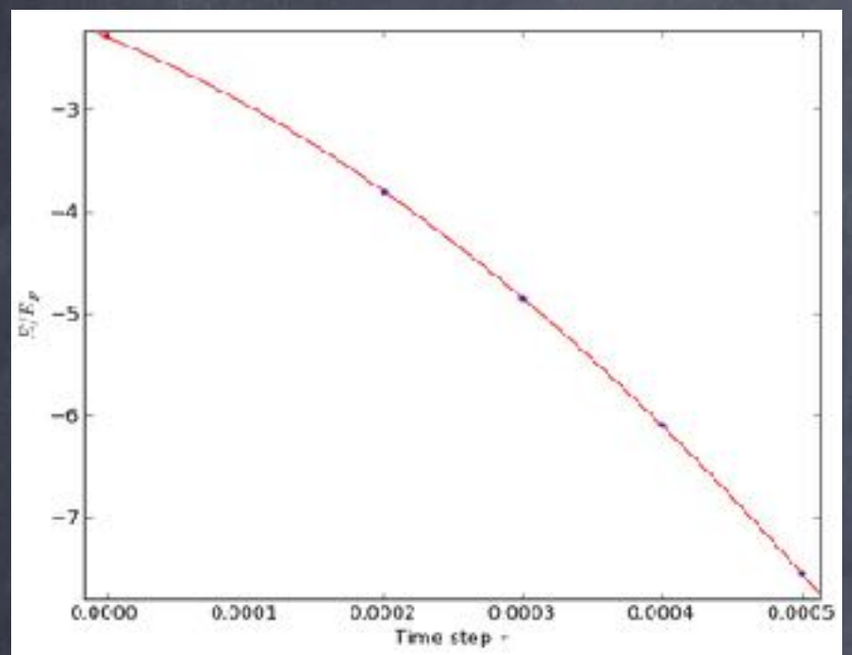
Stochastic Diagonal Dumping

- 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

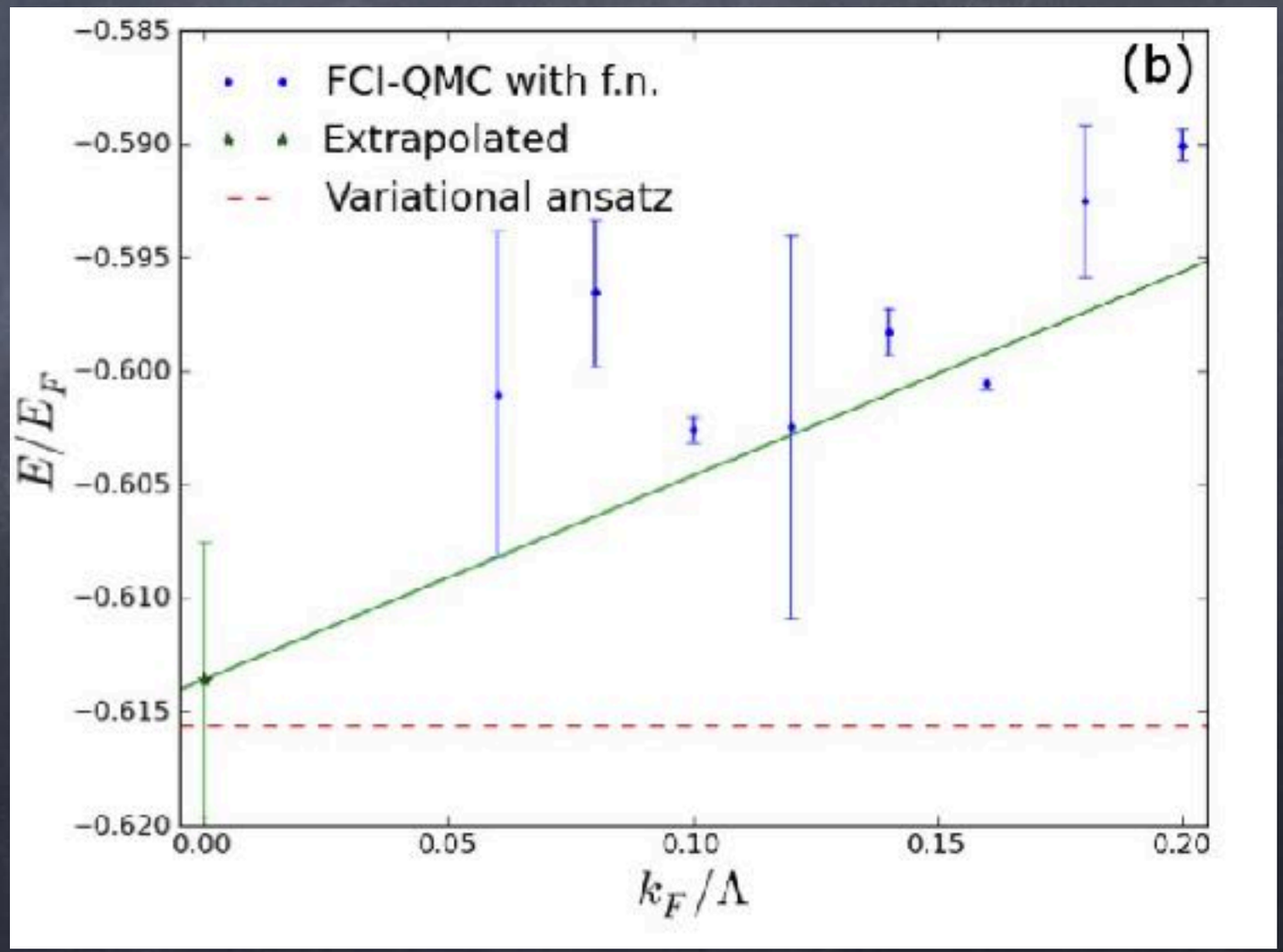
Formally correct, but 'bad' if $U_{\rm diag} \ll -1$

Add 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!



What have we done?

- Importance sampling with smart wave-function
- Partial Node
- Release Node
- QMC in the thermodynamic limit!
  - Fixed Node even with 10^6 connected terms (with a time step error)

Significantly improved over current state of art!

Now we are actually better then fixed node.

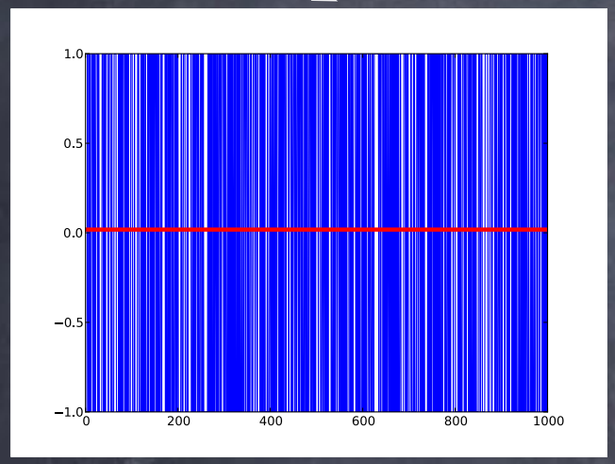
Better constraint and more examples soon ...

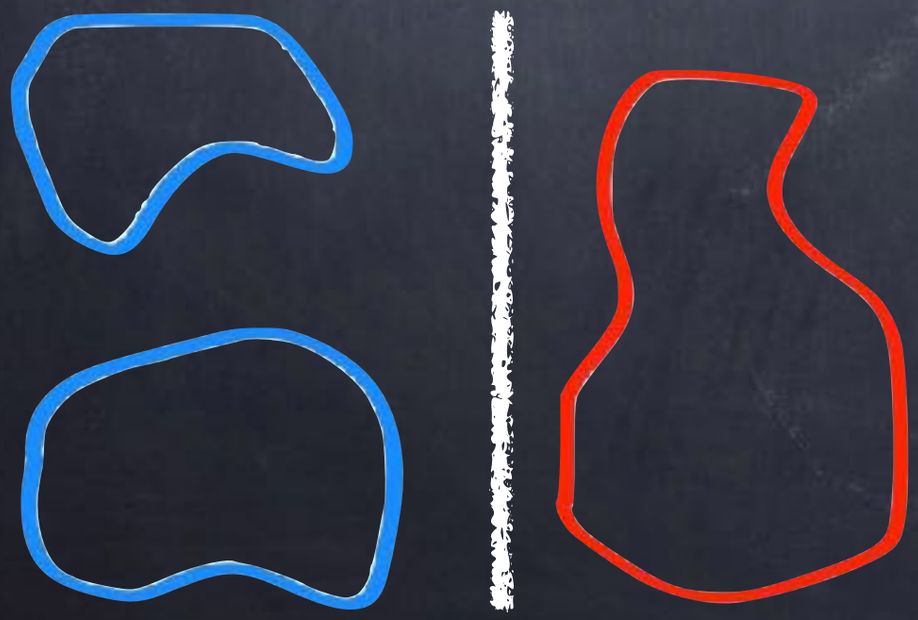
Story 3: Path Integrals

Goal: Further our understanding of what's hard and what's easy.

Signs from Permutations

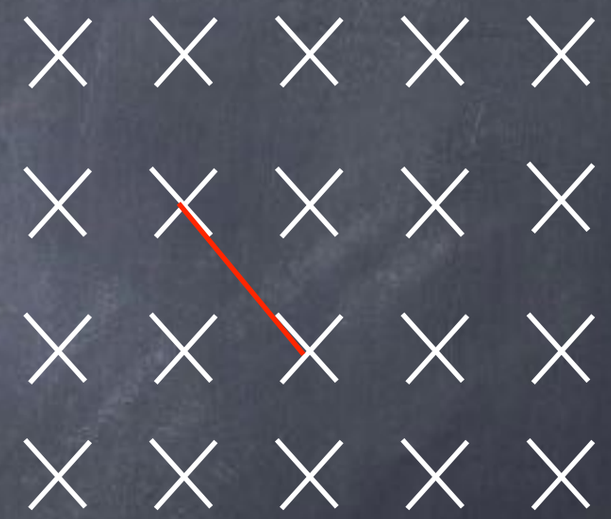
$$\langle E \rangle = \frac{\sum_{\pi,R} (-1)^{|\pi|} E(R) p(R,\pi)}{\sum_{\pi,R} (-1)^{|\pi|} p(R,\pi)}$$

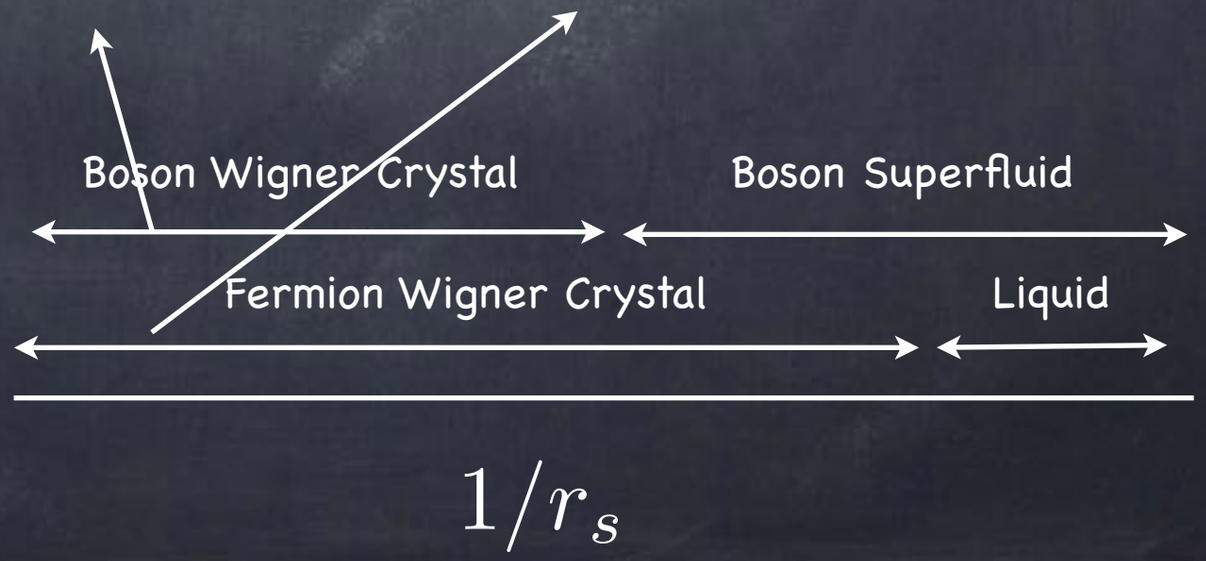




Boson

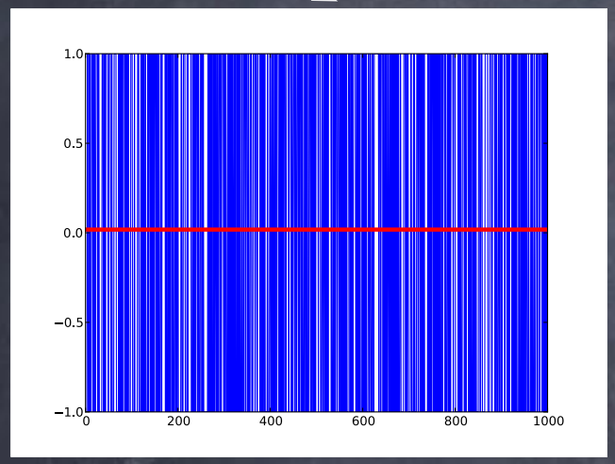
Fermion

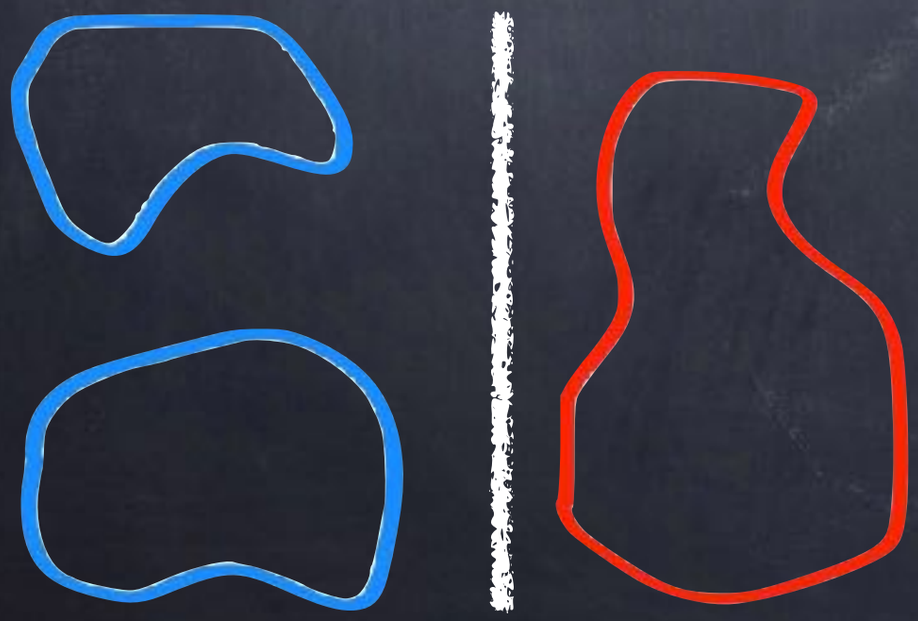




Signs from Permutations

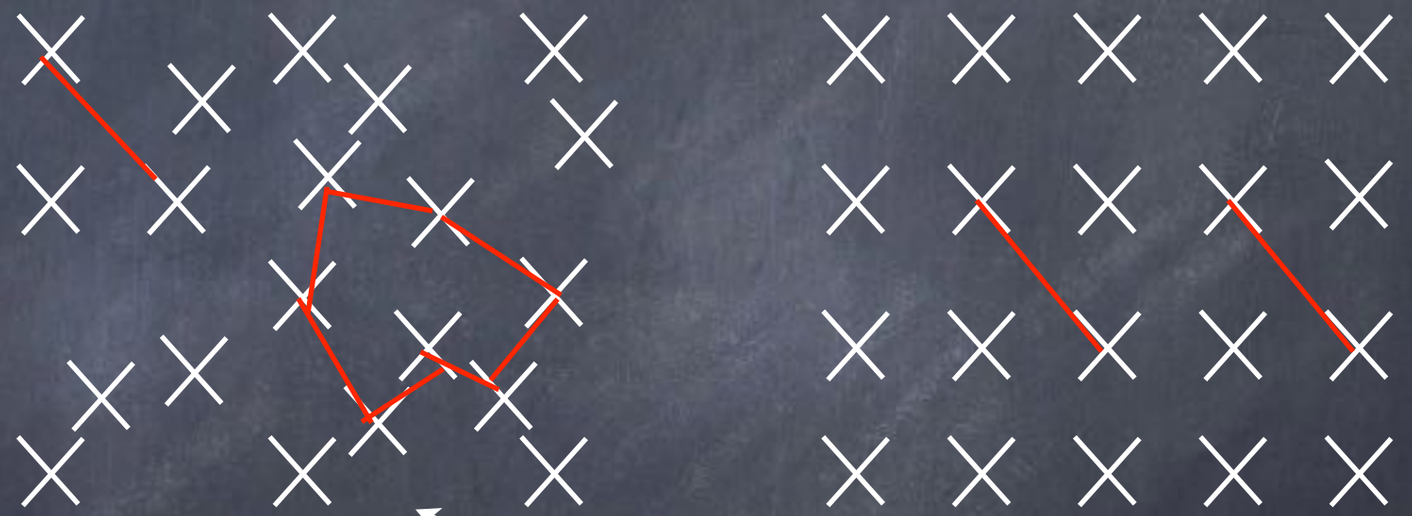
$$\langle E \rangle = \frac{\sum_{\pi,R} (-1)^{|\pi|} E(R) p(R,\pi)}{\sum_{\pi,R} (-1)^{|\pi|} p(R,\pi)}$$

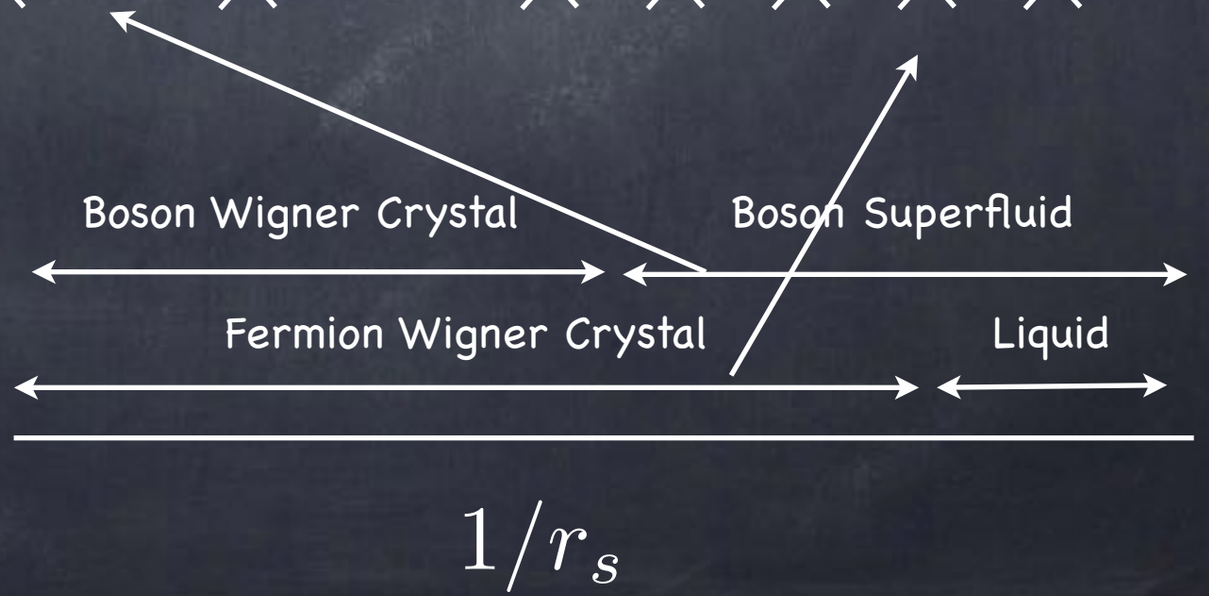




Boson

Fermion





First Case: Both Solids

Still a sign problem! - Sign exponentially small and dwarfed by noise!

Break configurations up into n groups.

Two possible contributions:

- Some sets of configurations unlikely (say big loops) and so contribution is small.
- Some sets of configurations likely but they subtract to a small number.

Both of these contribute to the 'sign problem' noise when you simulate.

Noise Type I

$$\frac{C_a + C_b - C_c + C_d - C_e + C_f}{C_a + C_b + C_c + C_d + C_e + C_f}$$

small (not many of the configs):

$$= \frac{C_a}{C_a + C_b} \frac{C_a + C_b}{C_a + C_b + C_c} \frac{C_a + C_b + C_c}{C_a + C_b + C_c + C_d} \cdots$$

relative error! (also can be done by importance sampling)

We can fix this! Like fixed node, we've uncovered some part of the noise that's actually easy.

Also makes our algorithms better -- don't spend exponettial work on the 'easy' stuff!

Noise Type II

big

$$\frac{C_a + C_b - C_c + C_d - C_e + C_f}{C_a + C_b + C_c + C_d + C_e + C_f}$$

small: That's a problem.

Q: Does this type of noise show up in solids that are both fermionic and bosonic?

A toy model:

Assume each particle is either in a pair permutation or isn't

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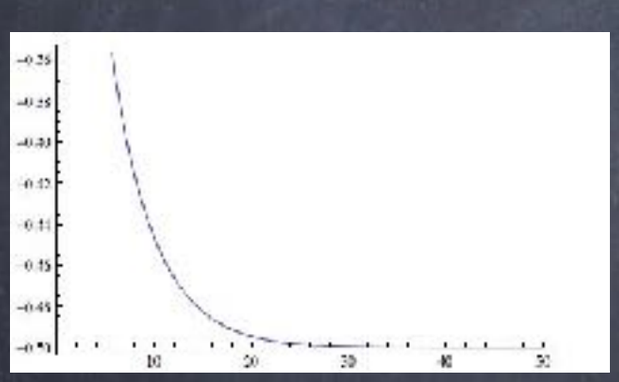
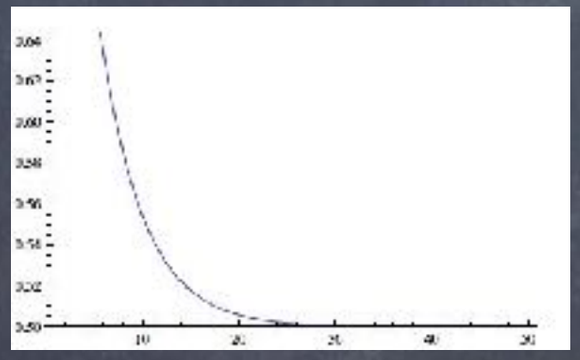
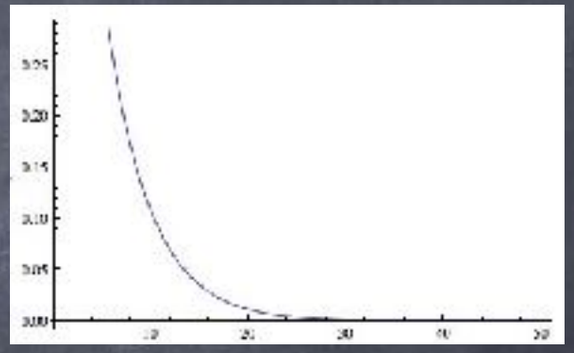
even configs - odd configs = exp small







Still a sign problem! (naively) - currently looking at smarter breakups.

Suggests an approximation:

Calculate p, use toy model answers.

Conclusions

- Wave-functions make QMC better then CCSD(T) for molecules
- Major improvements to FCI-QMC
- Starting to understand the true nature of the sign in path integrals

Fermions have exponentially small partition functions.

You might contribute to a small partition function because:

- positive and small "tractable"
- the small difference of two big terms. "hard"
- the small difference of two small terms. "tractable"
- the big difference of two big terms "tractable"

$$\frac{C_a + C_b - C_c + C_d - C_e + C_f}{C_a + C_b + C_c + C_d + C_e + C_f}$$

small (not many of the configs): $\frac{C_a}{C_a + C_b + C_c + C_d + C_e + C_f}$

$$= \frac{C_a}{C_a + C_b} \frac{C_a + C_b}{C_a + C_b + C_c} \frac{C_a + C_b + C_c}{C_a + C_b + C_c + C_d} \cdots$$

relative error! (also can be done by importance sampling)

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$$\frac{C_a + C_b - C_c + C_d - C_e + C_f}{C_a + C_b + C_c + C_d + C_e + C_f}$$

difference between small things: $\frac{C_c}{C_a + C_b + C_c + C_d + C_e + C_f}$

relative error! Sum or subtraction of small things is fine if we have relative error.

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$$\frac{C_a + C_b - C_c + C_d - C_e + C_f}{C_a + C_b + C_c + C_d + C_e + C_f}$$

big: relative error on each is 10% so total error is ~10%

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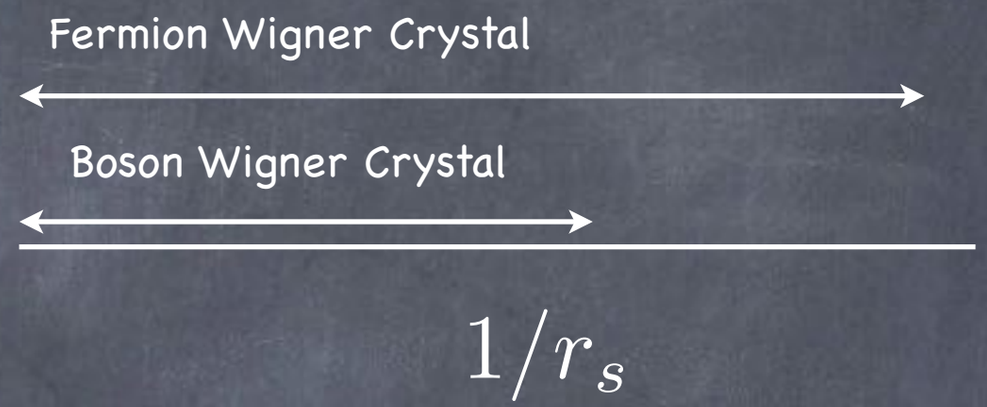
$$\frac{C_a + C_b - C_c + C_d - C_e + C_f}{C_a + C_b + C_c + C_d + C_e + C_f}$$

small: That's a problem.

Does that solve me?



A toy model:

1 1 1 1

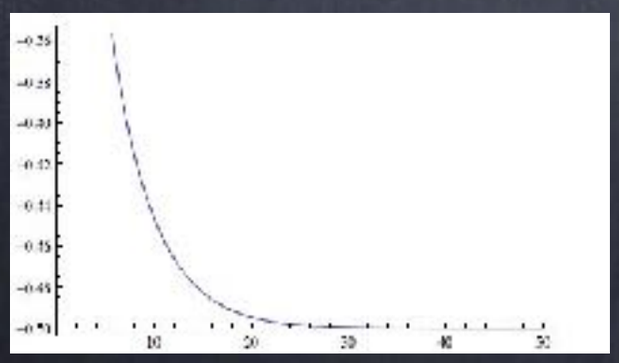
1 1 1 1

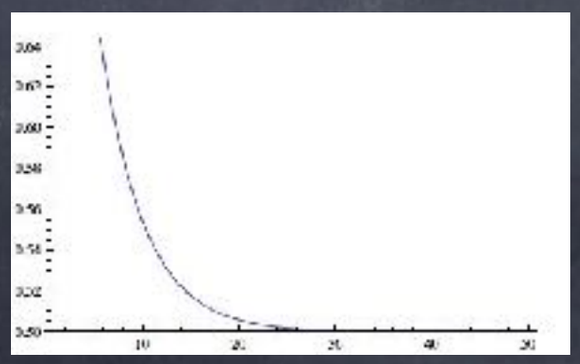
1 1 1 1

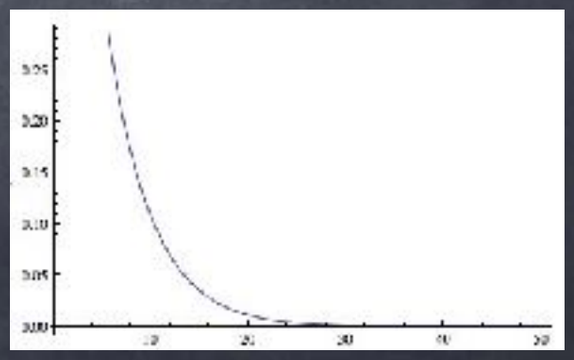
Sign problem still there!

2 1 1 1

even configs - odd configs = exp small

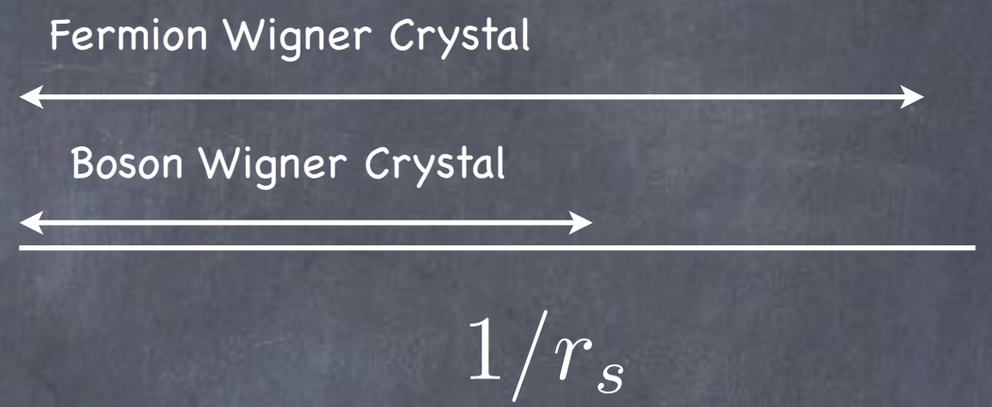




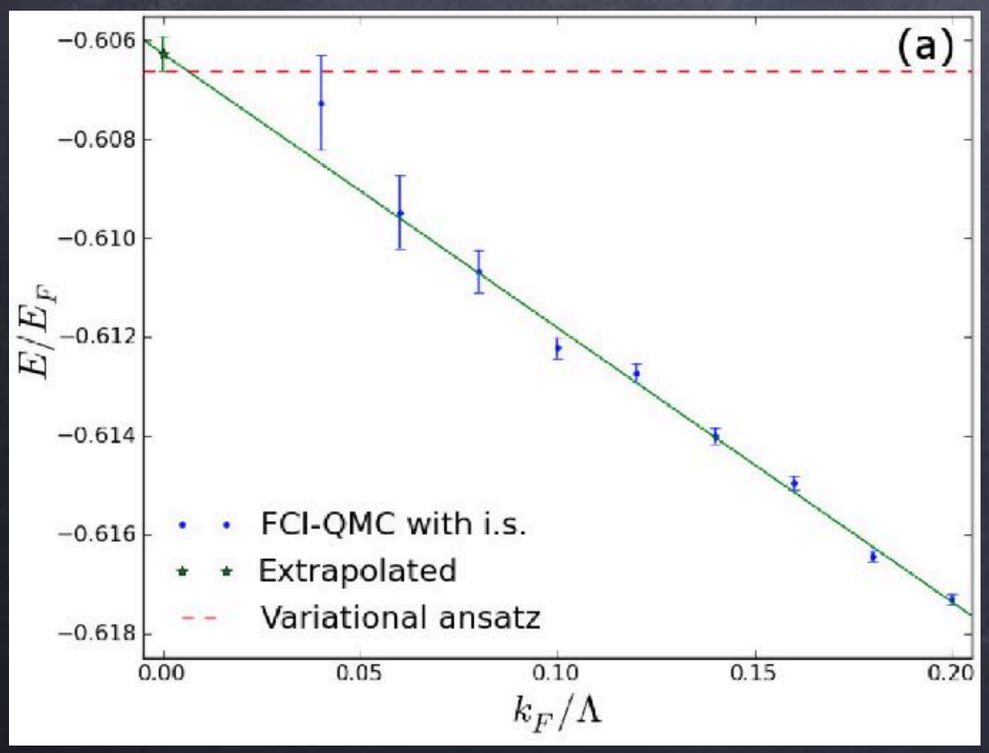


Suggests an approximation:
Calculate p, use toy model answers.

What about here?



Approximation breaks down because independence is really broken. Maybe we can assume large loops don't matter since they often cross nodes?


(a)
−0.606
−0.608
−0.610
−0.612
−0.614
−0.616
−0.618
E/E_F
FCI-QMC with i.s.
Extrapolated
Variational ansatz
0.00
0.05
0.10
0.15
0.20
k_F/Λ

Loops<1

Loops<2

Loops<3

Loops<4

All Permutations

$$\frac{\sum_i E_i s_i}{\sum_i s_i} \qquad \sum_i s_i = \frac{p(R,\pi_4)S(\pi_4)}{p(R,\pi_4)}$$

$$\frac{p(R,\pi_1)S(\pi_1)}{p(R,\pi_1)} \frac{p(R,\pi_2)S(\pi_2)}{p(R,\pi_1)S(\pi_1)} \frac{p(R,\pi_3)S(\pi_3)}{p(R,\pi_2)S(\pi_2)} \frac{p(R,\pi_4)S(\pi_4)}{p(R,\pi_3)S(\pi_3)} \frac{p(R,\pi_1)}{p(R,\pi_2)} \frac{p(R,\pi_2)}{p(R,\pi_3)} \frac{p(R,\pi_3)}{p(R,\pi_4)}$$

$$\frac{p(R,\pi_2)S(\pi_2)}{p(R,\pi_2)} \qquad \frac{p(R,\pi_1)S(\pi_1)}{p(R,\pi_2)}$$

$$\frac{p(R,\pi_1) - p(R,\pi_{2,o}) + p(R,\pi_{2,e})}{p(R,\pi_1)} = 1 + \frac{-p(R,\pi_{2,o}) + p(R,\pi_{2,e})}{p(R,\pi_1)}$$

$$\frac{p(R,\pi_2)S(\pi_2)}{p(R,\pi_3)} \qquad \frac{p(R,\pi_3)S(\pi_3)}{p(R,\pi_3)}$$

$$\frac{-p(R,\pi_{2,o}) + p(R,\pi_{2,e}) - p(R,\pi_{3,o}) + p(R,\pi_{3,e})}{-p(R,\pi_{2,o}) + p(R,\pi_{2,e})} = 1 + \frac{-p(R,\pi_{3,o}) + p(R,\pi_{3,e})}{-p(R,\pi_{2,o}) + p(R,\pi_{2,e})}$$

$$\sum_i s_i = \frac{p(R,\pi_4)S(\pi_4)}{p(R,\pi_4)}$$

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

$$\left(1+\frac{-p(R,\pi_{3,o})+p(R,\pi_{3,e})}{-p(R,\pi_{2,o})+p(R,\pi_{2,e})}\right)\left(1+\frac{-p(R,\pi_{4,o})+p(R,\pi_{4,e})}{-p(R,\pi_{3,o})+p(R,\pi_{3,e})}\right)\left(1+\frac{-p(R,\pi_{5,o})+p(R,\pi_{5,e})}{-p(R,\pi_{4,o})+p(R,\pi_{4,e})}\right)$$