Relativistic coupled clusters externally corrected by four-component DMRG

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There are three essential problems in computational relativistic chemistry: electrons moving at relativistic speeds, degenerate energy levels and dynamical correlation. Currently available quantum-chemical methods are capable of solving systems with one or two of these issues. However, there is a significant class of molecules, in which all the three effects are present. These are the heavier transition metal compounds, lanthanides and actinides with open d or f shells. For such systems, sufficiently precise numerical methods are not available. In this project, we propose to combine two numerical methods in order to address this challenging class of molecules. These are the relativistic versions of coupled clusters method and density matrix renormalization group (DMRG) method. According to our best knowledge, this is the first relativistic implementation of the coupled cluster method externally corrected by DMRG.

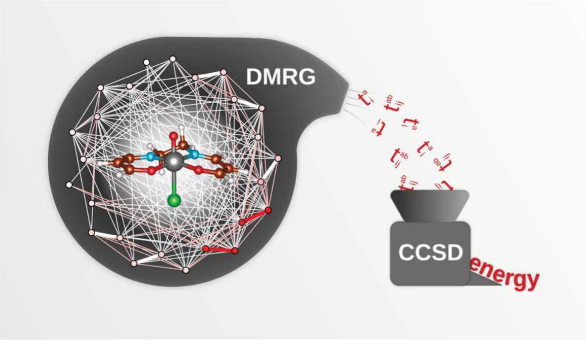

Figure 1: Graphical scheme of coupled clusters externally corrected by DMRG [2].

In the externally corrected approach, first a DMRG calculation is done on the most important part of the active space, keeping the rest of the system fixed. This accounts for the static correlation. Then a CC calculation is performed on the rest of the system, keeping in turn the DMRG part fixed. This captures the dynamical correlation. In other words, the DMRG calculation accounts for the multireference nature of the system, and the following CC calculation includes the effects of dynamical correlation. Already the simplest version thereof, the tailored CCSD (CC with single and double excitations) approach [1], yields very promising results [2]. Remarkably, all previous approaches based on the use of DMRG output in another method have so far been non-relativistic, leaving the relativistic domain unexplored - until now

References

1. T. Kinoshita, O. Hino, and R. J. Bartlett, *J. Chem. Phys.* **123** (2005), 074106.
2. L. Veis, A. Antalik, J. Brabec, F. Neese, O. Legeza, and J. Pittner, *J. Phys. Chem. Lett.* **7** (2016), 4072.