Convergence of many-body wavefunction expansions using a plane wave basis: From the homogeneous electron gas to the solid state

TCM Electronic Structure Discussion Group

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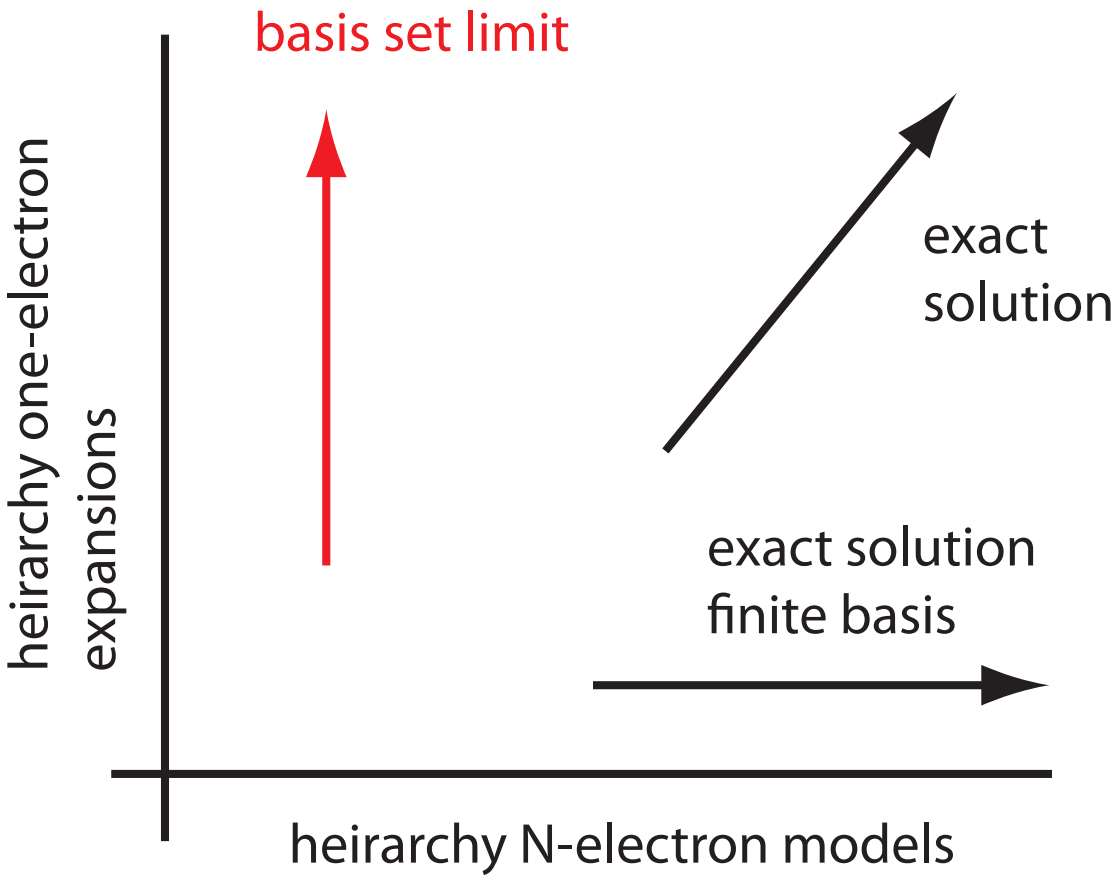
Determinantal Expansions



What is the Simulation Cell HEG?

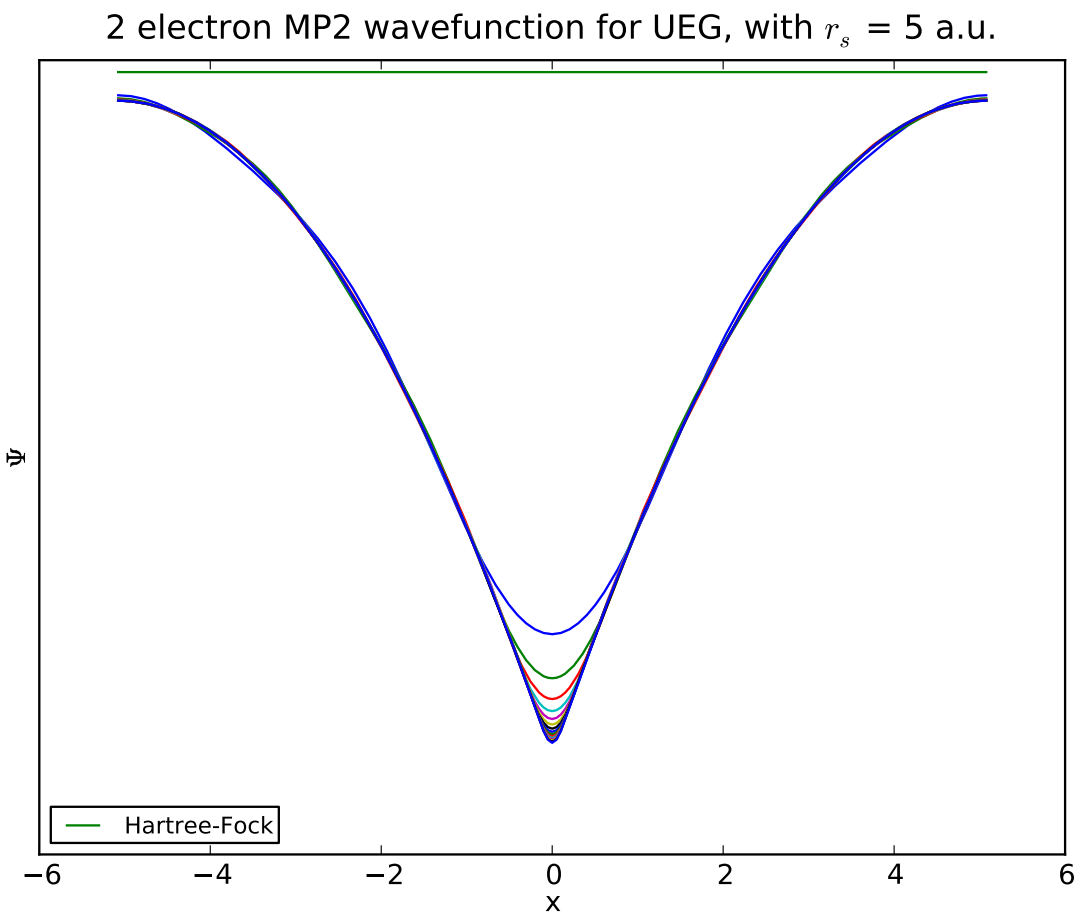
$$\hat{H} = \sum_{\alpha} -\frac{1}{2}\nabla_{\alpha}^{2} + \sum_{\alpha \neq \beta} \frac{1}{2}\hat{v}_{\alpha\beta} + \frac{1}{2}Nv_{\mathrm{M}}$$

- N electrons in a *periodic* (cubic) box of length L
- Uniform density: $\rho(\mathbf{r}) = \frac{N}{L^3}$
- Characteristic lengthscale: $r_s = \left(\frac{L^3}{\frac{4}{3}\pi N}\right)^{\frac{1}{3}}$
- Plane waves: $\psi_{js}(\mathbf{r}, \sigma) = \sqrt{\frac{1}{L^3}}\ e^{i\mathbf{k}_j \cdot \mathbf{r}}\ \delta_{s\sigma}$.
- Thermodynamic limit: $N \to \infty$, $\frac{N}{L^3} = \text{const.}$

Problems with Determinantal Expansions

- $|\Psi\rangle = \sum_{\mathbf{i}} c_{\mathbf{i}} |D_{\mathbf{i}}\rangle$
- Perturbative approaches - MP series and CCSD(T) - diverge in T.L.
- Size extensivity important - truncated CI will retrieve zero energy in T.L.

Electronic Cusps



[credit: George Booth]

- Lines show $(2n+1)^3$ k-points (from 27 to ∼16,000)
- (DFT) The density does not have e-e cusps
- (VMC) Jastrow factor

Overview

- 1) Simple theory to model basis set incompleteness: MP2

  Drawbacks: low-level, diverges, unphysical

  Benefits: analytic matrix elements, cheap, qualitative short-range cusp behaviour
- 2) Introduce momentum transfer vector based basis set truncation
- 3) Apply this to FCIQMC by re-summation of the projected energy
- 4) Apply to plane-wave solid-state systems (if time)

Second Order Møller-Plesset Theory (MP2)

- $H = \sum_\alpha F_\alpha + H'$
- Perturbing Hamiltonian couples in double excitations from the full N-fold excited states

$$E_{\mathrm{MP2}} = \sum_{i>j}^{\mathrm{occ}} \sum_{a>b}^{\mathrm{virt}} \frac{|\langle ij|\hat{v}|ab\rangle - \langle ij|\hat{v}|ba\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \qquad \text{(spinorbitals)}$$

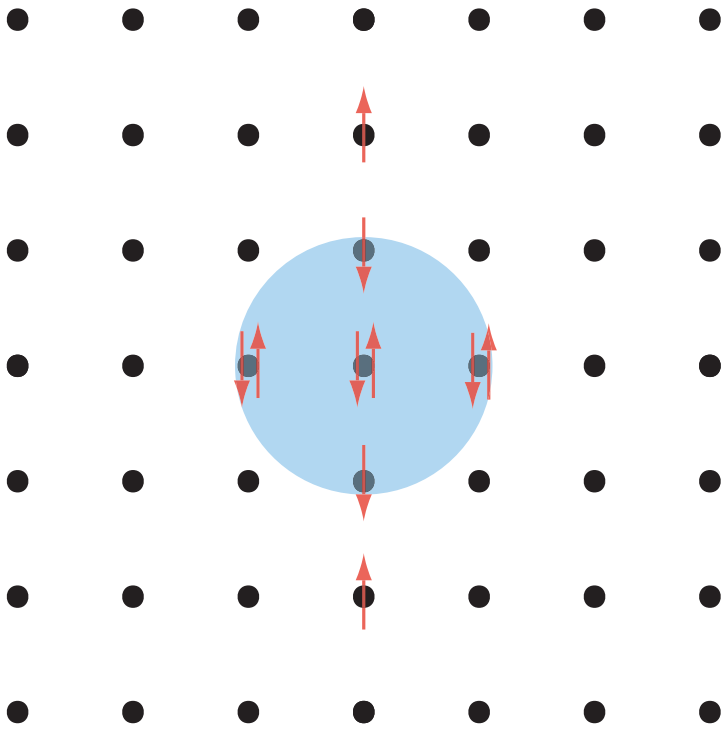
Double Excitations in k-space

- Transform MP2 expression into k-space representation:

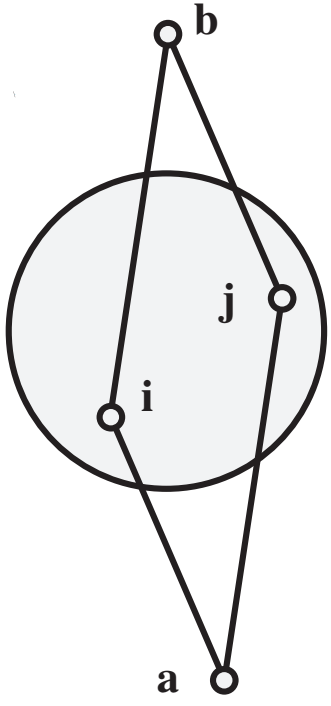
$$E_{\mathrm{MP2}} = \sum_{i>j}^{\mathrm{occ}} \sum_{a>b}^{\mathrm{virt}} \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_j - \mathbf{k}_b} \frac{2\, v^2_{\mathbf{k}_i - \mathbf{k}_a} - v_{\mathbf{k}_i - \mathbf{k}_a} v_{\mathbf{k}_j - \mathbf{k}_a}}{\Delta\epsilon}$$

- FT: $v_{\mathbf{k}_i - \mathbf{k}_a} = \frac{4\pi}{L^3 (\mathbf{k}_i - \mathbf{k}_a)^2}$
- These two terms are called 1) *direct* and 2) *cross* or *exchange-like* terms
- Momentum is conserved: $\mathbf{k}_i + \mathbf{k}_j = \mathbf{k}_a + \mathbf{k}_b$
- Can define a *momentum transfer vector*: $\mathbf{g} = \mathbf{k}_a - \mathbf{k}_i$

Double Excitations in k-space (2)



An excitation in the discrete regime



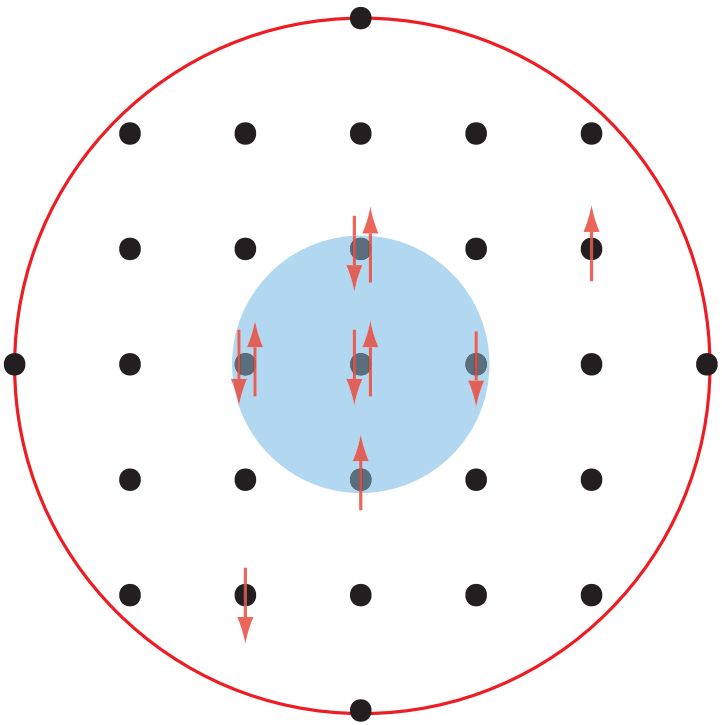
An excitation in the continuous regime (direct and cross shown)

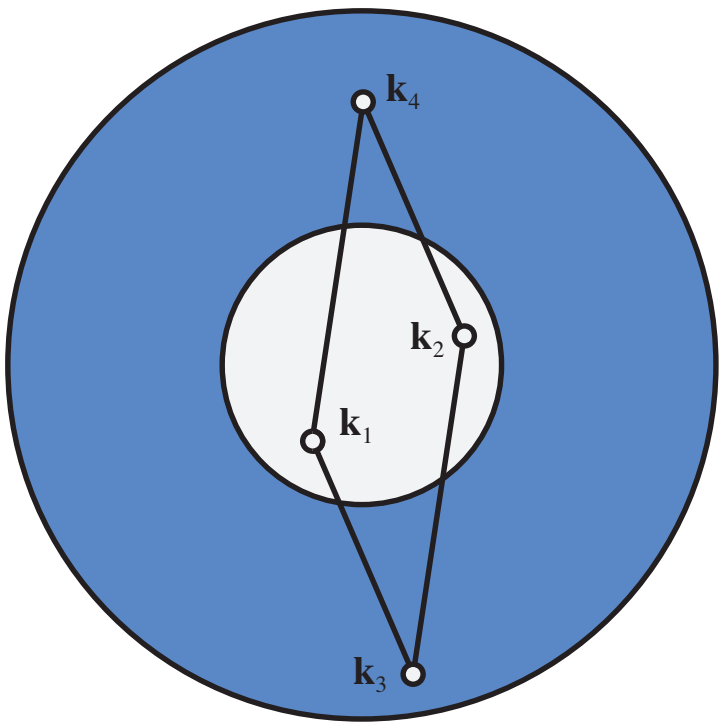
Introducing a Finite Basis Set

Use a kinetic energy $\frac{1}{2}k_c^2$ cutoff: $\sum_{ab\in\text{virt}} \rightarrow \sum_{\substack{k_f \leq k_a \leq k_c \\ k_f \leq k_b \leq k_c}}$

Allowed excitations now fall within a certain radius in k-space.

Call this E_k-cutoff.





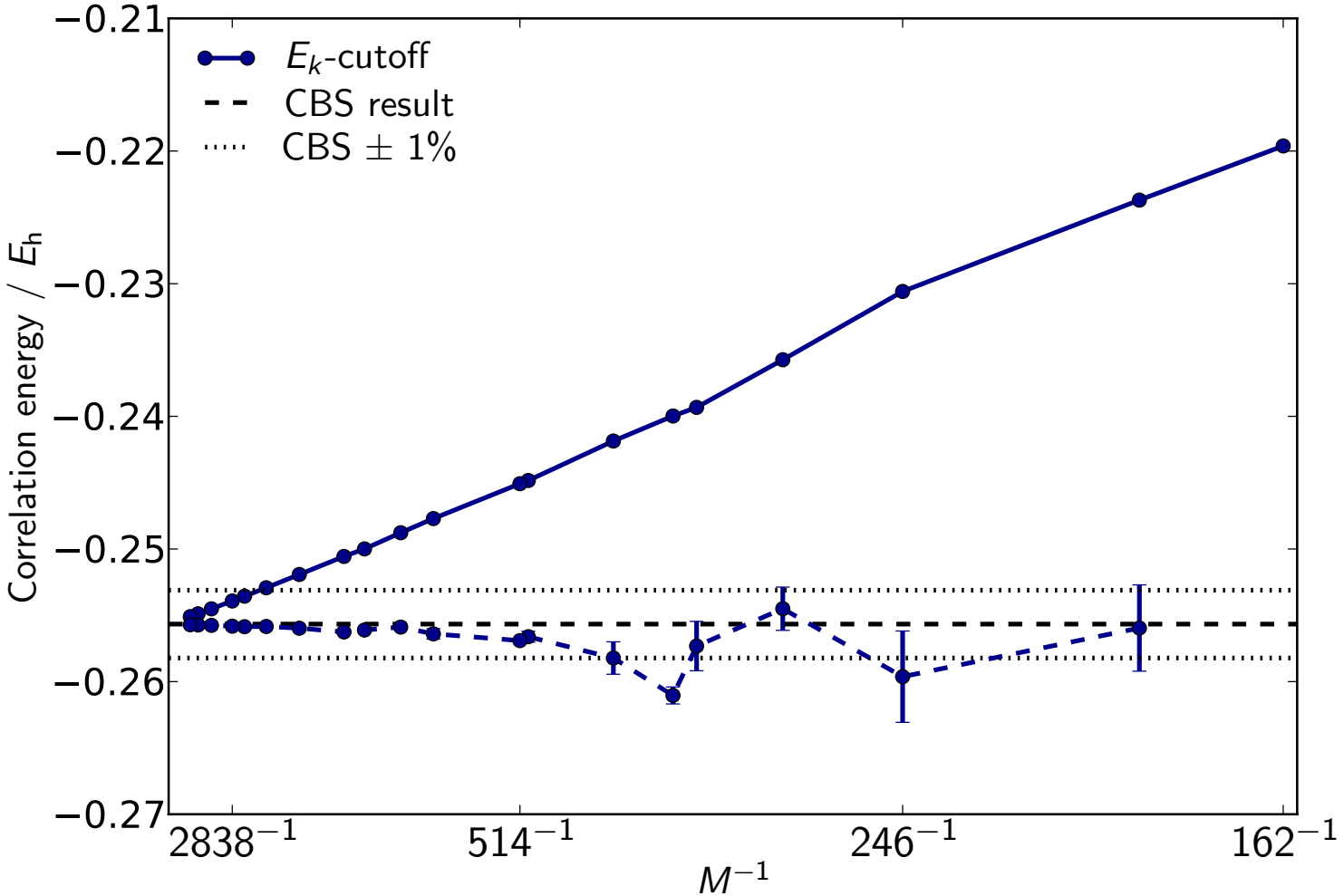
Analysis of the Limiting Behaviour

- E_k-cutoff: radius of k_c in k-space
- $\Delta E_{\mathrm{MP2}}(k_c) = E_{\mathrm{MP2}}(\infty) - E_{\mathrm{MP2}}(k_c)$ [basis set incompleteness error]
- $\Delta E_{\mathrm{MP2}}(k_c) =$

  $$\sum_{\substack{0\leq k_i\leq k_f \\ 0\leq k_j\leq k_f}} \sum_{\substack{k_a>k_c \\ k_b>k_c}} \delta_{\mathbf{k}_i-\mathbf{k}_a,\mathbf{k}_j-\mathbf{k}_b} \frac{2\ v^2_{\mathbf{k}_j-\mathbf{k}_a} - v_{\mathbf{k}_i-\mathbf{k}_a} v_{\mathbf{k}_j-\mathbf{k}_a}}{\Delta\epsilon}$$

- $\sum_{\substack{0\leq k_i\leq k_f \\ 0\leq k_j\leq k_f}}$: assume same power-law for each electron pair
- $\Delta\epsilon \propto k_a^2$, numerator $\propto 1/k_a^4$
- $\sum_{\substack{k_a\geq k_c \\ k_b\geq k_c}} \delta_{\mathbf{k}_i-\mathbf{k}_a,\mathbf{k}_j-\mathbf{k}_b}$: single sum over k_a
- $\Delta E_{\mathrm{MP2}}(k_c) \propto \sum_{k_a\geq k_c} \frac{1}{k_a^6}$
- $\Delta E_{\mathrm{MP2}}(k_c) \propto \int_{k_c}^{\infty} \mathrm{d}k_a\ \frac{1}{k_a^6}\ k_a^2 \propto \frac{1}{k_c^3}$.

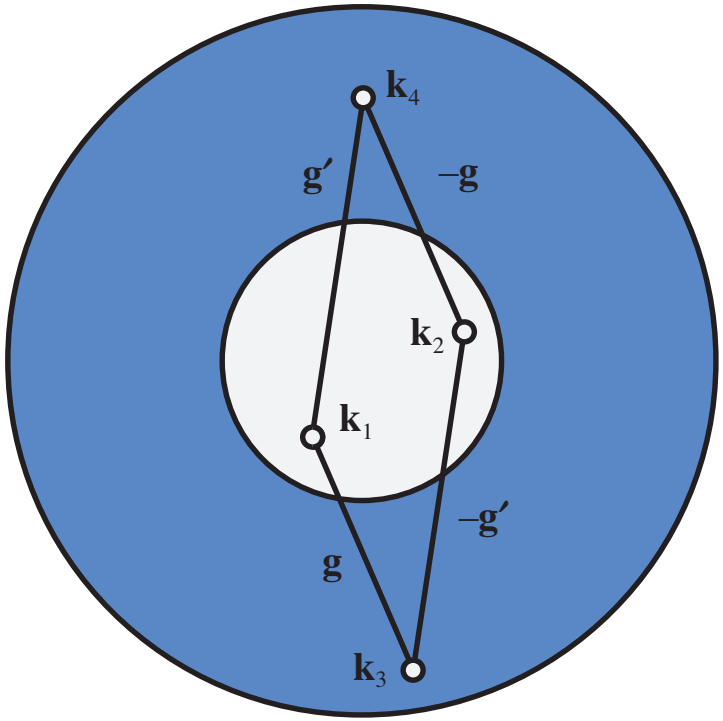
$1/k^3 \longrightarrow 1/M$



14 electrons, r_s=5.0 a.u.

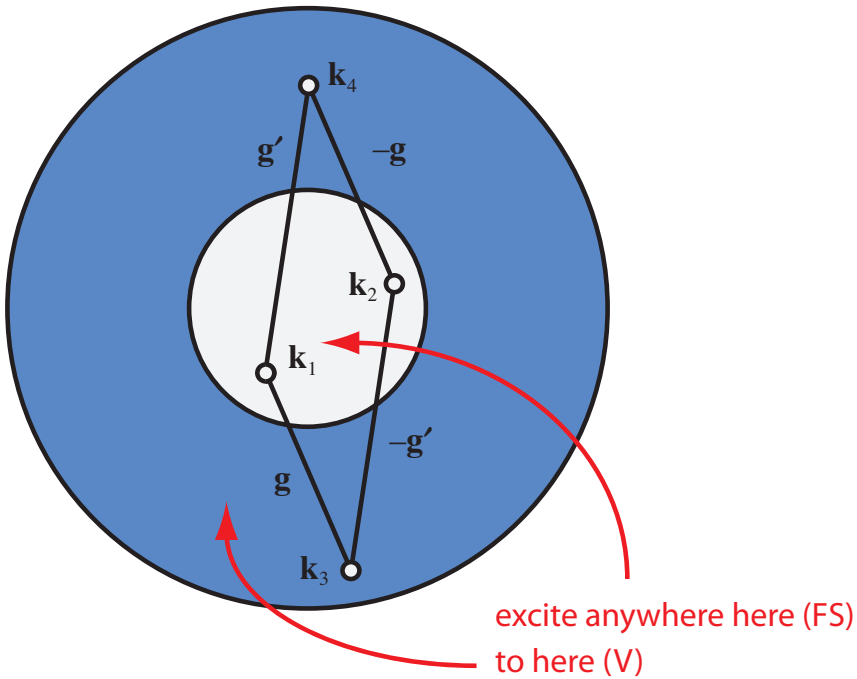
Momentum Transfer Vectors

- It is possible to define two momentum transfer vectors for an excitation.
- Seek to define basis sets using this, to see if there are better extrapolation properties.
- Show there are *three* sensible choices for basis sets
- Originates from basis set convergence work in solid state systems.



Momentum Transfer Vectors (2)

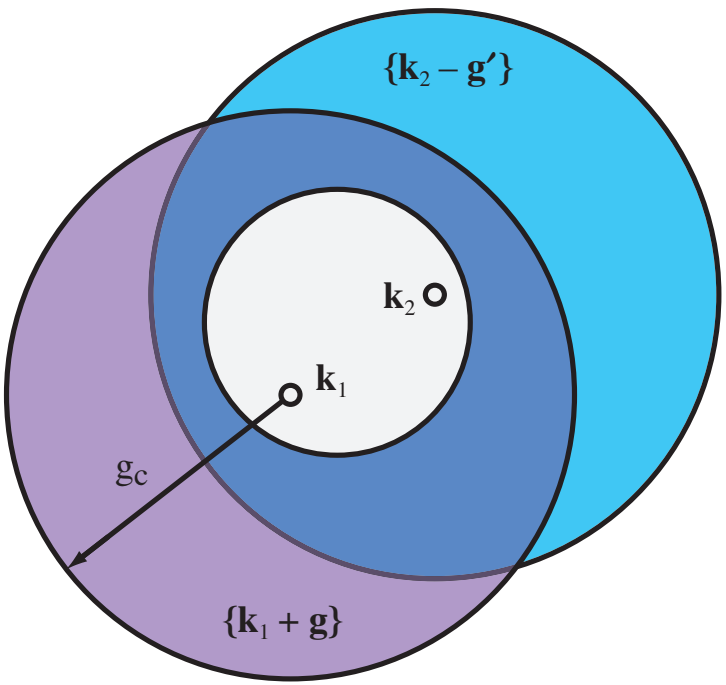
$$E_{\mathrm{MP2}} = \sum_{\mathrm{FS}} \sum_{\mathrm{V}} \delta_{\mathbf{g},\mathbf{g}'+\mathbf{k}_i-\mathbf{k}_j} \frac{\left(2\ v_{\mathbf{g}}^2 - v_{\mathbf{g}} v_{\mathbf{g}'}\right)}{\Delta\epsilon}$$

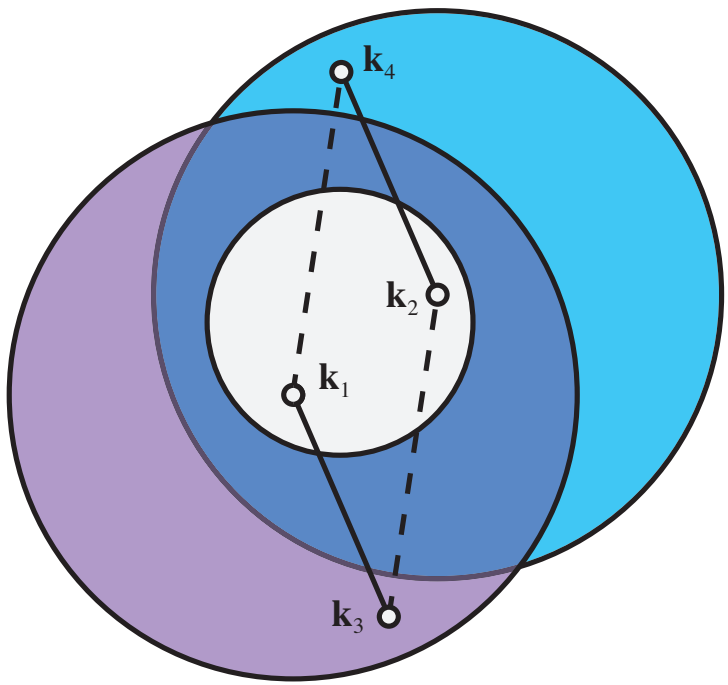


[disclaimer: these diagrams do not show volume excluded due to occupation effects]

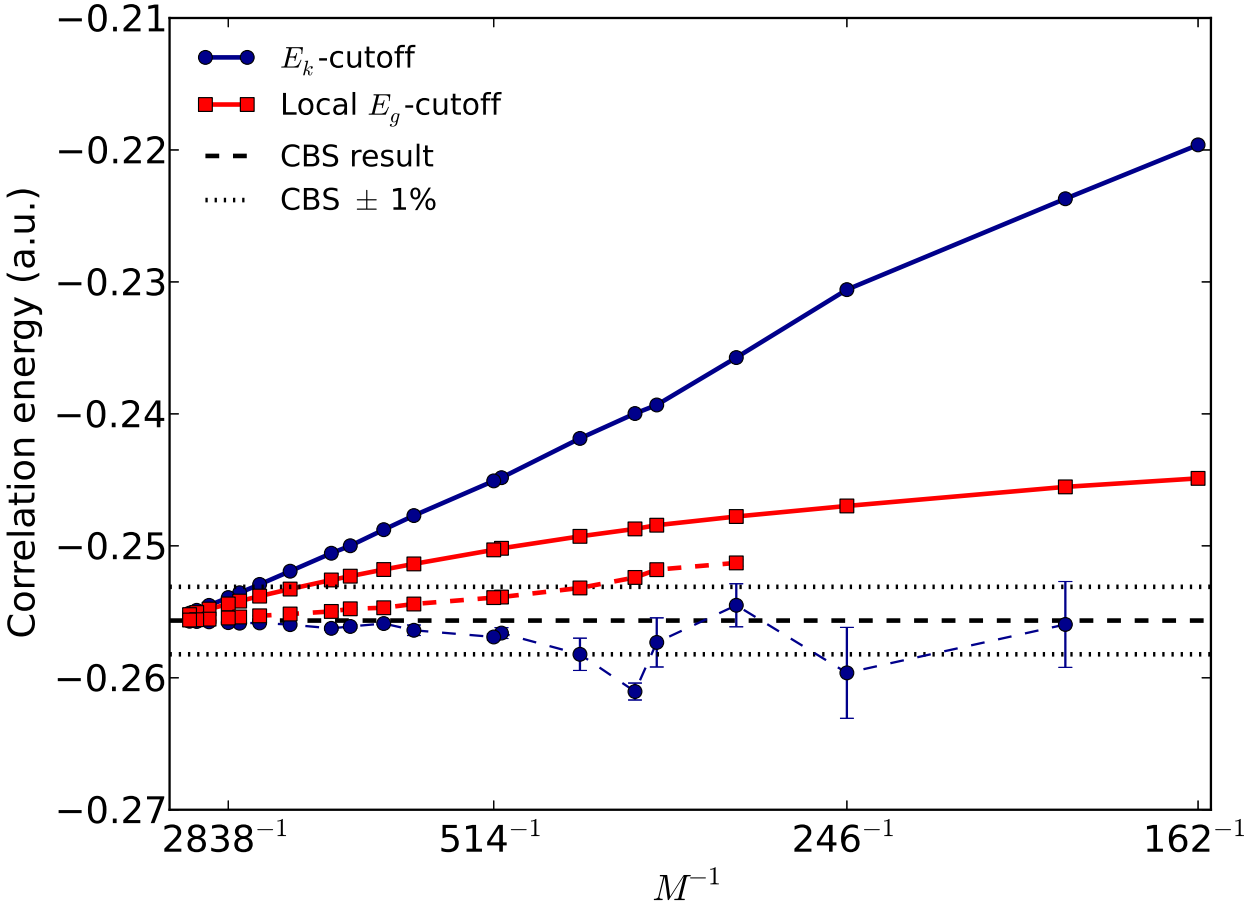
Local E_g-cutoff

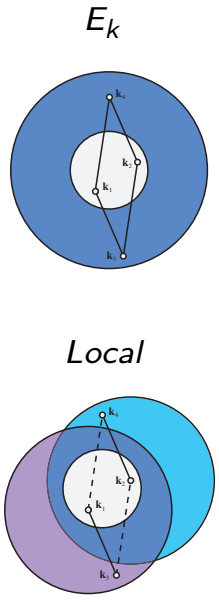
E_g-cutoff: radius of g_c in k-space, but bounds momentum transfer vector $\mathbf{g}$





Local E_g-cutoff (2)

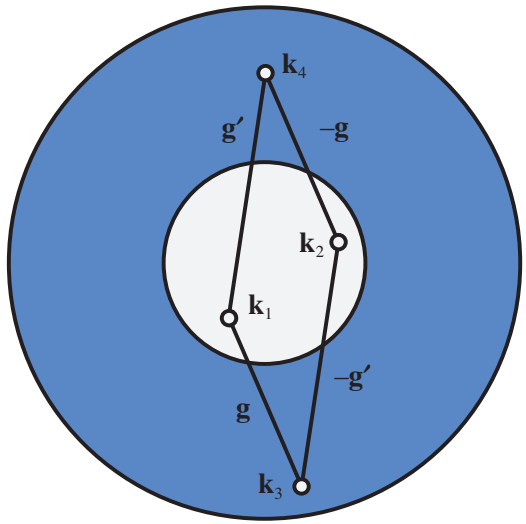




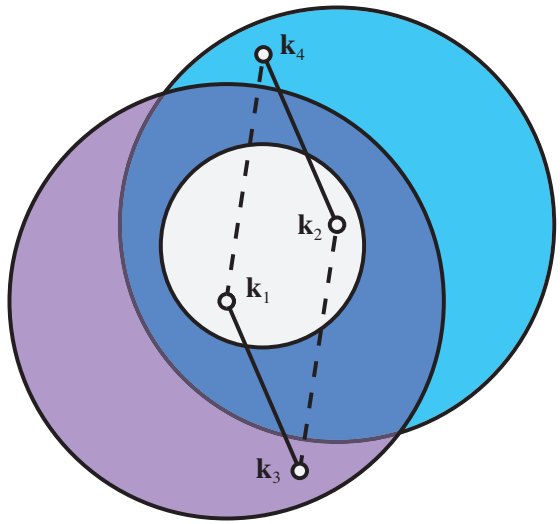
14 electrons, r_s=5.0 a.u.

Local E_g-cutoff (3)

- Treats electron coalescences on the same footing
- Different basis set per k-point/electron
- Spans further into k-space for the same number of functions per electron
- Loss of variationality w.r.t. CBS limit
- Breaks permutational symmetry
- Loss of size extensivity

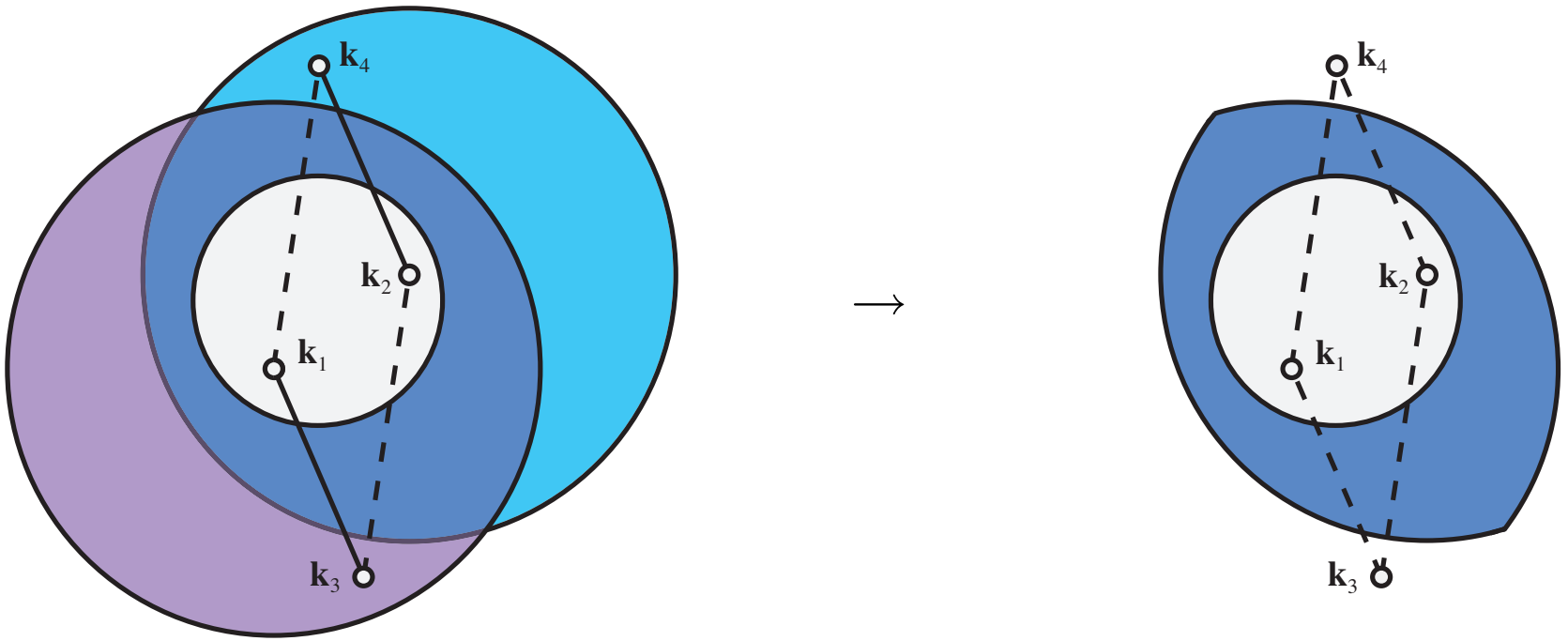


(E_k)

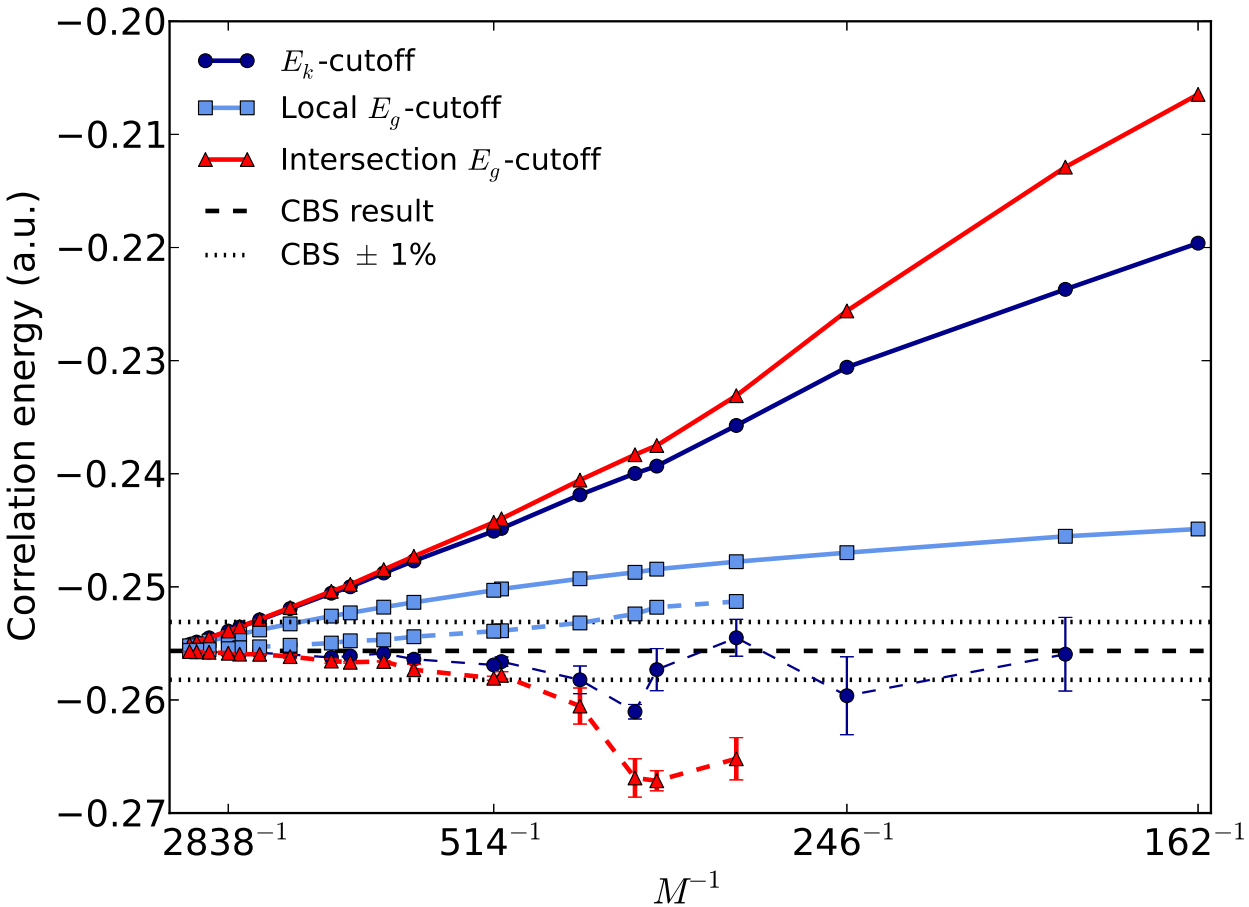


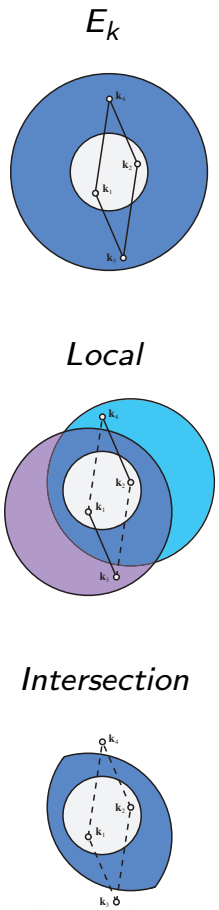
(local E_g)

Intersection E_g-cutoff



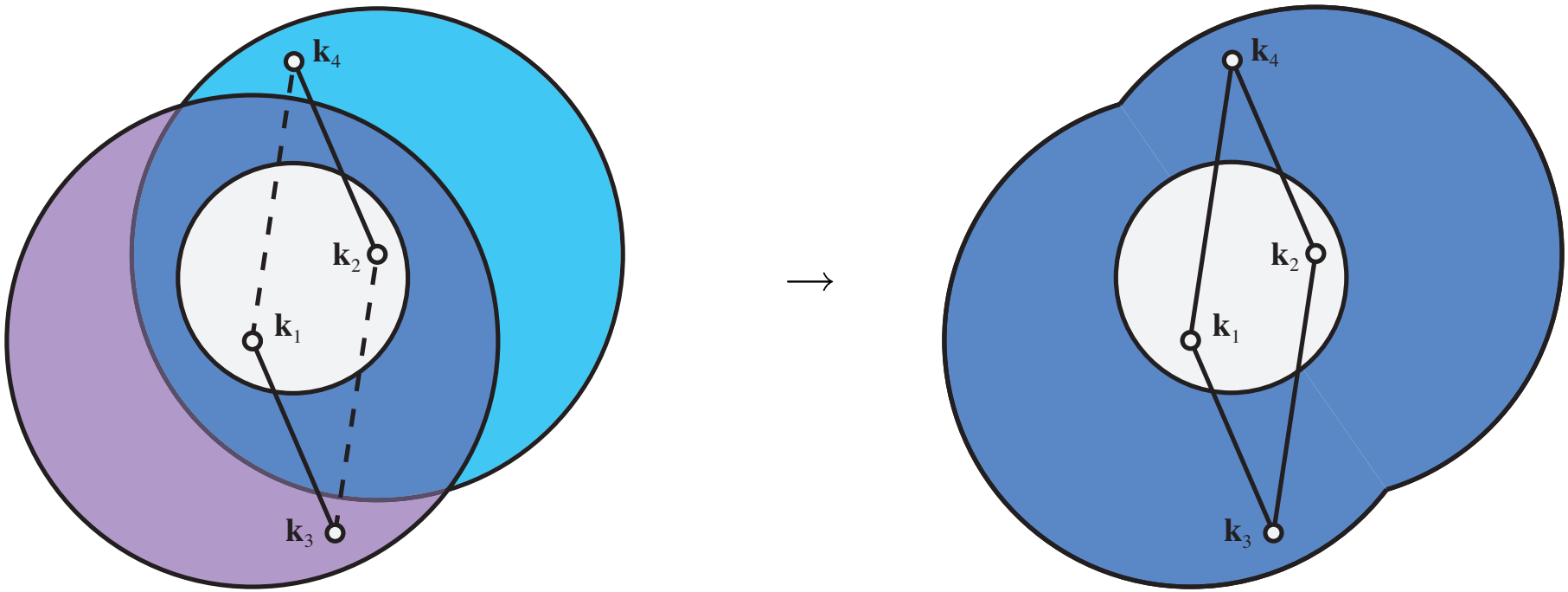
Intersection E_g-cutoff (2)



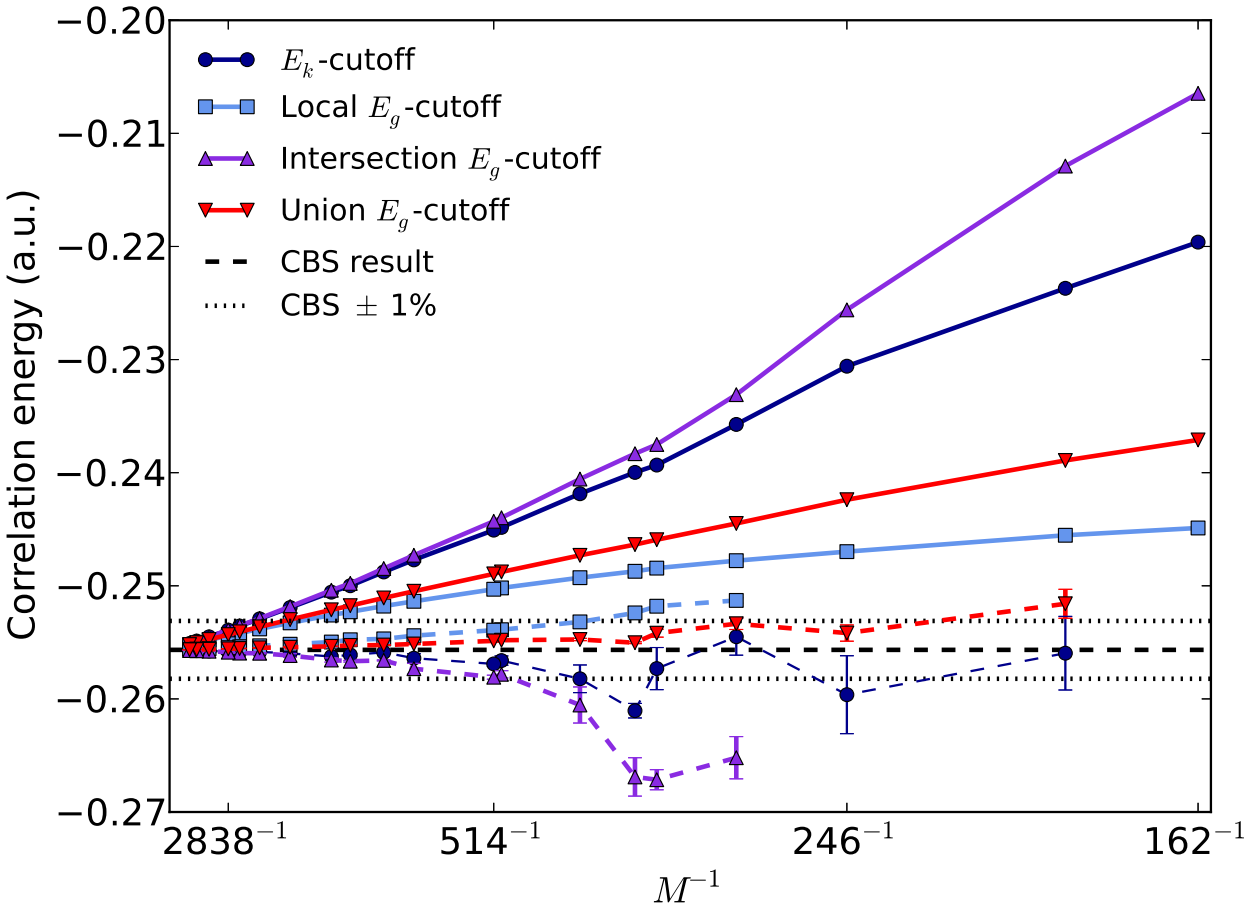


14 electrons, r_s=5.0 a.u.

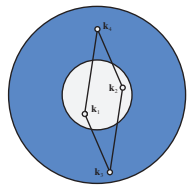
Union E_g-cutoff



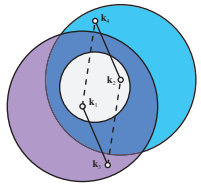
Union E_g-cutoff (2)



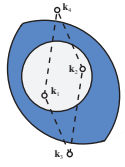
E_k



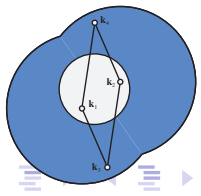
Local



Intersection

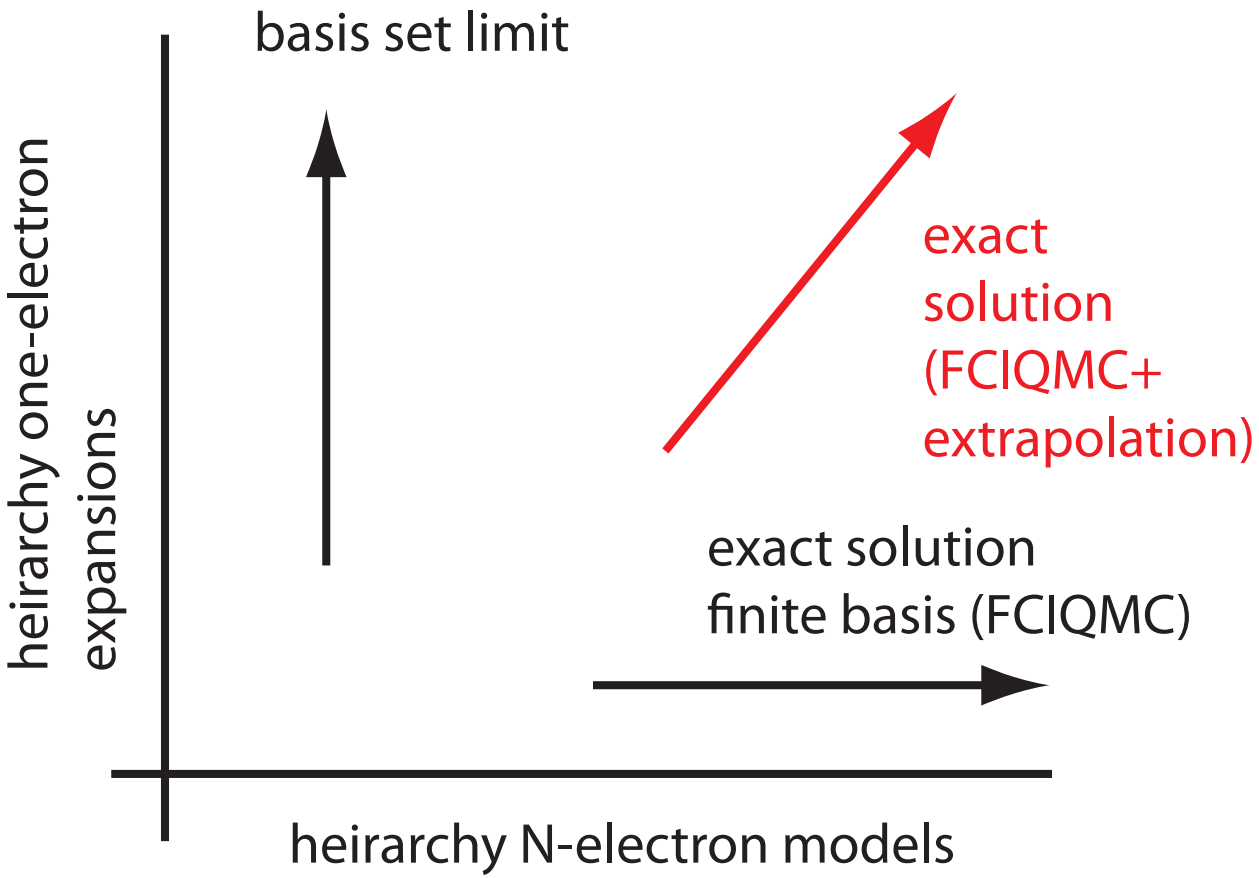


Union



14 electrons, r_s=5.0 a.u.

Determinantal Expansions



Application to FCIQMC

- Write wavefunction as a series of Slater Determinants

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

- Solve using a stochastic algorithm
- Energy can be found by projection onto a reference

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

- As before, FT:

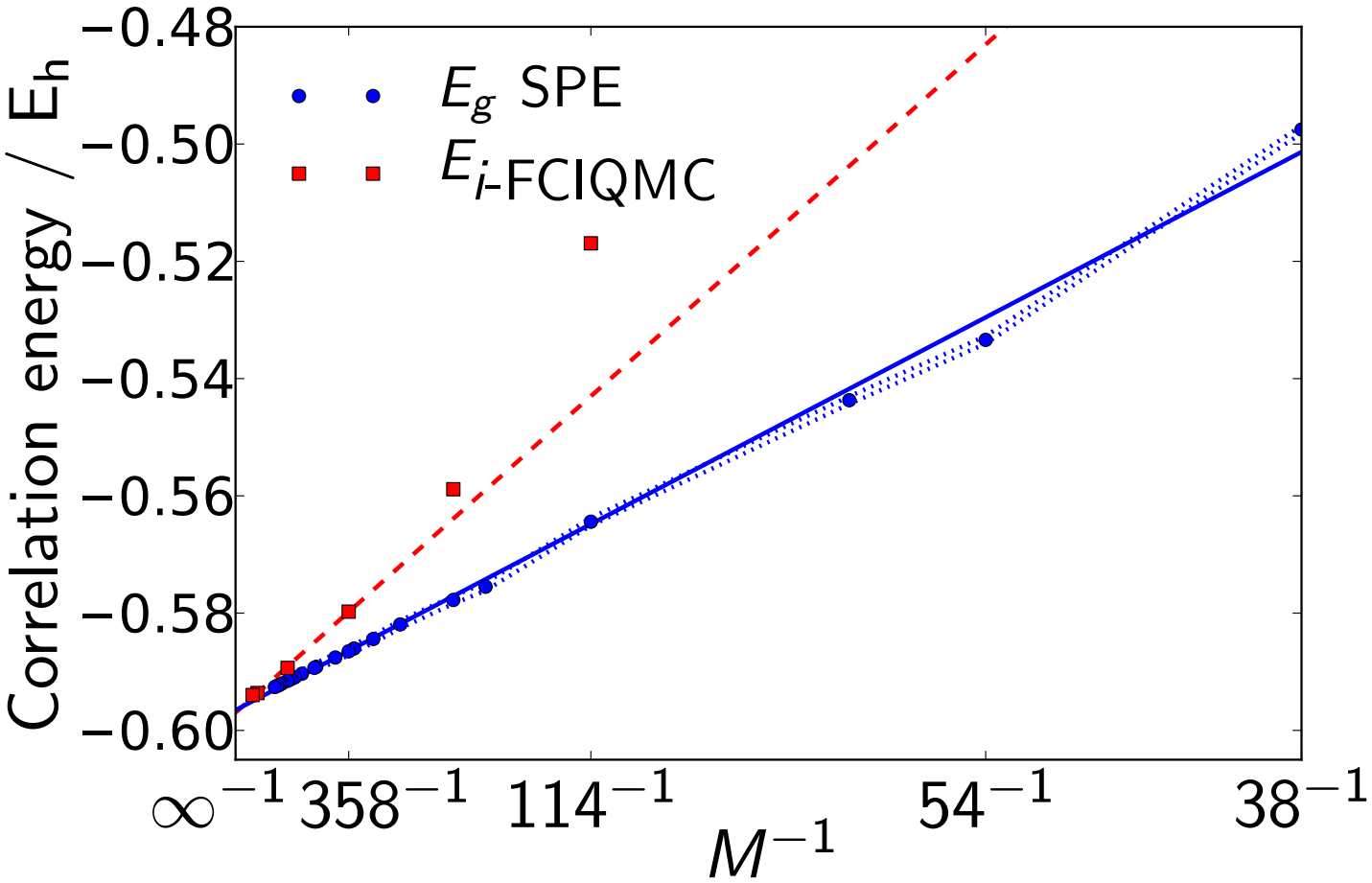
$$E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_j - \mathbf{k}_b} \left(v_{\mathbf{k}_i - \mathbf{k}_a} - v_{\mathbf{k}_j - \mathbf{k}_a} \right) \frac{c_{\mathbf{k}_i \mathbf{k}_j}^{\mathbf{k}_a \mathbf{k}_b}}{c_{\mathbf{0}}}$$

Application to FCIQMC (2)

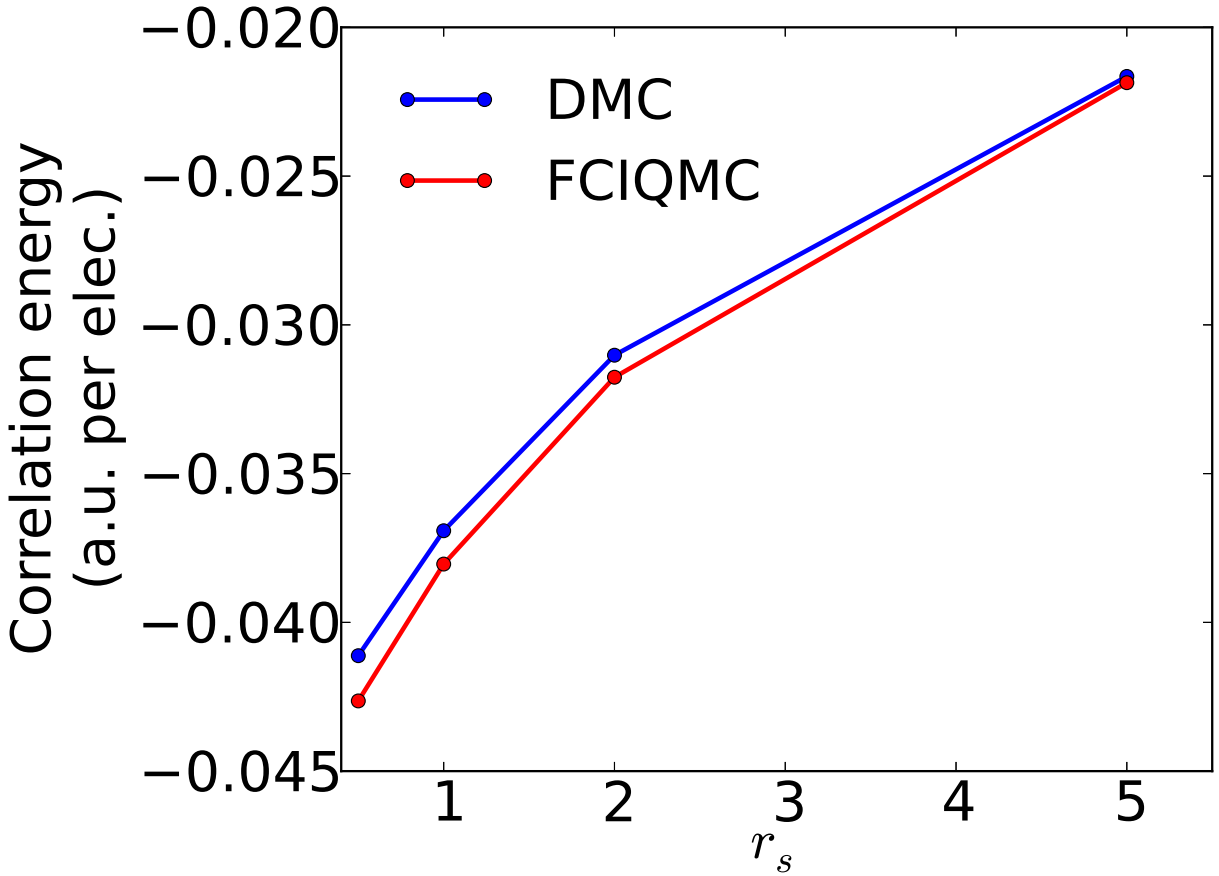
$$E_{\text{corr}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_j - \mathbf{k}_b} \left(v_{\mathbf{k}_i - \mathbf{k}_a} - v_{\mathbf{k}_j - \mathbf{k}_a} \right) \frac{c_{\mathbf{k}_i \mathbf{k}_j}^{\mathbf{k}_a \mathbf{k}_b}}{c_{\mathbf{0}}}$$

- Apply cutoffs as before
- Unlike before, this is now approximate
- Good enough for large M
- Extrapolation from a single calculation (SPE)

Application to FCIQMC (3)

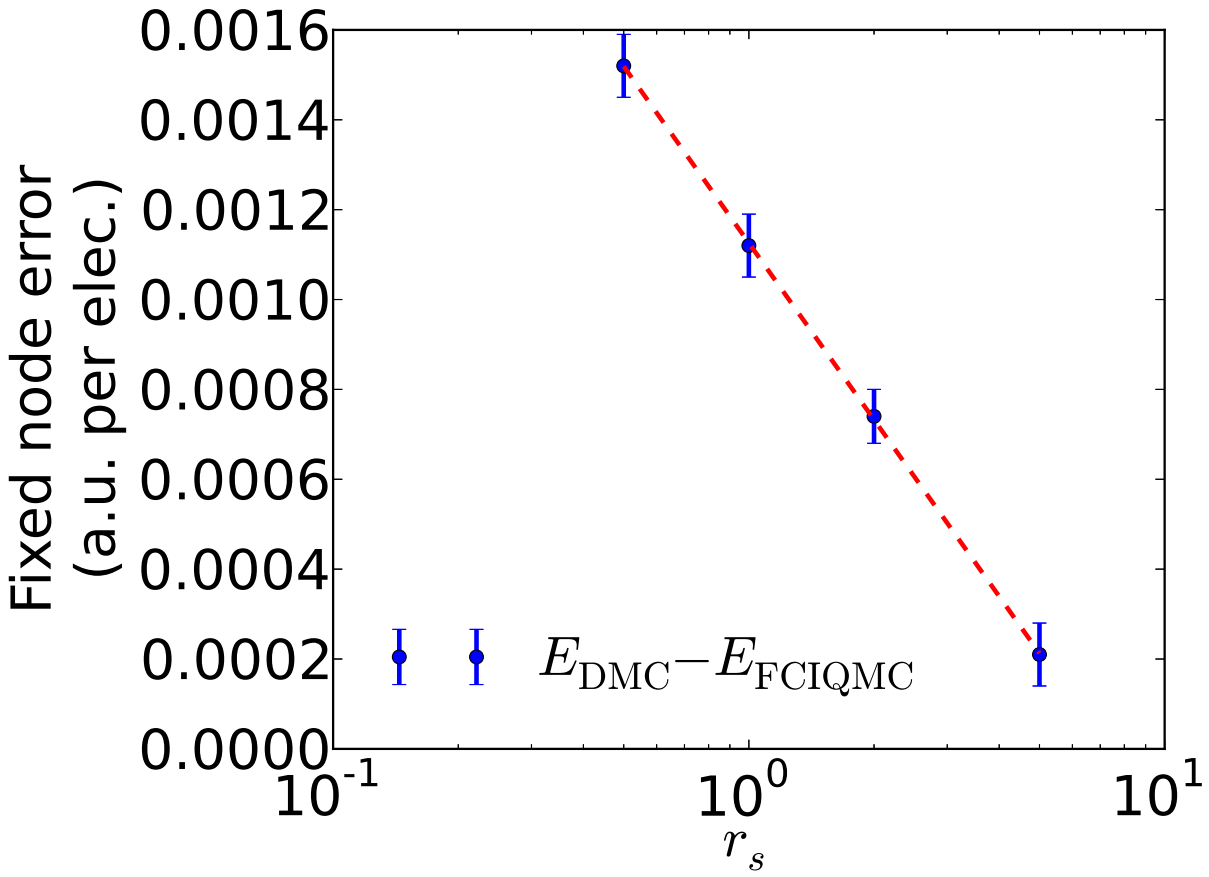


Comparison with DMC



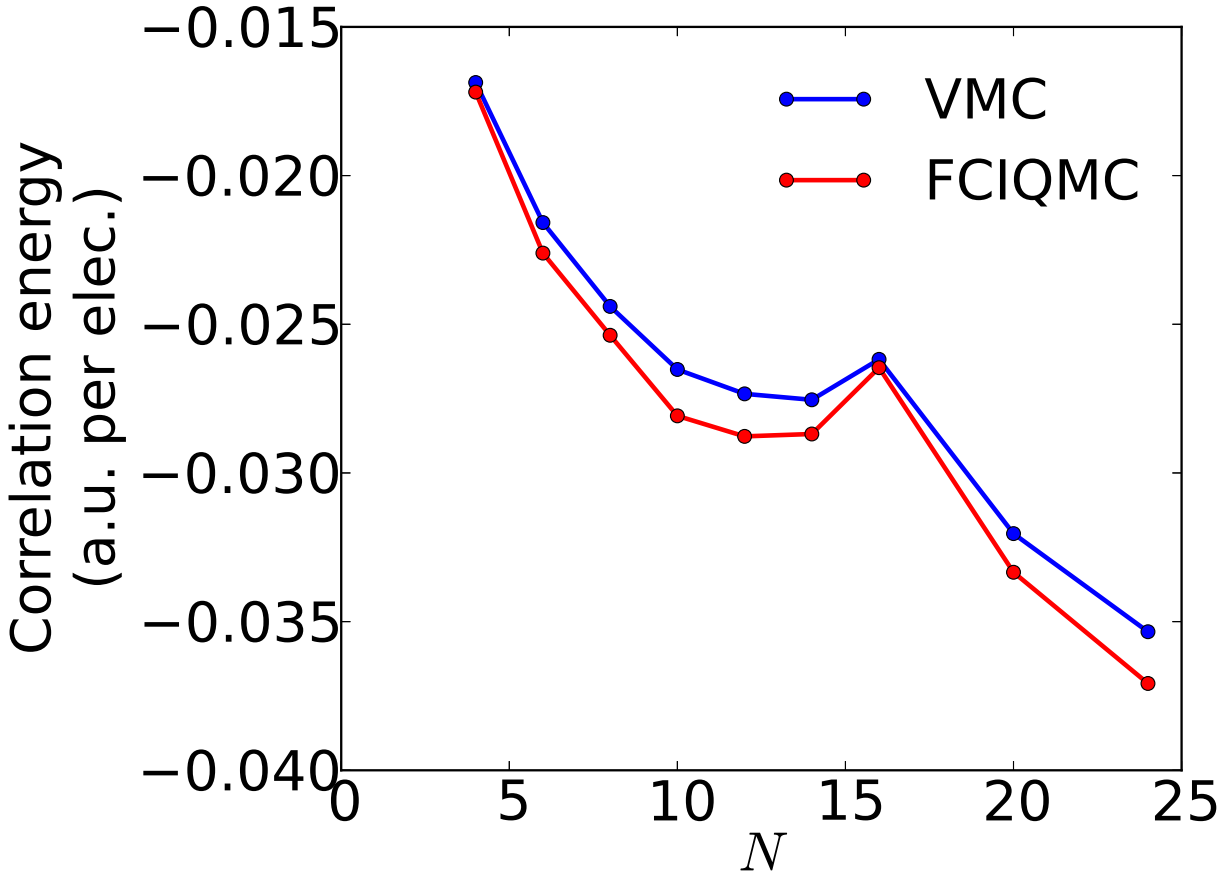
- $N = 14$ (Somewhat different trend than for 54 electrons)
- DMC results: Pablo López Ríos
- Consistent with: K.M. Rasch, L. Mitas, Chem. Phys. Lett. (2012), doi:10.1016/j.cplett.2012.01.016

Comparison with DMC (2)



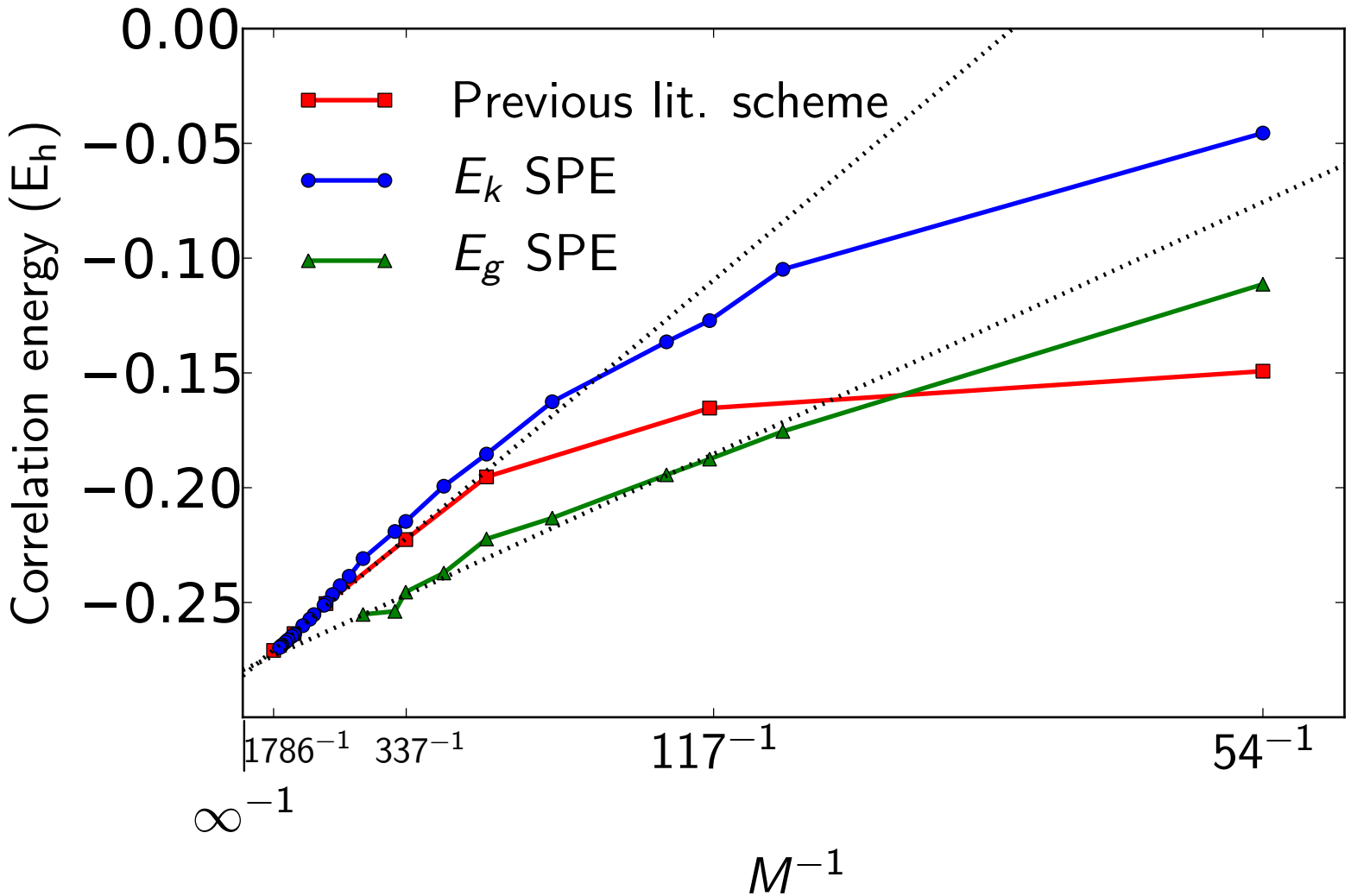
[DMC results: Pablo López Ríos]

Comparison with DMC (3)



[VMC results: Pablo López Ríos]

LiH solid


0.00
−0.05
−0.10
−0.15
−0.20
−0.25
Correlation energy (E_h)
Previous lit. scheme
E_k SPE
E_g SPE
1786^−1
337^−1
117^−1
54^−1
∞^−1
M^−1

Conclusions

- 1) Analyzed basis set incompleteness error for UEG
- 2) Found 1/M power-law holds for MP2
- 3) Discussed alternative momentum transfer vector basis sets
- 4) Applied this to FCIQMC by re-summation of the projected energy

Looking Ahead

- Twist-averaging to reach the thermodynamic limit
- More accurate electron gas energies (benchmark DMC fixed-node error)
- Does the CC series diverge for metals?

Acknowledgements

- Prof. Ali Alavi
- Dr. Andreas Grueneis (CCSD and RPA calculations; solid state applications) & VASP
- Dr. George Booth (MP2 and FCIQMC code)
- Dr. Pablo López Ríos (VMC/DMC) & CASINO
- Alavi Group
- EPSRC

References

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- i-FCIQMC: D Cleland, GH Booth, A Alavi, JCP 132 4, 041103 (2010)
- HEG/i-FCIQMC: JJS, GH Booth, A Gruneis, A Alavi, PRB 85, 081103(R) (2012)
- HEG/i-FCIQMC/Extrapolation: JJS, GH Booth, A Alavi, arXiv:1201.4691 [physics.comp-ph]
- MP2/Extrapolation/Solid State: upcoming