

Calculations of Optical Properties of Organic Molecular Aggregates Aiming to Avoid Some Drawbacks of TD-DFT and the Dipole Approximation

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Commonly used methods to compute optical properties based on DFT (density functional theory) - time dependent DFT, often used for molecules and clusters, and the dipole approximation, often used for solids and implemented in many codes - suffer from significant errors having to do with reliance on energies and shapes of Kohn-Sham orbitals, as they critically depend on integrals over overlapping orbitals with a kernel, which causes a string sensitivity. One consequence of that is strong underestimation of excitation energies with GGA functionals, another is artificial redshift of computed spectra of large molecules or molecular aggregates. We explore an alternative approach in which we compute frequency dependent polarizability which can be less dependent on the quality of the orbitals, and from there, the real, then the imaginary part of the dielectric constant, and ultimately the spectrum. We present calculations of absorption spectra of molecules and molecular aggregates that show that for some systems (specifically fullerene clusters) this approach is less sensitive to the specific DFT setup than (linear response) TD-DFT and the dipole approximation and results in more realistic spectra of molecular clusters. For single-molecule systems including oligomers, on the other hand, no advantage over TD-DFT is observed.

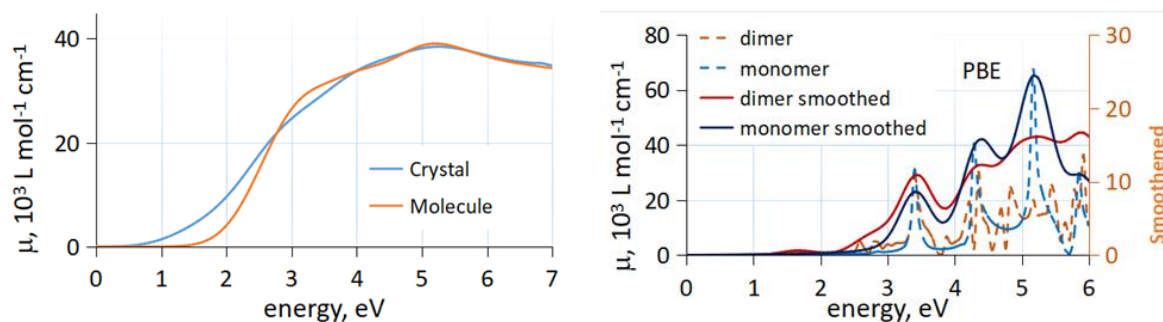


Figure 1. Left: the absorption spectrum of molecular and solid C60 computed with the popular dipole approximation showing an artificially large redshift in the solid state. Right: calculations using real polarizability as the starting point showing a realistic redshift due to aggregation with much better agreement with experiments (cf. to J Appl Spectrosc 77, 335 (2010) vs. Appl Phys Lett 94, 223307 (2009)).