DIFFUSION QUANTUM MONTE CARLO ON MULTIPLE POTENTIAL SURFACES: A SCALABLE APPROACH FOR CALCULATING SHIFTS IN TRANSITION FREQUENCIES IN CLUSTERS

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

An approach is described for applying Diffusion Monte Carlo (DMC) techniques to problems that involve two or more coupled potential energy surfaces. This technique combines surface hopping with traditional Diffusion Monte Carlo approaches. The accuracy and efficiency of this approach will be demonstrated through studies of the shifts in the frequencies of the fundamental and first overtone of the HF stretch in linear chains of HF. In the case of $(HF)_2$ the errors in the energies, calculated using DMC, are smaller than the statistical uncertainty of DMC. In this case, the vibrational excitation is localized in one of the monomers, but, as the number of HF monomers is increased to ten, the excitation becomes delocalized. Extensions of this approach to realistic studies of the IR spectrum of molecular clusters will be discussed.