Dielectric Response of Periodic Systems from Quantum Monte Carlo Calculations

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We present a novel approach to calculate the dielectric response of periodic systems in the quantum Monte Carlo formalism. We introduce a many-body generalization of the electric enthalpy, 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 highly-accurate diffusion quantum Monte Carlo calculations where the polarization is sampled iteratively via forward-walking. This approach has been validated for the case of an isolated hydrogen atom, and then applied to a periodic system, to calculate the dielectric susceptibility of molecular-hydrogen chains. The results found are in excellent agreement with the best estimates obtained from the extrapolation of highly-correlated quantum-chemistry calculations.