

Vibrational structure of asymmetric multi-well systems: a combined VCI and instanton approach

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Vibrational structure of systems with multiple symmetry-related minima on the potential energy surface can be difficult to solve. Vibrational wavefunctions are then delocalized and energy levels split due to tunneling between the minima. To obtain correct splitting values, it is necessary to converge vibrational energies to great accuracy, which becomes difficult using variational methods, even for moderately large systems. If minima are not symmetry related, but have either different frequencies (in case of partial isotopic substitution) or different energies (in case of different conformers), structure of vibrational levels can be described using a combination of tunneling contributions and differences in energies of wavefunctions localized in each minimum. Furthermore, amplitudes of vibrational eigenfunctions in each minimum depend on the ratios of tunneling contributions and energy differences. As a consequence, it is necessary to obtain good values for tunneling contributions in order to obtain good wavefunctions to use for, e.g. sampling of initial conditions in various mixed quantum-classical approaches used to model photoinduced processes.

In this talk we present an efficient method for computing vibrational structure of such systems. The idea of this combined method is to construct the Hamiltonian matrix in the basis of wavefunctions localized in the minima. Matrix elements that include states in the same minimum are obtained using vibrational configuration interaction (VCI) [1], while elements that include wavefunctions of different minima are computed using Jacobi field instanton (JFI) theory [2]. Such approach uses the best features of both methods. Instanton theory provides excellent tunneling matrix elements, but uses harmonic energies. On the other hand, VCI method provides excellent energies of localized wavefunctions, but provides a poor description of wavefunction in the barrier that separates two minima, which is crucial to obtain good tunneling contributions. Additional benefit of such approach is the fact that JFI method yields the approximate wavefunction around the instanton path that connects pairs of minima, which could in theory be used to sample nuclear coordinates in such systems. We demonstrate the accuracy of this method on the model 2D potential and partially deuterated malonaldehyde, as a real-life system with above properties.

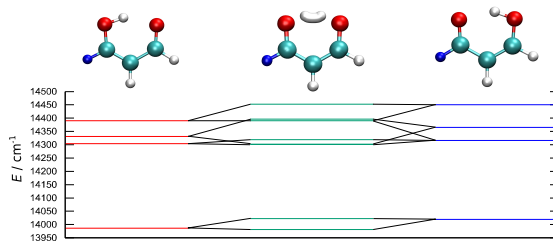


Fig. 1. Vibrational structure of partially deuterated malonaldehyde.

References:

- [1] K. Christoffel, J. Bowman, *Chemical Physics Letters*, **85**, (1982) 220-224.
- [2] M. Eraković, M. Cvitaš, *J. Chem. Phys.*, **153**, (2020) 134106.