

Wigner Gaussian dynamics: simulating the anharmonic and quantum ionic motion

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The atomic motion controls important features of materials, such as thermal transport, phase transitions, and vibrational spectra. However, the simulation of ionic dynamics is exceptionally challenging when quantum fluctuations are relevant (e.g., at low temperatures or with light atoms) and the energy landscape is anharmonic. In this work, we formulate the Time-Dependent Self-Consistent Harmonic Approximation (TDSCHA) in the Wigner framework, paving the way for the efficient computation of the nuclear motion in systems with sizable quantum and thermal anharmonic fluctuations. Besides the improved numerical efficiency, the Wigner formalism unveils the classical limit of TDSCHA and provides a link with the many-body perturbation theory of Feynman diagrams.

We further extend the method to account for the non-linear couplings between phonons and photons, responsible, e.g., for a nonvanishing Raman signal in high-symmetry Raman inactive crystals, firstly discussed by Rasetti and Fermi. We benchmark the method in phase III of high-pressure hydrogen *ab initio*. The nonlinear photon-phonon coupling reshapes the IR spectra and explains the high-frequency shoulder of the H₂ vibron observed in experiments.

The Wigner TDSCHA is computationally cheap and derived from first principles: it is unbiased by assumptions on the phonon-phonon and phonon-photon scattering and does not depend on empirical parameters. Therefore, the method can be adopted in unsupervised high-throughput calculations.