FCIQMC, CCMC and finite electron gases

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FCIQMC & CCMC in a nutshell

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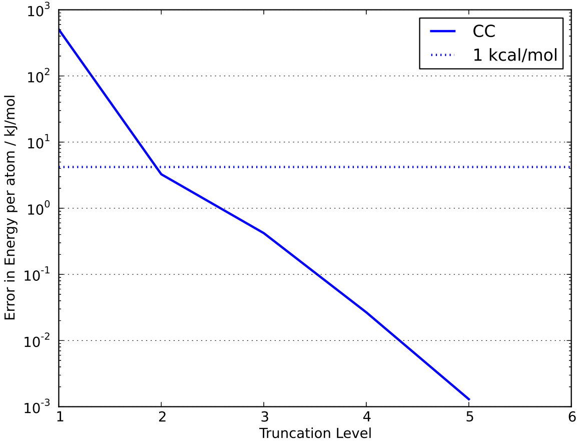
CC Theories can be truncated size-consistently at excitation levels.

Size Consistency



1 kcal/mol = 10 meV

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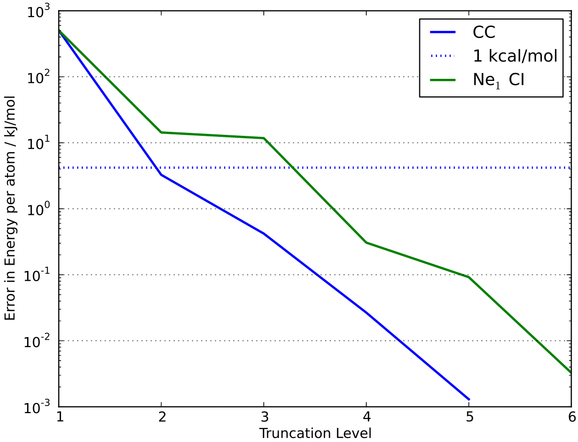

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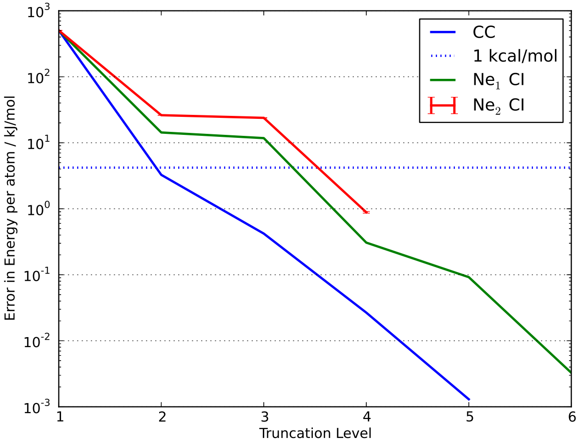

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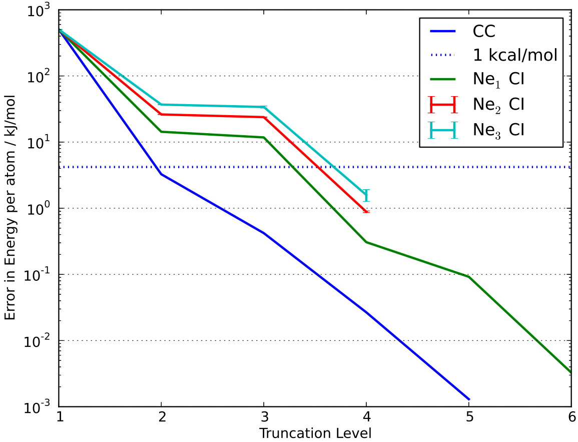

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When do they work?

FCIQMC

- Still small systems, but bigger than exact diagonalization.
- Some systems are easy with low plateau (Hubbard low U, UEG low r_s), others hard (high U, r_s, alkanes)
- i-FCIQMC, semi-stochastic, real weights make more tractable.
- Still have to try a system to find out if it can be investigated.

CCMC

- Size-consistent excitation level truncation allows much larger systems to be investigated.
- Plateaux also vary with system difficulty.
- Multi-reference systems are much harder.
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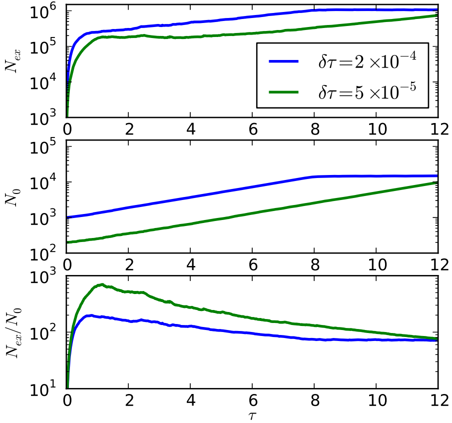
We would like to know if it's possible to do a calculation without having to try. How can we measure difficulty?

Finding Plateaux



Ne cc-pVQZ CCSDTQ. space=1.4×10^7 excitors

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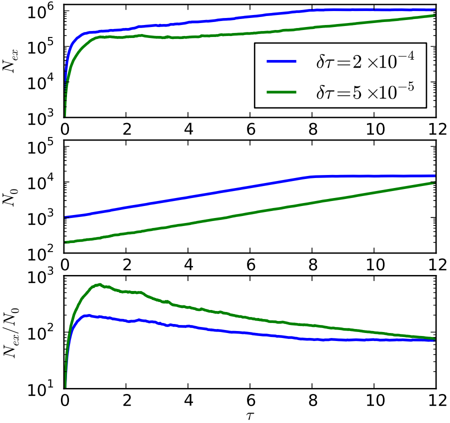

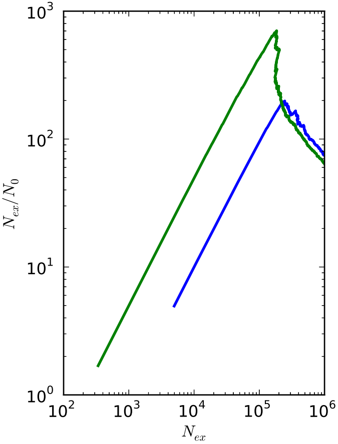

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In Praise of Automation

- Plateau finding automated at $N_{\text{ex}}(\tau_{\max})$ where

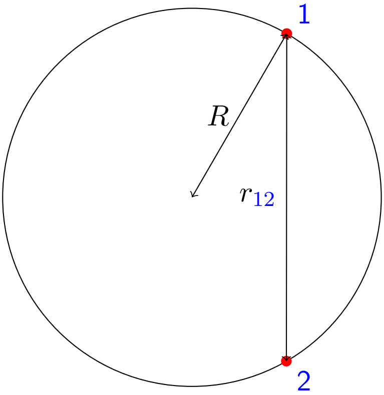
$$\tau_{\max} = \max_{\tau} \frac{N_{\text{ex}}}{N_0}.$$

- Error bars come from standard deviation of 10 largest values.
- Energy analysis automated by fitting form of $N_{\text{ex}}(\tau)$ and finding equilibrated N_{ex}, N_0, E_{proj} and S.

Finite Electron Gases

- The Uniform Electron Gas comes in many guises.
- Most commonly it is expressed in a periodically repeating cell.
- r_s characterises the density.
- $\varepsilon_{\mathrm{corr}}(r_s)$ for $N \to \infty$ is well-known and used for LDA.
- Loos and Gill have been concentrating on UEGs in other geometries (ring, sphere, glome ...).
- These have different $\varepsilon_{\mathrm{corr}}(r_s)$ which can be used to make an improved density functional.
- Can we use FCIQMC to calculate $\varepsilon_{\mathrm{corr}}(r_s)$?

Ringium

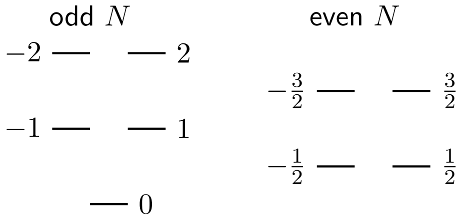


- Electrons confined on a ring radius R.
- $r_s = \pi R/n$.
- Kinetic Energy is one-dimensional.
- Coulomb interaction is through-space (i.e. $1/r_{12}$) not around ring.
- HF orbitals just $e^{im\phi}$.

Ringium basis

Restricted Hartree–Fock orbitals for $M_L = 0$ are

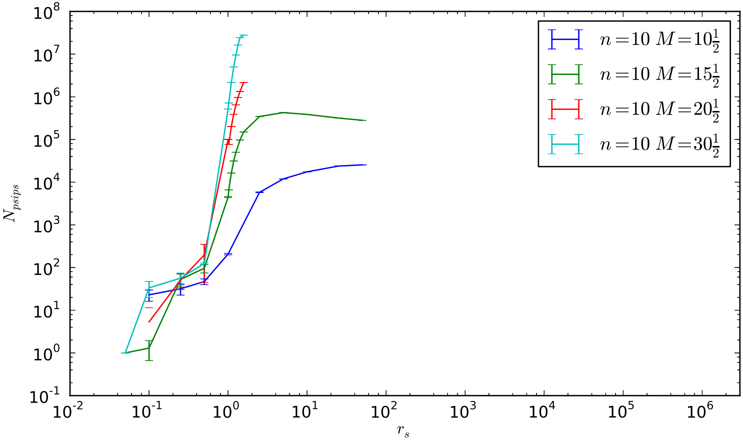
$$\chi_m(\phi) = e^{2\pi i m \phi} \text{ with } \begin{cases} m \in Z & \text{for odd } N \\ m = \frac{2n+1}{2}, n \in Z & \text{for even } N \end{cases}$$



M indicates the maximum value of m.

1D Coulomb enforces nodes making ringium is spin-blind.

FCIQMC Plateau heights vs r_s



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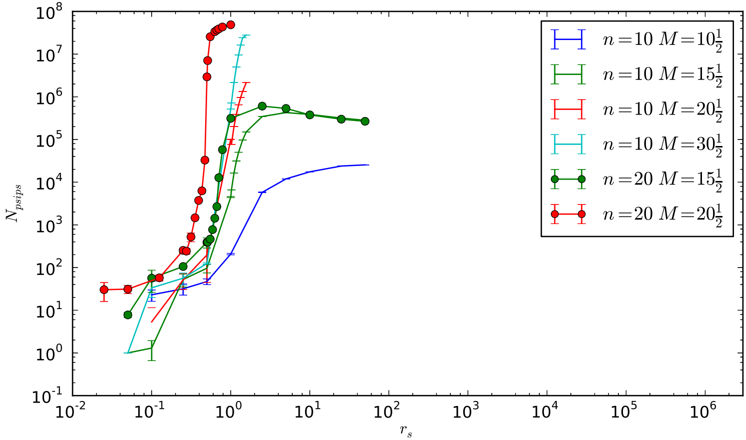

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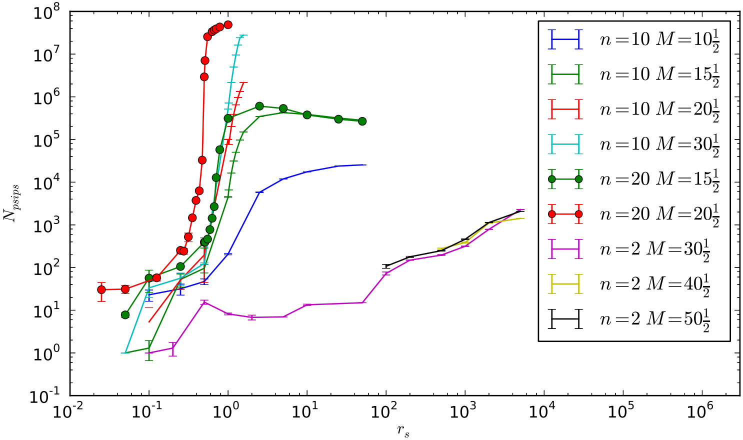
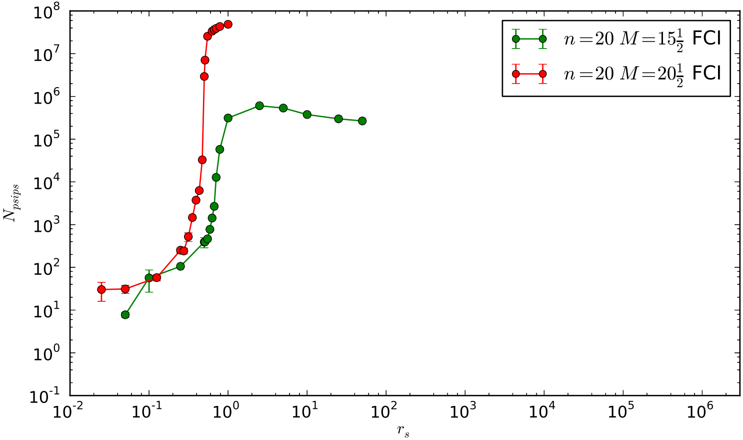


CCMC Plateau heights vs r_s



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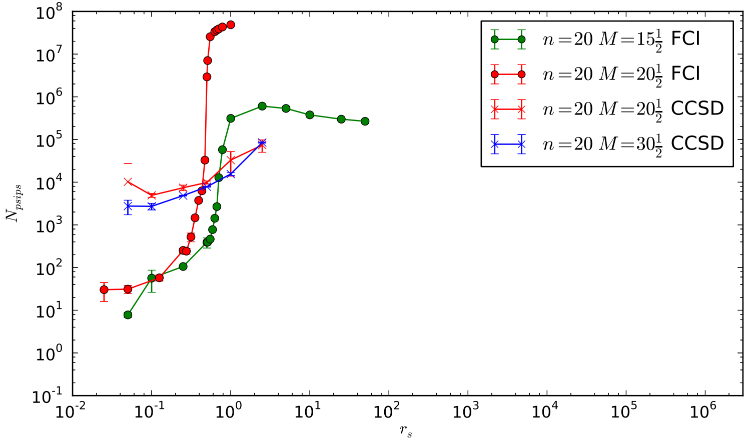

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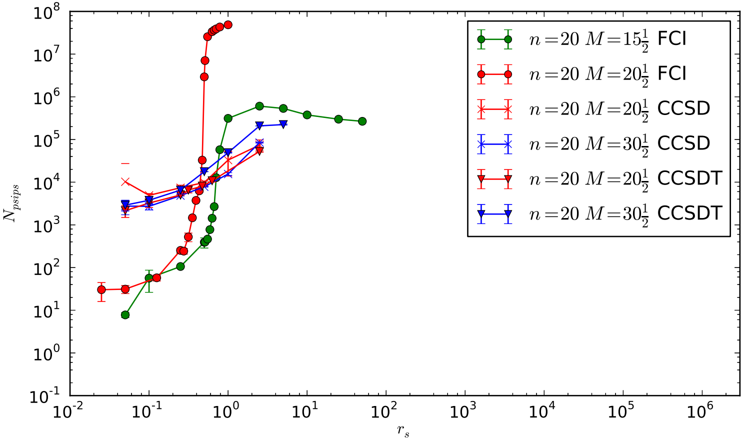

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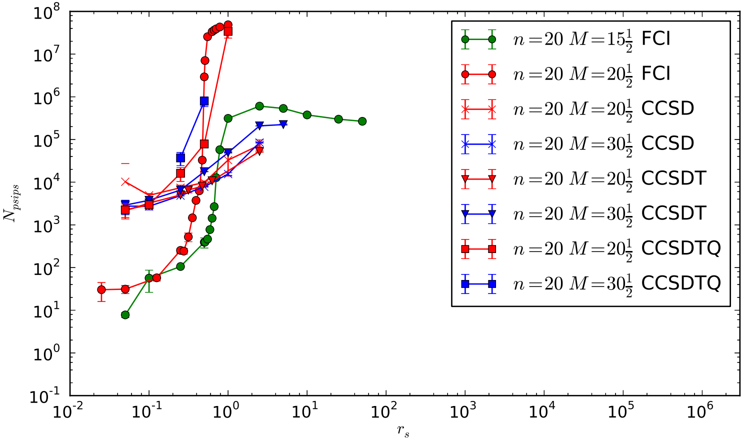

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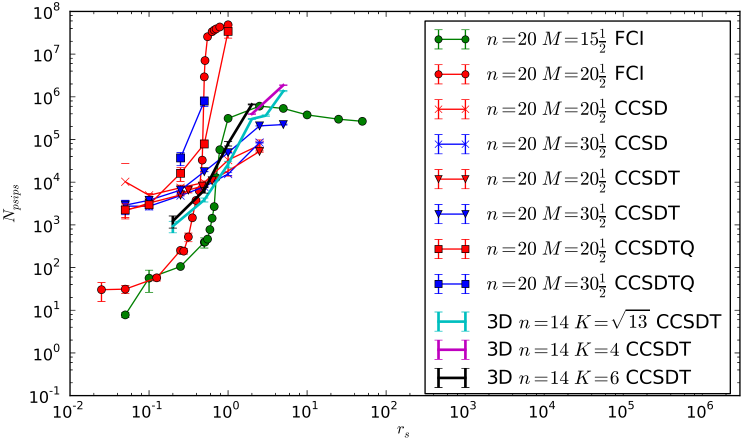

Thoughts

- For 1D and 3D UEG, rapid change of behaviour between easy and hard at $r_s \approx 1$.
- As r_s increases, both FCIQMC and CCMC reach a constant plateau height.
- Structure of Hamiltonian dominated by r_s^{-1} off-diagonal over r_s^{-2} diagonal.
- CCMC plateaux usually smaller than FCIQMC's.
- 3D UEG with FCIQMC/CCMC probably possible.

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THE ROYAL SOCIETY