General Order Coupled-Cluster in the 4-Component Framework

Lasse Kragh Sørensen[1], **Jeppe Olsen**[2], **Timo Fleig**[3]

[1] *Theoretische Chemie, Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany*

[2] *Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark*

[3] *Laboratoire de Chimie et Physique Quantiques, I.R.S.A.M.C., Université Paul Sabatier, Toulouse, France*

We present the initial implementation of a string-based general-order coupled cluster [1] method which fully accounts for relativistic effects within the four-component framework [2]. The method opens the way for the treatment of multi-reference problems through a state-selective expansion of the model space. Unlike the previously reported version[3], where the evaluation of the coupled cluster vector function is carried out via relativistic configuration interaction expansions, the current version is commutator-driven and therefore has the correct scaling.

We demonstrate some of the capabilities of the new method in calculations of complete potential energy curves of the HBi molecule. The inclusion of spin-orbit interaction and higher excitations than coupled cluster double excitations, either by multi-reference model spaces or the inclusion of full iterative triple and quadruple excitations, leads to highly accurate results for spectral constants of HBi.

Due to the correct scaling, the new code also opens the possibility doing inner-valence/outer-core correlation/polarization which is often be very significant if high accuracy is desired. The importance of these effects on HBi are demonstrated.

Additional truncation schemes of the coupled cluster hierarchy not only based on excitation level n but also on the flipping of the Kramers projection ΔM_k is shown along with additional schemes exploiting the Generalized Active Space (GAS) concept to achieve a more compact representation of the wavefunction.

[1] L. K. Sørensen, J. Olsen and T. Fleig, *In Preparation*

[2] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC08 (2008), written by L. Visscher, H. J. Aa. Jensen, and T. Saue, with new contributions from R. Bast, S. Dubillard, K. G. Dyall, U. Ekström, E. Eliav, T. Fleig, A. S. P. Gomes, T. U. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, P. Sałek, and J. Sikkema (see http://dirac.chem.sdu.dk)

[3] T. Fleig, L. K. Sørensen and J. Olsen, *tca* 118 (2007) 347