EXPLORING ROTATION-VIBRATION COUPLING IN HIGHLY FLUXIONAL MOLECULES USING SURFACE HOPPING DIFFUSION MONTE CARLO

ANDREW S. PETIT, and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210*.

Diffusion Monte Carlo (DMC) has widely been shown to be a powerful technique for studying ro-vibrational states of highly fluxional molecules and clusters. An extension of DMC to multiple potential energy surfaces (PESs) based on the Tully surface hopping approach[a] has previously been developed by our group.[b] Here, we report an application of this approach to the calculation of rotationally excited states of systems with pronounced rotation-vibration coupling and large-amplitude, zero-point vibrational motion. More specifically, for a chosen value of J, each walker in the DMC ensemble is expanded in a symmetric top basis. The expansion coefficients are updated each time-step based on the action of the rigid-rotor asymmetric top Hamiltonian. This Hamiltonian is constructed using the inverse moment of inertia tensor evaluated in the Eckart frame at the walker's position in configuration space. Each walker is then localized onto a single, K-dependent effective PES, and the effective potential energy associated with the walker's position on that surface determines the evolution of its weight in the DMC ensemble. Preliminary results of the application of this methodology to model systems such as H_3^+ and H_2D^+ will be discussed as well as its prospect for accurately evaluating ro-vibrational states of systems like CH_5^+. Finally, a comparison of this technique with our previously developed fixed-node DMC approach for the evaluation of ro-vibrational energies and wave functions will be presented.[c]

[a] J. C. Tully, J. Chem. Phys. 93, 1061 (1990).
[b] A.B. McCoy, Chem. Phys. Lett. 321, 71 (2000).
[c] A. S. Petit, B. A. Wellen, and A. B. McCoy, J. Chem. Phys. 136, 074101 (2012).