DIFFUSION MONTE CARLO USING MACHINE LEARNING POTENTIAL ENERGY SURFACES

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Diffusion Monte Carlo (DMC) is a technique for obtaining the ground-state solution to the vibrational time-independent Schrödinger equation based on a stochastic sampling of an electronic potential energy surface (PES). To obtain accurate results, one needs a globally-accurate PES. Ideally, the electronic energies used in DMC are calculated at the CCSD(T) level of theory. Recently, neural networks have shown promise to provide accurate post-Hartree corrections to the electronic energy at the cost of a standard Hartree-Fock calculation[ab]. These neural network surfaces, however, have only been validated using a small sampling of the available configurations of the system. DMC, by design, samples the entire region of the PES that is sampled by the vibrational ground state wave function.

Despite the speed of the neural network potential relative to a calculation at a high level of theory such as CCSD(T), the necessity of the evaluation of the Hartree-Fock energy for every one of the thousands of DMC configurations over tens of thousands of time-steps makes this computationally challenging. To this end, we have developed a DMC algorithm to take advantage of massively parallel high performance computing environments. In addition, to further alleviate the computational cost, we have incorporated importance sampling into the algorithm to reduce the overall number of configurations required to adequately sample the PES. Combined, these two optimizations push the calculation back into the realm of computational feasibility. We have benchmarked the calculation on the water monomer and the CH_5^+ molecular ion. We plan to extend this work to larger systems, such as large water clusters or a simple Criegee intermediate, where running the DMC with traditional electronic structure would be intractable.

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[a] Welborn, M. , Cheng, L., Miller, T. M. JCTC. 2018 14 (9), 4772-4779

[b] Cheng, L., Kovachki, N. B., Welborn, M., Miller, T. M. JCTC. 2019 15 (12), 6668-6677