

Linear absorption spectroscopy from explicitly time-dependent equation-of-motion coupled-cluster theory

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Time-domain approaches to the *ab initio* description of light-matter interactions are becoming increasingly common, as they display a number of potential advantages over their frequency-domain counterparts [1]. One of the most well known advantages of a time-dependent formalism is that it can lead to a drastic reduction in the storage requirements for excited-state computations on large systems. For example, in a frequency-domain computation, obtaining information about broad spectral features in molecules with large densities of states may require the determination of hundreds of excited-state wave functions [2], each of which must be stored either in main computer memory or on disk. Explicitly time-dependent approaches, however, yield similar information from the analysis of a single time-domain signal and require the storage of only a handful of wave-function-sized objects.

In this work, we present an approach to explicitly time-dependent equation-of-motion coupled cluster (TD-EOM-CC) theory based on the time-propagation of a coupled-cluster dipole function, rather than the wave function itself. The dipole-function-based TD-EOM-CC formalism introduces no approximation and requires the time-evolution of only one time-dependent quantity: either the left or right dipole function, contrary to formalisms based on the time-propagation of the coupled-cluster wave function, which requires both left and right wave functions to be propagated. Due to the invariance of the obtained spectra to one's choice of propagating the right or left dipole function, in principle, the dipole-function-based TD-EOM-CC formalism reduces the computational effort required to evaluate a given component of a linear absorption line shape by a factor of two, when compared to its wave-function-based counterpart.

We validate the approach by computing the linear absorption spectra at the second-order approximate coupled-cluster singles and doubles (CC2) level of theory for a set of small closed-shell molecules. We also consider the ability of TD-EOM-CC2 to predict extreme ultraviolet (XUV) spectra for third-row cations belonging to the Neon-isoelectronic sequence. In general, we observe good agreement between TD-EOM-CC2 and the experimentally-obtained spectra. We are currently implementing a TD-EOM-CCSD variant of the method and extending the formalism in order to capture chiro-optical properties.

References:

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