USING FIXED-NODE DIFFUSION MONTE CARLO TO PROBE ROTATION-VIBRATION COUPLING IN HIGHLY FLUXIONAL ASYMMETRIC TOP MOLECULES

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Our group has developed a fixed-node Diffusion Monte Carlo (DMC) methodology that can be used to describe rotationally excited states of highly fluxional symmetric top molecules.[a] This technique has been thoroughly benchmarked using rotationally excited states of H_3^+, H_3O^+, and NH_3 with $J \leq 12$.[b] Here, we report a recently developed extension of this methodology to asymmetric top molecules which undergo large amplitude, zero-point vibrational motion. The nodal surfaces used in the fixed-node DMC calculations are obtained from rigid-rotor wave functions calculated using the system's ground state vibrationally averaged rotational constants. The algorithms used to evaluate node crossing and re-crossing are generalized to account for the pronounced curvature exhibited by the nodal surfaces of asymmetric top molecules with $\kappa \approx 0$ due to the strong mixing of two or more symmetric top basis functions. Finally, the insight that can be obtained from these calculations into the nature and strength of the vibration-rotation coupling present in highly fluxional asymmetric top molecules will be briefly discussed and further elaborated on in the following talk.

[a] A. S. Petit and A. B. McCoy, J. Phys. Chem. A 113, 12706 (2009).
[b] A. S. Petit, B. A. Wellen, and A. B. McCoy, J. Chem. Phys. 136, 074101 (2012).