Anharmonic Vibrational Spectra from Quartic Potentials to Discrete Variable Representation: Scaling Strategies for Hydrogen-Bonded and Weakly-Bound Molecular Clusters

Qian-Rui Huang[1]

[1]*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*

Abstract

Vibrational spectra of hydrogen-bonded clusters and weakly-bound complexes are often poorly described by the double-harmonic approximation, where mode-mode coupling and higher-order terms in the potential and dipole surfaces give rise to additional spectral features - overtones, combination bands, and Fermi resonances - beyond what the double-harmonic approximation predicts.

We present two complementary anharmonic vibrational analysis methods developed in-house. The first, a Quartic-Potential vibrational configuration interaction (QP-VCI) approach with analytical ladder-operator Hamiltonian matrix elements, is scalable to ~40 normal modes and extends to much larger systems (up to 100+ modes) via a perturbative basis-selection scheme (QP-PT2). The second, a Discrete Variable Representation (DVR) approach on Gauss-Hermite grids, targets more strongly-coupled systems; while the full-grid formulation is limited to ~12 modes, a one-dimensional product-basis reformulation (FBR-1D) - structurally analogous to the QP-VCI matrix elements - substantially improves both speed and accuracy over prior product-basis schemes and extends the accessible range further. We illustrate the physical insight both methods provide through case studies of Fermi resonance and combination-band coupling in ionic hydrogen-bonded dimers and protonated water clusters, and discuss ongoing work extending these approaches toward larger systems, including a tensor-network (DMRG) treatment of the DVR Hamiltonian.