Real-time response from imaginary-time simulation: Hacking quantum statistics with Path Integral Monte Carlo

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The electric field response is a fundamental property of matter, which in case of atoms and molecules, culminates in polarizability. The static and dynamic multipole polarizabilities are the origins of all kinds of spectral phenomena, such as infrared activity, optical dispersion, and x-ray scattering. Often the full response is indeed divided into electronic and rovibrational effects in the Born-Oppenheimer approximation, which neglects their coupling to each other and the finite temperature. In a recent work [1], we go beyond the Born-Oppenheimer approximation in an ab initio path integral Monte Carlo simulation (PIMC), which enables us to study the combined electronic, rovibrational and nonadiabatic effects on the total dynamic polarizability.

Unfortunately, estimating dynamic properties is a notorious challenge with real-space Quantum Monte Carlo (QMC) methods, such as PIMC. While the variants of QMC excel in complex quantum statistical many-body problems, they usually operate in imaginary time. Theoretically, the generalized susceptibilities, or the quantum correlation functions in the imaginary domain can be analytically continued to yield the real-time response properties. However, the practical implementation is an ill-posed inversion problem, which defies even the most sophisticated methods. Here we focus on a particular numerical approach: Maximum Entropy method (MaxEnt) [2]. While MaxEnt has its flaws, it provides convincing estimates of the exact multipole spectra, dynamic polarizabilities, and accurate van der Waals coefficients of several small atomic and molecular systems.

References

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