Multi-Reference Electron Correlation Methods in the Relativistic 4-Component Regime

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Electronic structure calculations on heavy-element systems require an adequate treatment of special relativity, but in particular highly efficient methods for the description of electron correlation due to the large number of electrons. The frequently occurring near-degeneracy situations in combination with spin-orbit coupling call for multi-reference methods in the ab-initio treatment of dynamical electron correlation. The starting point for such calculations is favorably a relativistic Multi-Configuration (MC) SCF state including spin-orbit coupling.

Recent developments along these lines in the 4-component electronic structure package `DIRAC` [1] include general-order multi-reference Coupled-Cluster [2] and general-order multi-reference configuration interaction (CI). The essential features of the large-scale CI implementation [3] as well as its modular incorporation in a new second-order Kramers-restricted MCSCF program [4,5] are discussed in some detail. These methods are applied to the actinide compound UO_2 [6] where ground and excited states are investigated.

[1] `DIRAC`, a relativistic ab initio electronic structure program Written by H. J. Aa. Jensen, T. Saue, L. Visscher with contributions from V. Bakken, E. Eliav, T. Enevoldsen, T. Fleig, O. Fossgaard, T. Helgaker, J. Laerdahl, C. V. Larsen, P. Norman, J. Olsen, M. Pernpointner, J. K. Pedersen, K. Ruud, P. Salek, J. N. P. van Stralen, J. Thyssen, O. Visser, and T. Winther.

[2] L. K. Sørensen, T. Fleig, J. Olsen, *Chem. Phys. Lett.*, to be published.

[3] T. Fleig, J. Olsen, L. Visscher, *J. Chem. Phys.*, 119:2963, 2003.

[4] H.J.Aa. Jensen, K.G. Dyall, T. Saue, K. Fægri, *J. Chem. Phys.*, 104:4083, 1996.

[5] J. Thyssen, H.J.Aa. Jensen, T. Fleig, *J. Chem. Phys.*, to be published.

[6] T. Fleig, H.J.Aa. Jensen, J. Olsen, L. Visscher *J. Chem. Phys.*, to be submitted.