Absorption Spectra of Solids from Periodic Equation-of-Motion Coupled-Cluster Theory

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As an important technique to study the interaction between light and materials, absorption spectroscopy has been widely used in the areas of photovoltaics, photocatalysis, light-emitting diodes, and more. The ability to simulate optical absorption spectra from first principles is of great importance both to complement experiments and to predict properties of new materials. On the other hand, recent years have seen rapid development of wavefunction-based quantum chemistry methods incorporating periodic boundary conditions, where accurate predictions have been made for periodic solids. Here, we present ab initio absorption spectra of three-dimensional solids calculated using Gaussian-based periodic equation-of-motion coupled-cluster theory with single and double excitations (EOM-CCSD). The spectra are calculated efficiently by solving a system of linear equations at each frequency, giving access to an energy range of tens of eV without explicit enumeration of excited states. We assess the impact of Brillouin zone sampling, for which it is hard to achieve convergence due to the cost of EOM-CCSD. Our results show that the excitonic effects that dominate the low-energy part of optical spectra of semiconductors and insulators are well described by EOM-CCSD, and our most converged spectra exhibit lineshapes that are in good agreement with experiment. Detailed discussions on various approximations, including the basis-set dependence, the frozen-orbital approximation, and partitioning of the EOM ansatz will be provided.