Equation-of-Motion Coupled-Cluster Theory Revisited: Size-Extensive Computation of Properties and Transition Moments

Jürgen Gauss

Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany

In recent years, Equation-of-Motion Coupled-Cluster (EOM-CC) theory [1] has evolved to a powerful tool for the reliable and accurate computation of excitation energies, ionization potentials, electron affinities, etc. A pending problem nevertheless is the lack of size-extensivity in the computation of properties and in particular of transition moments using the various EOM-CC schemes (see, e.g., the discussion in [2]).

This talk demonstrates how the size-extensivity problem in EOM-CC theory can be cured via an appropriate modification of the corresponding expressions for expectation values and transition properties [3]. The required modifications are exact in the full configuration-interaction (FCI) limit and consist in the elimination of the unwanted disconnected contributions, in this way providing connected expressions for properties and transition moments. The close relationship of the resulting expressions to those obtained via coupled-cluster response theory [4] is emphasized.

Numerical examples for the computation of EOM-CC properties and transition moments are given with an emphasis on the differences between the results from the traditional and the modified expressions. In particular, we discuss the computation of spin-orbit coupling constants using EOM-CC theory [5,6].

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