APPLICATION OF QUANTUM DIFFUSION MONTE CARLO METHODS TO THE STUDY OF EXCITED VIBRATIONAL STATES IN MOLECULAR CLUSTERS.

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Quantum Diffusion Monte Carlo (QDMC) emerged recently as a useful method for modelling structure and spectroscopy of molecular clusters. The advantages of the method include flexibility and extendability to large clusters; however the method is applied most easily to the ground vibrational state. Calculation of excited states is still a challenge. A new approach was suggested by us for (QDMC), calculation of intermolecular exited states; the approach is based on nodal surface optimization. Several exited vibrational states at J=0 for $H_2O..CO$ and $H_2O..N_2$ clusters were studied in the present work. Intramolecular fundamentals of $H_2O..CO$ were also studied using a combination of QDMC, and an adiabatic approximation based on frequency separation between inter- and intramolecular vibrations. Variational treatment in a Morse basis is used for the stretch excitations. QDMC is employed to calculate the distribution of intermolecular configurations, and to evaluate the influence of intermolecular zero-point motion on intramolecular frequency shifts; this influence is quite substantial. The dependence of the potential on intermolecular coordinates was obtained using ab initio Moller Plesset perturbation theory calculations.

References:

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