

Linear and non-linear dielectric response of periodic systems from quantum Monte Carlo

Paolo Umari

DEMOCRITOS, CNR-INFM

Trieste, Italy

We present a novel approach that allows to calculate the dielectric response of periodic systems in the quantum Monte Carlo formalism¹. We employ a many-body generalization for the electric enthalpy functional, where the coupling with the field is expressed via the Berry-phase formulation for the macroscopic polarization. A self-consistent local Hamiltonian then determines the ground-state wavefunction, allowing for accurate diffusion quantum Monte Carlo calculations where the polarization's fixed point is estimated from the average on an iterative sequence. The polarization is sampled through forward-walking. This approach has been validated for the case of the polarizability of an isolated hydrogen atom, and then applied to a periodic system. We then calculate the linear susceptibility of molecular-hydrogen chains with different bond-length alternations. The results found are in excellent agreement with the best estimates obtained from the extrapolation of quantum-chemistry calculations. By adopting trial wavefunctions obtained from Hartree-Fock, we can then calculate with great accuracy the second hyper-susceptibility. Finally, we assess the importance of electronic correlations for the calculated linear and non-linear susceptibilities.

[1] P. Umari, A. J. Williamson, G. Galli, and N. Marzari, *Phys. Rev. Lett.*, **95**, 207602 (2005).