EXTENSIONS OF FIXED-NODE DIFFUSION MONTE CARLO TO THE STUDY OF THE ROTATIONALLY EXCITED STATES OF H_2D^+

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Diffusion Monte Carlo (DMC) has been shown to be a highly successful technique for treating quantum zero-point effects of very floppy molecules and clusters. Our group has developed a fixed-node DMC methodology that allows us to expand the application of the approach to studies of rotationally excited states of such systems. We recently applied this approach to the study of H_3^+.[a] We chose this system because of the availability of a global potential energy surface of spectroscopic accuracy, and the results of converged variational calculations have been reported that can be used to assess the accuracy of the DMC calculations. As a symmetric top molecule, the nodal structures of the rotationally excited states of H_3^+ are well known and can be used in fixed-node DMC calculations. We have recently extended this methodology to asymmetric top molecules, using H_2D^+ as a test system for these types of molecules as it has a κ value near zero. Here, we describe these extensions and present the results of DMC calculations of representative rotationally excited states of H_2D^+.

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