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Towards a determinant space representation of the electronic wave function in the solid state

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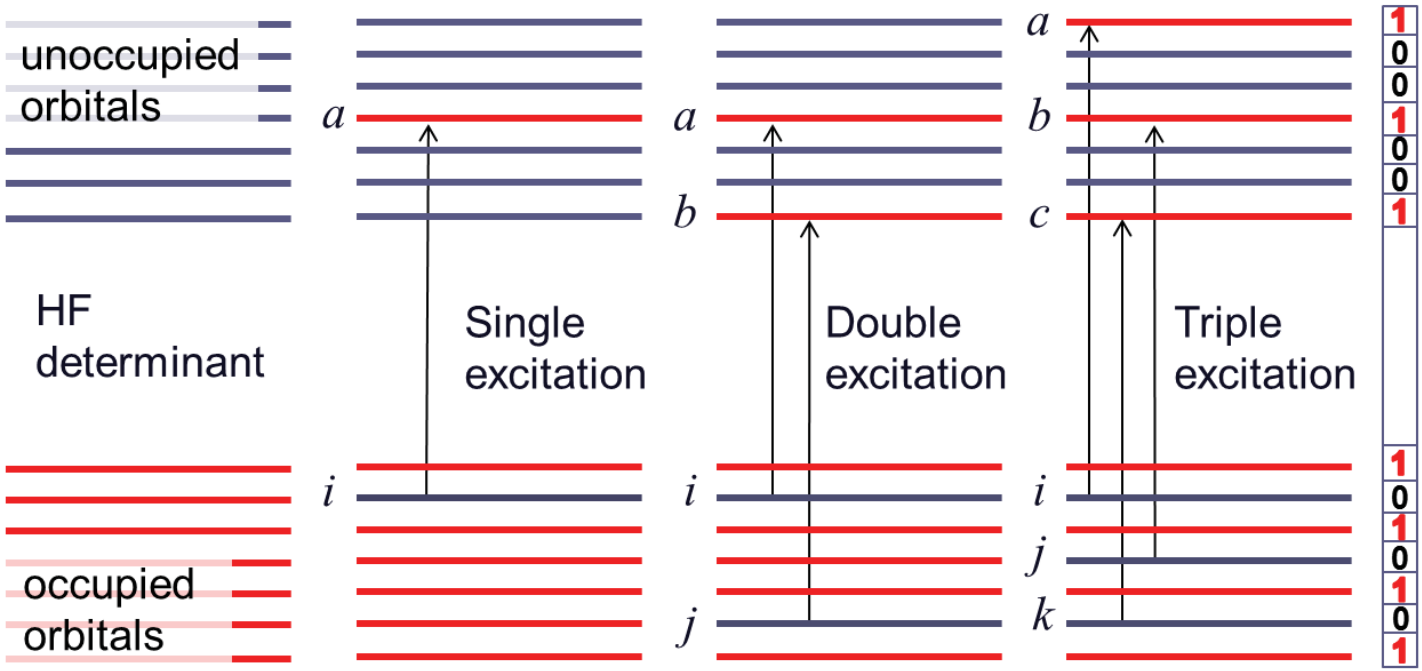
16th Workshop on Computational Physics and Materials Science:

Total Energy and Force Methods

Fock space

- Functional space of quantum chemical methods giving rise to antisymmetric determinants



Exponentially large space becomes systematically complete as the basis set increases in size

Full variational optimization: FCI or exact diagonalization

How to reduce the complexity of the wavefunction?

- Single-reference (diagrammatic) methods:
  - MP2, CCSD, CCSD(T), …
  - Established hierarchy for molecules
  - Polynomial scaling, but relies on qualitative HF
  - Periodic MP2: Schutz, Scuseria, Manby, Kresse, Hutter …
- Multi-reference methods:
  - General CI (CAS), tensor factorizations (MPS/CPS), …
  - Required for stronger correlations
  - Variational optimization and exponential cost in general
- QMC?

FCIQMC motivation

- FCI wavefunction -> discrete, coarse-grained walker snapshot
- Stochastic evolution according to ITSE
- Full wavefunction & properties arise after appropriate time-averaging

- Lose:
  - Vector-arithmetic operations
- Gain:
  - Tractible wavefunction storage and manipulation
  - Computational effort sampling a determinant $\propto$ amplitude
  - Large-scale parallelization

JCP 131, 054106 (2009)

Projector Monte Carlo

- Imaginary-time S.E. $\dfrac{\partial \psi}{\partial \beta} = -H\psi$
- Solution given in eigenbasis as

$$\psi(r,\beta) = \sum_n c_n e^{-\beta(E_n - S)} \left| \Psi_n \right\rangle$$

- Slater determinant space allows for linearization of propagator

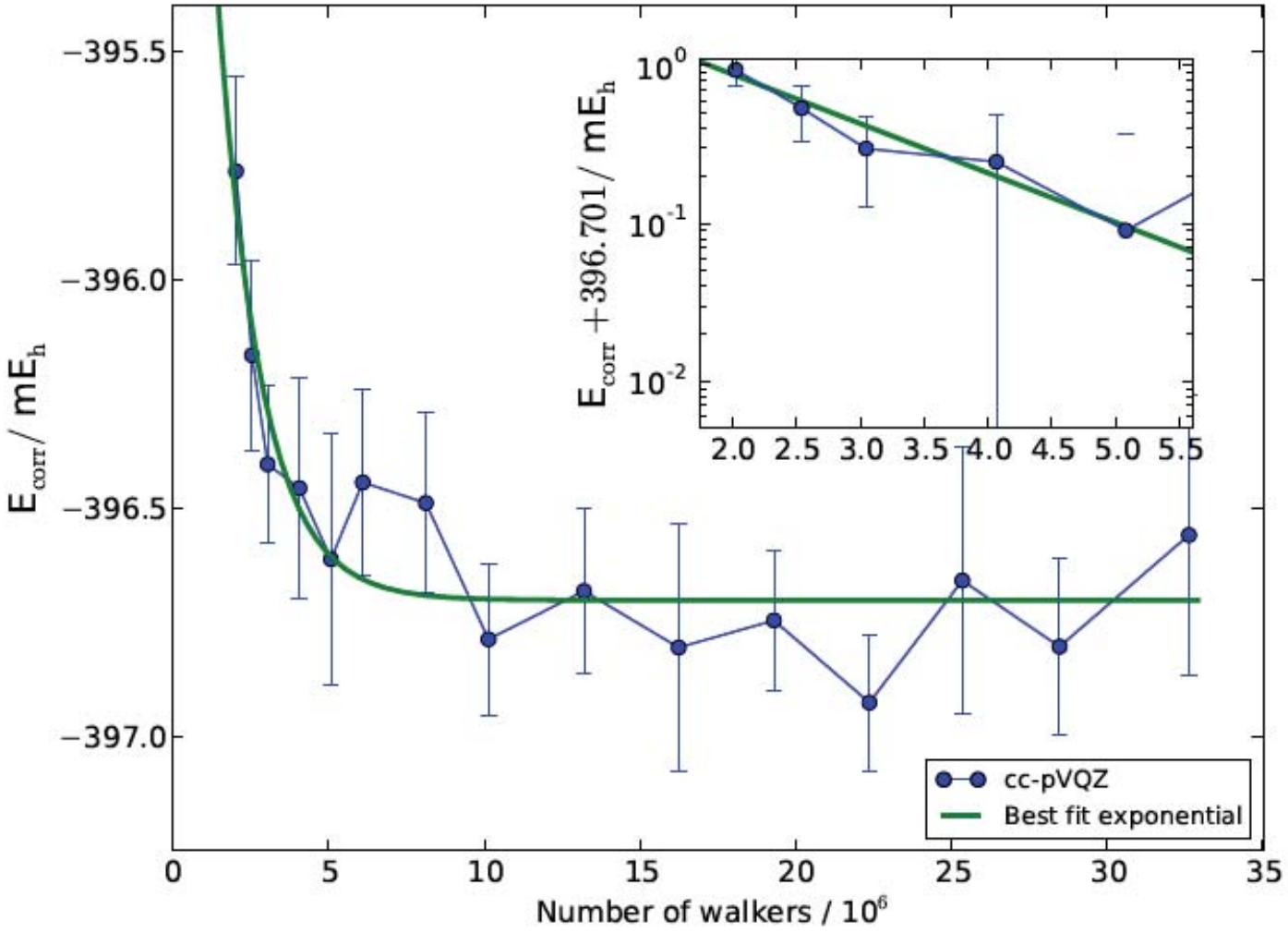
$$\frac{\partial C_i}{\partial \beta} = (H_{ii} - S)C_i + \sum_{j \neq i} H_{ij} C_j$$

Initiator approximation

- Annihilation events are crucial for breaking sign-symmetry of solutions and overcome sign problem
- For high annihilation rate and minimization of noise propagation -> initiator approximation
- Low weighted determinants are propagated with a truncated hamiltonian over the occupied space only
- Systematically improvable

JCP 132, 041103 (2011)

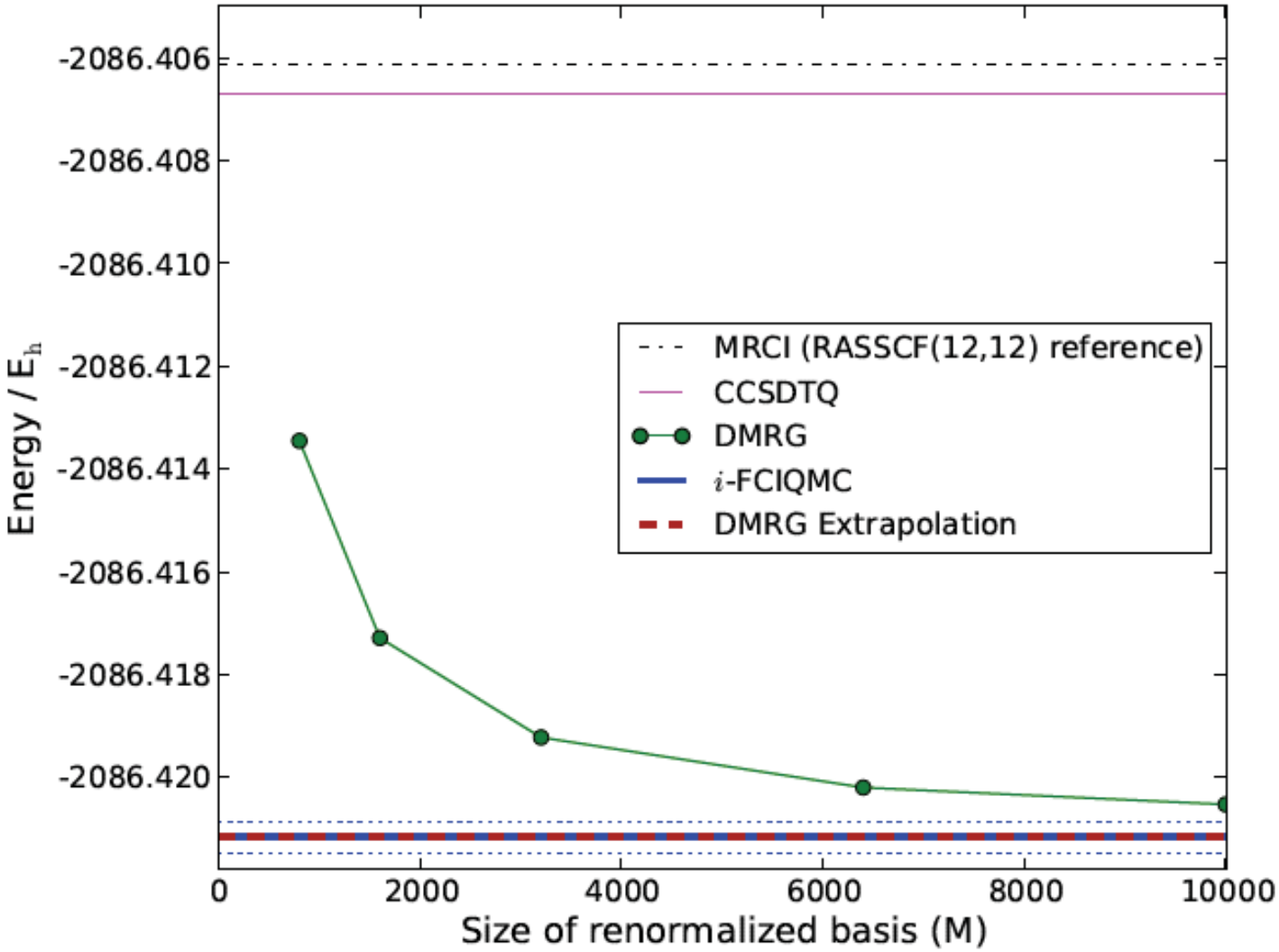
Carbon Dimer



- cc-pVQZ basis set
- Many small chemical systems treated to high accuracy

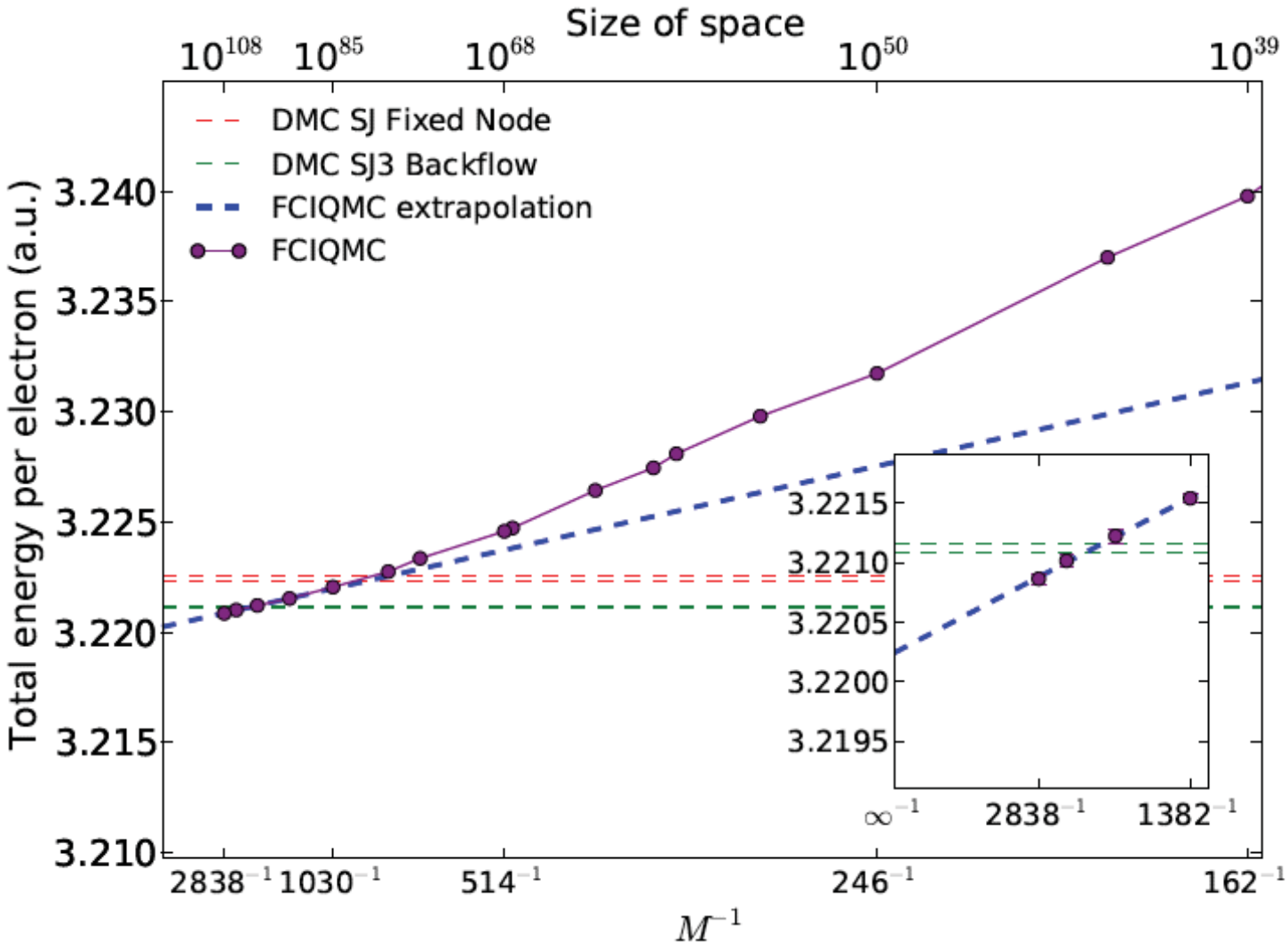
JCP 135, 084104 (2011)

Chromium dimer



10^{14} determinants. FCI vector would require 60,000 TB RAM

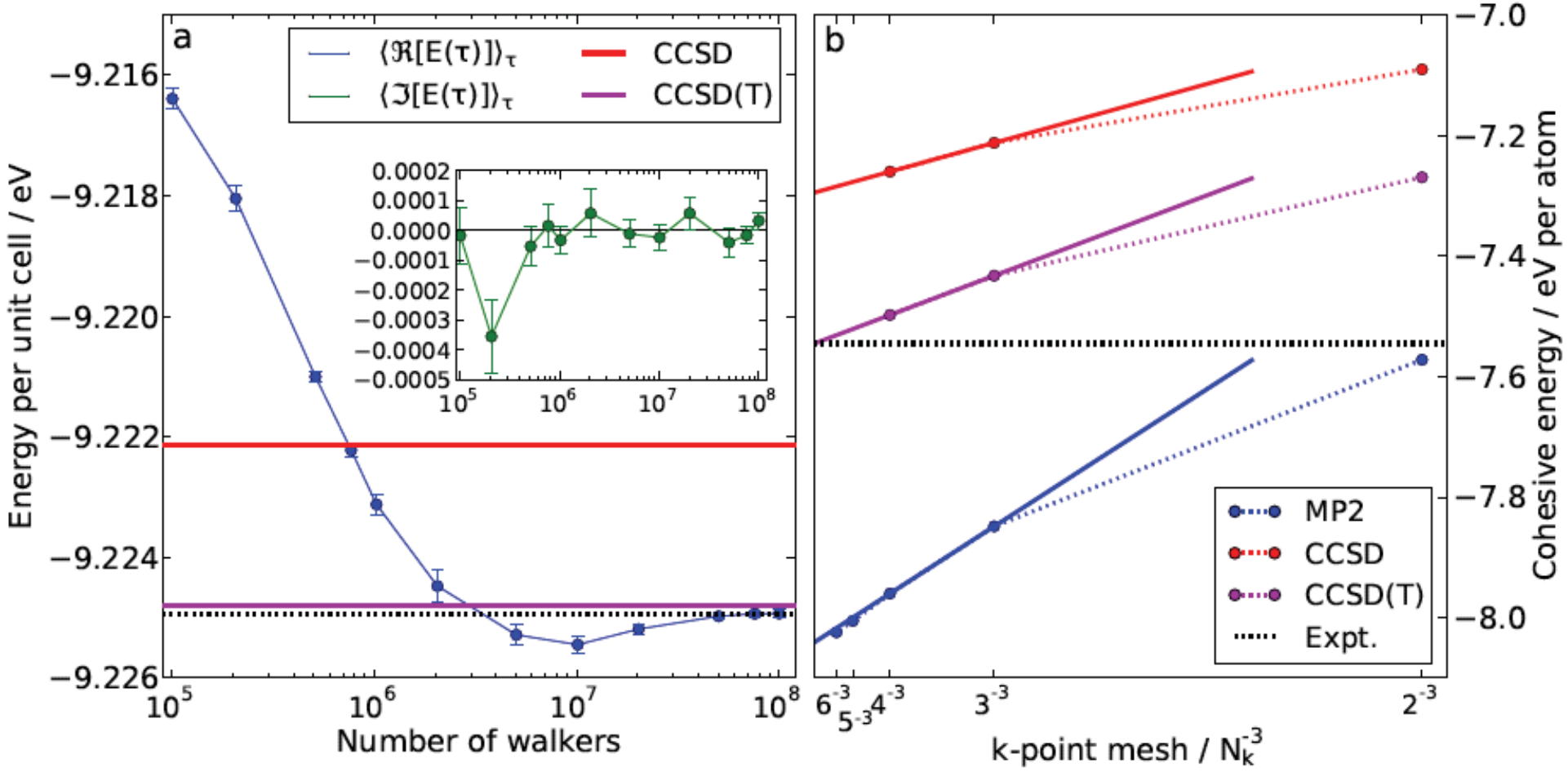
Uniform Electron Gas



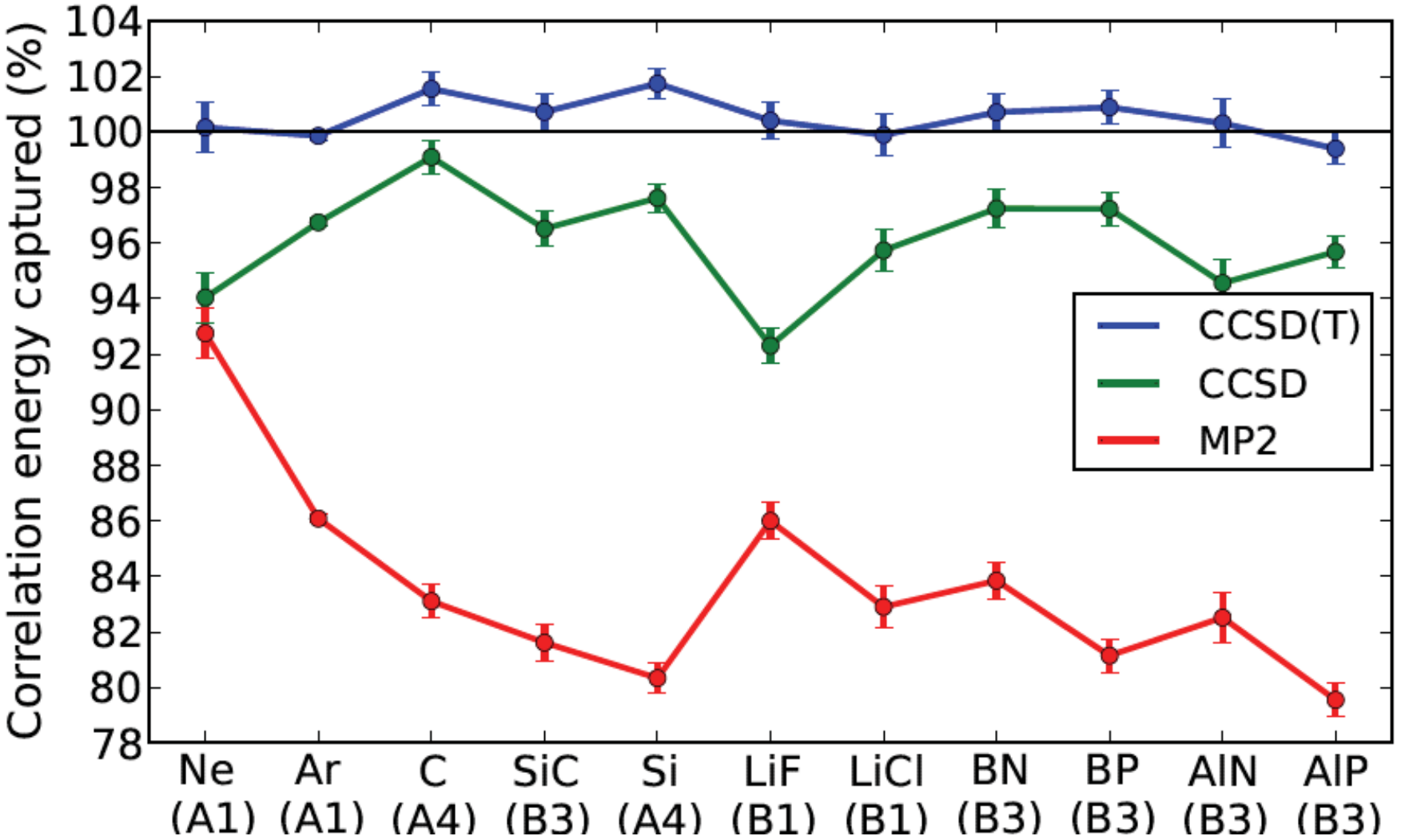
- r_s=0.5 a_0 54 electrons in a plane wave basis

PRB 85, 081103 (2012)

Lithium Hydride convergence



- 3x3x3 mesh -> 27 k-points sampled: Complex walker dynamic with sub-meV accuracy
- 54 electrons in 54 bands: 10^{30} determinants
- A first implementation of high-level quantum chemical methods in the solid state



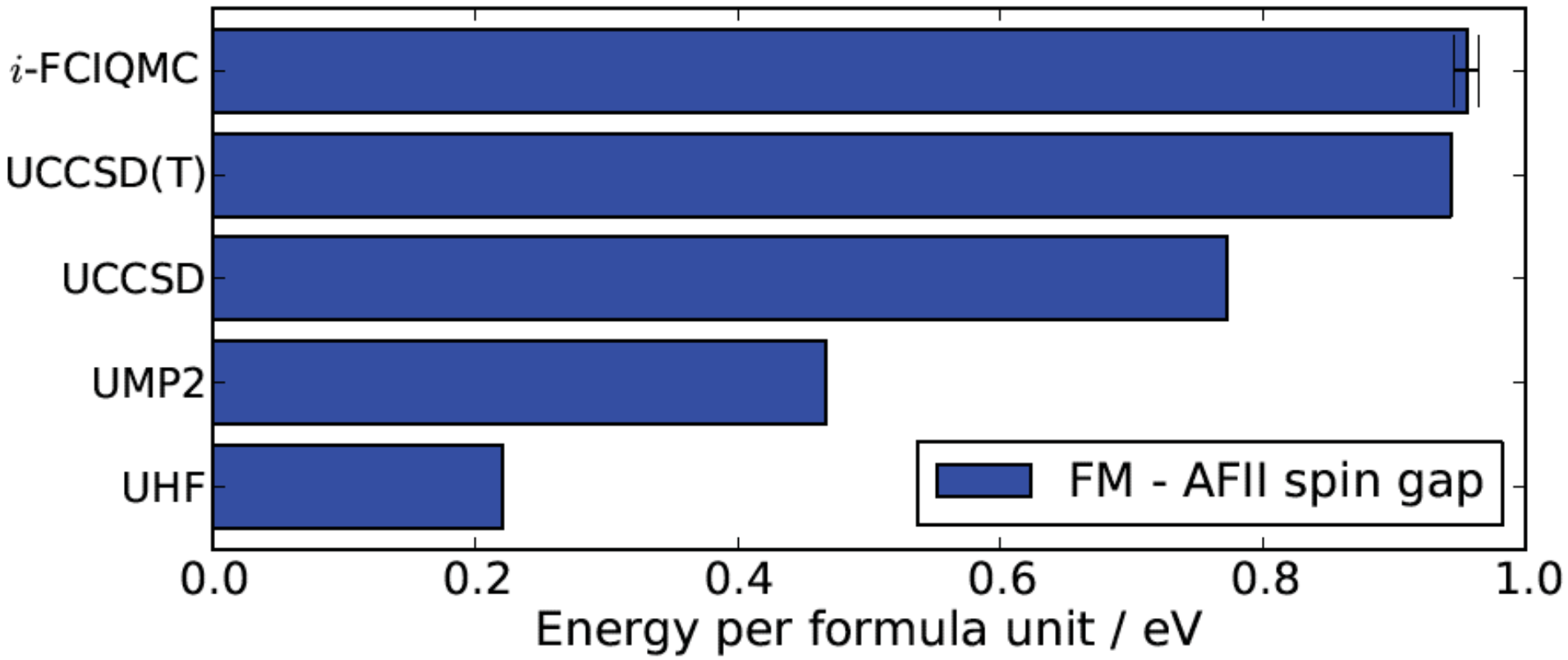
- 2x2x2 cells: (64e, 64o) and (80e, 72o) for LiF and LiCl
- Experimental lattice constants with A1 = fcc, A4 = diamond, B1 = rock-salt, B3 = zinc-blende
- 2-300 million walkers for *i*-FCIQMC calculations

Nature (2013)

	LiH	C	BN	AlP
MP2	–2.386	–8.039	–7.149	–4.629
CCSD	–2.454	–7.295	–6.572	–4.107
CCSD(T)	–2.483	–7.545	–6.782	–4.347
Experiment	–2.487	–7.545	–6.758	–4.322

- CCSD(T) with MAE of 0.03 eV, compared to 0.2 eV (PBE)

AFII-FM spin gap in Nickel Oxide



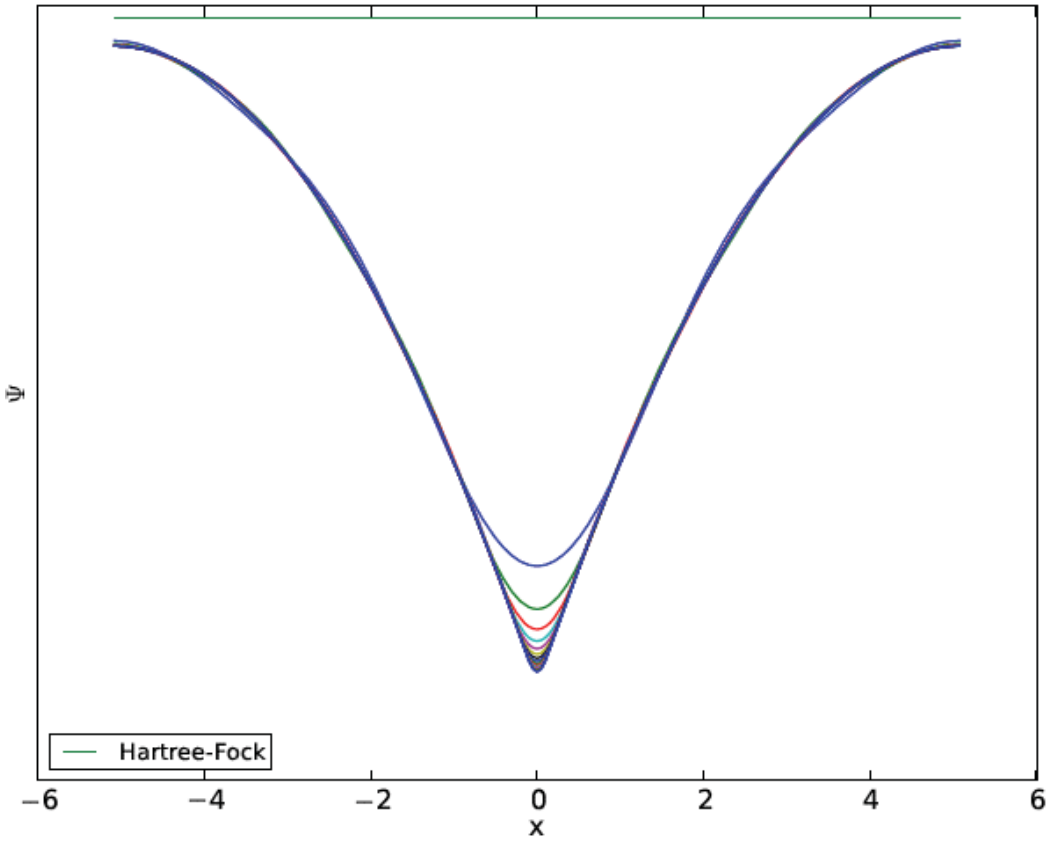
- Unrestricted reference
- Two formula units
- 32 electrons in 38 UHF bands

Problem 1: Slow convergence wrt basis size

- Improved orbital representation?
  - MP2 natural orbitals: factor of 2-10x saving in orbital space depending on sparsity of electron density.
  - Will fail for stronger correlation effects

JCTC 7, 2780 (2011)

- Root of the problem: electron-electron cusps in PW(/gaussian) basis

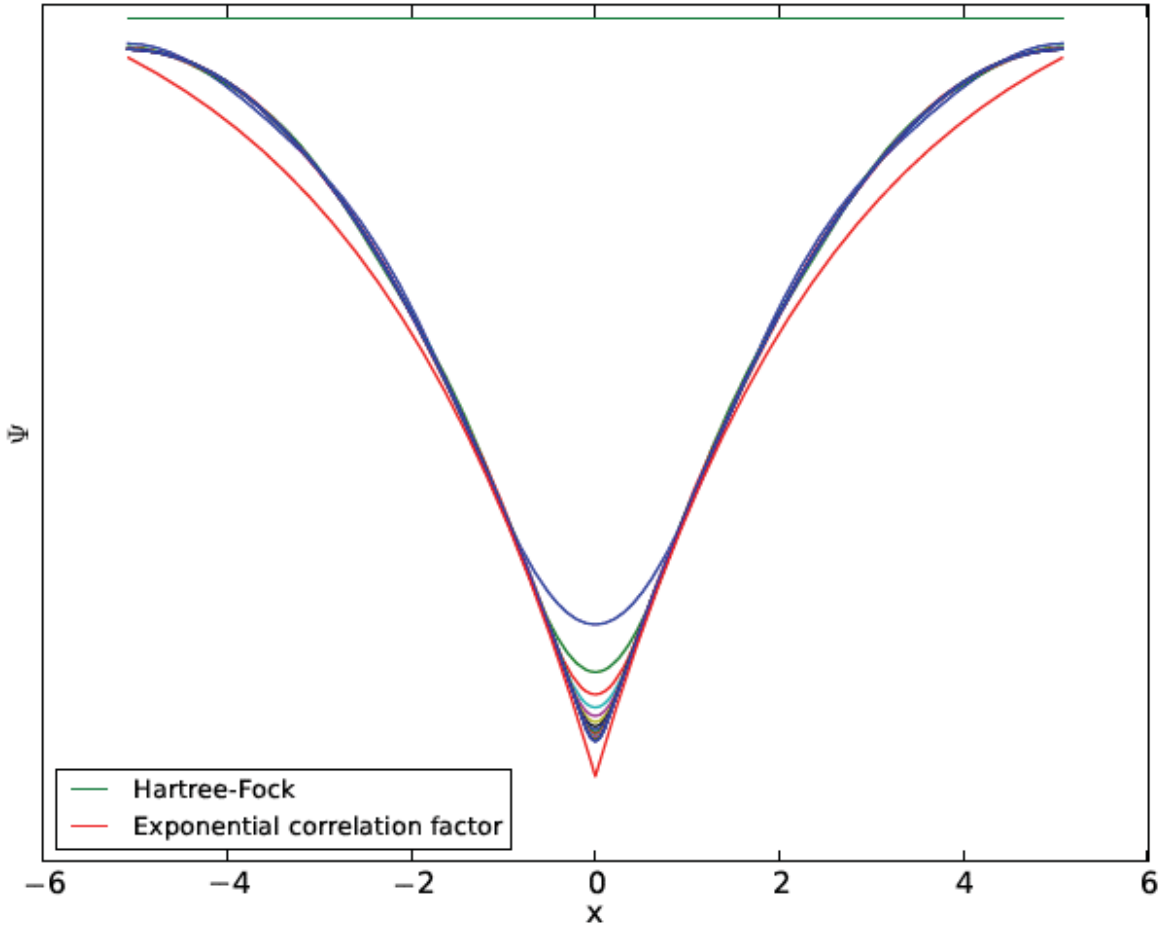


- $r_s = 5\ a_0$
- 2 electron UEG wavefunction
- 27-50,000 plane waves

- Add explicitly correlated component to the wavefunction: R12/F12 methods

$$\left|u_{ij}\right\rangle = T_{ab}^{ij}\left|ab\right\rangle + t^{ij}\hat{Q}_{12}f(r_{12})\left|ij\right\rangle$$

$$f(r_{12}) = \frac{1}{\gamma}(1 - e^{-\gamma r_{12}})$$

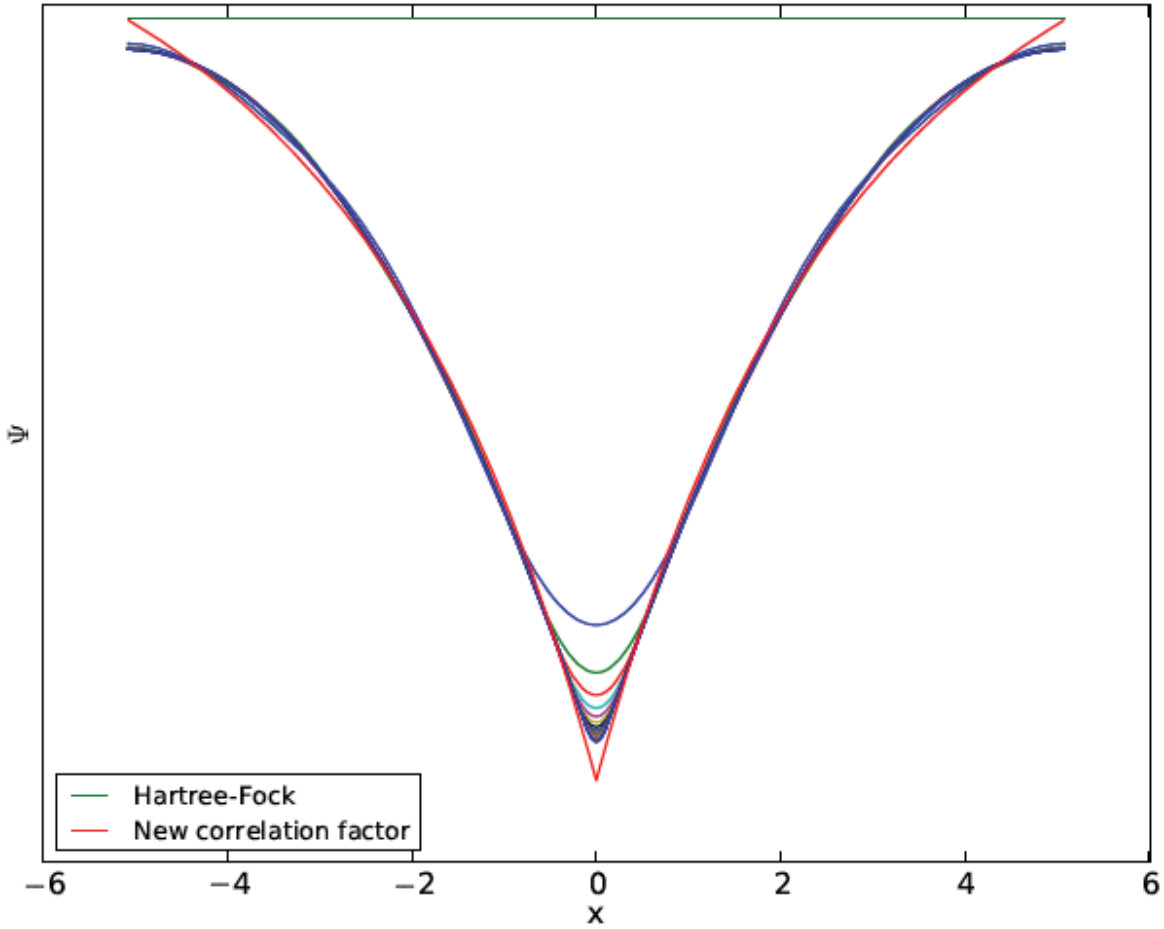


- In molecular systems, $f(r_{12})$ taken to be of exponential form

- Add explicitly correlated component to the wavefunction: R12/F12 methods

$$\left|u_{ij}\right\rangle = T_{ab}^{ij}\left|ab\right\rangle + t^{ij}\hat{Q}_{12}f(r_{12})\left|ij\right\rangle$$

$$f(r_{12}) = -\frac{1}{\gamma^2}\frac{(1-e^{-\gamma r_{12}})}{r_{12}}$$

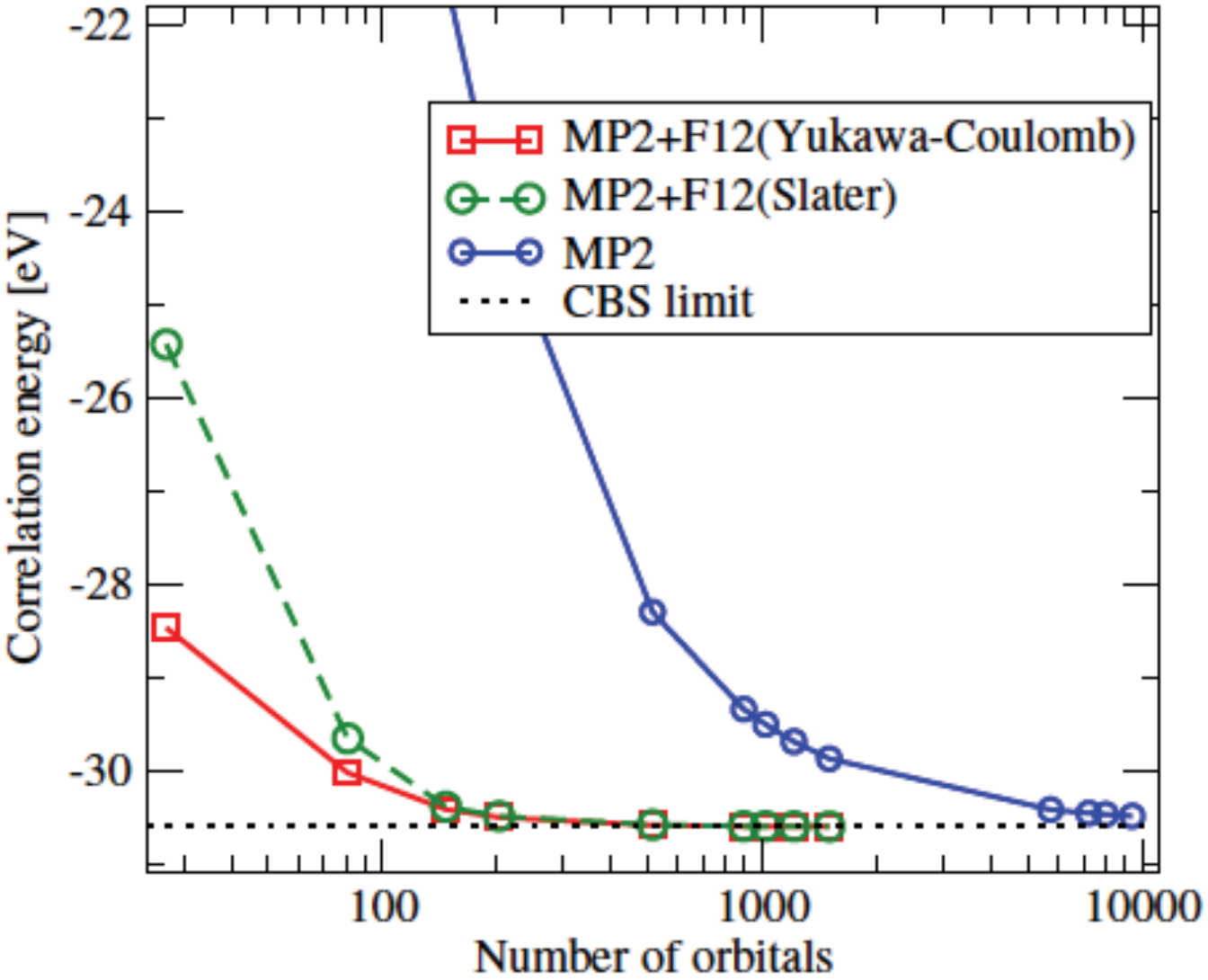


- Via perturbation theory can find "exact" form of correlation hole for new optimal correlation factor for the solid-state

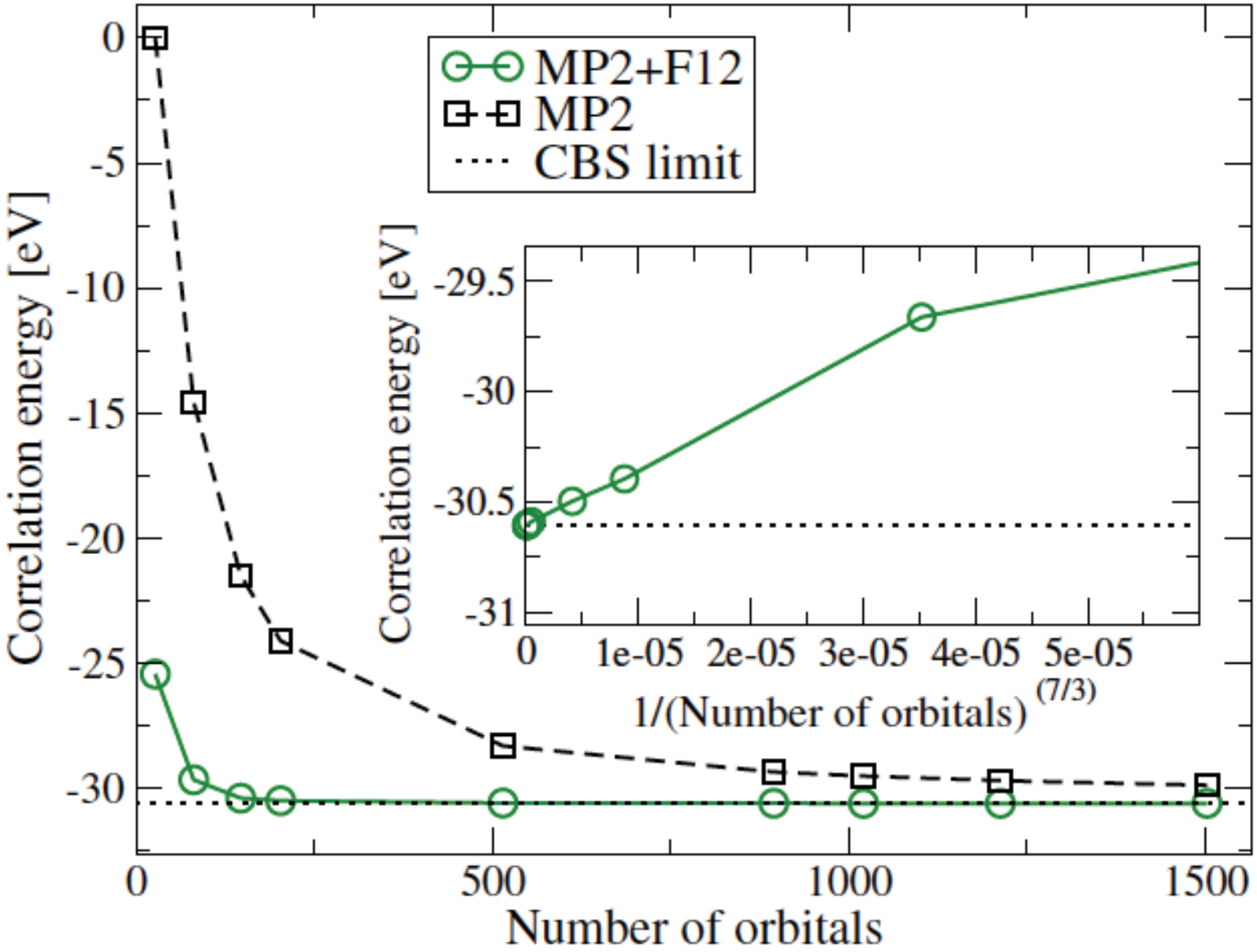
- Can be generalized for FCIQMC in two ways

- Required on-the-fly calculation of density matrices -> forces

JCP 137, 164112 (2012)



- 54 electrons, r_s= 5 a_0


MP2+F12
MP2
CBS limit
Correlation energy [eV]
Number of orbitals
0
-5
-10
-15
-20
-25
-30
0
500
1000
1500
-29.5
-30
-30.5
-31
1e-05
2e-05
3e-05
4e-05
5e-05
1/(Number of orbitals)^(7/3)

Problem 2: Excited states in FCIQMC

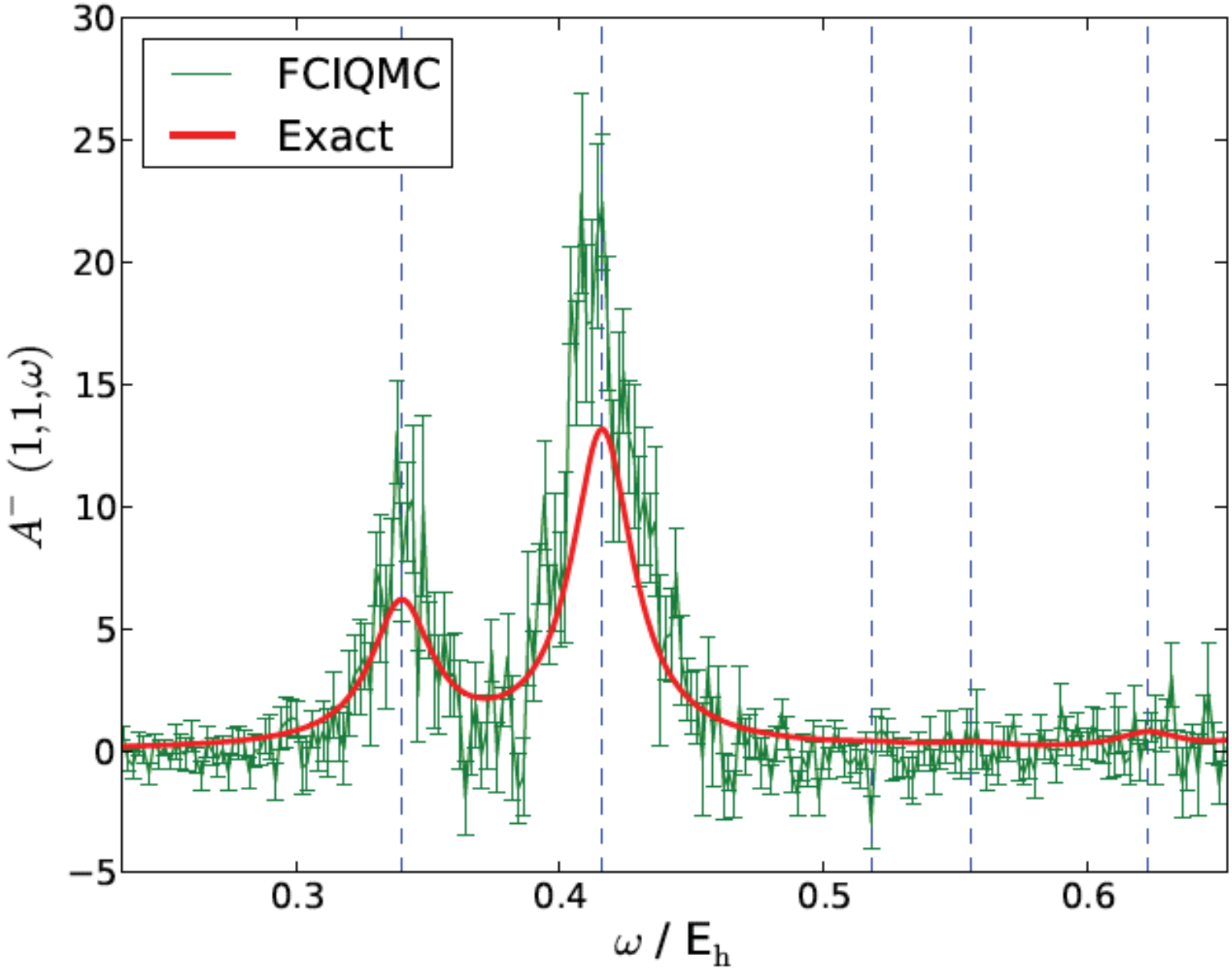
- By construction, FCIQMC exponentially filters out excited states
- Change the propagator for stable convergence to exact excited states

$$\psi(r,\beta) = \sum_n c_n e^{-\beta(E_n - S)} \left| \Psi_n \right\rangle$$

$$\Rightarrow \sum_n c_n e^{-\beta^2(E_n - S)^2} \left| \Psi_n \right\rangle$$

- No requirement for nodal constraint, analytic continuation or orthogonalization
- As with the ground state: no uncontrolled approximations
- Expensive: Additional factor of $\left(\beta \times \Delta E\right)^{-1}$ compared to GS

JCP 137, 191102 (2012)



- Be_2 molecular system

Problem 3: Slow convergence wrt supercell??

- DMFT? FCIQMC as impurity solver?
- DMET (Garnet Chan PRL 109, 186404 (2012))
  - Frequency independent analogue of DMFT
  - Self-consistently solve coupled mean-field problem on whole system and high-level calculation on selected 'impurity' orbitals
  - "Exact" mean-field coupling from bath orbitals for effect of environment

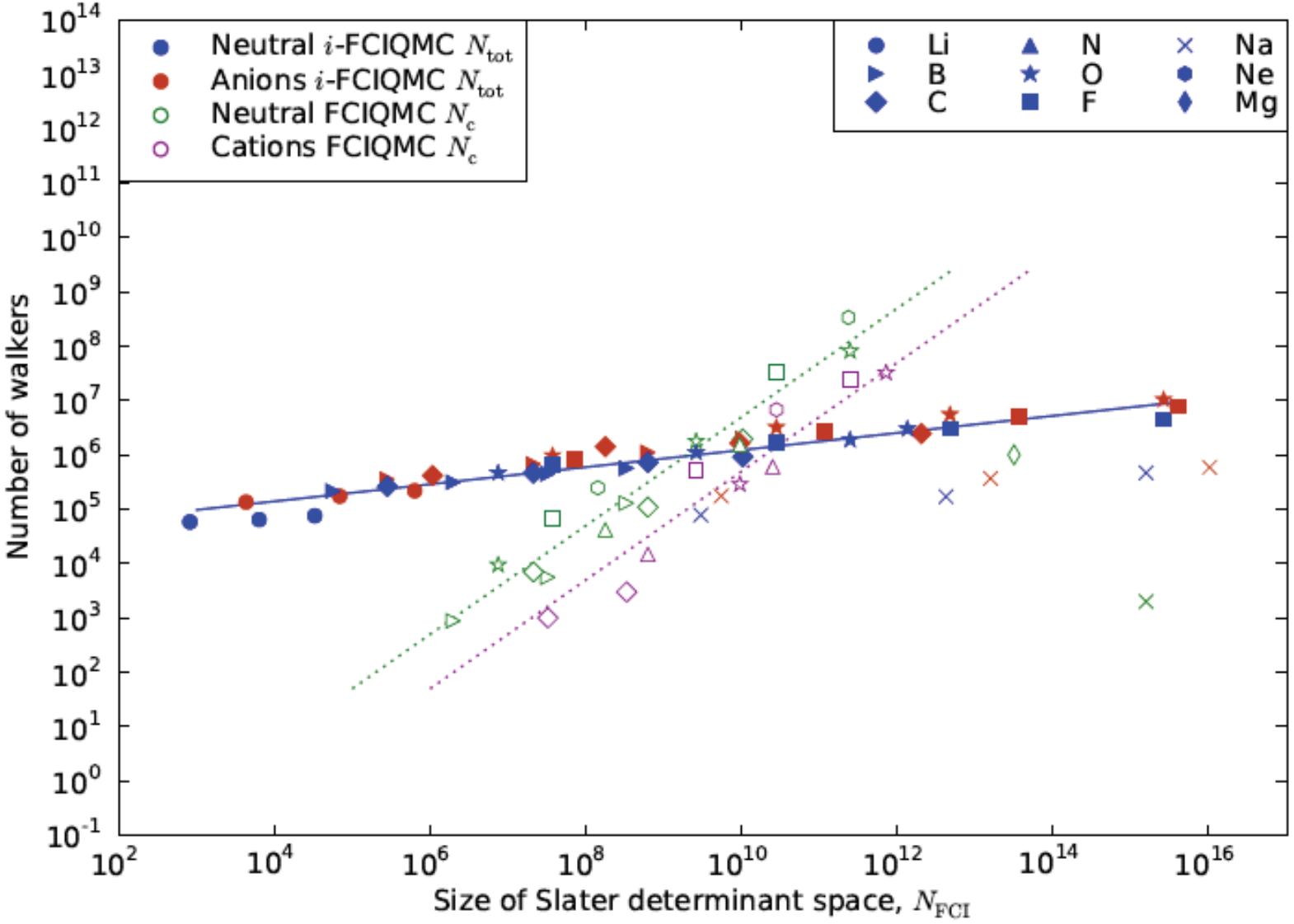
Thanks

- C. Filippi, R. Martin & N. Binggneli

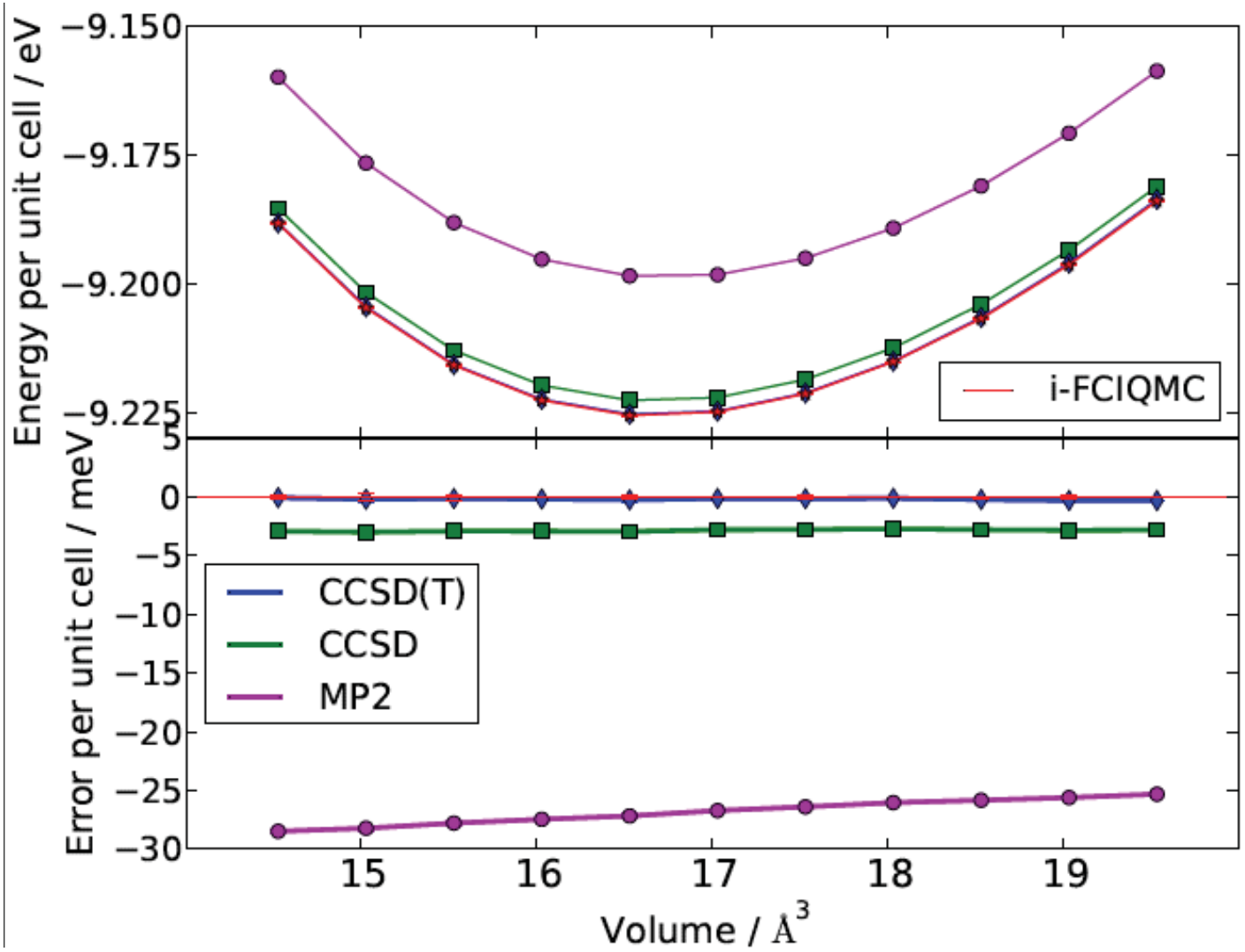
- Ali Alavi
- Garnet Chan (Excited States, DMET, Explicit correlation)
- Andreas Grüneis (VASP, Explicit correlation)
- Georg Kresse (VASP)
- James Shepherd (UEG)
- David Tew (Explicit correlation)
- Simon Smart

- FCIQMC is now in MOLPRO for molecular calculations

Scaling


Neutral i-FCIQMC N_{tot}
Anions i-FCIQMC N_{tot}
Neutral FCIQMC N_{c}
Cations FCIQMC N_{c}
Li
B
C
N
O
F
Na
Ne
Mg
Number of walkers
Size of Slater determinant space, N_{FCI}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
10^{8}
10^{9}
10^{10}
10^{11}
10^{12}
10^{13}
10^{14}
10^{2}
10^{4}
10^{6}
10^{8}
10^{10}
10^{12}
10^{14}
10^{16}

LiH EOS


Energy per unit cell / eV
−9.150
−9.175
−9.200
−9.225
i-FCIQMC
Error per unit cell / meV
5
0
−5
−10
−15
−20
−25
−30
CCSD(T)
CCSD
MP2
15
16
17
18
19
Volume / Å^3