A novel framework for deriving triples and quadruples corrections to the CCSD energy

Janus J. Eriksen[†], **Kasper Kristensen**[†], **Thomas Kjærgaard**[†], **Poul Jørgensen**[†], **and Jürgen Gauss**[‡]

[†]*qLEAP Center for Theoretical Chemistry, Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark.*
[‡]*Institut für Physikalische Chemie, Johannes Gutenberg–Universität Mainz, Duesbergweg 10–14, D–55128 Mainz, Germany.*

Using the coupled cluster energy Lagrangian technique, we have performed a perturbation analysis, in which the CCSD state is considered as the unperturbed reference state and the fluctuation potential and the effect of triple and quadruple excitations as perturbations. By counting orders in the fluctuation potential in the expansion away from the CCSD energy point towards the CCSDT or CCSDTQ energies (depending on truncation level), amplitudes and Lagrange multipliers that carry orders are derived and used in conjunction with Wigner's $2n + 1$ and $2n + 2$ rules to determine energy corrections from the energy Lagrangian. The analysis reveals that approximate triples and quadruples may be introduced in a hierarchical fashion at different levels of accuracy; the models resulting form this hierarchy encompass— to lowest order—the models of the CC(m)PT(n) hierarchy. However, the two hierarchies begin to differ at higher orders owing to the different pictures in which they are derived and established, namely EOM–CC and coupled cluster energy Lagrangian theory, respectively. In the present work, we seek to uncover these differences.