Accurate total energy derivatives from correlated sampling diffusion Monte Carlo calculations

Tom Poole[a], Prof. Matthew Foulkes[a], Dr. James Spencer[a,b], and Prof. Peter Haynes[a,b]

[a]*Department of Physics, Imperial College London*
London, UK
[b]*Department of Materials, Imperial College London*
London, UK

Quantum Monte Carlo (QMC) methods are powerful techniques for calculating the electronic structure of atoms, molecules and solids with an accuracy comparable to the standard ab initio methods of quantum chemistry. The two most commonly used methods, variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo (DMC), rely on the statistical sampling of an accurate many-body wave function with a computational cost that scales favourably when compared to post-Hartree-Fock methods such as configuration interaction and coupled cluster calculations. This makes the QMC approach the ideal tool for computing the total energies of large collections of interacting quantum particles where conventional density functional theory methods fail to capture the role of dispersion interactions or electronic correlation.

Despite a number of advances in the area, the extraction of total energy derivatives, required for force calculations, remains problematic. This poster presents a method for correlating DMC simulations performed on two similar systems, which leads to a large reduction in the error of the energy difference between the systems when compared to independently obtained results. Accurate energy differences form the basis for finite difference estimates of total energy derivatives, where it is shown that for increasingly small displacements the stochastic error in the energy gradient remains constant. Results are presented for atomic force calculations on the water molecule and pressure calculations of solid hydrogen phases.