The Homogeneous Electron Gas: Beyond Fixed Nodes

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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 $1\mathrm{mE_h}$ 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].

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