Local Treatment of Electron Excitations within EOM-CCSD Method

Tatiana Korona[1] and Hans-Joachim Werner

Institut für Theoretische Chemie,
Universität Stuttgart,
Pfaffenwaldring 55, D-70569 Stuttgart, Germany

The Equation-of-Motion coupled cluster method restricted to single and double excitations (EOM-CCSD) and singlet excited states is formulated in a basis of nonorthogonal local orbitals. In the calculation of excited states only excitations from localized molecular orbitals into subspaces (domains) of the local basis are allowed, which strongly reduces the number of EOM-CCSD amplitudes to be optimized. Unlike in the local theories for the ground state, the domains cannot be simply restricted to the atomic orbitals that are spacially close to the localized occupied orbitals. The appropriate choice of orbital domains becomes thus the main problem in the local treatment of electron excitations. The most promising method of the proper selection of domains is based on an analysis of a wave function computed by some more approximate (and cheaper) theory, like e.g. configuration-interaction singles (CIS). Test calculations for the local EOM-CCSD approach were performed on the basis of a preliminary implementation within the conventional EOM-CCSD code. The excitation energies computed by the local method reproduce the conventional EOM-CCSD excitation energies with an accuracy of 0.1-0.2 eV for several low-lying excited singlet states.

[1]Permanent address: Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland