Absorption in Al_{13} cluster using Real-Time TDDFT: transitions involving the continuum

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Unlike noble-metal nanoparticles (NPs) the localized surface plasmon resonance (LSPR) in Aluminum NPs occurs in the ultra-violet (UV) making them suitable for plasmonic application in the UV. This has stemmed research interest [1] in Al NPs and clusters despite their high sensitivity to oxidation and the difficulties in optical measurements high in the UV. From theoretical aspect optical properties of Al clusters is difficult to obtain as the LSPR is above the ionization energy implying transitions that involve contribution from states which are largely part of the continuum, in particular for the anion. To this end, quantum mechanical calculations of Al clusters from different groups differ radically as evidenced by optical absorption in and neutral [2, 3] charged [4, 5] Al_{13}.

In this work we present a systematic way to obtain absorption spectra for Al clusters within the framework of real-time time-dependent density-functional theory using the real-space code octopus [6]. This is done by systematic incorporation of contributions from “discretized" continuum states (which are not required to be explicitly calculated within RT-TDDFT,) to the propagation of occupied Kohn-Sham orbitals. The results are compared with linear-response TDDFT calculations where excited states are explicitly calculated. This comparison showed the advantages of grid based RT-TDDFT calculations which give correct spectra for all charge states, +1, neutral, and -1, of the Al_{13} cluster.

References

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Keywords: TDDFT, real-time, Metal clusters, DFT.