

Exploring amplitude functions in the coupled-cluster framework – an alternative approach to convergence improvement

Zsuzsanna É. Mihálka¹, Jozef Noga¹

¹ Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, Ilkovičova 6, SK-84125 Bratislava, Slovakia

C16

The single reference (SR) coupled-cluster (CC) formalism is a well established method in electronic structure theory and its variants are routinely applied to the correlation problem. The corresponding nonlinear equations are usually solved in an iterative fashion. However, in certain cases (e.g., bond dissociation), the conventional iterative process which starts from the first order Møller–Plesset (MP) amplitudes converges slowly or not at all. Several remedies — extrapolation techniques, a different iteration route – have been proposed, one of the best known examples is the direct inversion in the iterative subspace (DIIS) [1, 2] method.

We present an alternative approach, which is a result of a broader investigation: if the perturbational parameter λ formally appearing in many-body perturbation theory (MBPT) and relatedly, the CC framework, is included explicitly in the Hamiltonian and the CC formalism, all quantities involved (correlation energy, amplitudes) become functions of λ . Employing the MP partitioning, properties of the resulting λ -dependent amplitude functions are discussed.

Based on known values of the CC amplitudes $\mathbf{T}(\lambda)$ at different $|\lambda| < 1$ points (which are easier to obtain), we take advantage of the discussed properties of $\mathbf{T}(\lambda)$ to estimate the CC amplitudes without solving the relevant equations at $\lambda = 1$ (corresponding to the original, physical problem), an idea which has been tested successfully in the context of MBPT [3]. While we explore this idea only in the SR case, it can also be generalized to other CC schemes designed to treat systems where strong correlation plays an important role.

We limit ourselves to CC truncated at the level of singles and doubles (CCSD), and investigate the adequacy of the approximate amplitudes provided by this procedure. Aiming at improving the convergence pattern of the solution process, this set of amplitudes can also be used as the starting point for the CCSD iterations, and combined with DIIS it can resolve the divergence issues of the conventional sequence [4].

The project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under the funding scheme No. 945478 - SASPRO2.

[1] P. Pulay, Chem. Phys. Lett., **73** (1980), 393–398.

[2] G. E. Scuseria, T. J. Lee, H. F. Schaefer III, Chem. Phys. Lett., **130** (1986), 236–239.

[3] Z. É. Mihálka, P. R. Surján, Phys. Rev. A, **96** (2017), 062106.

[4] Z. É. Mihálka, J. Noga, Mol. Phys., DOI: 10.1080/00268976.2022.2140084.