A Full Configuration Interaction QMC Perspective on the Homogeneous Electron Gas

James Shepherd

Quantum Monte Carlo in the Apuan Alps
31st July 2012

Why?

- A real challenge for FCI(QMC)
- ...a new method in fully-periodic calculations
- Model systems can give physical insight without added complexity of real systems
- ...an application with development in mind
- Exact (finite/complete basis) energy benchmarks
- What does the wavefunction look like?

70 years of history...

- 1934 Wigner crystal
- 1956 Landau theory of Fermi liquids
- 1957 Gell-Mann & Brueckner RPA
- 1962 Overhauser spin/charge density waves
- 1980 Ceperley-Alder QMC

...and so much more.

DMC: very successful

Phase transitions, spectral functions, effective mass, QP renomalization factor

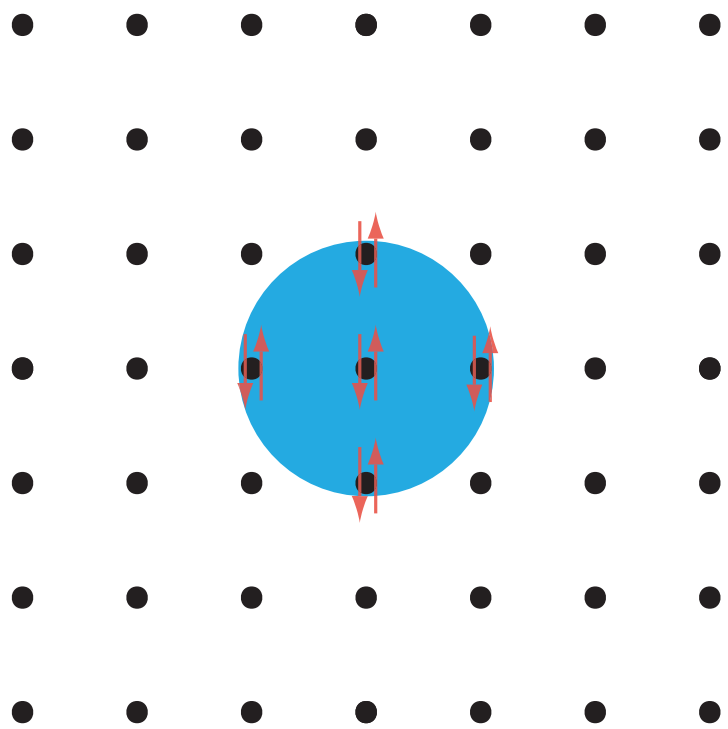
(Ceperley, Needs, Holzmann, Drummond, Foulkes, Ballone, Gurturbay etc. etc.)

Post-HF quantum chemistry: new studies of the solid state (e.g. LiH)

(Schutz, Manby, Kresse, Stoll, Fulde etc. etc.)

Open question: what does $|\Psi\rangle = \sum_{\mathbf{i}} c_{\mathbf{i}} |D_{\mathbf{i}}\rangle$ look like?

$$\hat{H} = \sum_{\alpha} -\frac{1}{2}\nabla_{\alpha}^{2} + \sum_{\alpha\neq\beta} \frac{1}{2}\hat{v}_{\alpha\beta} + \text{const.}$$



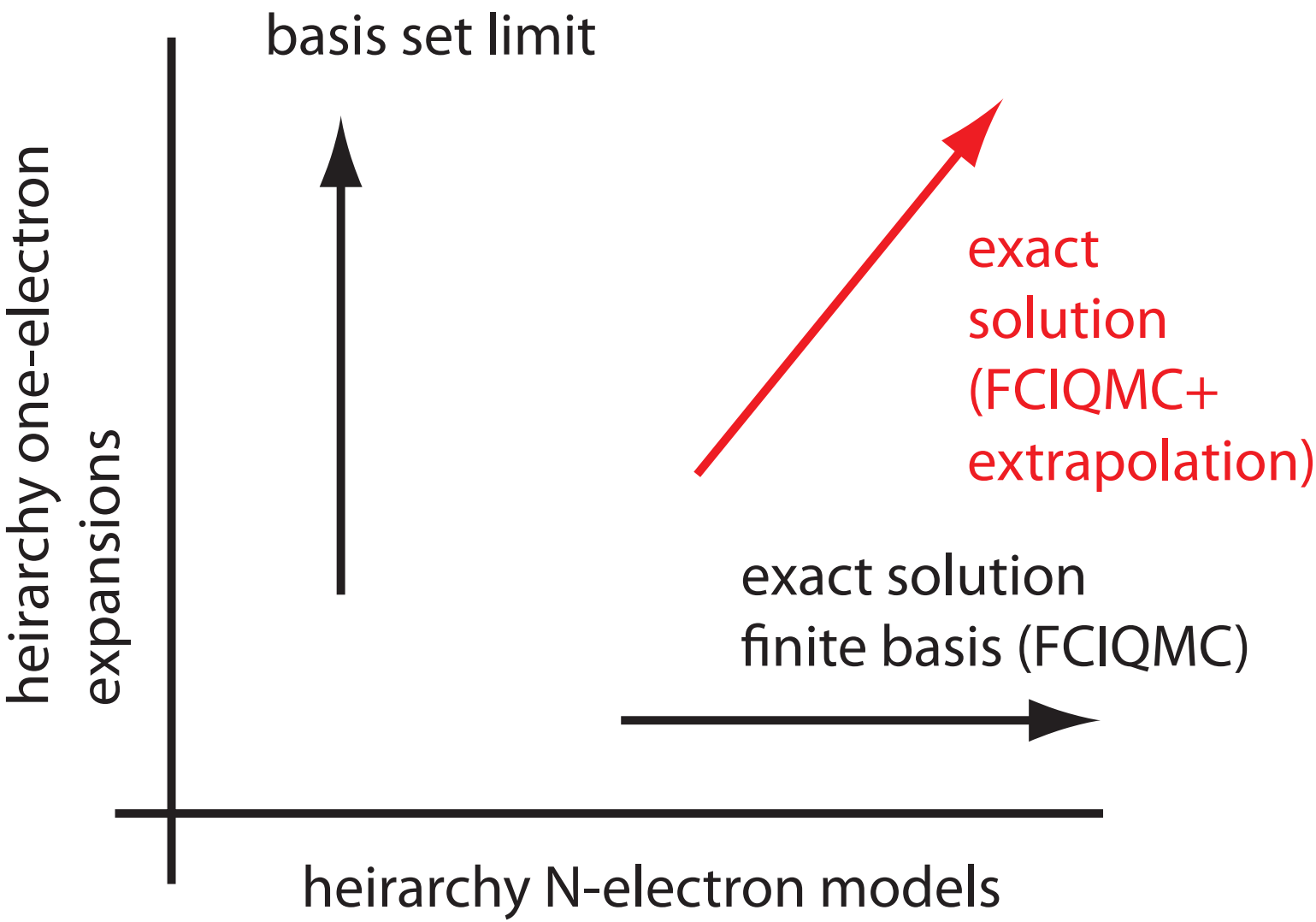
$$\psi_{\mathbf{k}} = \sqrt{\frac{1}{L^3}}\; e^{i\mathbf{k}\cdot\mathbf{r}}\; \delta_{s\sigma}$$

Finite particle number: N

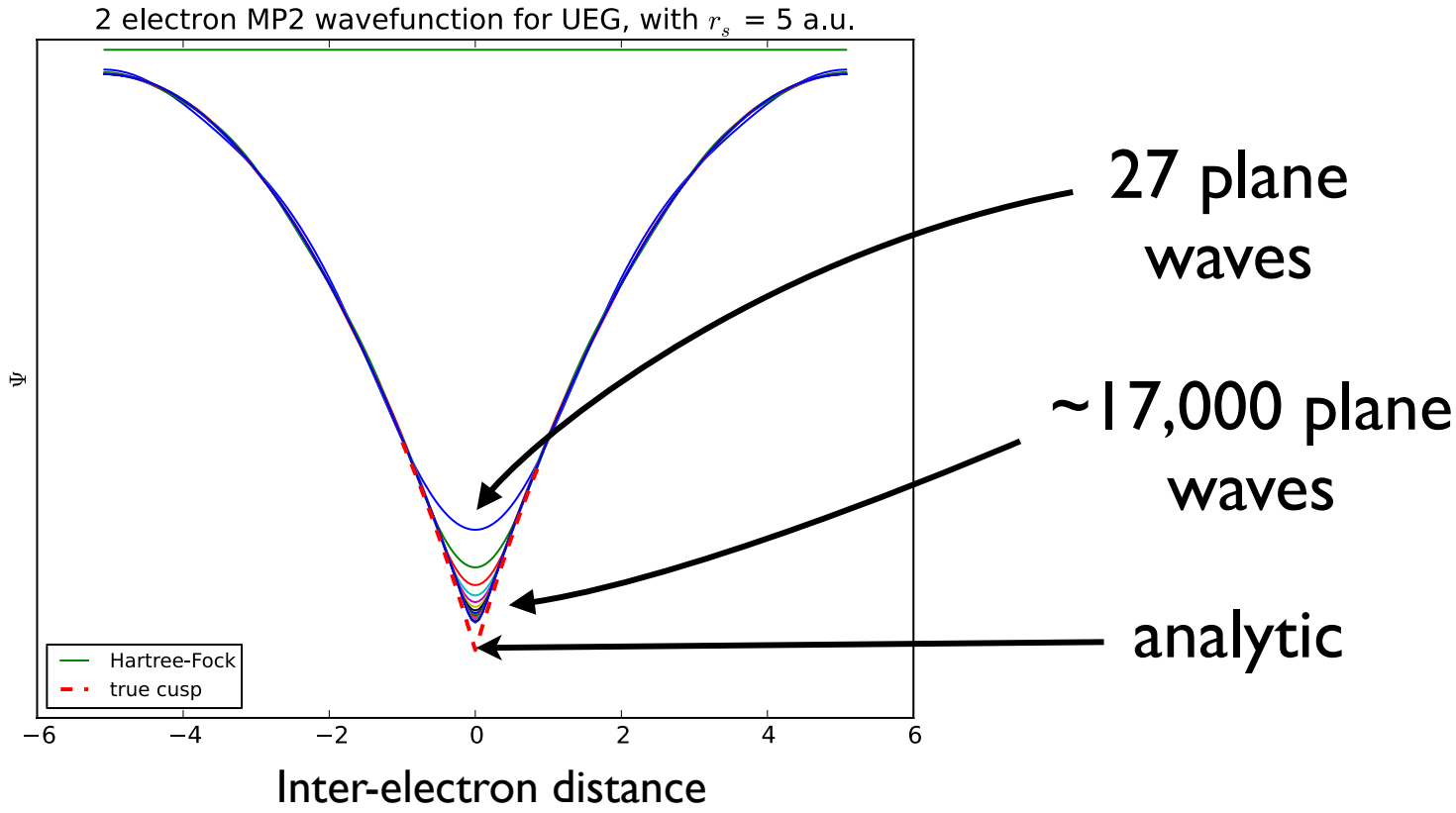
Uniform density: r_s

(I am discussing 3D but will show 2D schematics)

Using $|\Psi\rangle = \sum_{\mathbf{i}} c_{\mathbf{i}} |D_{\mathbf{i}}\rangle$ to solve $\hat{H}\Psi = E\Psi$



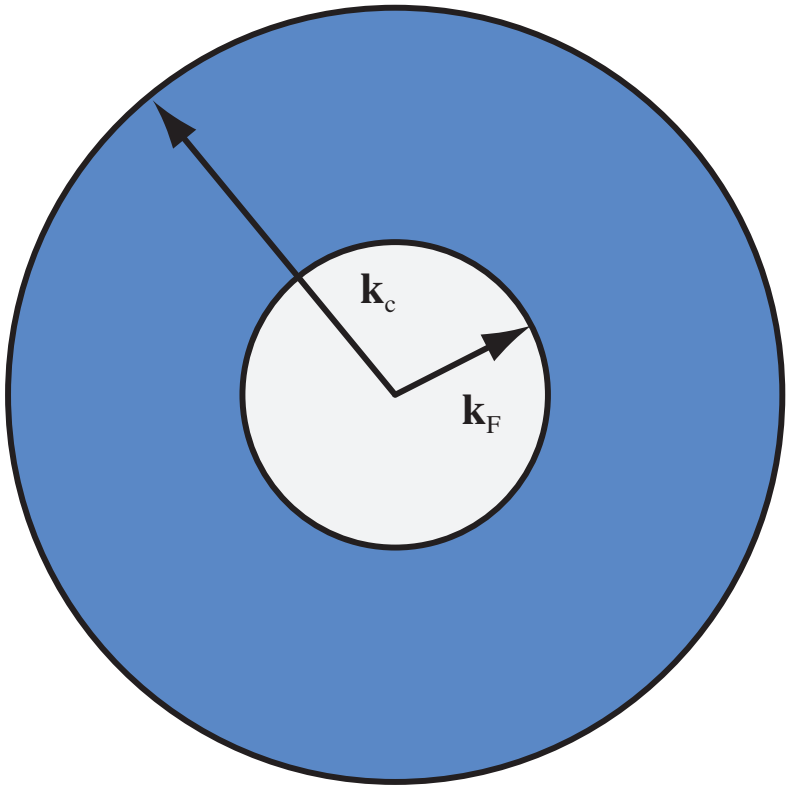
The problem with determinantal expansions...



... simulation-cell HEG has large amounts of dynamic correlation at real metal r_s-values

figure due to George Booth

Perturbative approaches (MP2, CCD(T)) diverge...



Simulate M with consistent N

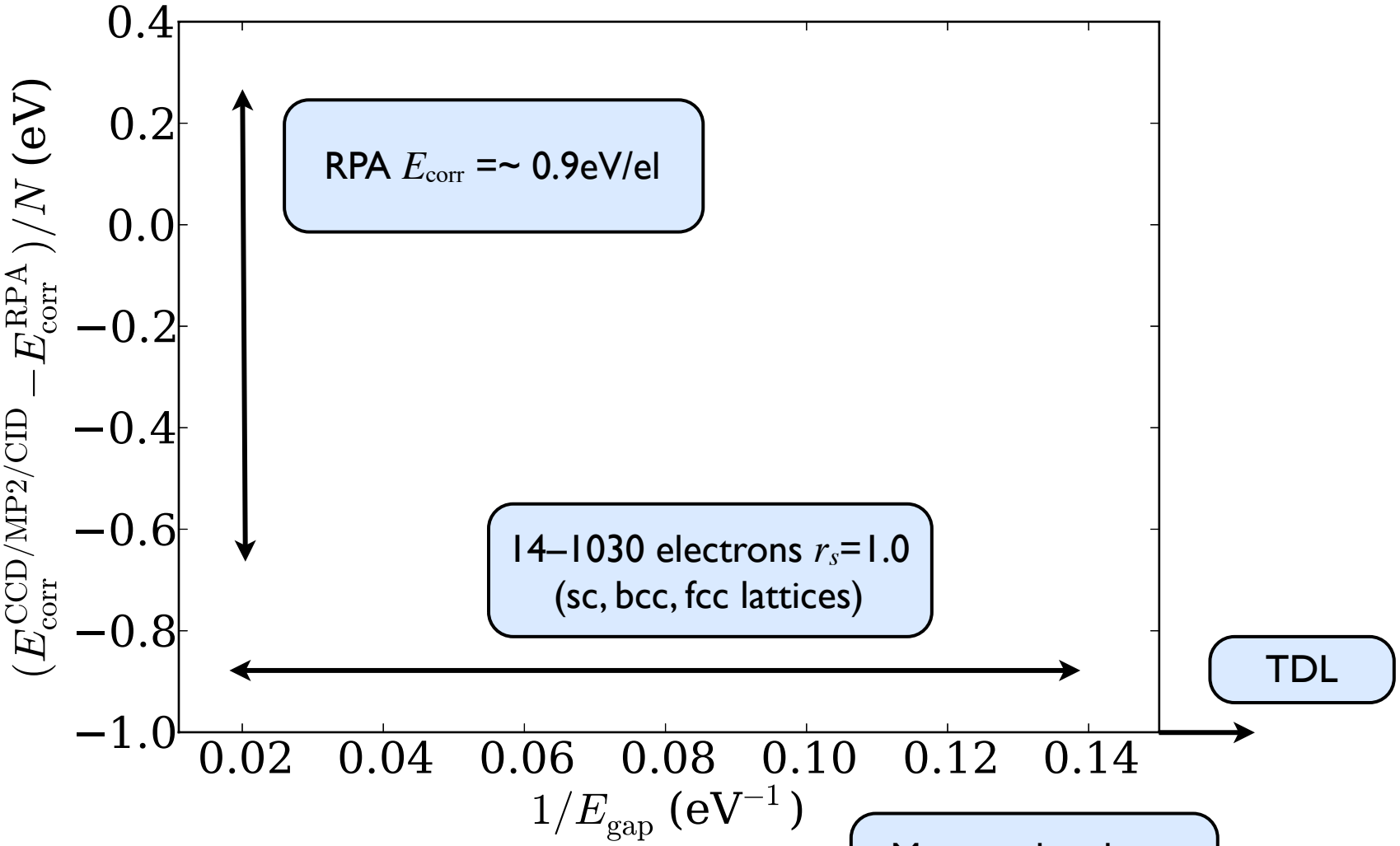
↓

Measure band gap (closes in TDL)

↓

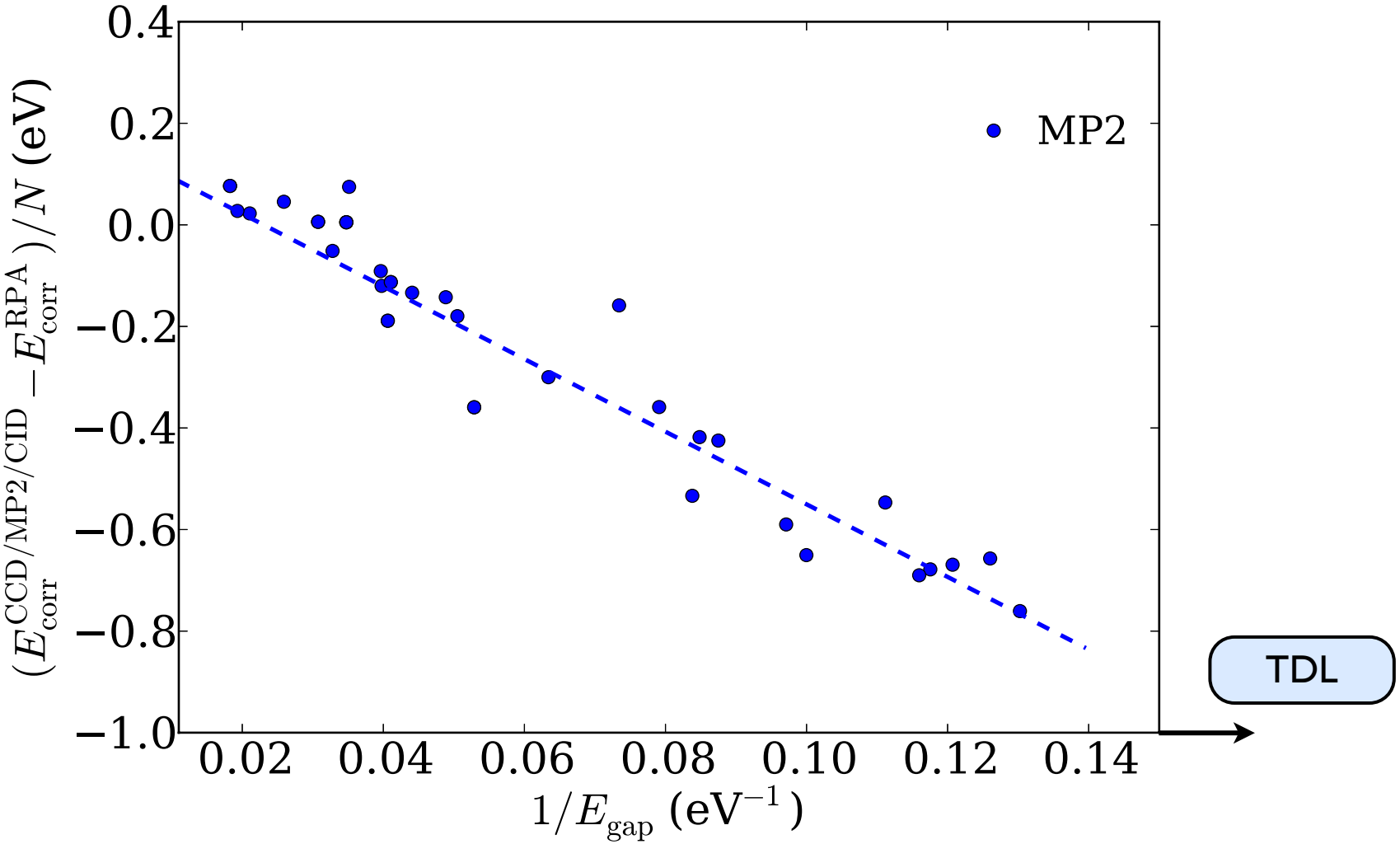
Take difference w.r.t RPA

Take difference w.r.t RPA



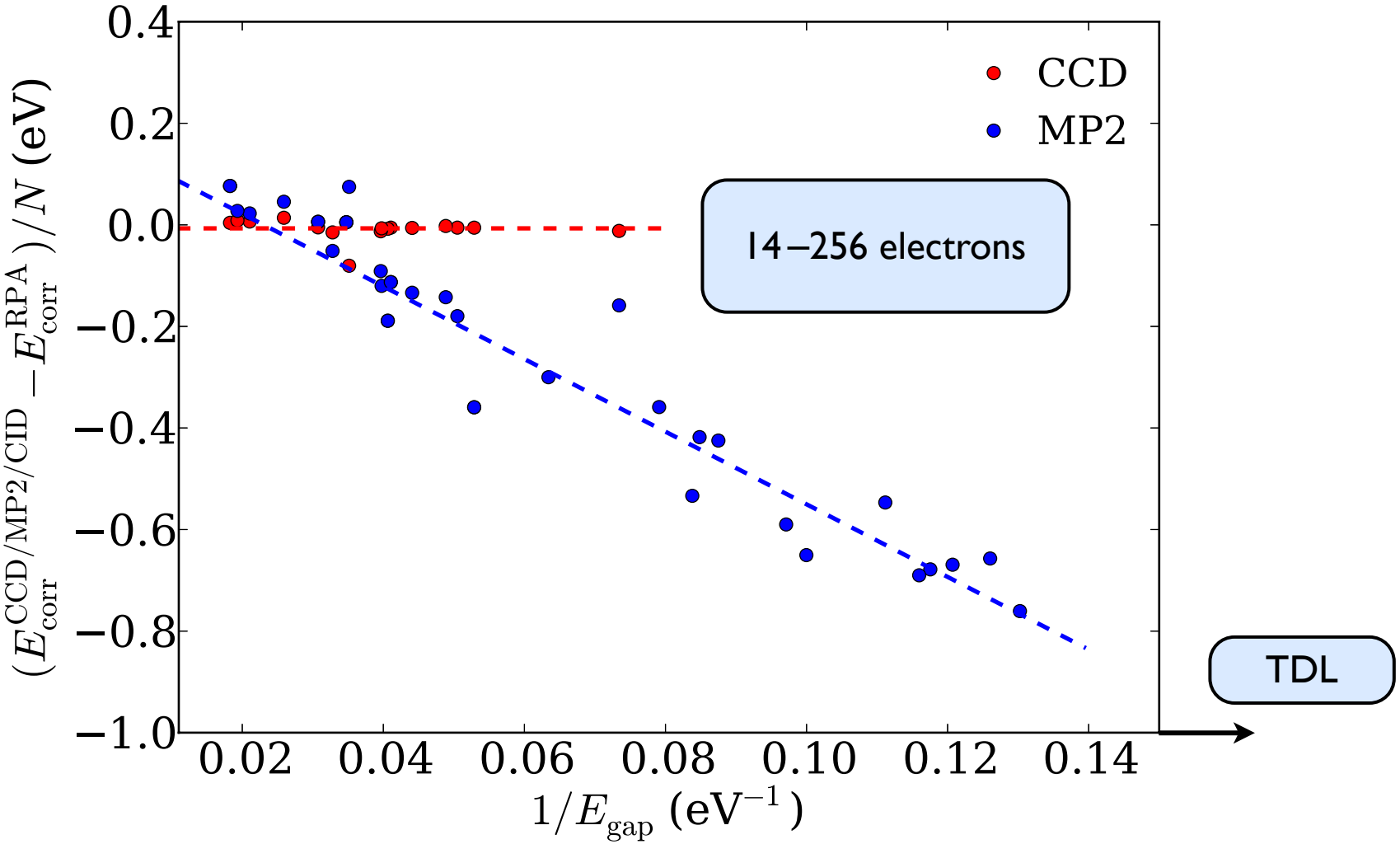
Measure band gap (closes in TDL)

MP2 diverges...



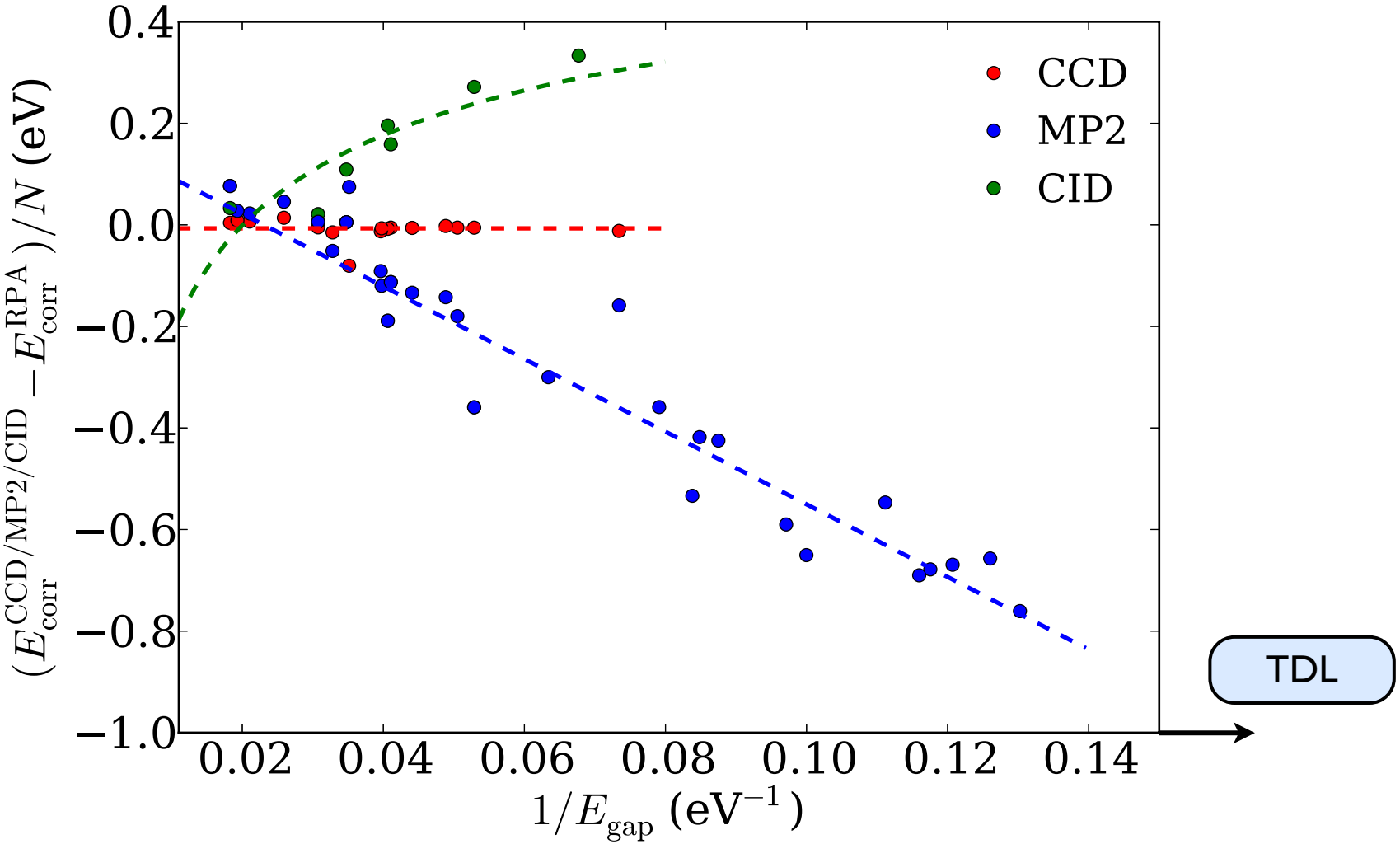
RPA due to Andreas Grueneis, VASP

CCD converges...



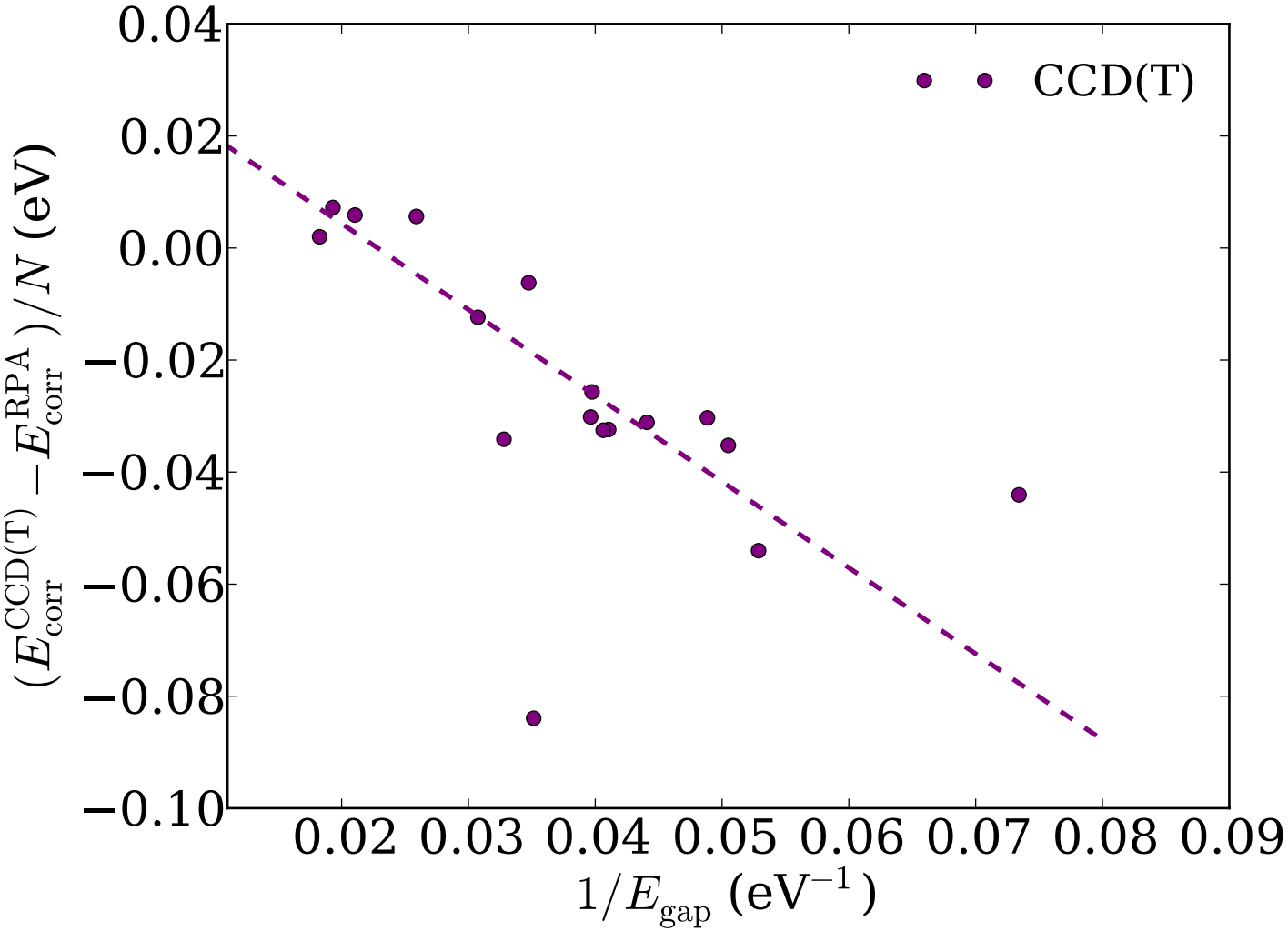
RPA/CCD due to Andreas Grueneis, VASP

CID goes to zero (C.E./elec)...



RPA/CCD due to Andreas Grueneis, VASP

...and CCD(T) diverges.



RPA/CCD(T) due to Andreas Grueneis, VASP

FCIQMC

$$|\Psi\rangle = \sum_{\mathbf{i}} c_{\mathbf{i}} |D_{\mathbf{i}}\rangle$$

+

$$\Psi_0 = \lim_{\tau\to\infty} e^{-\tau(\hat{H}-S)}\Psi_{\tau=0}$$

$$\downarrow$$

$$-\frac{dc_{\mathbf{i}}}{d\tau} = (H_{\mathbf{ii}} - S)c_{\mathbf{i}} + \sum_{\mathbf{j}\neq\mathbf{i}} H_{\mathbf{ij}} c_{\mathbf{j}}$$

FCIQMC: GH Booth, AJW Thom, A Alavi, JCP 131 5, 054106 (2009)

FCIQMC

Walker population

Spawning

$$-\overbrace{\frac{dc_{\mathbf{i}}}{d\tau}} = \underbrace{(H_{\mathbf{ii}} - S)c_{\mathbf{i}}} + \overbrace{\sum_{\mathbf{j}\neq\mathbf{i}} H_{\mathbf{ij}} c_{\mathbf{j}}}$$

Death/cloning

Instantaneous $\Psi(\tau), H_{\mathbf{ij}}(\tau)$

FCIQMC: GH Booth, AJW Thom, A Alavi, JCP 131 5, 054106 (2009)

Initiator FCIQMC (i-FCIQMC)

Coupling of $\Psi(\tau), H_{\mathbf{ij}}(\tau)$

Only consider $H_{\mathbf{ij}}$ over those determinants with a certain population

$$-\frac{dc_{\mathbf{i}}}{d\tau} = (H_{\mathbf{ii}} - S)c_{\mathbf{i}} + \sum_{\mathbf{j}\neq\mathbf{i}} H_{\mathbf{ij}} c_{\mathbf{j}}$$

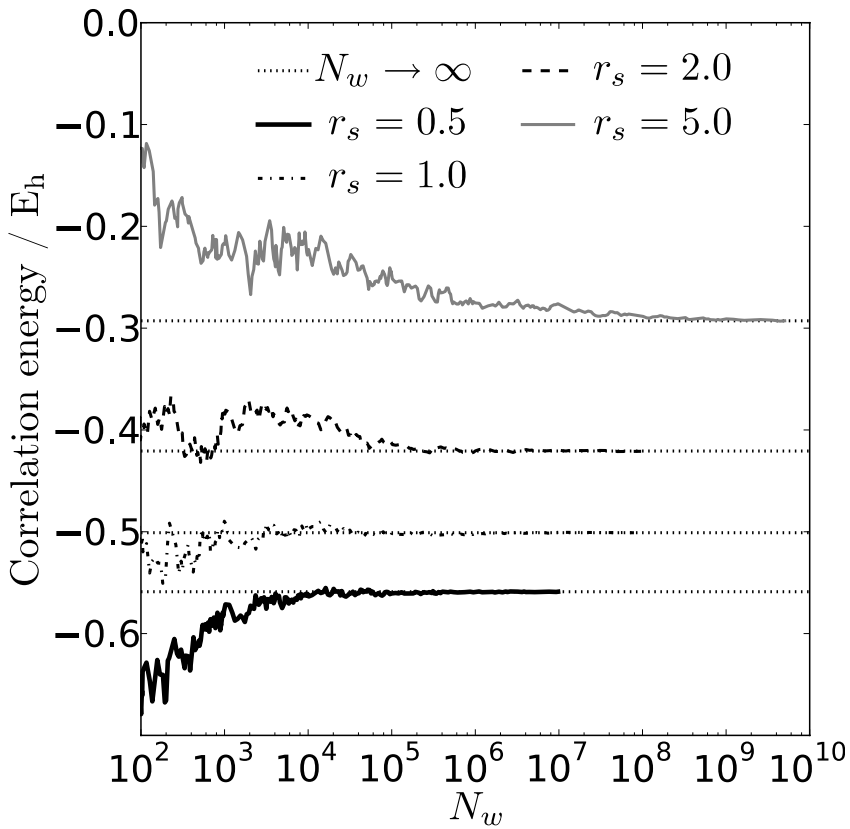
Stabilises S over a much larger range of walker populations

$N_w \to \infty$ limit must be found

i-FCIQMC: D Cleland, GH Booth, A Alavi, JCP 132 4, 041103 (2010)

Initiator FCIQMC (i-FCIQMC)

$N_w \to \infty$ limit must be found

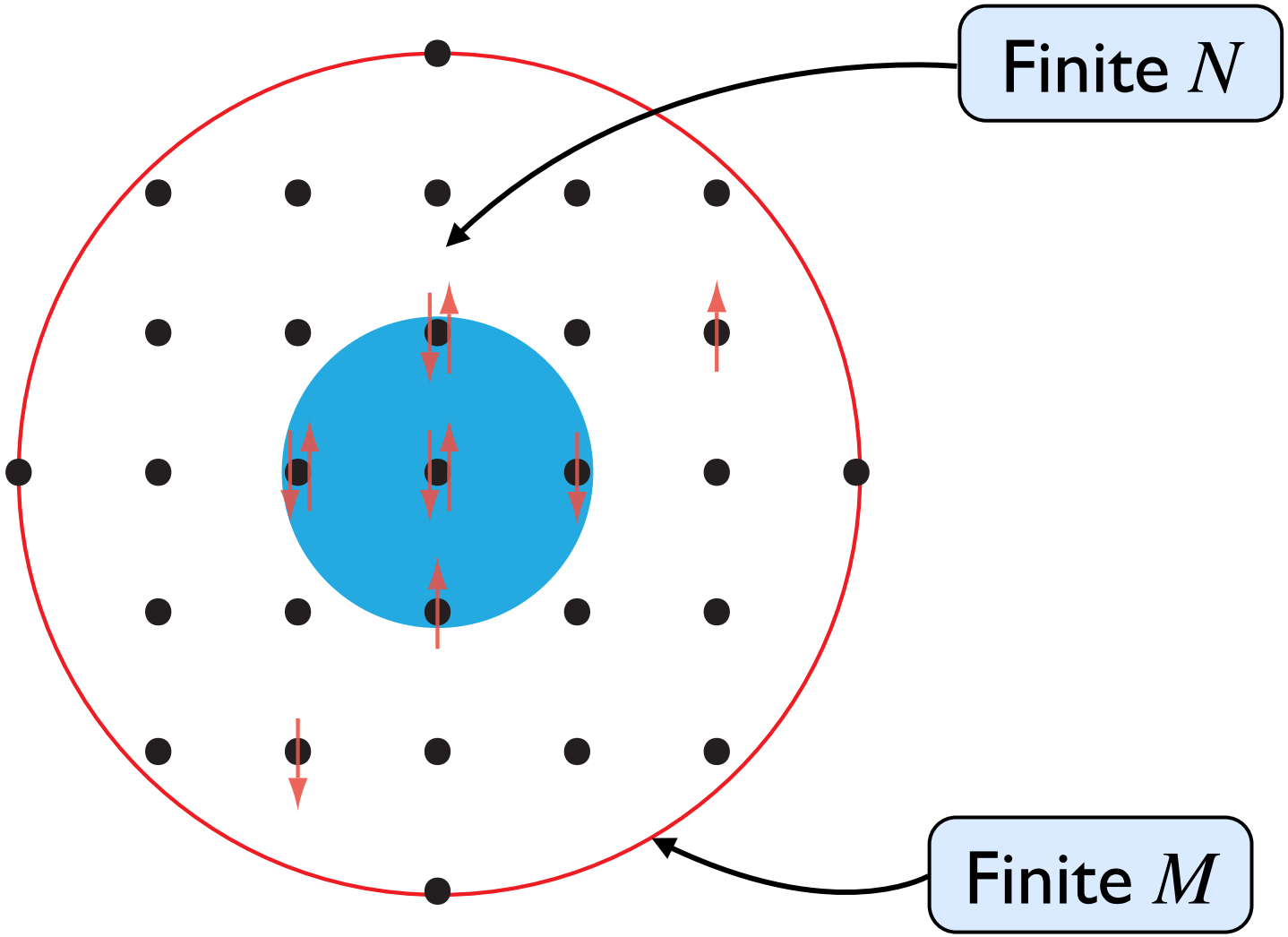


i-FCIQMC/HEG/extrap/initiator error: JJS, GH Booth, A. Alavi, JCP, 136, 244101 (2012)

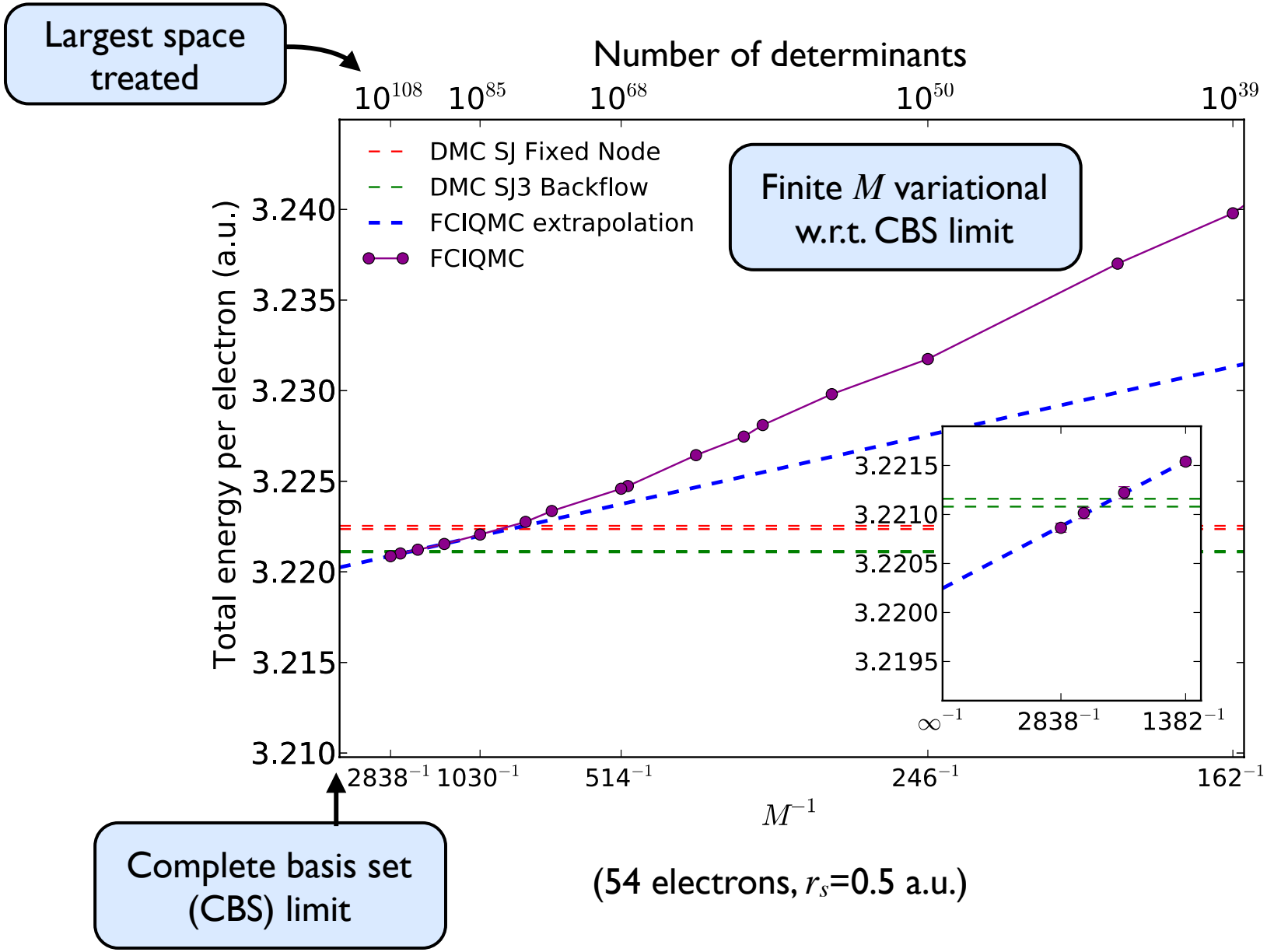
Overview

- Introduction
- Plane wave basis set incompleteness error
- Comparison with DMC and finite size effects
- Insights from the FCIQMC wavefunction

Plane wave basis sets



CBS limit is recovered as $1/M$...

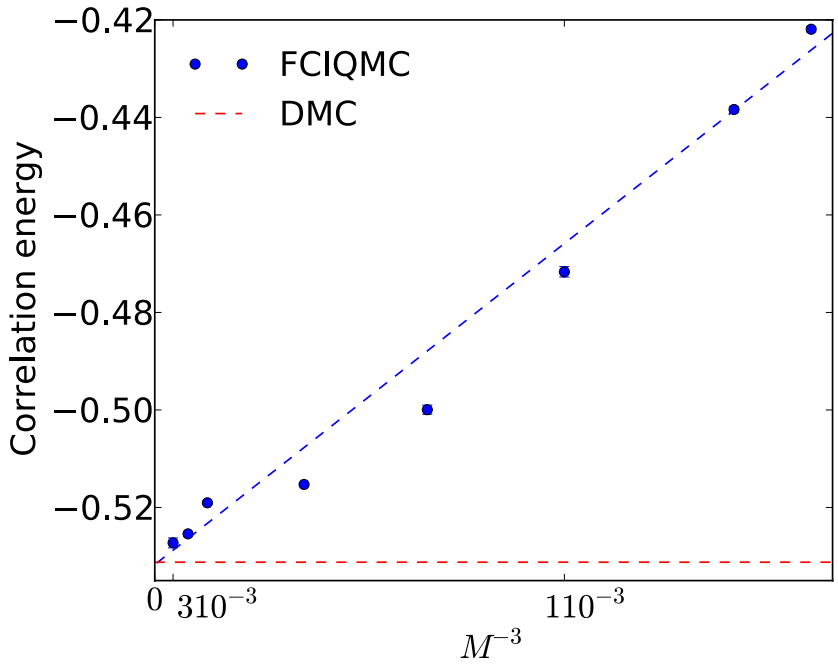


(54 electrons, r_s=0.5 a.u.)

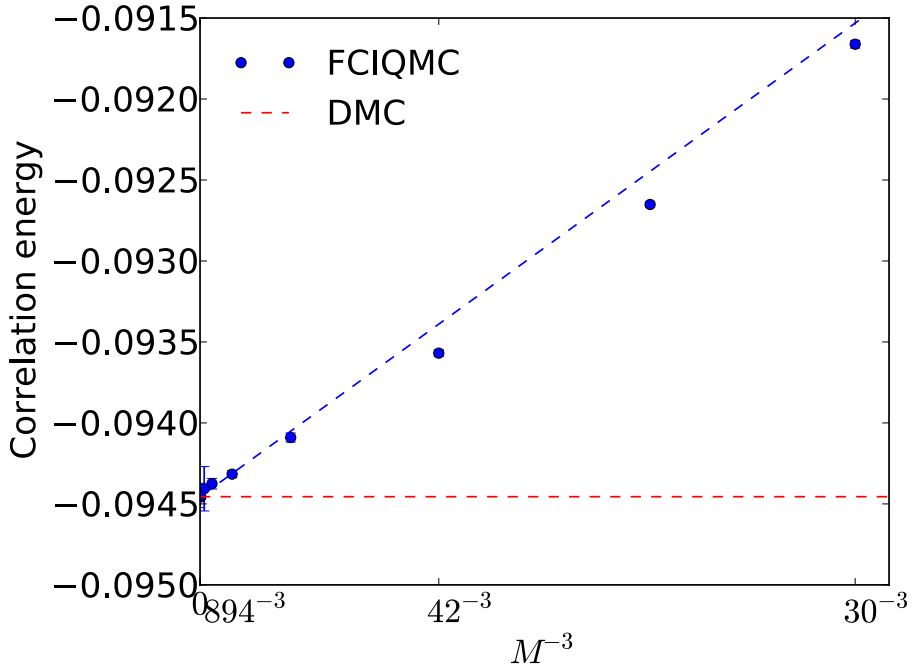
i-FCIQMC/HEG: JJS, GH Booth, A Gruneis, A Alavi, PRB, 85, 081103(R) (2012)

Spin-polarization/dimension dependent…

e.g. 1D spin-polarized, $1/M^3$



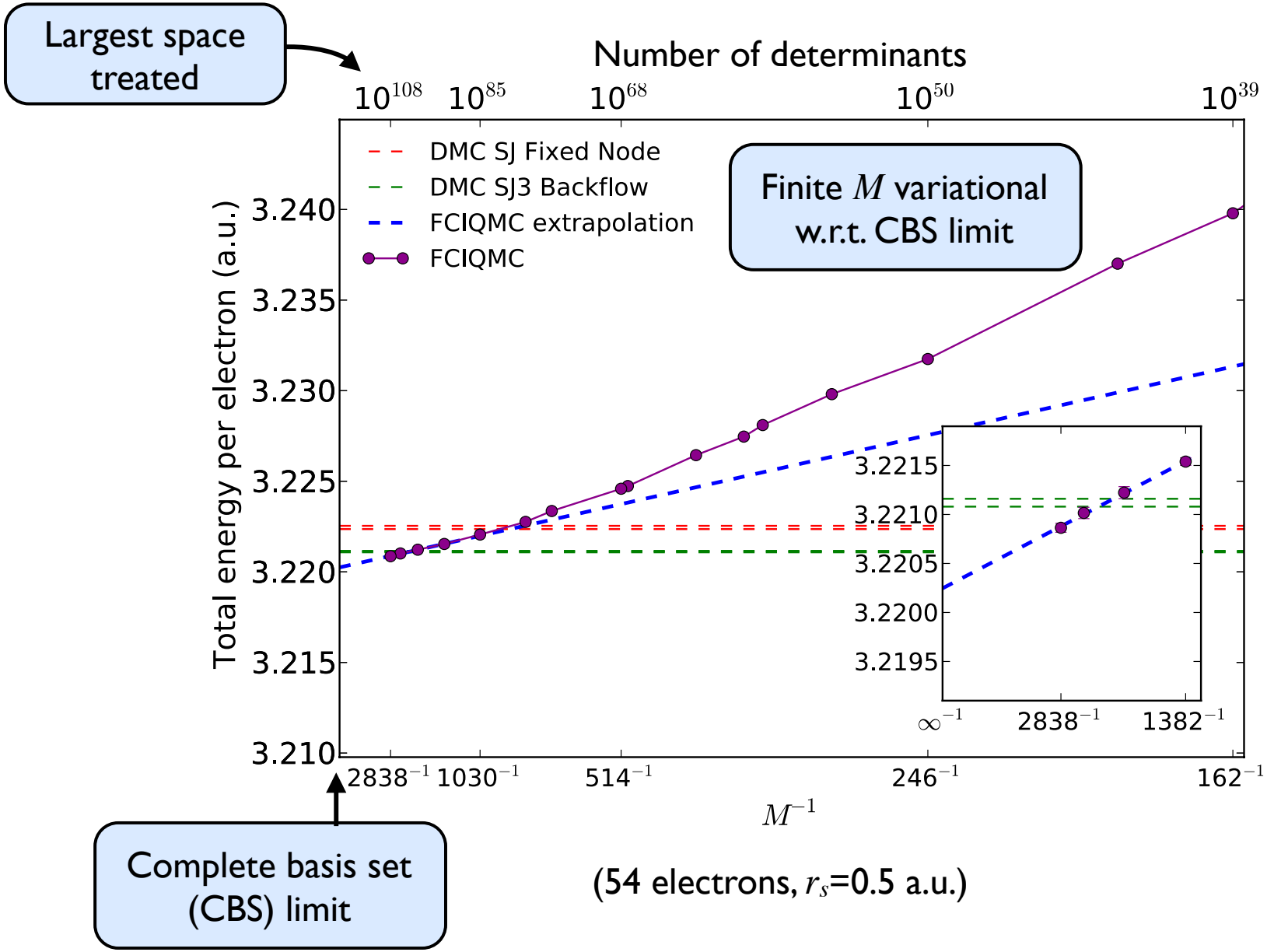
25 electrons, 1D ferromagnetic



5 electrons, 1D ferromagnetic

due to Jennifer Mohr

CBS limit is recovered as $1/M$...



(54 electrons, r_s=0.5 a.u.)

i-FCIQMC/HEG: JJS, GH Booth, A Gruneis, A Alavi, PRB, 85, 081103(R) (2012)

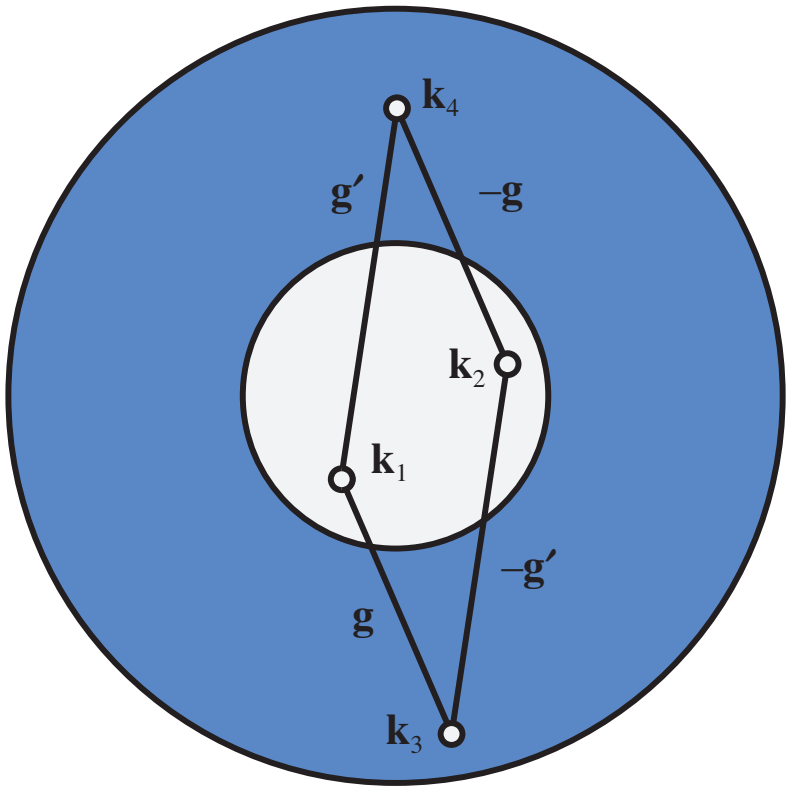
$$E_{\text{corr}} = \sum_{\mathbf{j}\in\{\text{doubles}\}} \langle D_{\mathbf{j}} | H | D_{\mathbf{0}} \rangle \frac{c_{\mathbf{j}}}{c_{\mathbf{0}}}$$

$$E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_j - \mathbf{k}_b} \left(v_{\mathbf{k}_i - \mathbf{k}_a} - v_{\mathbf{k}_j - \mathbf{k}_a} \right) \frac{c_{\mathbf{k}_i \mathbf{k}_j}^{\mathbf{k}_a \mathbf{k}_b}}{c_{\mathbf{0}}}$$

Pairwise addition of virtual contributions

HEG/extrapolation: JJS, A Gruneis, GH Booth, G Kresse, A Alavi, PRB, 86, 035111 (2012).

Consider a different definition of basis set



- It is possible to define two momentum transfer vectors for an excitation.
- Show there are *three* sensible choices for basis sets based on this.
- Originates from basis set convergence work in solid state systems.

HEG/extrapolation: JJS, A Gruneis, GH Booth, G Kresse, A Alavi, PRB, 86, 035111 (2012).

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$$E_{\text{corr}} = \sum_{\mathbf{j}\in\{\text{doubles}\}} \langle D_{\mathbf{j}} | H | D_{\mathbf{0}} \rangle \frac{c_{\mathbf{j}}}{c_{\mathbf{0}}}$$

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Pairwise addition of virtual contributions

Assume fixed

HEG/extrapolation: JJS, A Gruneis, GH Booth, G Kresse, A Alavi, PRB, 86, 035111 (2012).

Consider a different definition of basis set

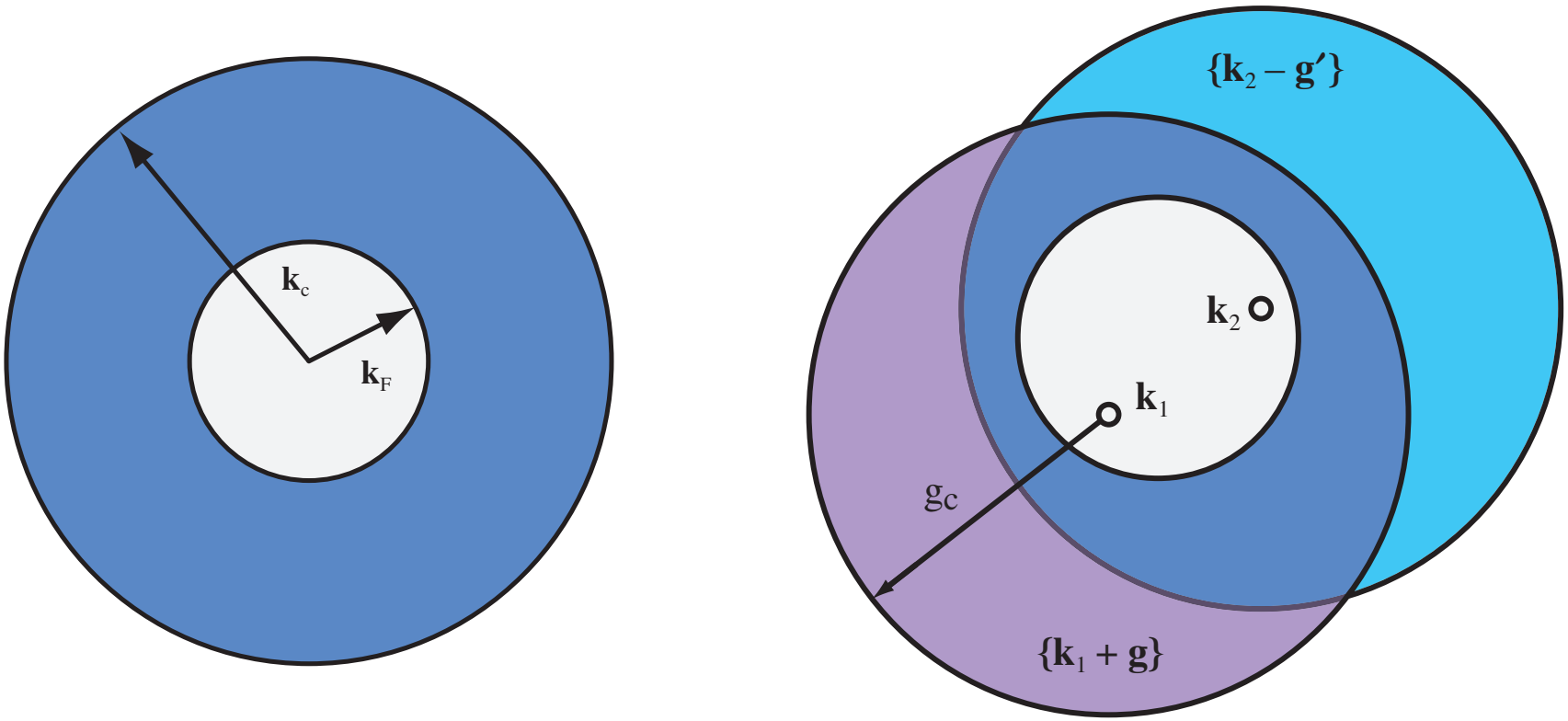
$$E_{\text{corr}} = \sum_{\mathbf{j}\in\{\text{doubles}\}} \langle D_{\mathbf{j}} \mid H \mid D_{\mathbf{0}} \rangle \frac{c_{\mathbf{j}}}{c_{\mathbf{0}}}$$

$$E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_j - \mathbf{k}_b} \left(v_{\mathbf{k}_i - \mathbf{k}_a} - v_{\mathbf{k}_j - \mathbf{k}_a} \right) \frac{c_{\mathbf{k}_i \mathbf{k}_j}^{\mathbf{k}_a \mathbf{k}_b}}{c_{\mathbf{0}}}$$

$$\sum_{ab}^{k_c} F(k) \longrightarrow \sum_{ab}^{g_c} F(g)$$

HEG/extrapolation: JJS, A Gruneis, GH Booth, G Kresse, A Alavi, PRB, 86, 035111 (2012).

$$\sum_{ab}^{k_c} F(k) \longrightarrow \sum_{ab}^{g_c} F(g)$$



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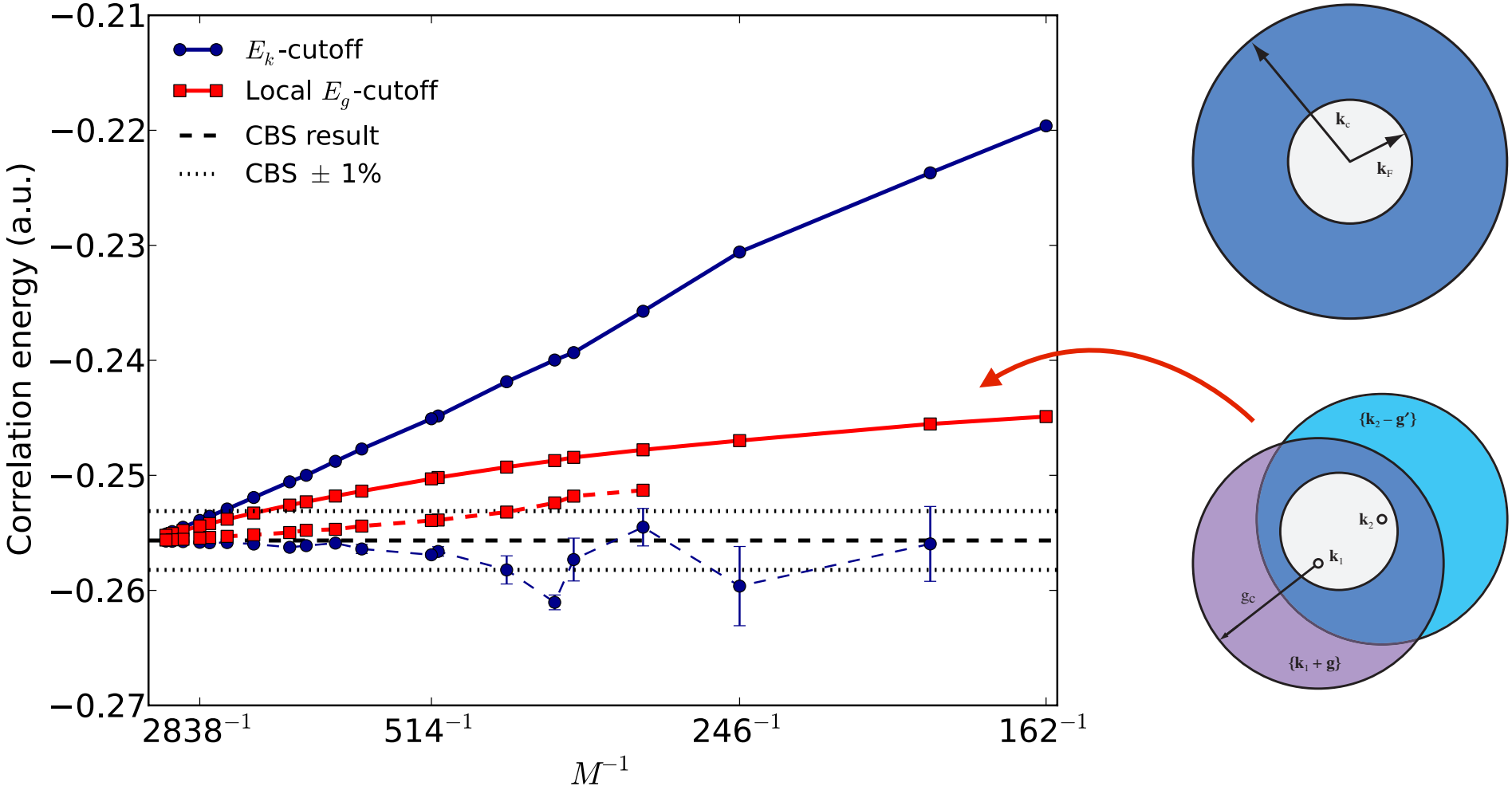

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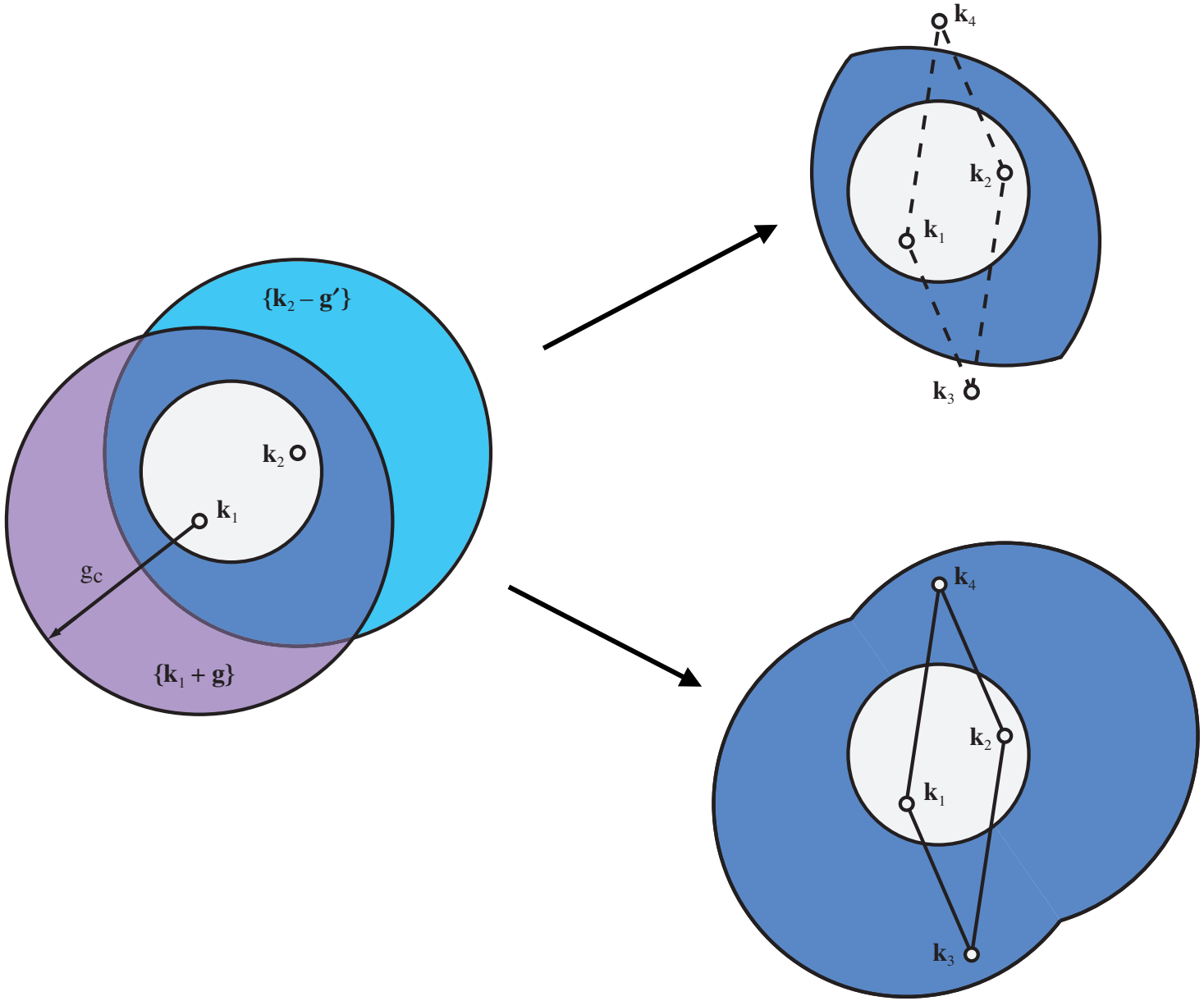

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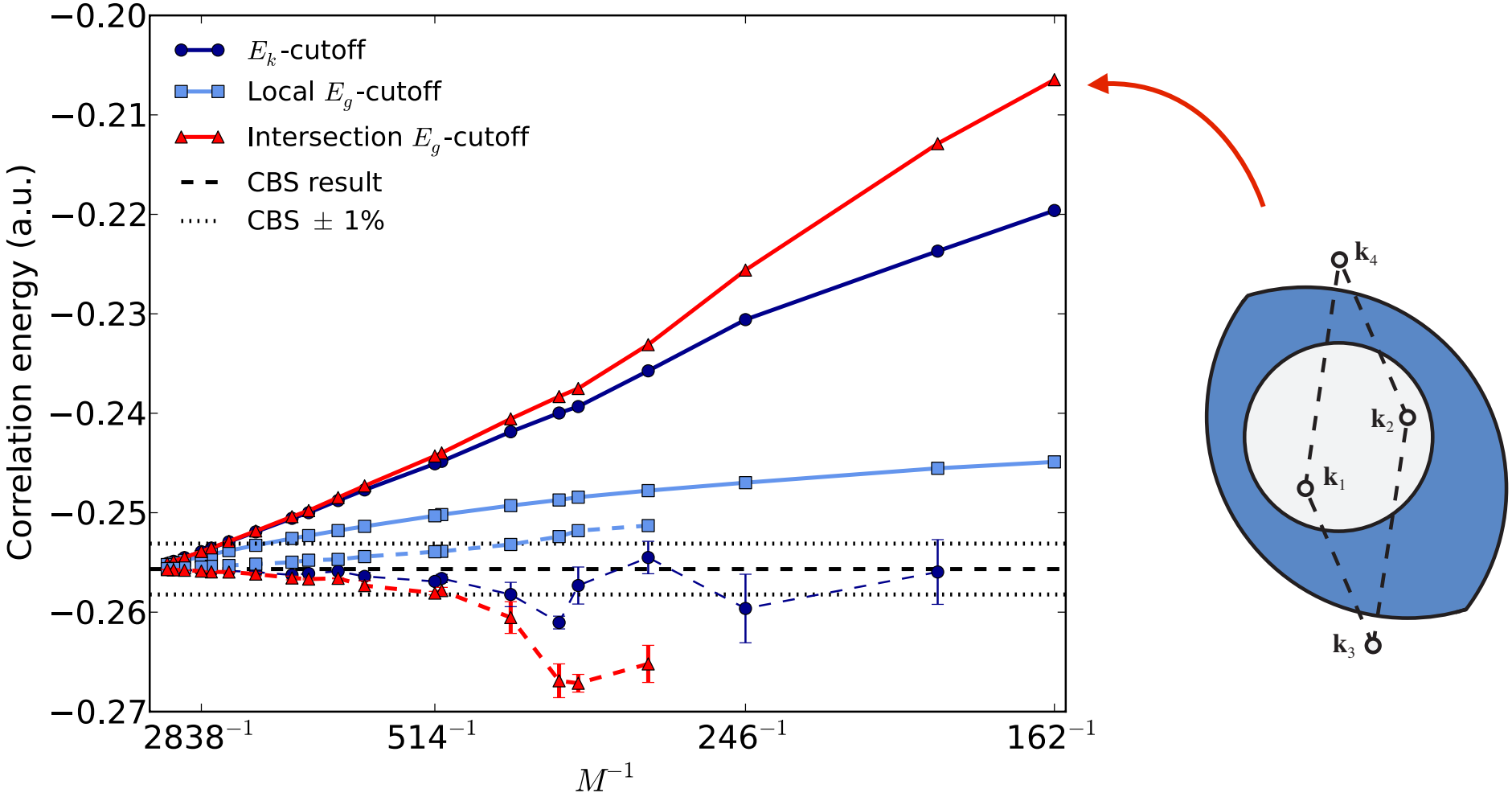

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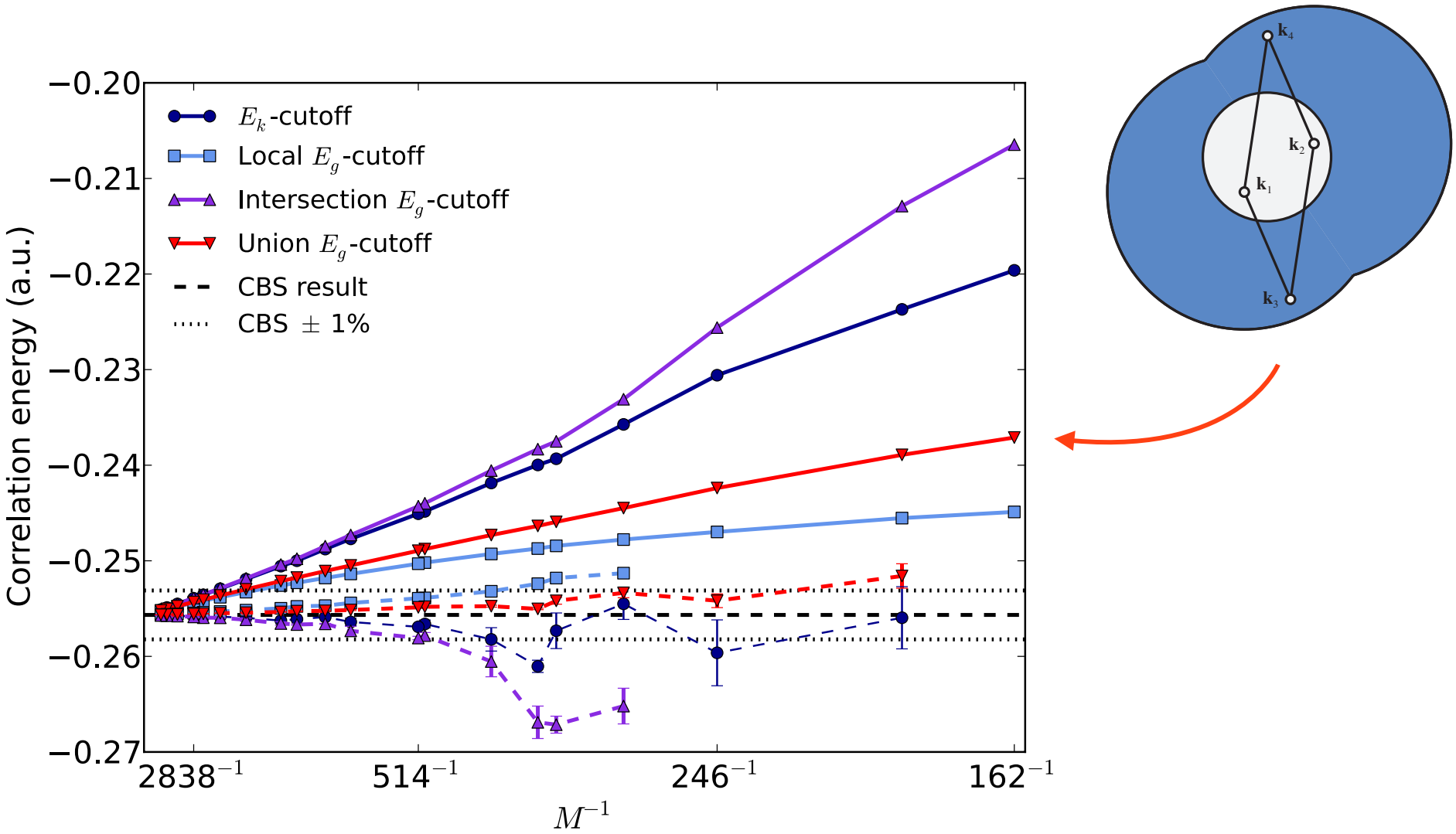


HEG/extrapolation: JJS, A Gruneis, GH Booth, G Kresse, A Alavi, PRB, 86, 035111 (2012).

For multi-reference calculations, there is a trade-off...

$$E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_j - \mathbf{k}_b} \left(v_{\mathbf{k}_i - \mathbf{k}_a} - v_{\mathbf{k}_j - \mathbf{k}_a} \right) \frac{c_{\mathbf{k}_i \mathbf{k}_j}^{\mathbf{k}_a \mathbf{k}_b}}{c_{\mathbf{0}}}$$

$$\sum_{ab}^{k_c} F(k)$$

Slower/less accurate extrapolation

$$\sum_{ab}^{g_c} F(g)$$

Neglects coefficient relaxation

HEG/extrapolation: JJS, A Gruneis, GH Booth, G Kresse, A Alavi, PRB, 86, 035111 (2012).

r_s	M	k extrapolation	g extrapolation
0.5	1850	-0.5969(3)	-0.5959(7)
1.0	1850	-0.5325(4)	-0.5316(4)
2.0	1850	-0.4447(4)	-0.444(1)
5.0	778	-0.306(1)	-0.307(1)

For multi-reference calculations, there is a trade-off...

$$E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_j - \mathbf{k}_b} \left(v_{\mathbf{k}_i - \mathbf{k}_a} - v_{\mathbf{k}_j - \mathbf{k}_a} \right) \frac{c_{\mathbf{k}_i \mathbf{k}_j}^{\mathbf{k}_a \mathbf{k}_b}}{c_{\mathbf{0}}}$$

$$\sum_{ab}^{g_c} F(g)$$

- Single (multi-reference) calculation
- Immediate CBS estimate
- Systematically improvable

HEG/extrapolation: JJS, A Gruneis, GH Booth, G Kresse, A Alavi, PRB, 86, 035111 (2012).

Overview

- Introduction
- Plane wave basis set incompleteness error
- Comparison with DMC and finite size effects
- Insights from the FCIQMC wavefunction

How good are the HF nodes?

- Single-determinant Slater-Jastrow wavefunction
- Real-space propagation using a Green's function propagator
- Makes the Schrödinger equation diffusive
- Must enforce anti-symmetry explicitly:

$$f(\mathbf{x},\tau) = \Psi(\mathbf{x},\tau)\phi_T(\mathbf{x})$$

- How good are the trial wavefunction's nodes? (infer from energy)

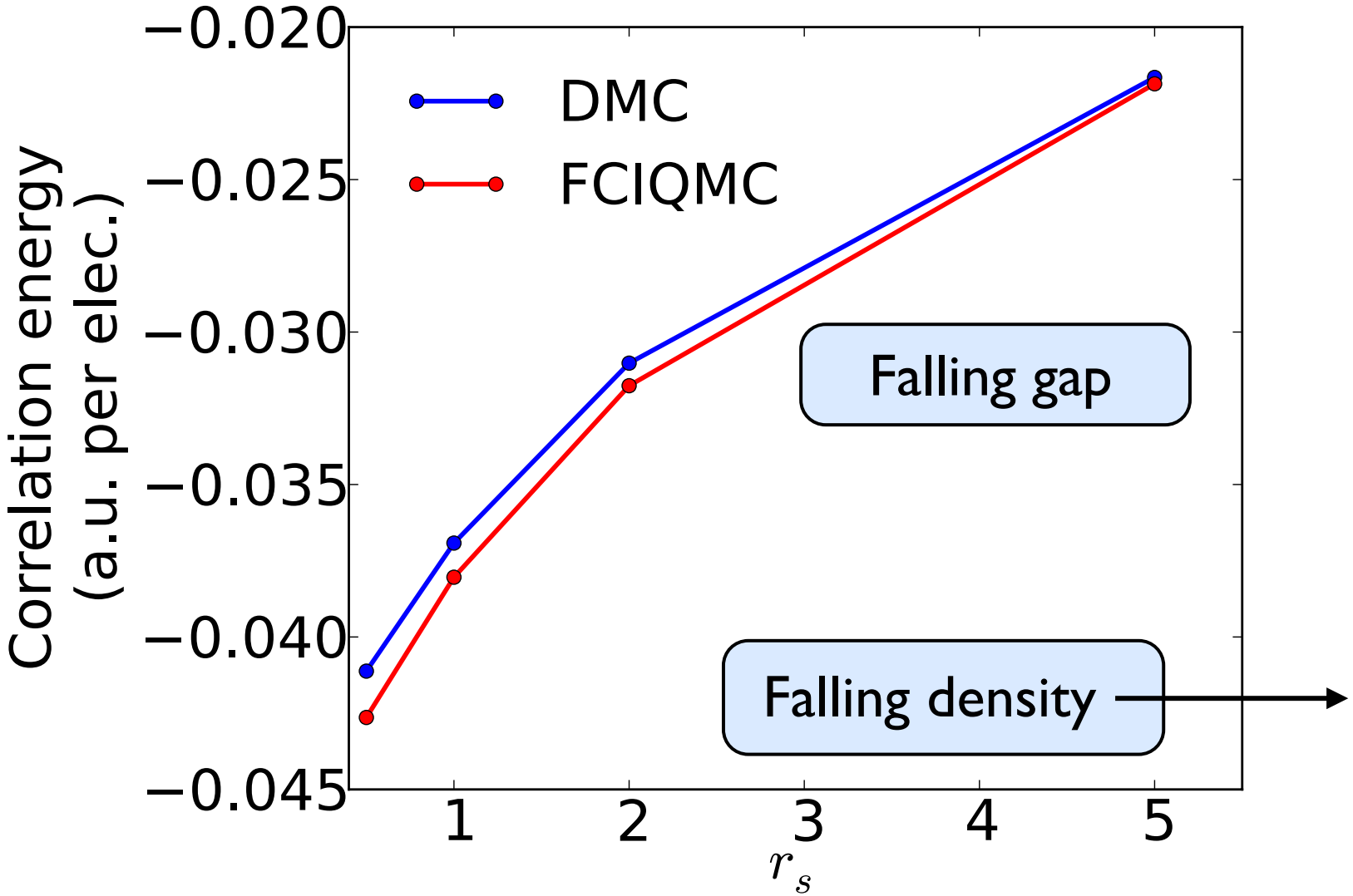
i-FCIQMC, exact except for:

- Basis set incompleteness error
- Initiator error

DMC, exact except for:

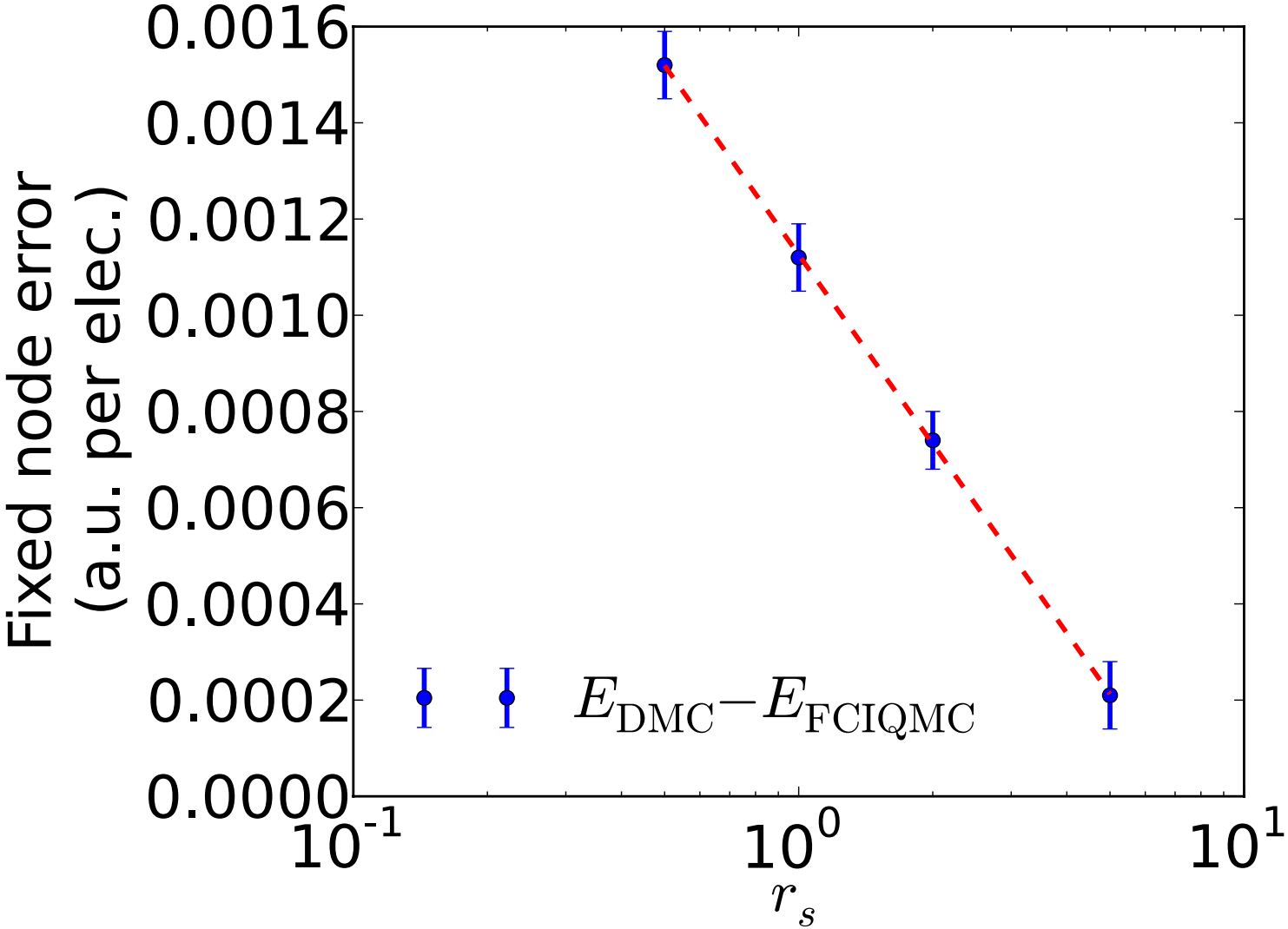
- Fixed-node error (after backflow)
- (Time-step error)

CASINO: RJ Needs, MD Towler, ND Drummond and P Lopez Rios, J. Phys.: Condensed Matter 22, 023201 (2010).
Backflow: P. Lopez Rios, A. Ma, ND Drummond, MD Towler and RJ Needs, Phys. Rev. E 74, 066701 (2006)



14 electron system

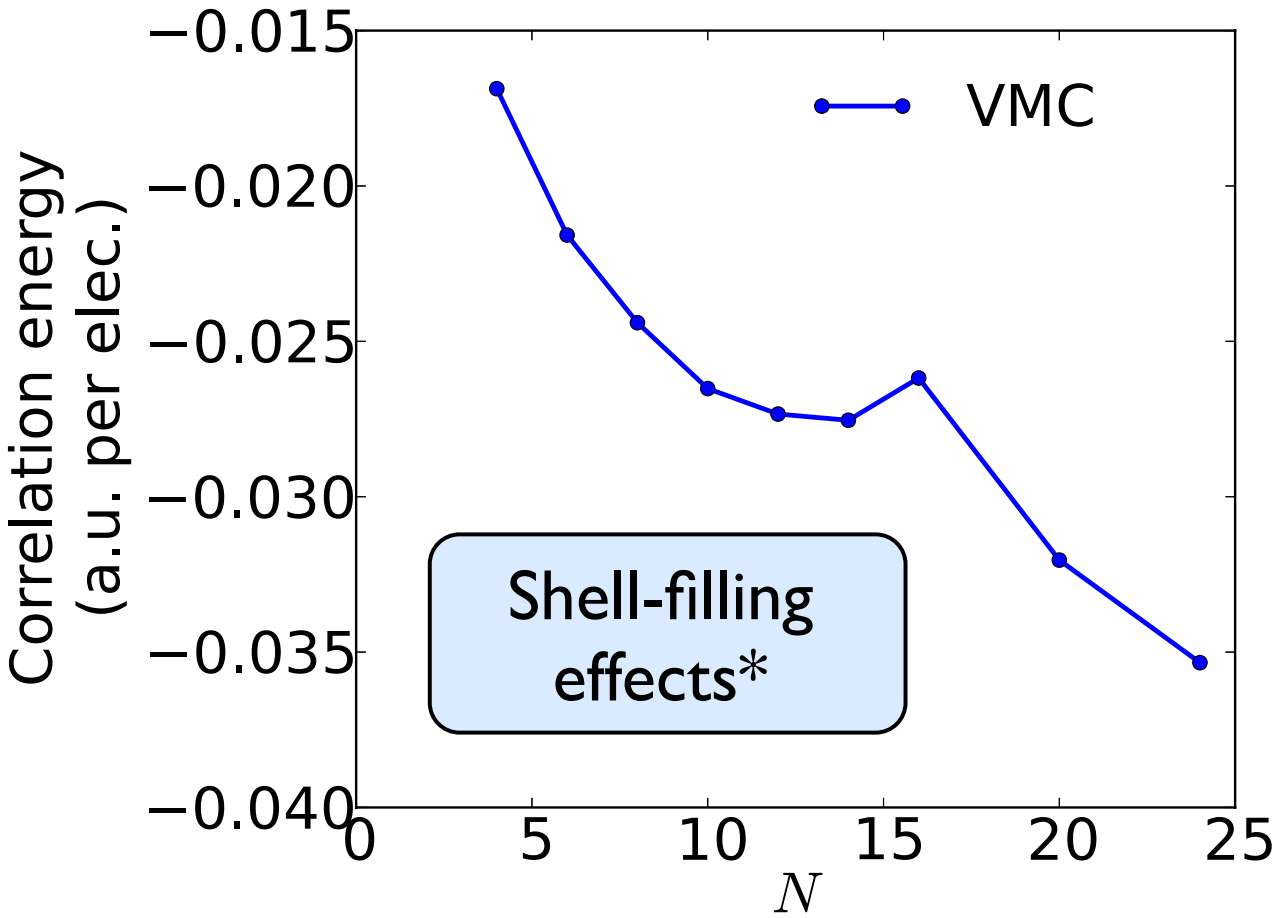
Consistent with:
K.M. Rasch, L. Mitas, Chem. Phys. Lett. 528, 59 (2012)
Y Kwon, D. M. Ceperley and R. M. Martin, Phys. Rev. B 58, 6800 (1998).



14 electron system

DMC results due to Pablo López-Ríos

The correlation energy undulates with changing N...

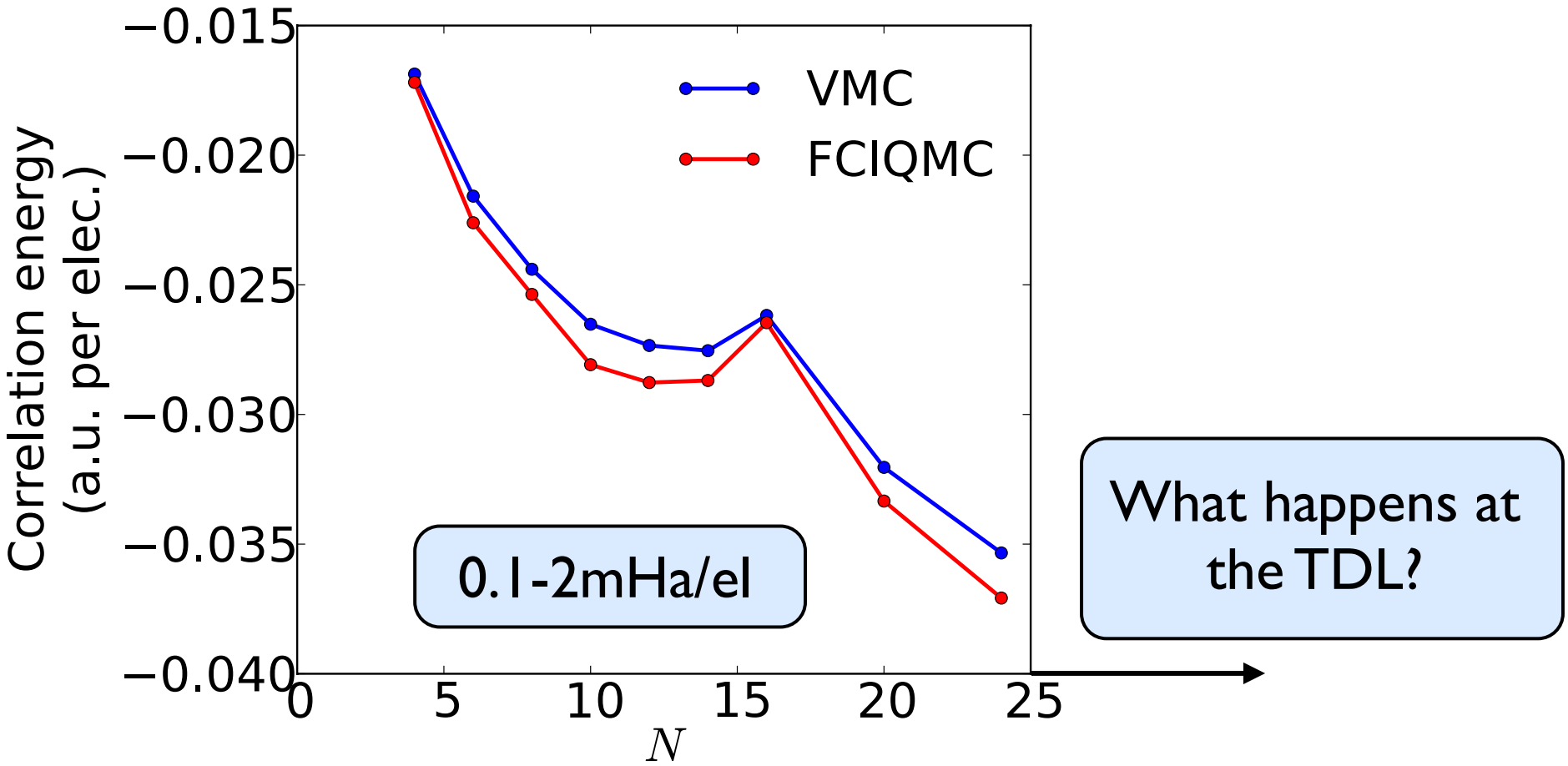


(r_s=1.0 a.u.)

VMC results due to Pablo López-Ríos

*Non-zero twist angle

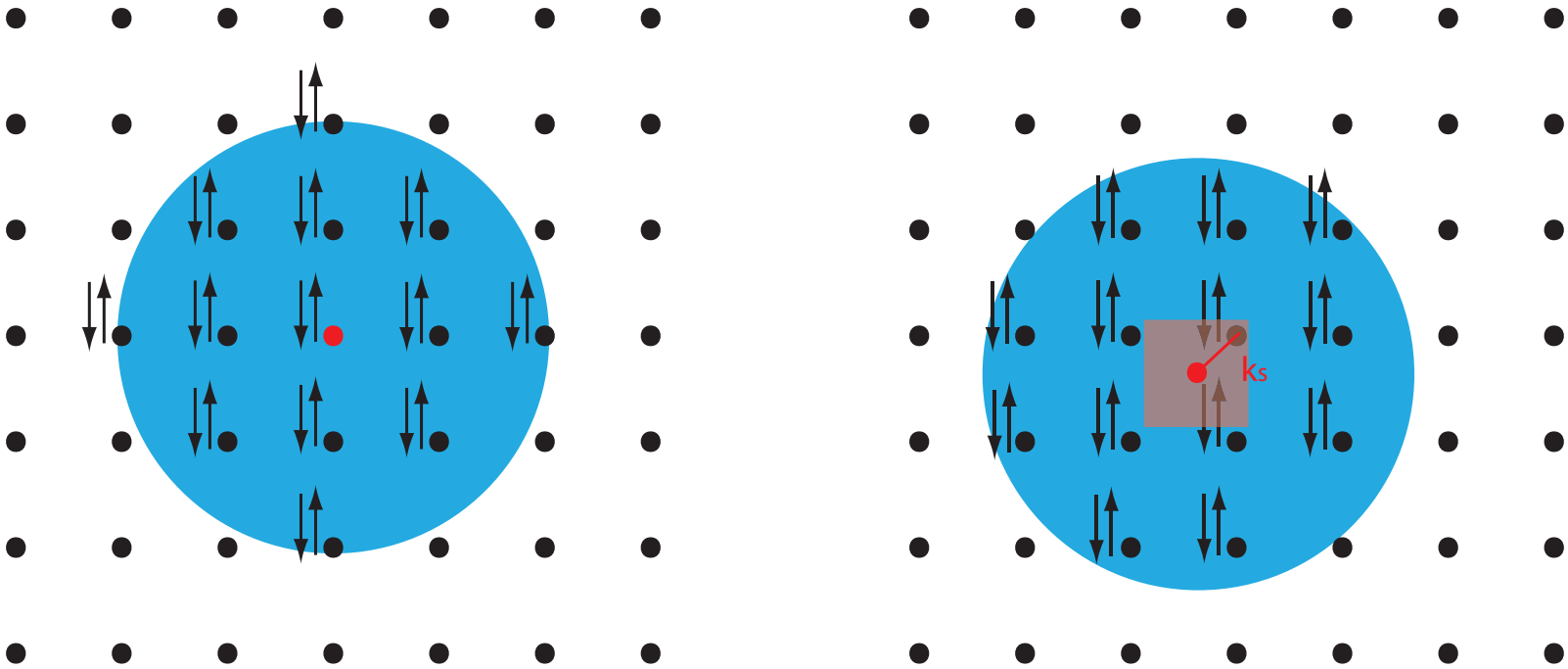
...but so does the gap.



(r_s=1.0 a.u.)

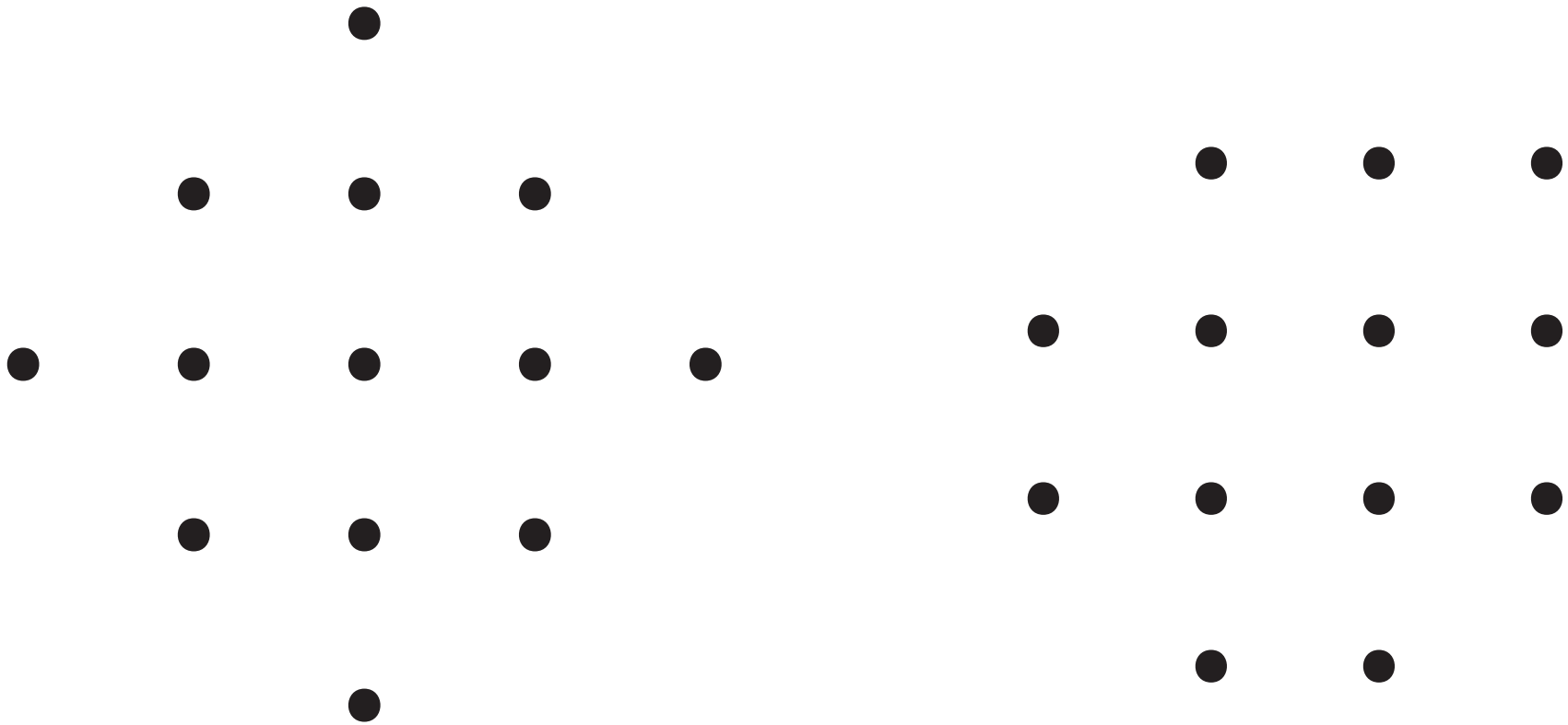
VMC results due to Pablo López-Ríos

Simulation cell HEG systems can resemble clusters of electrons in k-space more than the continuum picture of a sphere



Offset can cause 'repopulation'

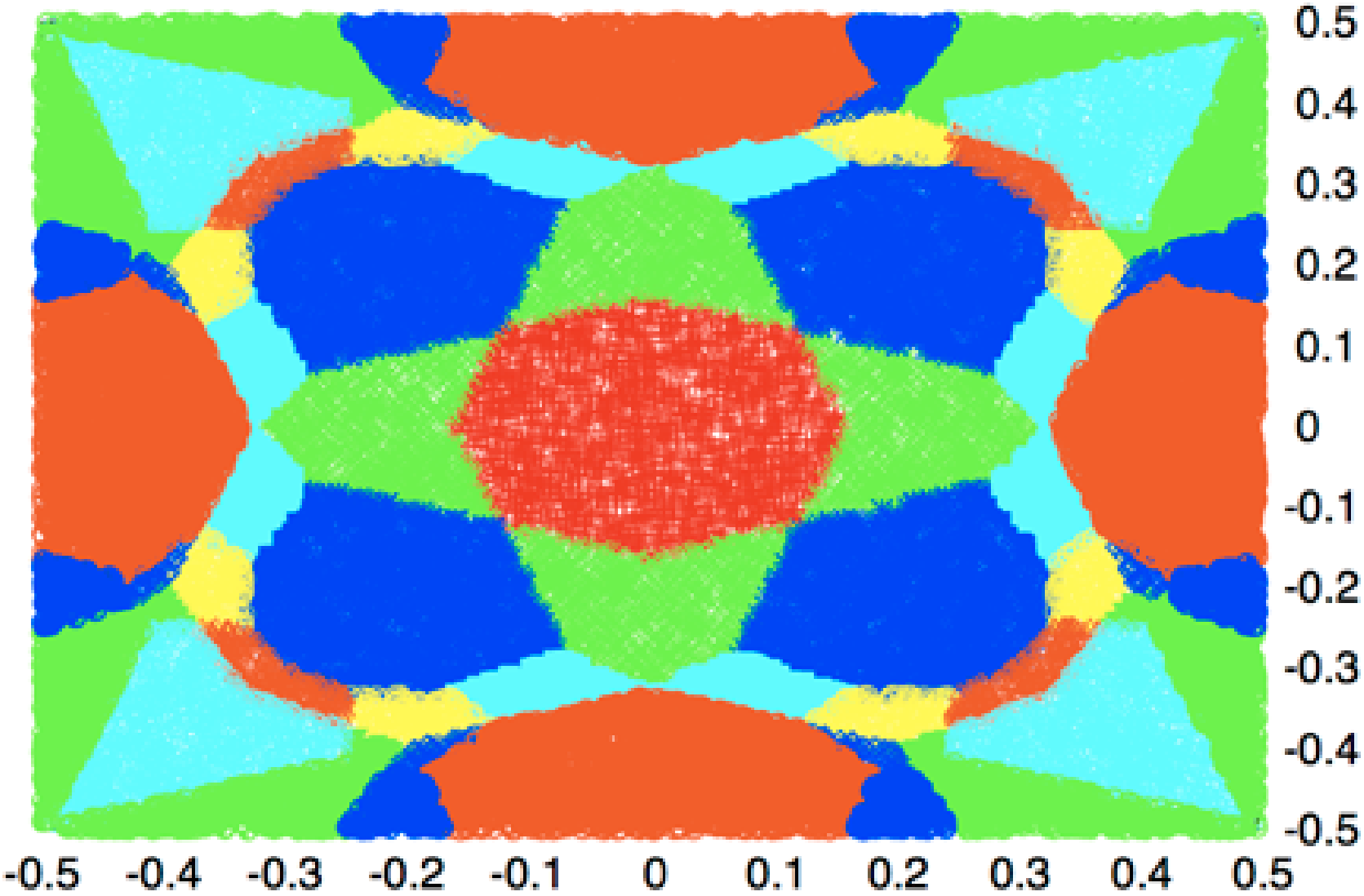
C Lin, F-H Zong, D M Ceperley, Phys Rev E 64, 016702 (2001)
N Drummond, R Needs, A Sorouri, W Foulkes, Phys Rev B, 78, 125106 (2008)

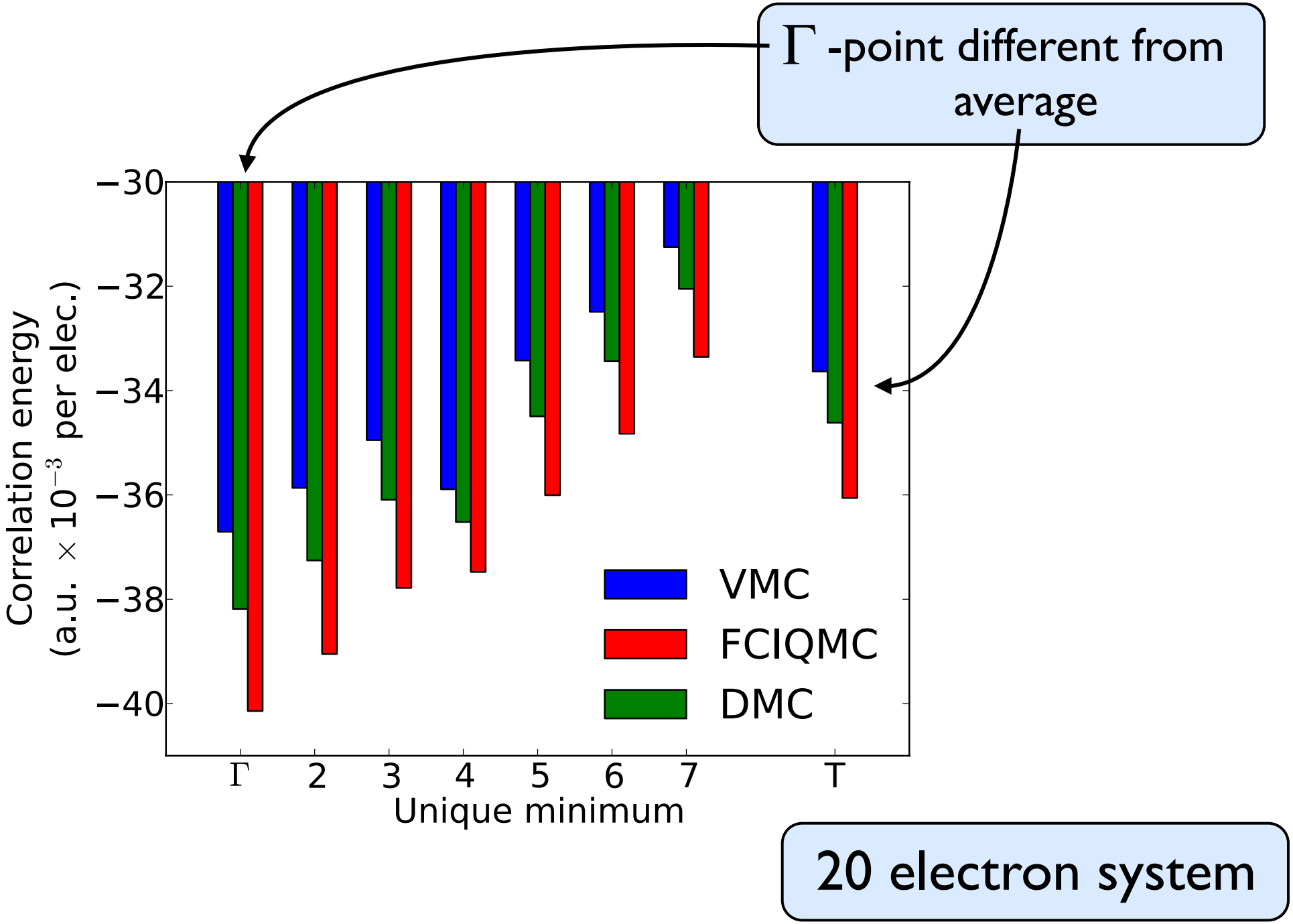


These now have different correlation energies…

(HF changes regardless)

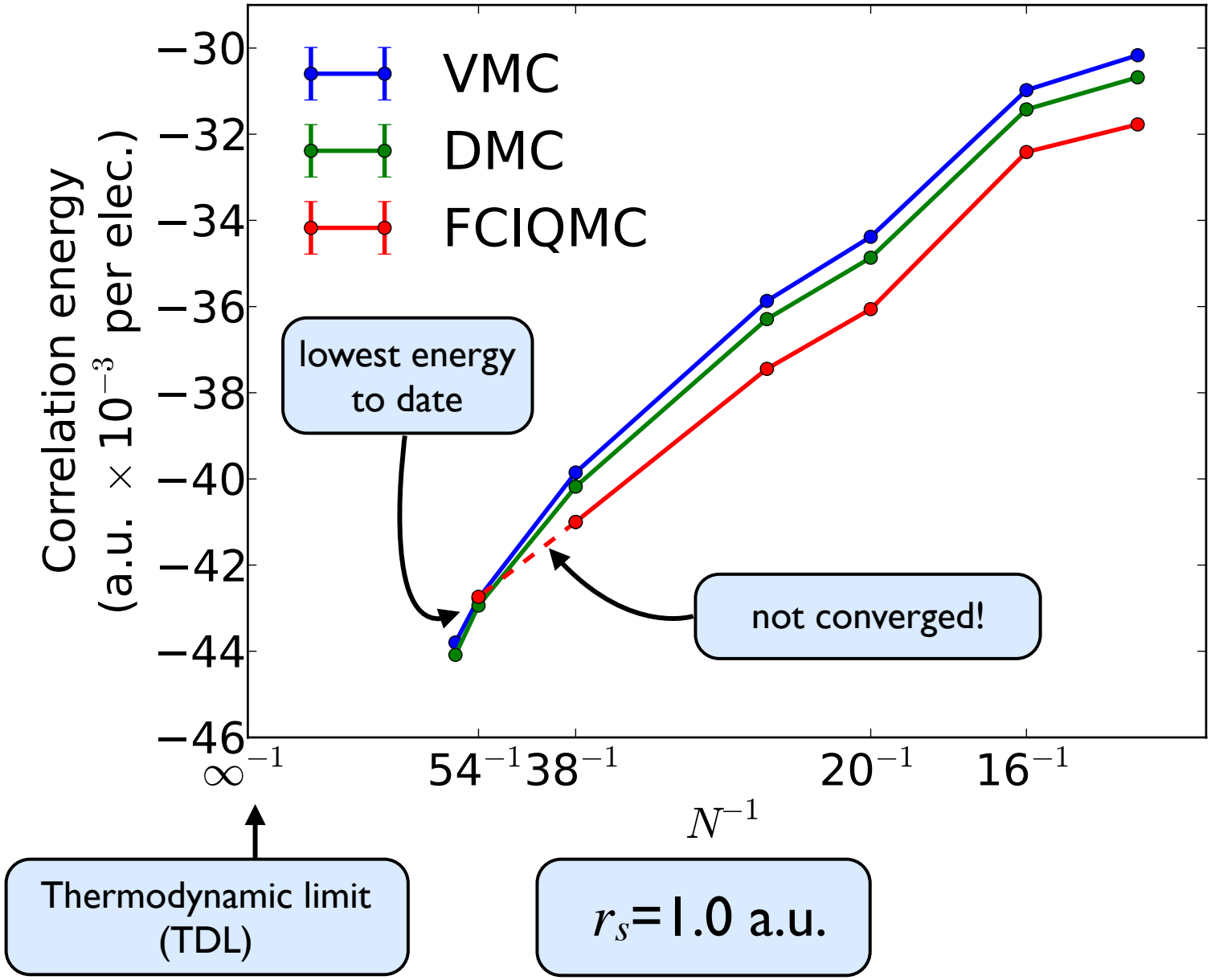
54 electron system





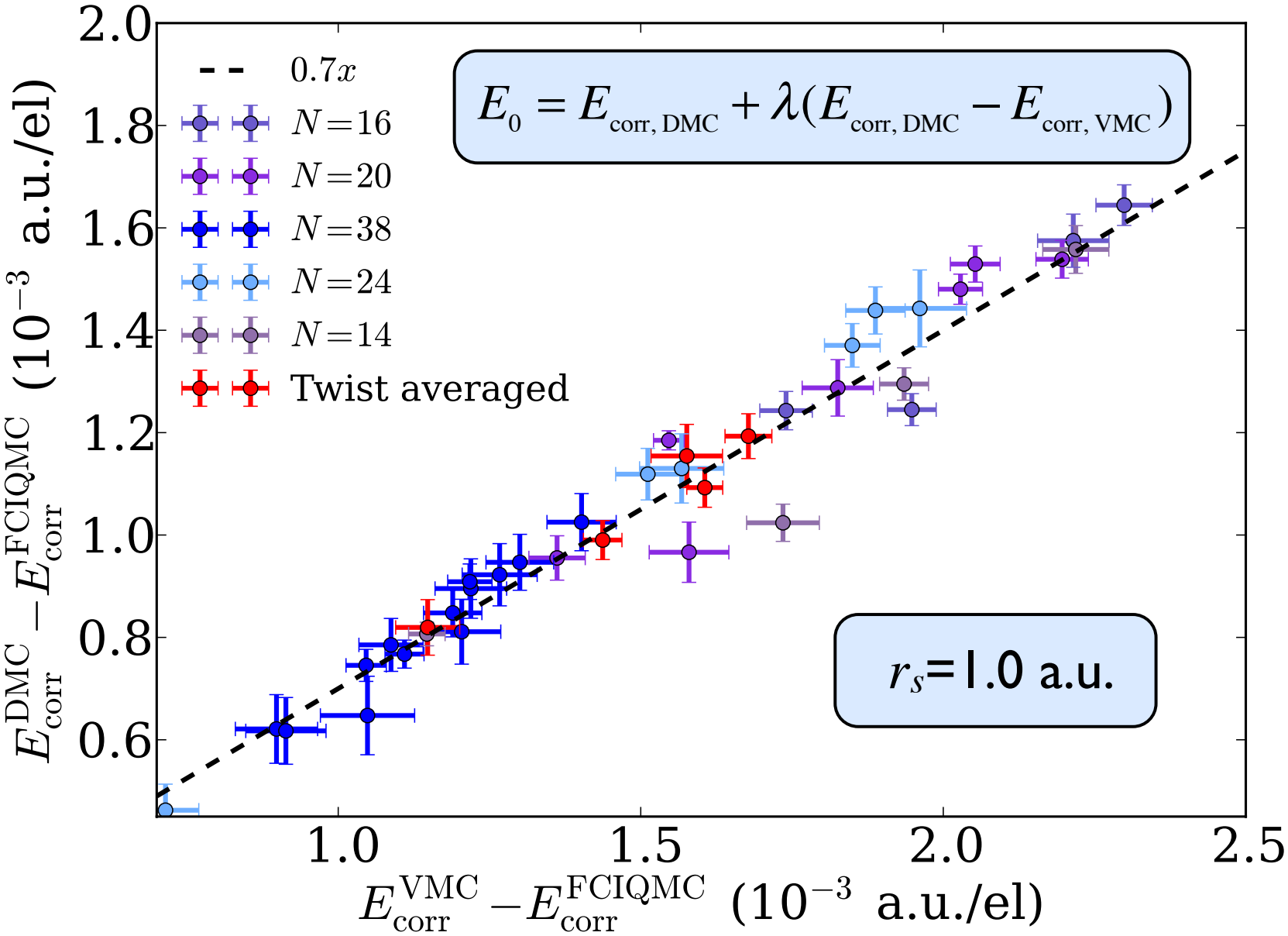
DMC/VMC results due to Pablo López-Ríos

Twist-averaging yields a smooth pattern with N...



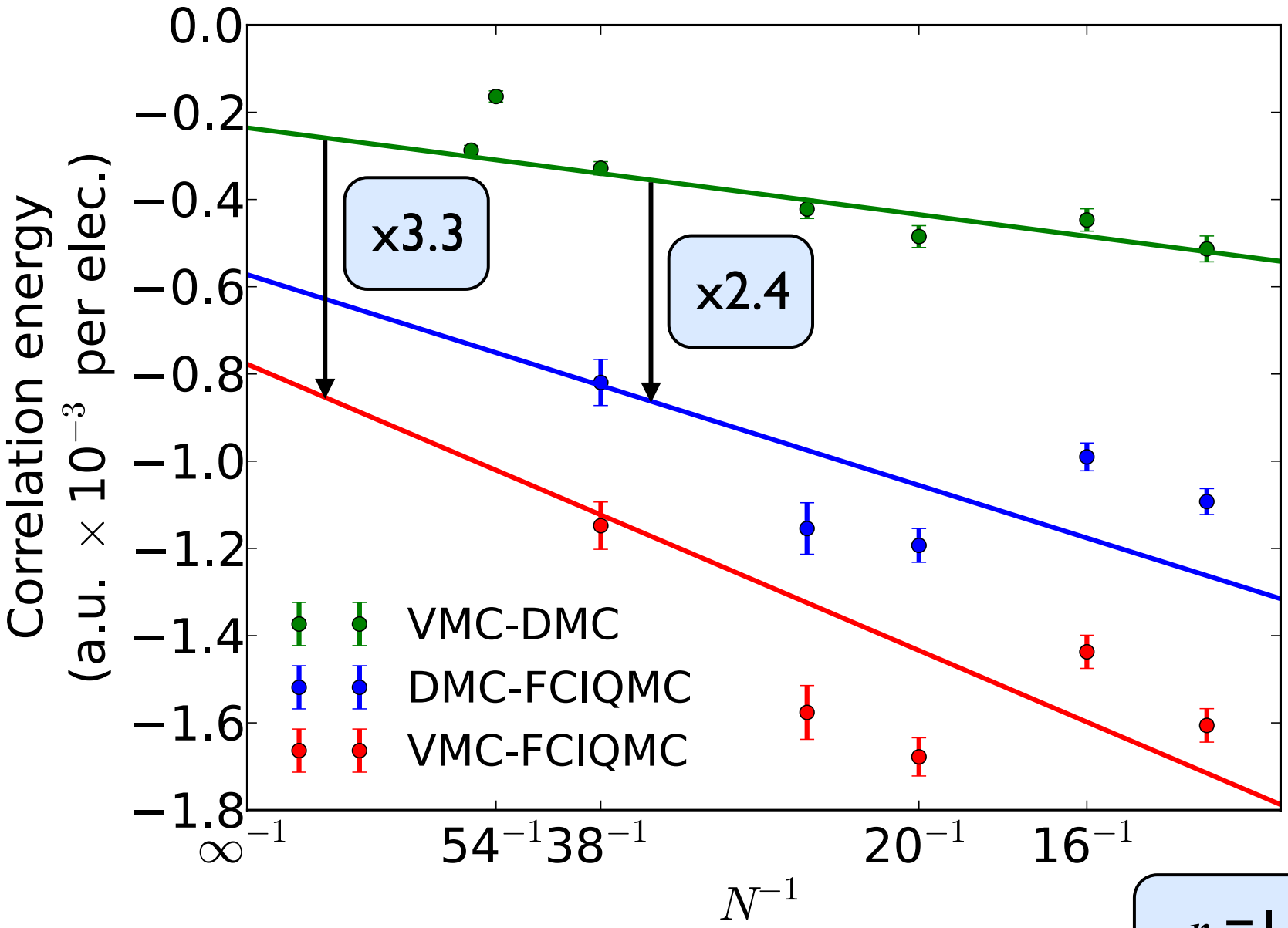
DMC/VMC results due to Pablo López-Ríos

With an underlying relationship



DMC/VMC results due to Pablo López-Ríos

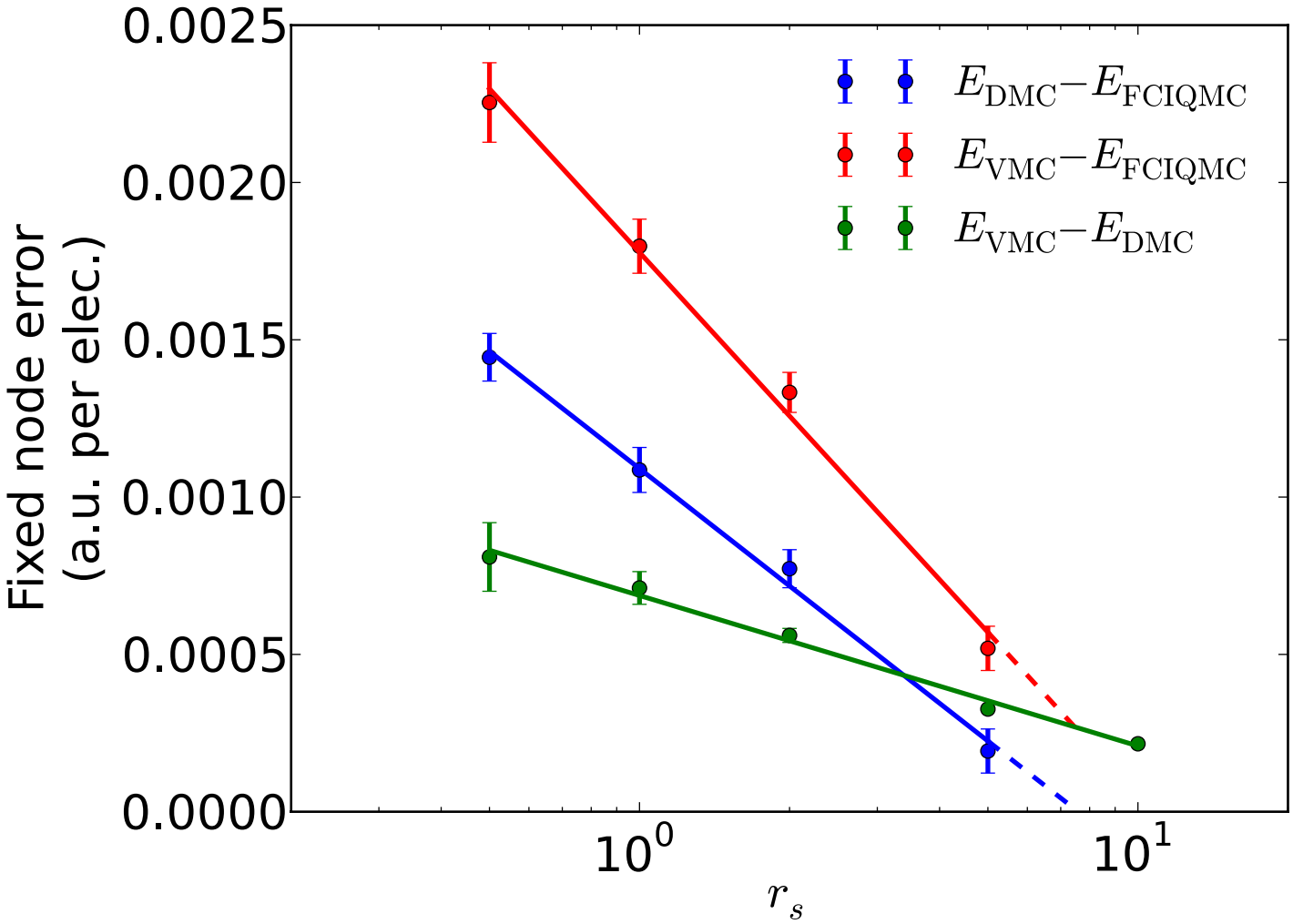
Using this relationship...



r_s=1.0 a.u.

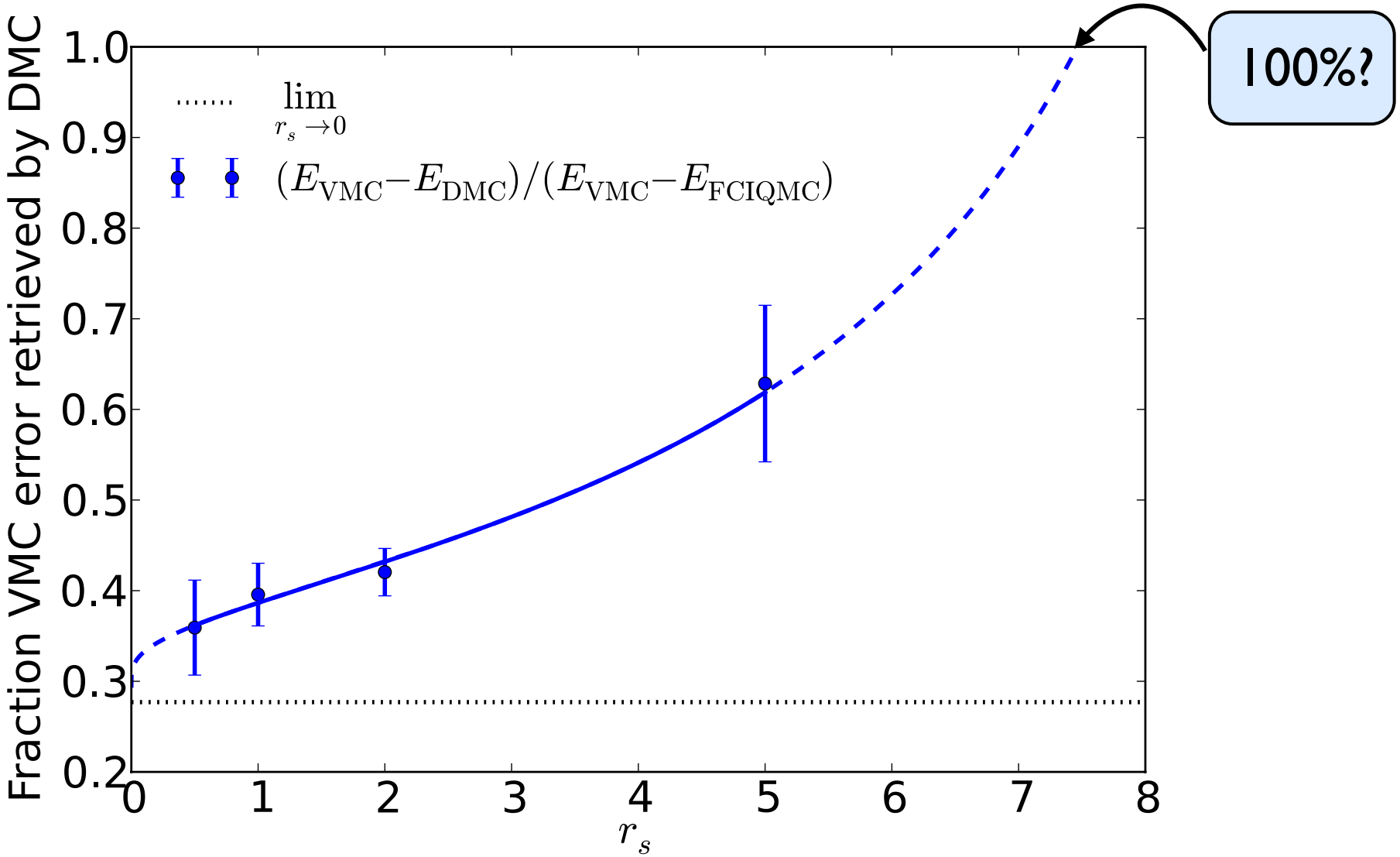
DMC/VMC results due to Pablo López-Ríos

Ratios are hopefully fairly constant with N, so return to 14 electrons...



DMC/VMC results due to Pablo López-Ríos

How well does DMC do in retrieving the missing correlation energy in VMC?



DMC/VMC results due to Pablo López-Ríos

Overview

- Introduction
- Plane wave basis set incompleteness error
- Comparison with DMC and finite size effects
- Insights from the FCIQMC wavefunction

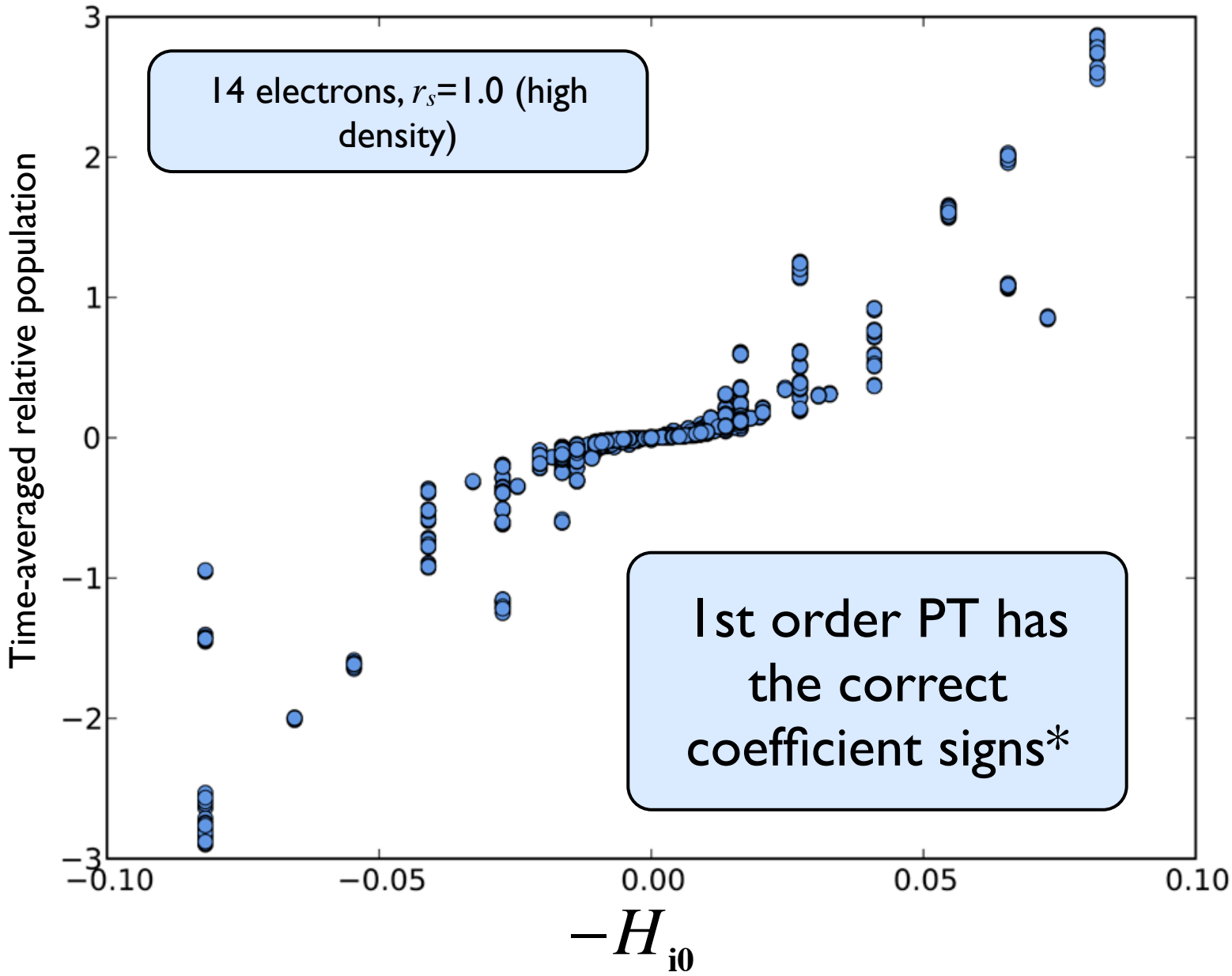
What about the wavefunction?

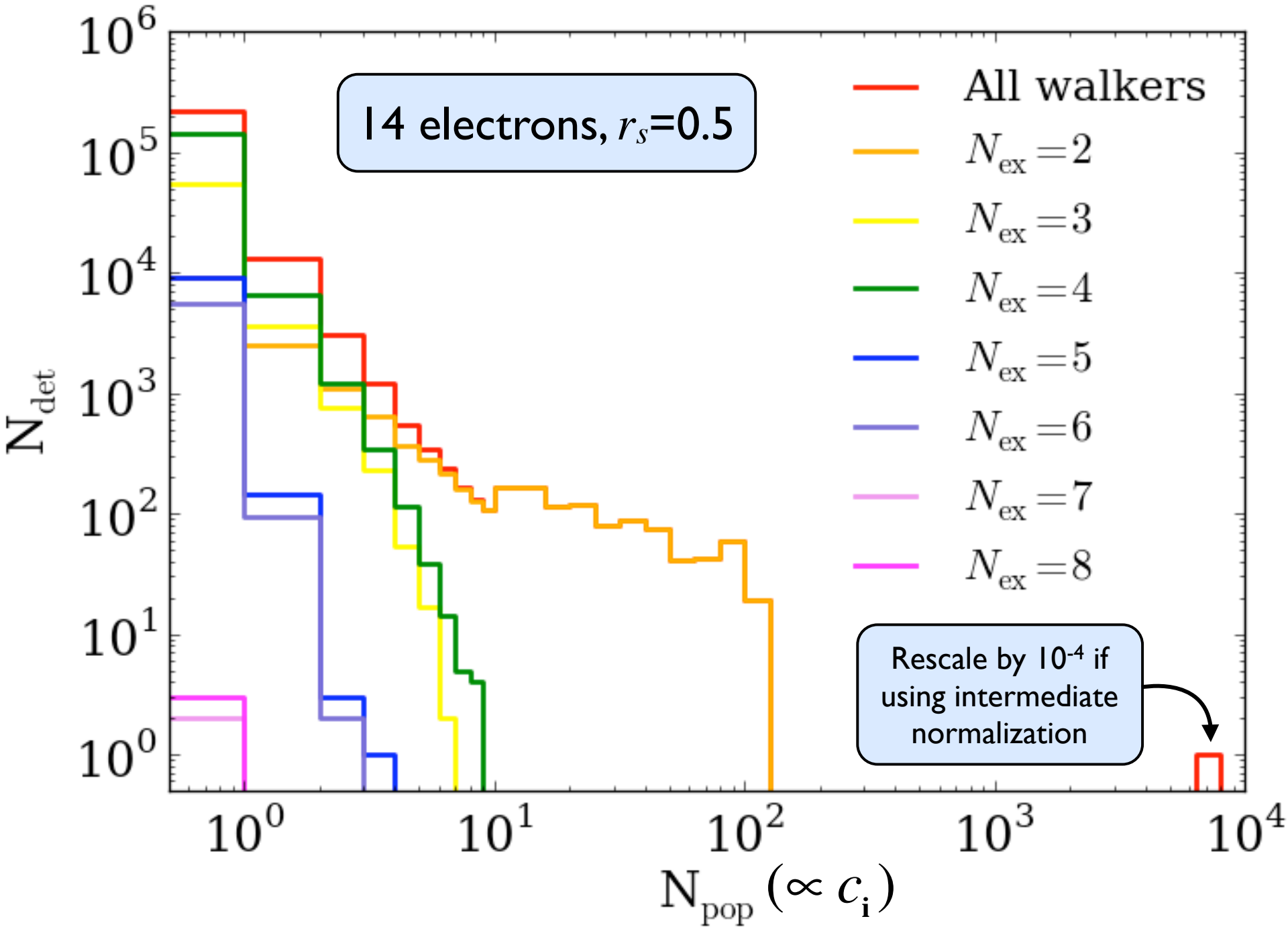
i-FCIQMC directly simulates a representation of the wavefunction (walkers)

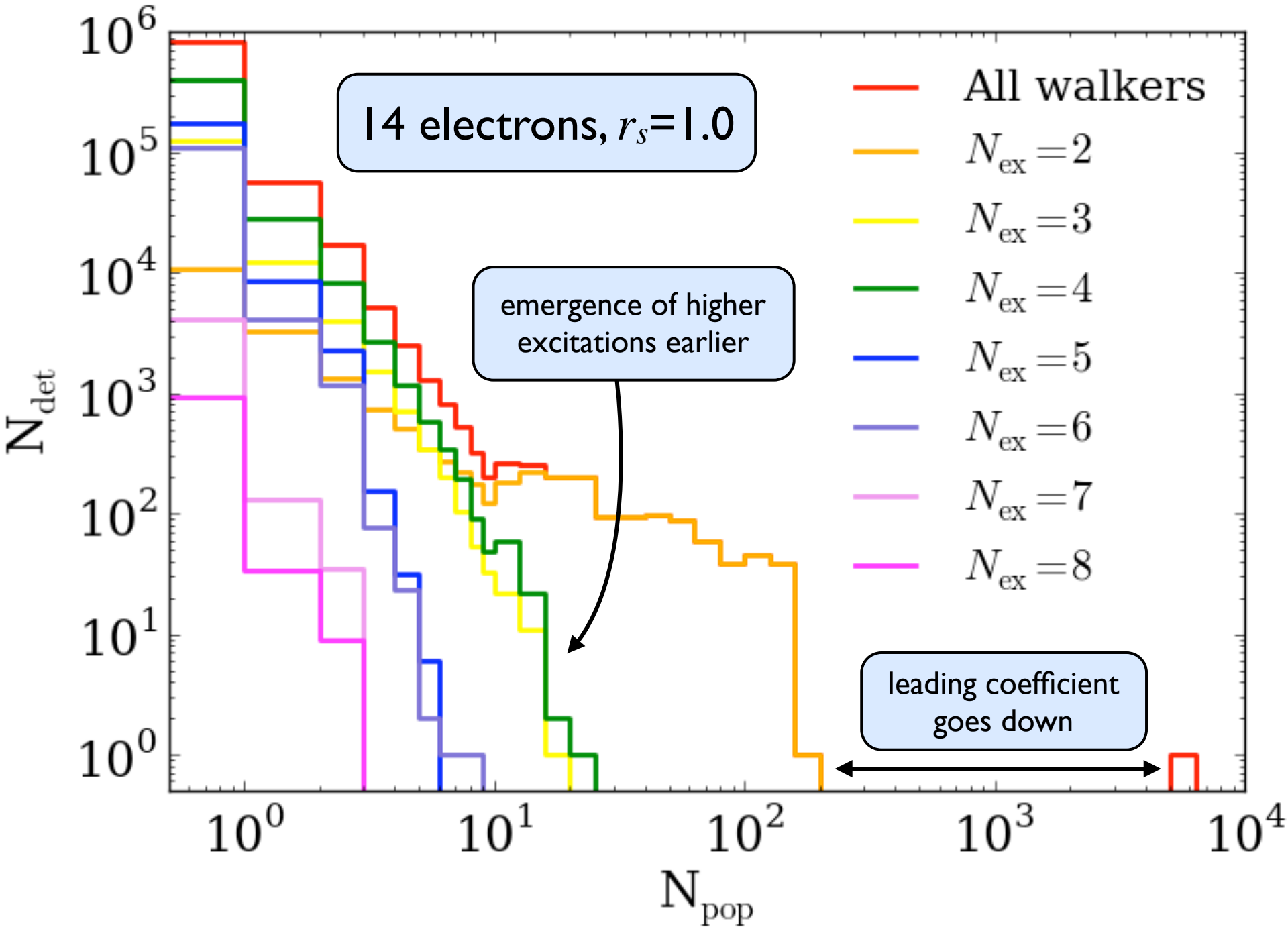
- Is the wavefunction recognisably multi-reference?
- What are the most important excitations?
- How does this compare with molecules?
- ...or other theories?

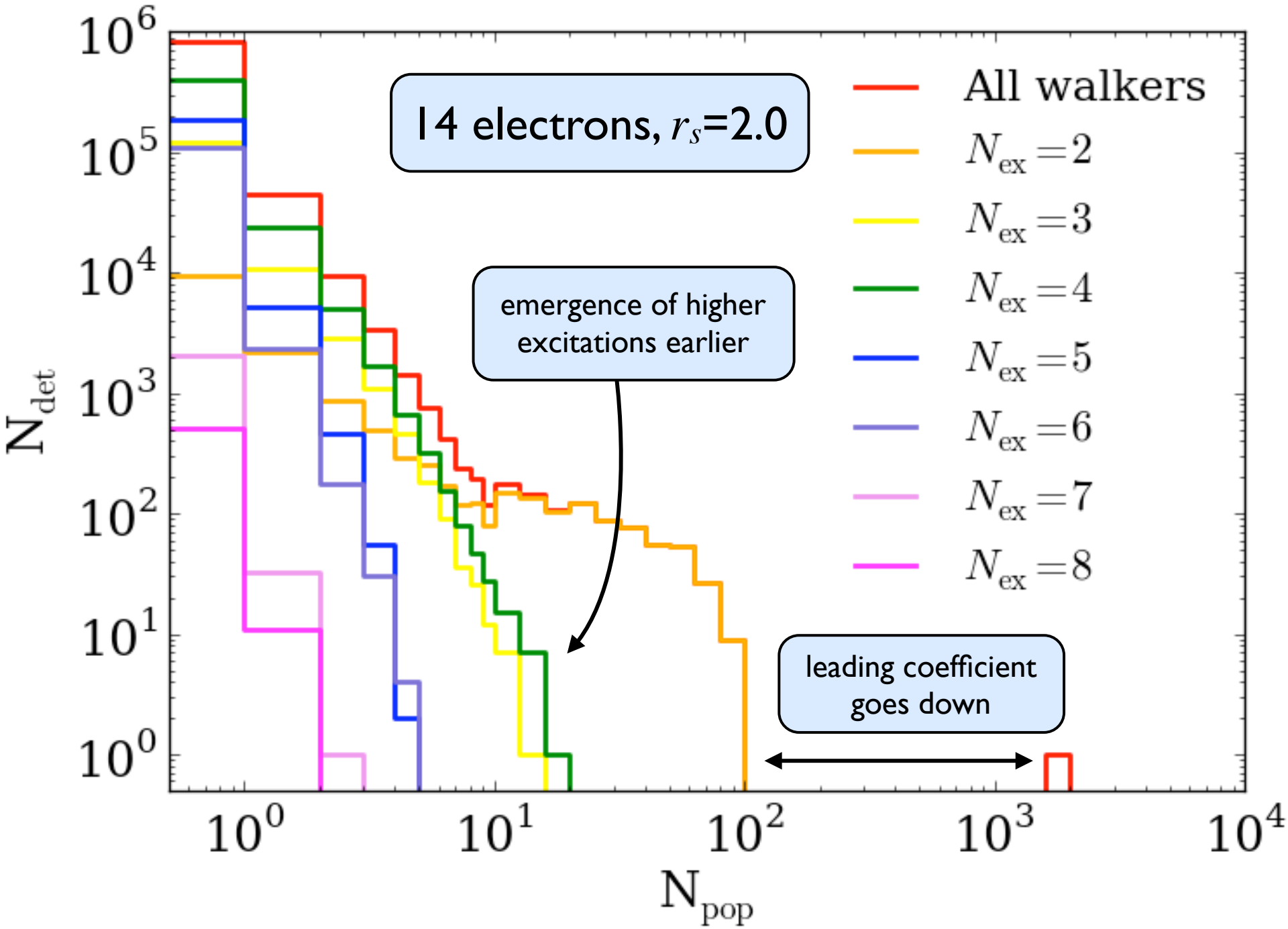
(Speculative/preliminary)

A remarkably simple 'sign structure'?

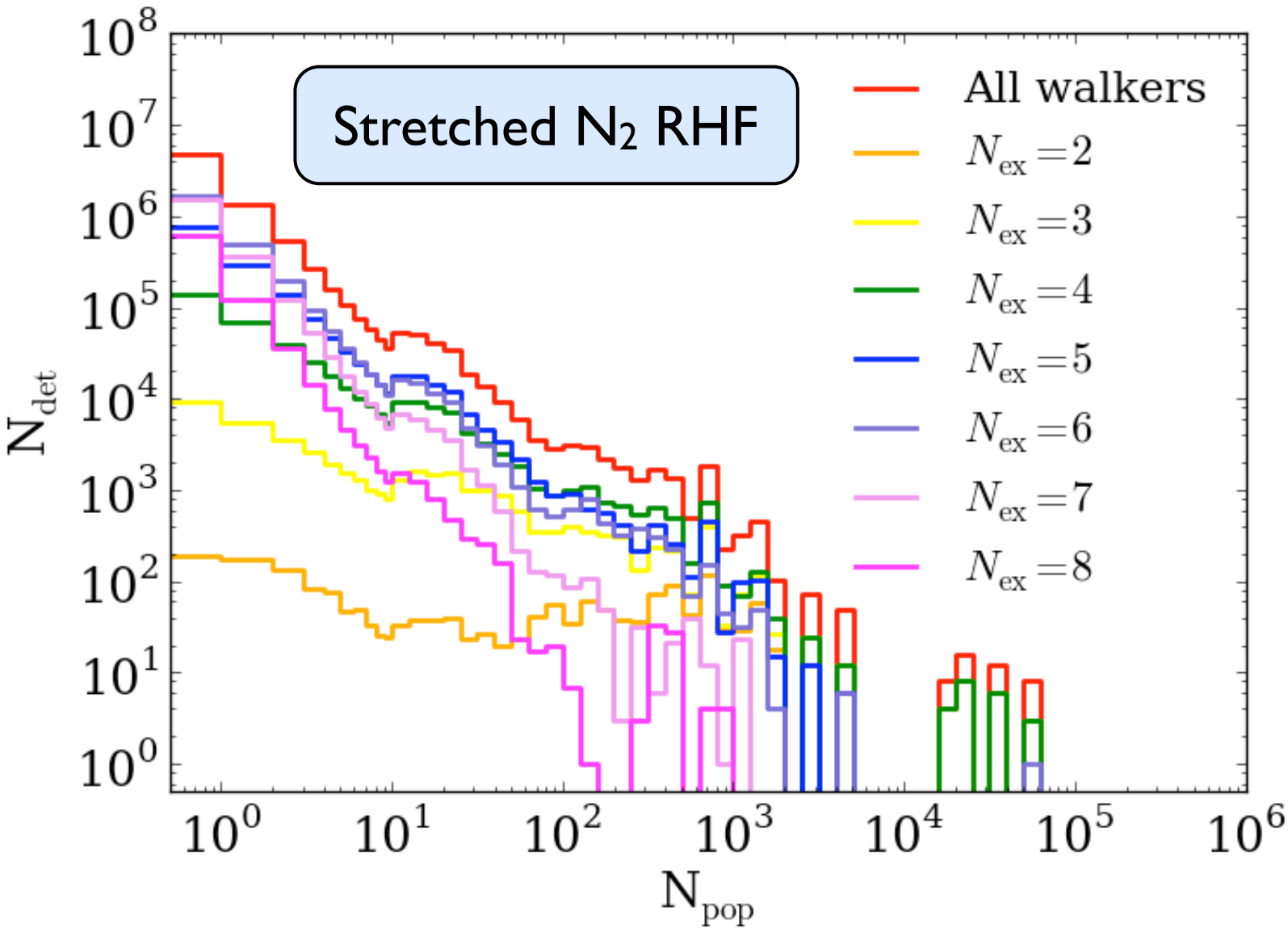



14 electrons, r_s=0.5
All walkers
$N_{ex}=2$
$N_{ex}=3$
$N_{ex}=4$
$N_{ex}=5$
$N_{ex}=6$
$N_{ex}=7$
$N_{ex}=8$
Rescale by 10^{-4} if using intermediate normalization
N_{det}
N_{pop} ($\propto c_i$)
10^0
10^1
10^2
10^3
10^4
10^5
10^6

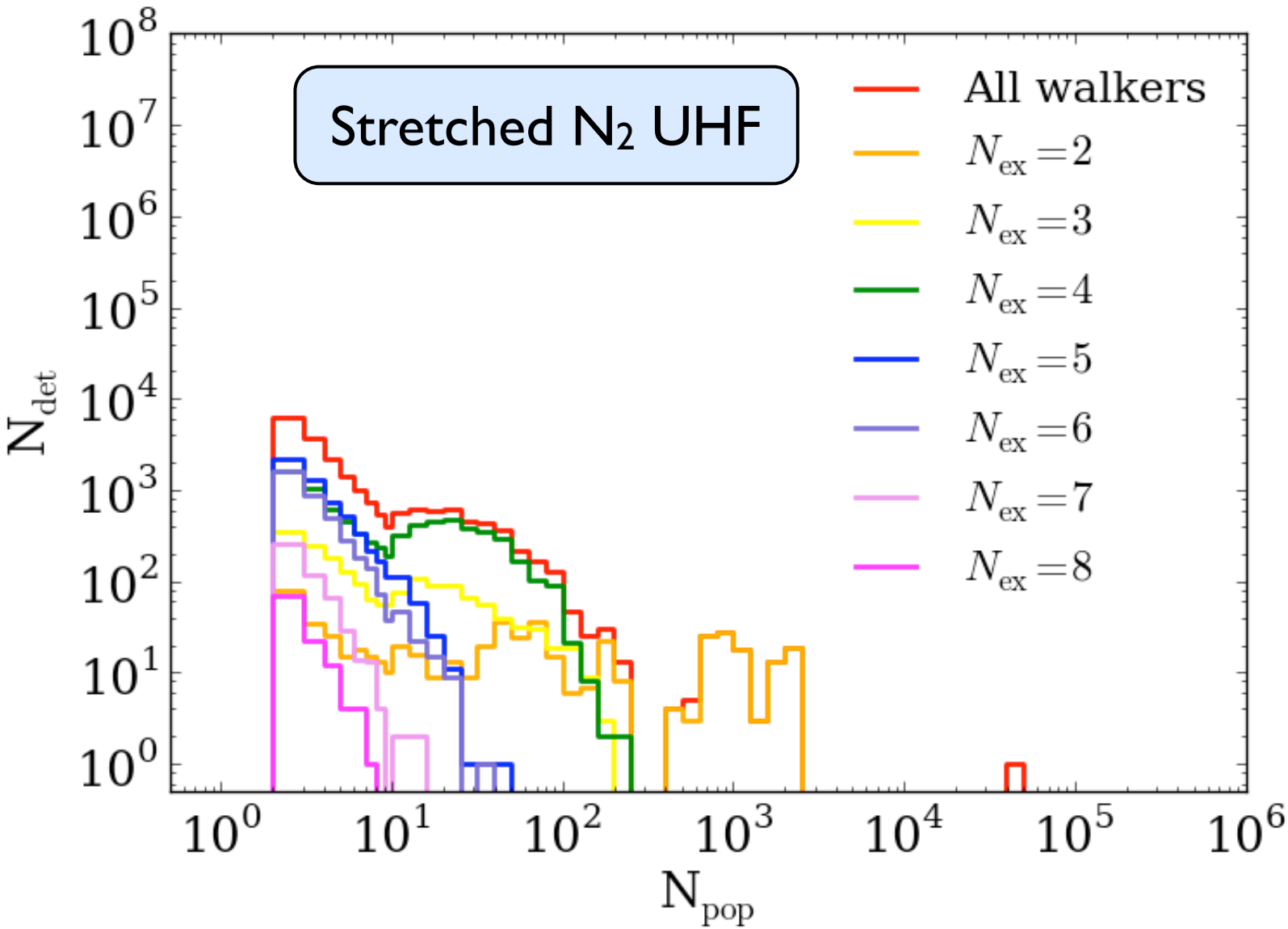

14 electrons, r_s=1.0
emergence of higher excitations earlier
leading coefficient goes down
All walkers
$N_{ex}=2$
$N_{ex}=3$
$N_{ex}=4$
$N_{ex}=5$
$N_{ex}=6$
$N_{ex}=7$
$N_{ex}=8$
N_{det}
N_{pop}
10^0
10^1
10^2
10^3
10^4
10^5
10^6

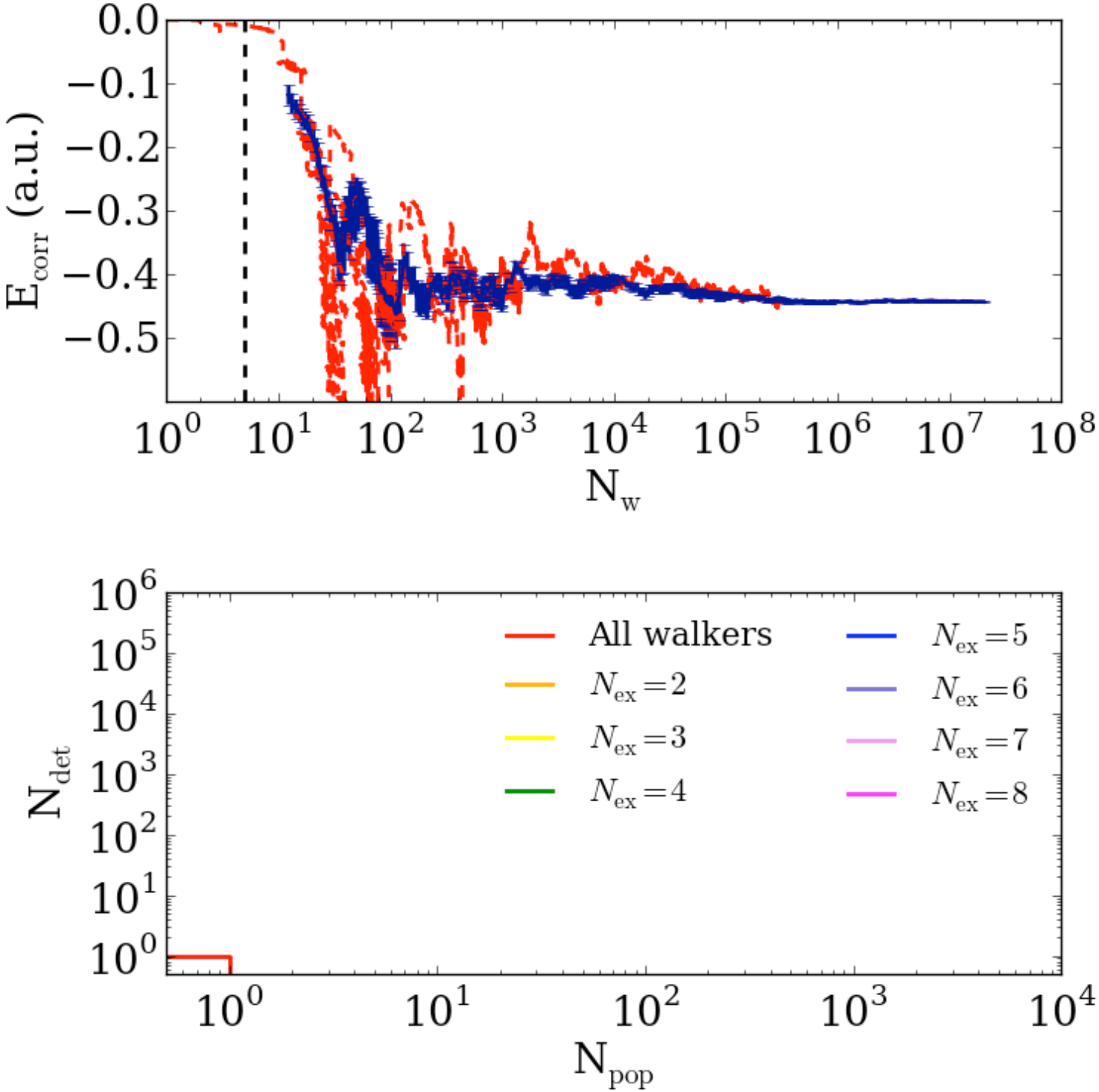

14 electrons, r_s=2.0
emergence of higher excitations earlier
leading coefficient goes down
All walkers
$N_{ex}=2$
$N_{ex}=3$
$N_{ex}=4$
$N_{ex}=5$
$N_{ex}=6$
$N_{ex}=7$
$N_{ex}=8$
N_{det}
N_{pop}
10^0
10^1
10^2
10^3
10^4
10^5
10^6

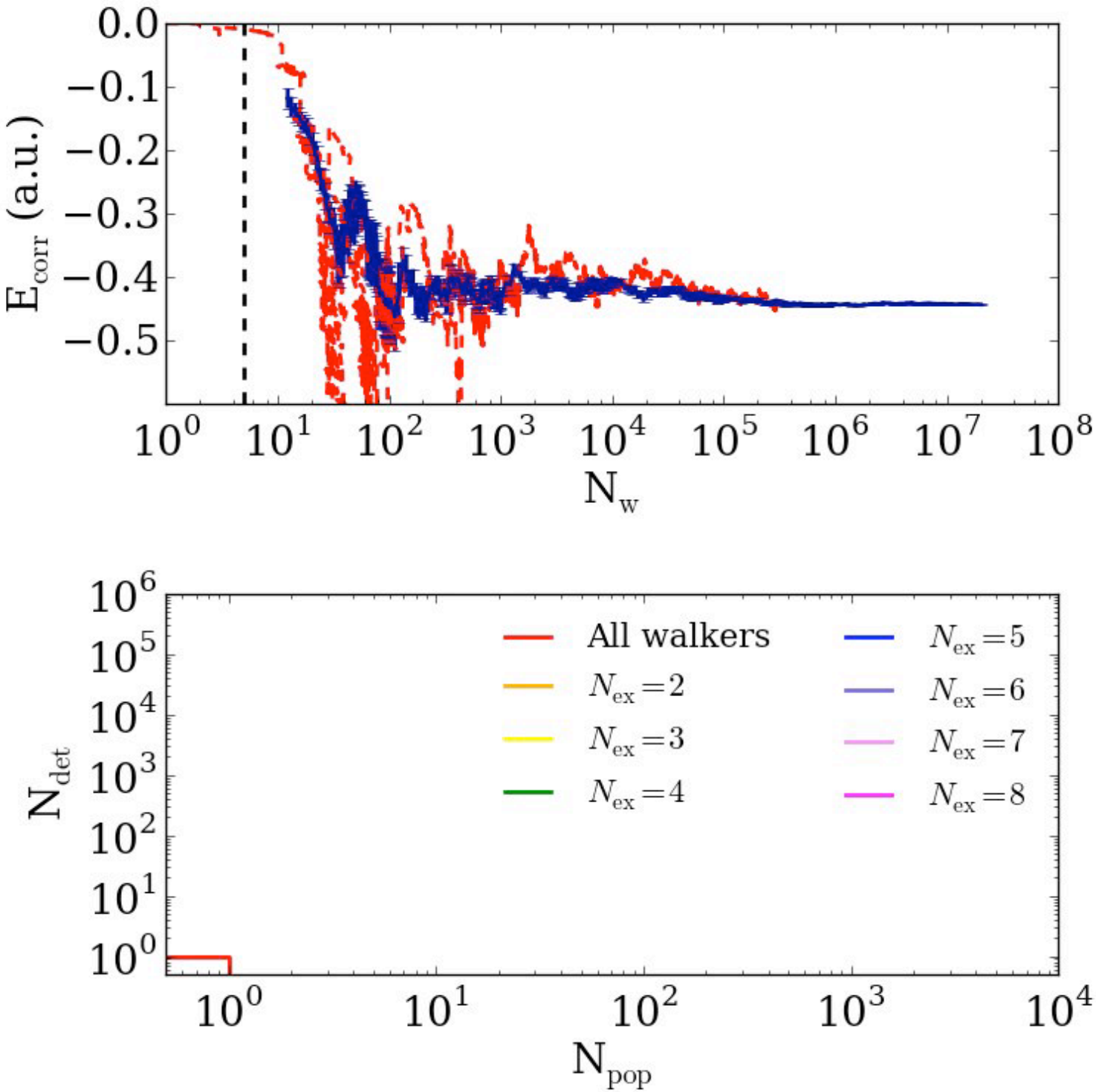
How does this relate to molecules?



How does this relate to molecules?




0.0
−0.1
−0.2
−0.3
−0.4
−0.5
E_corr (a.u.)
10^0 10^1 10^2 10^3 10^4 10^5 10^6 10^7 10^8
N_w
10^6
10^5
10^4
10^3
10^2
10^1
10^0
N_det
All walkers
N_ex = 2
N_ex = 3
N_ex = 4
N_ex = 5
N_ex = 6
N_ex = 7
N_ex = 8
10^0 10^1 10^2 10^3 10^4
N_pop


0.0
−0.1
−0.2
−0.3
−0.4
−0.5
E_corr (a.u.)
10^0 10^1 10^2 10^3 10^4 10^5 10^6 10^7 10^8
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10^0
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All walkers
N_ex = 2
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N_ex = 6
N_ex = 7
N_ex = 8
10^0 10^1 10^2 10^3 10^4
N_pop

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- HEG/diverences: JJS *et al.* in preparation