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

P. SANDLER, V. BUCH, Department of Physical Chemistry and the Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel.

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$_2$O$_x$CO and H$_2$O$_x$N$_2$ clusters were studied in the present work. Intramolecular fundamentals of H$_2$O$_x$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: