Ab initio approach based on the Mulitpole Hamitonian toward optical responses beyond the dipole approximation

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Abstract: Localized electric field around a metal nano-structures has played a vital role in modern nano-optical science and engineering. The interaction between molecules with such a localized field can go beyond our understandings of the light-matter interaction under the dipole approximation. In the dipole approximation, the light has long wavelength than a molecular scale and therefore a molecule is excited by a spatially uniform field. In a sharp contrast, the localized field can excited molecule non-uniformly, thus violating the dipole approximation. Most available ab initio calculations software have modules to simulate excited states and/or spectroscopy under the dipole approximation. For theoretical study beyond the dipole approximation, we have developed a method based on the multipole Hamiltonian. I will explain this method and applications for electronic excitations with localized field showing unique non-linear response and optical forces. Also the interaction between localized field and molecular vibrations are discussed.