Excitation and Response Properties of Polymers and Molecules using Time-Dependent Current-DFT

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Time-dependent density-functional theory has the potential to be a very versatile method to calculate various excitation and response properties of large molecular systems. However, the static axial polarizability of conjugated oligomers obtained within this method is greatly overestimated when using the standard adiabatic local density approximation (ALDA). This local approximation but also the more advanced generalized gradient approximation is unable to describe the highly nonlocal exchange and correlation effects found in these quasi-one-dimensional systems. We have found a successful approach towards the solution of this longstanding problem by using time-dependent current-density-functional theory[1], in which we describe these ultranonlocal exchange-correlation effects within a local current description. For the prototype polyacetylene and many other systems excellent agreement with high level ab initio quantum chemical methods was obtained using the Vignale-Kohn (VK) current-functional [2]. For these long chains we have obtained the excitation energies and oscillator strengths and we can explain the large reduction of the static polarizability by the way in which the VK-functional modifies these excitation properties. We also obtained the excitation energies for a set of atoms and benchmark molecules [3]. These results show that the VK functional fails for particular transitions.

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