A Semiclassical Divide-and-Conquer Method for Spectroscopic Calculations of High Dimensional Molecular Systems

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Several quantum approaches to vibrational spectroscopy are nowadays available. Among them we recall the variational perturbation theory (VPT2),[1] the Multiconfigurational Time Dependent Hartree (MCTDH)[2] and the vibrational configuration interaction (VCI).[3] Quantum effects like Zero Point Energy and overtones can be recovered only in a quantum picture, but a purely quantum treatment is too demanding for molecules with more than few dozens of degrees of freedom, due to the well known curse of dimensionality problem.[4]

Semiclassical theory represents a very powerful tool to properly account for quantum effects.[5, 7, 6, 8, 9, 10] In particular, the Time Averaged version of the quantum propagator has been shown to be very accurate for small molecules.[11, 12] Despite that, medium and large sized molecules are out of reach, since the approach runs out of steam when the dimensionality increases, being limited to about 25-30 degrees of freedom.

In this work a new semiclassical divide-and-conquer approach is presented with the aim to demonstrate that quantum dynamics simulations of high dimensional systems are doable.[13] The accuracy and efficiency of the method are firstly tested on small molecules, for which exact results are available.[14] Then the method is applied to the calculation of the quantum vibrational spectrum of a C_{60} Fullerene molecule, a system characterized by 174 degrees of freedom. Results show that the approach can accurately account for quantum anharmonicities, purely quantum features like overtones, and removal of degeneracy when the molecular symmetry is broken.

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