# EXTENSIONS TO GUIDED DIFFUSION MONTE CARLO FOR EXCITED STATES

JACOB M FINNEY, ANNE B McCOY, *Department of Chemistry, University of Washington, Seattle, WA, USA*.

Diffusion Monte Carlo (DMC) is a stochastic method that is used to obtain the ground state energy and ground state wave function of a system of interest. DMC requires a potential energy surface (PES) that describes all degrees of freedom of the system. We have found that the use of guiding functions, functions that describe some of the vibrational degrees of freedom within the system, allow improved sampling of the ground state wave function if the guiding function is chosen carefully.[a] [b] While this enables us to used DMC to study larger systems, to obtain spectra we will also need to calculate the excited state energies and matrix elements of the dipole moment operator involving the ground and excited state wave functions. In this work we explore the use of excited state guiding functions for the evaluation of vibrationally excited states. Specifically, we combine the approaches taken from previous work using ground state guided DMC simulations and fixed-node approaches, which we have used to obtain excited state wave functions from unguided DMC calculations. This approach has been applied to studies of OH stretching vibrations in $H_2O$ and $H_3O_2^-$ , where comparisons to previous studies can be made. Various approaches for obtaining the intensities from the ground and excited state DMC wave functions are explored.[c]

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

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

[c] Barnett, R. N., Reynolds, P. J., Lester Jr., W. A., *J. Chem. Phys.* (1992), **96**, 2141-2154