

Energy Gradients for Excited States within the TD-DFT Formalism.

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Abstract

TD-DFT based methodology for calculating energy gradients with respect to the position of nuclei of molecules in excited states is presented. It allows for exploring excited state geometries by locating energy minima as well as transition states of photochemical reactions.

Despite an enormous success in dealing with ground state properties, for a long time DFT could not be rigorously applied to excited states. This has recently changed with the development of time dependent density functional theory (TDDFT)[Casida, 1995]. TDDFT has now become the methodology of choice for studying excitation energies of large systems. However, work on the calculations of excited states energy gradients with respect to nuclei positions has started only recently [Caillie and Amos, 1999, Caillie and Amos, 2000], and the methodology is not yet in widespread use.

We have developed energy gradients of excited states in a form suitable for implementation in ADF[van Gisbergen, 1999]. While the basic outline of the work follows to large extent Ref. [Caillie and Amos, 1999, Caillie and Amos, 2000] the presented theory is augmented to make use of optimization techniques present in the ADF code, such as frozen core approximation and linear scaling.

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