A FULLY AB INITIO APPROACH TO THE EVALUATION OF VIBRATIONAL SPECTRA USING GAUSSIAN BASIS SETS

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We have developed a black-box method to evaluate vibrational spectra using only the information provided by semi-classical *ab initio* molecular dynamics simulations. Using a distributed Gaussian basis set centered at the points sampled by an AIMD trajectories and a local harmonic approximation to the potential at each point, it is possible to obtain accurate vibrational spectra. By exploiting the locality of molecular vibrations, this method is applicable to the evaluation of spectra systems of moderate size. The judicious choice of Gaussian width parameters as well as selection augmentation of the basis with appropriate harmonic basis functions can lead to high-fidelity spectra even for relatively short trajectories.

This method provides a complement to perturbative approaches, as it treats low-frequency vibrations accurately and is amenable to systems with multiple low-lying energetic minima. Furthermore, by running more AIMD trajectories, it is possible to refine the vibrational spectrum obtained.