GUIDED DIFFUSION MONTE CARLO BASED ON BONDING ENVIRONMENT: AN EFFICIENT APPROACH FOR STUDYING MOLECULAR VIBRATIONS IN PATHOLOGICAL SYSTEMS

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Diffusion Monte Carlo (DMC) is a technique that can be used to obtain the ground state energy and ground state wave function given a potential energy surface (PES) that fully describes the system of interest. However, one complication with this technique is that in order to obtain accurate results for molecular systems that have couplings between the high and low frequency vibrations, large ensemble sizes are needed. [a] One approach to combat these large ensemble sizes is to use a guiding function to describe the high-frequency vibrations. This approach has been applied to studies of neutral water clusters, protonated water clusters, and CH_5^+, where a significant reduction in the ensemble sizes that were needed in the simulations was achieved. [b] [c] An extension of this idea has been used to obtain excited state information in the coordinates described by the guiding functions.

In this work, I will describe the applications of this approach to systems with large coupling among the vibrational degrees of freedom. The use of a guiding function that describes the ground state wave function of the high-frequency vibrations allow us to use smaller ensemble sizes, while producing ground state energies and wave functions that are as accurate or more accurate than those obtained using traditional DMC approaches. By using an excited state guiding function in the degrees of freedom that are being excited, we can obtain the excited state energy and wave functions through fixed-node DMC. With these wave functions in hand, we can also obtain overlaps between the ground state and first excited state, allowing us to evaluate intensities. This approach provides accurate representations of the excited state energy and the intensity of the transition from the ground state as long as the guiding functions for the ground and excited states provide fairly accurate representations of the wave functions along the excited degree of freedom.

[a] Mallory, J. D. and Mandelshtam, V. A., *J. Phys. Chem. A* (2015), **119**, 6504-6515.

[b] Lee, V. G. M. and McCoy, A.B., *J. Phys. Chem. A* (2019), **123**, 37, 8063-8070.

[c] Finney, J. M., DiRisio, R. J., McCoy, A.B., *J. Phys. Chem. A* (2020), **124**, 45, 9567-9577.