
Divide-and-Conquer Semiclassical Dynamics: A Viable Method for Vibrational Spectra Calculations of High Dimensional and Anharmonic Molecular Systems

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The prediction of accurate vibrational frequencies is often necessary for the interpretation of experimental outcomes, especially when sources of strong anharmonic effects such as hydrogen bonding are present. Unfortunately, the most relevant stumbling block to fill in the gap between theory and experiment is usually represented by dimensionality problems, when quantum mechanical effects like Zero Point Energy, quantum anharmonicities, and overtones cannot be neglected. In this circumstance quantum applications are generally limited to small and medium sized molecules. One possible alternative is represented by Semiclassical theory, which allows to recover accurate spectral densities by taking advantage of quantities arising from classical mechanics simulations.^[1-5] In particular, here we present a method, called Semiclassical “Divide-and-Conquer”, able to reproduce spectra of high-dimensional molecular systems accurately.^[6,7] The method is first validated by performing spectra of small and medium sized molecules, and then it is used to calculate the spectra of benzene and a C₆₀ model, which is made of 174 degrees of freedom. Then, we show results of variously sized-water clusters characterized by strong hydrogen-bonding that red shifts the involved OH stretches.^[8] Finally, the method is combined with ab-initio molecular dynamics to abandon the necessity to employ pre-fitted Potential Energy Surfaces, and applied to study supramolecular systems like the protonated glycine dimer and hydrogen-tagged protonated glycine.^[9]

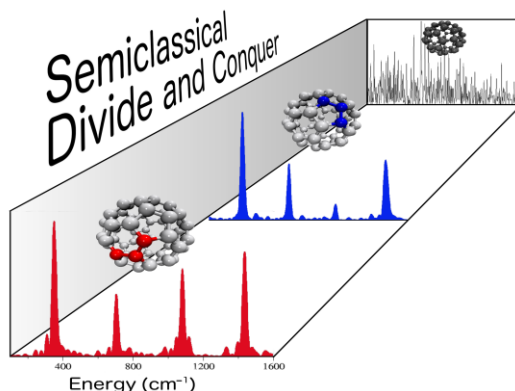


Figure 1: Pictorial representation of the Divide-and-Conquer strategy.

References

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