APPLYING QUANTUM MONTE CARLO TO THE ELECTRONIC STRUCTURE PROBLEM

ANDREW D POWELL, RICHARD DAWES, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*.

Two distinct types of Quantum Monte Carlo (QMC) calculations are applied to electronic structure problems such as calculating potential energy curves and producing benchmark values for reaction barriers. First, Variational and Diffusion Monte Carlo (VMC and DMC) methods using a trial wavefunction subject to the fixed node approximation were tested using the CASINO code.[1] Next, Full Configuration Interaction Quantum Monte Carlo (FCIQMC), along with its initiator extension (i-FCIQMC) were tested using the NECI code.[2] FCIQMC seeks the FCI energy for a specific basis set. At a reduced cost, the efficient i-FCIQMC method can be applied to systems in which the standard FCIQMC approach proves to be too costly. Since all of these methods are statistical approaches, uncertainties (error-bars) are introduced for each calculated energy. This study tests the performance of the methods relative to traditional quantum chemistry for some benchmark systems.

References: [1] R. J. Needs et al., J. Phys.: Condensed Matter 22, 023201 (2010). [2] G. H. Booth et al., J. Chem. Phys. 131, 054106 (2009).