The Homogeneous Electron Gas: Beyond Fixed Nodes II

James J. Shepherd[(a)*], George Booth[(a)], Andreas Grüneis[(a,b)], Pablo López-Ríos[(c)], Richard J. Needs[(c)], Georg Kresse[(b)] and Ali Alavi[(a)†]

(a) The University Chemical Laboratory, University of Cambridge, UK (b) University of Vienna, Faculty of Physics and Center for Computational Materials Science, Austria
(c) TCM Group, Cavendish Laboratory, University of Cambridge, UK. Emails: *js615@cam.ac.uk, †asa10@cam.ac.uk

Introduction

The variational and diffusion Monte Carlo (DMC) methods have had unparallelled success in describing the ground state of the homogeneous electron gas (HEG) [1]. Over the past three decades, these theories have been methodically improved to yield increasingly accurate energies over a wide variety of densities. In spite of this however, they are still thought to contain residual error due to the fixed-node (FN) approximation and, although these are somewhat alleviated by use of homogeneous backflow transformations, the errors are thought to be around 10^{-3} a.u. per electron [2,3]. It is our intention here to use the newly-developed full configuration interaction quantum Monte Carlo (FCIQMC) method [4], in particular its *initiator* adaptation [5], to find the FCI energies of finite electron gases [6-8]. Employing the Vienna ab-initio simulation package (VASP) [9], we compare these to approximate quantum chemical methods for a variety of basis set sizes. Removing the remaining source of error in these energies, basis set incompleteness error, we compare the resultant exact energies to DMC energies obtained using the CASINO program [10].

Exact Energies from FCIQMC

The aim of FCIQMC is to solve the imaginary time Schrödinger equation,

$$\hat{H}\Psi(\tau) = -\frac{\partial\Psi(\tau)}{\partial\tau},$$

by performing a long-time integration to project out the ground state in which the wavefunction is expressed in a Slater determinant basis,

$$\Psi(\tau) = \sum_{\mathbf{i}} C_{\mathbf{i}}|D_{\mathbf{i}}\rangle.$$

The resultant FCI equations,

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

are solved using a stochastic representation of the wavefunction, based on walkers,

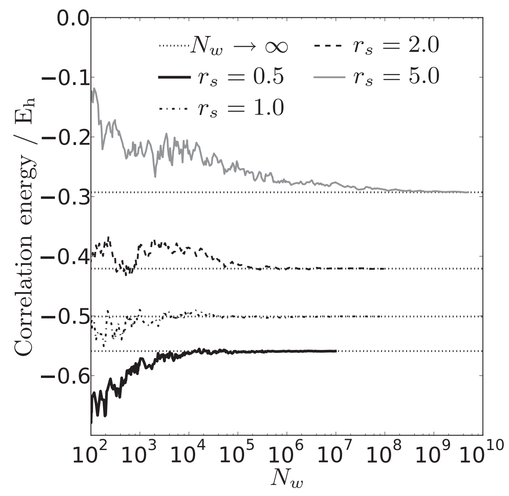
$$C_{\mathbf{i}} \propto N_{\mathbf{i}}$$

and spawning, annhiliation and death/cloning events in Slater determinant space. When the shift (S) is equal to the total energy, these coefficients will stabilise at the exact FCI wavefunction for a sufficient number of walkers. We seek to solve these equations for the plane-wave HEG Hamiltonian,

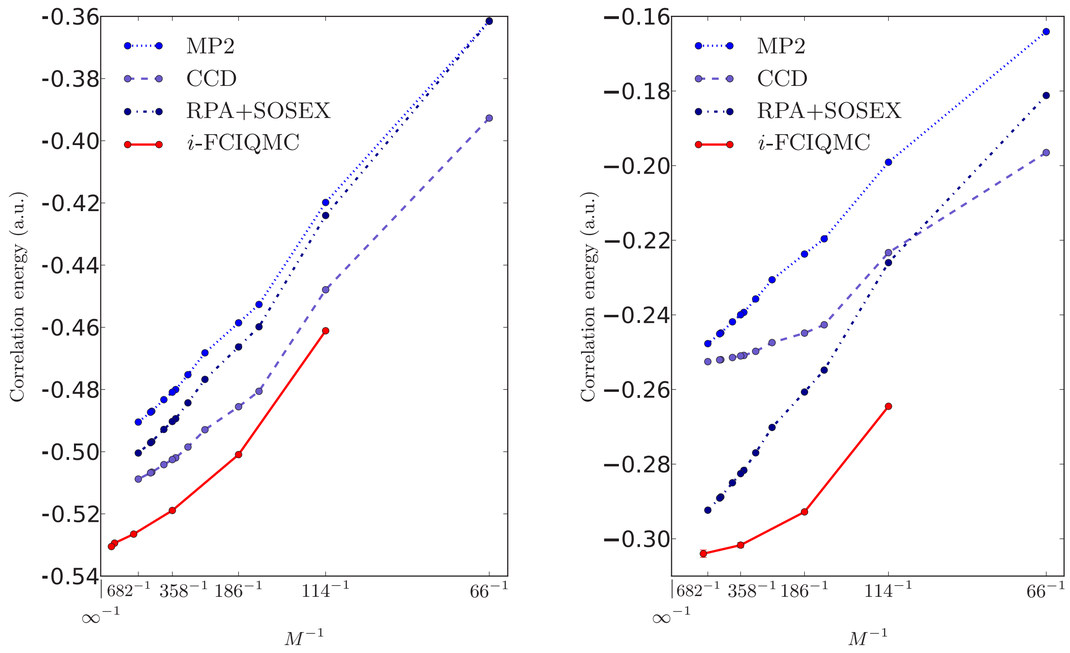
$$\hat{H} = \sum_{\alpha} -\frac{1}{2}\nabla_{\alpha}^2 + \frac{1}{2L^3}\sum_{\alpha\neq\beta}\sum_{\mathbf{q}\neq\mathbf{0}} v_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{r}_{\alpha}-\mathbf{r}_{\beta})} + \frac{1}{2}\hat{N}v_{\mathrm{M}}$$

The Initiator Adaptation

In the *initiator* adaptation to FCIQMC, when considering flux onto an empty site, only those determinants exceeding a certain population size are considered. This stabilises populations at a greater range of walker numbers (N_w) allowing for more correlation energy estimates to be found. However, the infinite walker number limit needs to be recovered. This is demonstrated for the N=14 system (right). This also shows that as the density is lowered, the difficulty in convergence rises due to a rising correlation strength.



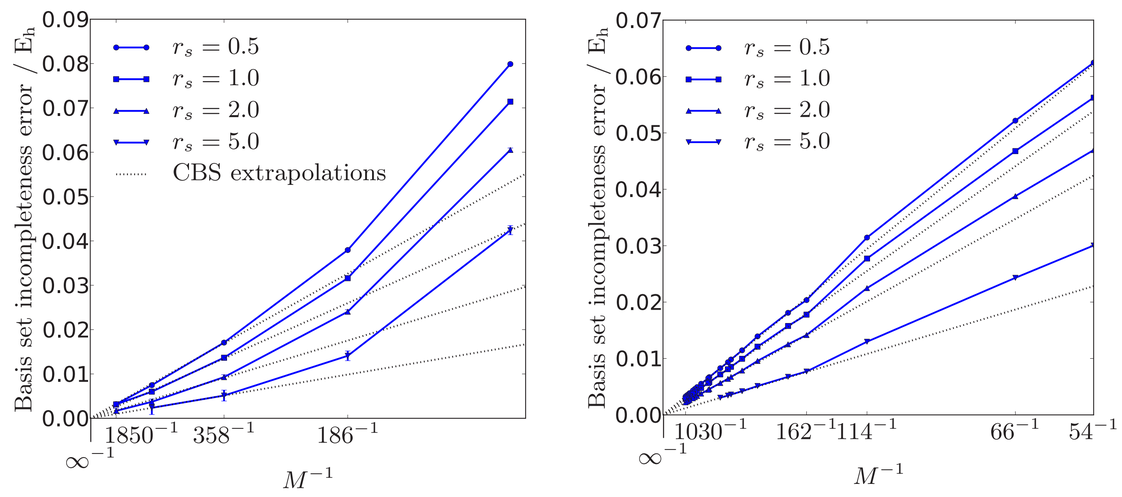
Benchmarking Finite-Basis Energies



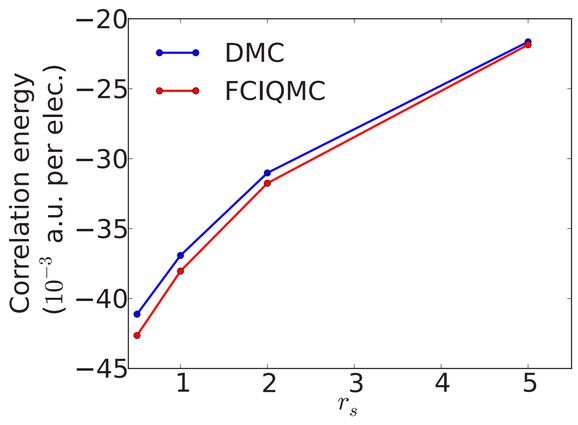
N=14 absolute correlation energies for r_s=1.0 (left) and r_s=5.0 (right) are compared between i-FCIQMC and more approximate methods.

Efficient Removal of Basis Set Incompleteness Error

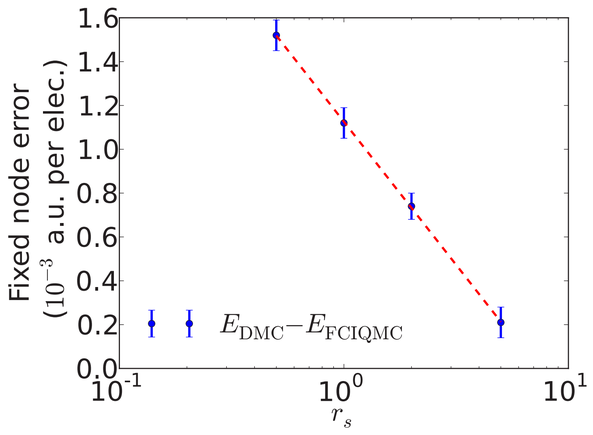
Basis set error can be removed by extrapolation in a manner similar to molecular systems, and similarly behaves as $1/M$ where M is the number of basis functions (left). In recent studies [7,8] we have found that improved convergence properties result from using basis set truncations which are different for each electron pair and based on the momentum transfer vector (right), rather than a conventional sphere in reciprocal space.



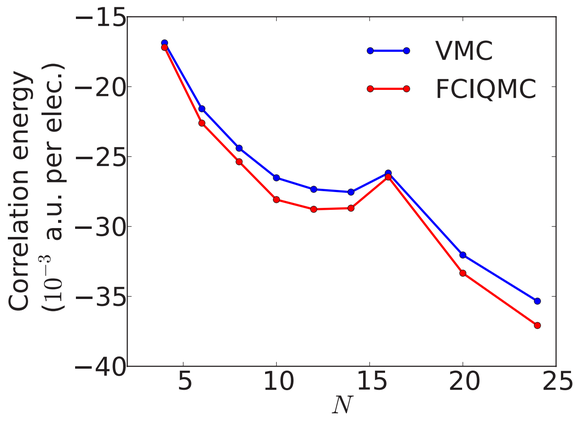
Quantifying Residual Error in Diffusion Monte Carlo



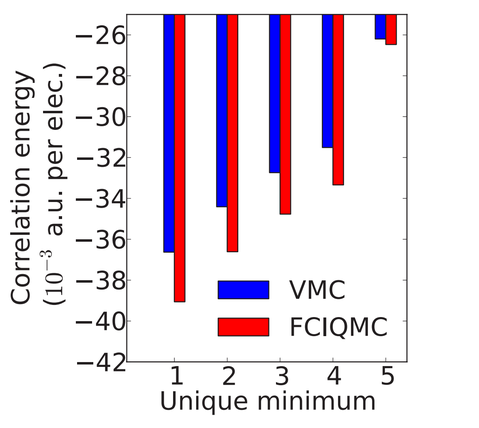
Comparison between (complete basis set) FCIQMC and DMC energies for a range of densities (N=14). The difference can be attributed to error due to the fixed-node approximation.



The error decreases with falling density, empircally found as Log(r_s) (N=14). The decrease of fixed-node error with lowered density is consistent with previous findings in the HEG[3].



The FCIQMC-DMC energy gap changes rapidly with changing electron number (non-zero twist angle), apparently reflecting the shell-filling effects that also cause fluctuation in the correlation energy, due to finite size effects.



The energy gap also changes dramatically for different minima in the simulation-cell first Brillouin zone. For the N=16 example shown, there are only 5 unique ground-state correlation energies.

References: [1] W. M. C. Foulkes, L. Mitas, R. J. Needs, G. Rajagopal, Rev. Mod. Phys., 73, 33, (2001). [2] P. López Ríos, A. Ma, N. D. Drummond, M. D. Towler and R. J. Needs, Phys. Rev. E 74, 066701 (2006). [3] Y. Kwon, D. M. Ceperley, R. M. Martin, Phys. Rev. B, 58, 6800 (1998). [4] G. H. Booth, A. J. W. Thom, A. Alavi, J Chem Phys, 131, 050106, (2009). [5] D. Cleland, G. H. Booth, A. Alavi, J Chem Phys 132, 041103, (2010). [6] J. J. Shepherd, G. H. Booth, A. Gruneis, A Alavi, Phys. Rev. B 85, 081103(R) (2012). [7] J. J. Shepherd, G. H. Booth, A Alavi, arXiv:1201.4691 (2012). [8] J. J. Shepherd, A. Gruneis, G. H. Booth, G Kresse, A Alavi, arXiv:1202.4990 (2012). [9] http://www.vasp.at/. [10] R.J. Needs, M.D. Towler, N.D. Drummond and P. López Ríos, J. Phys.: Condensed Matter 22, 023201 (2010).

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