The Homogeneous Electron Gas: Beyond Fixed Nodes II

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Introduction

The variational and diffusion Monte Carlo (DMC) methods have had unparalleled 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 $10^{-1}$ 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,

$$i\frac{d\Psi}{dt} = -\hat{H}\Psi$$

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

$$\Psi(t) = \sum_{\Delta \Gamma} \langle \Delta \Gamma | \Psi(t=\infty) \rangle | \Delta \Gamma \rangle.$$  

The resultant FCI equations,

$$-i \frac{d}{dt} \langle \Delta \Gamma | \Psi(t=\infty) \rangle = \langle \Delta \Gamma | \hat{H} \rangle = \sum_{\Phi} \sum_{k} v_{\Phi k} \langle \Delta \Gamma | \Phi \rangle a_{k}^{\dagger} + \sum_{k} a_{k} \langle \Phi | \Delta \Gamma \rangle C_{\Phi}$$

are solved using a stochastic representation of the wavefunction, based on walkers, $\Gamma_i \times N_{\Delta}$ and spawning, annihilation and death/ cloning events in Slater determinant space. When the shift (S) is equal to the total energy, these events will stabilise the exact FCI wavefunction for a sufficient number of walkers. We seek to solve these equations for the plane-wave HEG Hamiltonian,

$$\hat{H} = \sum_{k} v_{k} a_{k}^{\dagger} a_{k} + \frac{1}{2} \sum_{k} \sum_{k'} \hbar \omega_{kk'} a_{k}^{\dagger} a_{k'} + \frac{1}{2} \mathcal{N} \hbar \omega_{0}.$$  

Benchmarking Finite-Basis Energies

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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 ($N_{\Delta}$) 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.

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/$N_{\Delta}$ where $N_{\Delta}$ 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

The energy gap 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: