The full dielectric response from time-dependent density functional theory

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Microscopic structure of different materials is often studied using spectroscopic methods that probe optical transitions, i.e. dipole allowed electronic excitations. Measurement of the full momentum dependent dielectric response provides a more comprehensive picture of the electronic structure, as it additionally describes e.g. plasmon dispersion and generalized oscillator strengths. Among the experimental techniques that can access these transitions, non-resonant inelastic x-ray scattering (NRIXS) attracts considerable interest because of its applicability for various materials in a wide energy range, thus being capable for studying vibrational and valence as well as core electron excitations. Furthermore, NRIXS allows experiments at extreme conditions. The rapid development in the experimental technique has led to increased need for reliable computational methods, and here time-dependent density functional theory (TDDFT) is becoming a standard tool for studying the electronic excitations.

In this work we present a scheme to simulate the NRIXS (and similarly the electron energy loss) spectrum of molecular systems, i.e. the dynamic structure factor. The method relies on calculating the density-density response function using TDDFT. This function describes the quantum fluctuations of electron density at different times and is closely related to the material's dynamic structure factor. Our method utilises the calculation of the time-dependent electronic density under an influence of external electric field using the real-space computer code OCTOPUS.[1, 2]

We describe the theory behind the presented scheme and show results for some small benchmarking molecular systems comparing them with experimental spectra and other calculations. Finally, we discuss the new information that can be obtained from the momentum transfer dependent NRIXS spectrum, and the connection to optical photoabsorption spectrum.

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