

SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CM1405

STSM title: Efficient Simulation of Core Spectroscopies with Relativistic Electronic Structure Methods

STSM start and end date: 01/02/2019 to 28/02/2019

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PURPOSE OF THE STSM:

The overall purpose of the short scientific mission (STSM) was to implement the Core-Valence separation (CVS) within the Equation-Of-Motion (EOM) Coupled-Cluster (CC) method based on the 4-component Hamiltonian in the Dirac relativistic electronic structure package.

This would allow to accurately simulate X-ray phenomena, such as X-ray absorption spectroscopy (XAS) and X-ray photo-electron spectroscopy (XPS) across the entire periodic table. In particular, it would enable the study of K- and L-edges of both light ($Z=1$ to ~ 30) and heavy ($Z>30$) elements (and the M-edges for the latter), since an accurate description of relativistic effects is absolutely essential to properly describe the properties of the innermost electrons of atoms and molecules

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The core of this project involved both theoretical and code developments. Hence, a good understanding of both the theory and the computational environment was required before proceeding to the implementation and application stages. Week 1 was thus devoted to the understanding of the theoretical background: first, the study of relativistic quantum chemistry; the implications that relativity has on chemical systems and the methods (4- and 2-component etc.) used to treat it. Second, the study of the Equation-Of-Motion (EOM) Coupled-Cluster (CC) theory, in particular the diagrammatic derivation of the EOM-CC equations and the particular features of the formulation of EOM-CC for relativistic Hamiltonians.

On the computational side, the first step was to get acquainted with the DIRAC code. Therefore, during the first week, time was spent on the practical aspects of how to run calculations with it. In week 2, the focus was on gaining deeper knowledge on how the code is organized, with a particular focus on understanding the organization of its coupled-cluster module. This was indeed essential to identify which sections were to be modified, not only with respect to how to add the new functionality, but also for it to be efficient, avoiding redundant code. Once the theoretical basis was set, the EOM—CCSD equations were re-derived introducing the CVS approximation. Different levels of the CVS approximation have been proposed, based on what terms are retained or dropped in the equations.

In order to get further insight of the problem, in week 2 a study of the computational complexity of the model was carried out, through an operation count study. In this study, the cost of the standard (hereafter referred to as “full-space”) EOM-CCSD model was compared against the different levels of approximation proposed in the analytical (referred to as “compressed”) CVS scheme we are developing (enforcing core-valence separation, coupling it to the use of a frozen-core treatment in solving the CCSD equations, eliminating contributions from determinants made up configurations). In week 2 we have also started mapping out the modifications to the code which would be required to implement the “compressed” approach. This continued through weeks 3 and

4, since these involve significant modifications to the code, that require careful consideration.

Before proceeding to the implementation of the “compressed” CVS method, in week 3 we extended the projection-based CVS approximation recently implemented DIRAC, to allow for a frozen-core treatment of the CCSD equations for the ground state and of eliminating of doubly excited/ionized determinants). As this CVS scheme is based on projecting out undesired elements of the Hamiltonian matrix in the “full-space” method, it will be inefficient for large-scale applications. However, apart from providing a first programming assignment, it has the advantages of (a) allowing us to perform exploratory studies on relatively small but nevertheless interesting systems; (b) it provides us with a reference implementation with which to verify the implementation of the “compressed” approach.

In week 4, we started to test the projection-based implementation and to carry out pilot calculations with it, in view of preparing a manuscript for publication. We have also started formalizing the strategies to be taken in the implementation of the “compressed” approach.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

Our first main result is the computational complexity analysis, which underscores the importance of carrying out the implementation of the “compressed” approach. From this analysis, we have also investigated the conditions for which the “compressed approach would be most favourable.

As an example, we have considered the case of the M-edge absorption and ionization for the $\text{UO}_2\text{Cl}_4^{2-}$ system, a component of the $\text{Cs}_2\text{UO}_2\text{Cl}_4$ system for which there are accurate experimental results for the K, L and M edges of the uranium atom. For this system, which contains 248 electrons, we have determined that the commonly used CVS approach of demarcating the core/valence separation with a single threshold, and including in the core the electrons of the K, L and M edges (about 48), we can expect the cost of the calculations to be reduced to about half of that of one using projection techniques. Furthermore, if instead of a single threshold we define an interval containing only the M edge, we may expect a roughly tenfold cost reduction with respect to projection. It should be noted that these reductions are mostly due to lowering the amount of memory required in the calculations, a factor which is often the bottleneck in quantum chemical calculations.

A second main result is the extension of the projection-based CVS implementation. The functionality for enforcing the frozen-core treatment of the CCSD equations for the ground state was not previously available in Dirac. As mentioned above, this implementation will serve as benchmark for the implementation of “compressed” approach, and is currently being used to carry out XPS and XAS energy calculation. To the best of our knowledge, this is the first time such calculations are carried out with 4-component based Hamiltonians, and exploiting molecular double point group symmetry, and we expect to have a manuscript ready for publication in the near future.

A third result is the validation of the projection-based implementation. Apart from comparing 4-component results of the projection and “full-space” calculations for model systems (and verifying discrepancies of no more than 0.1 eV), we have successfully verified the implementation, running with a non-relativistic Hamiltonian, against those in the DALTON and Q-CHEM codes.

FUTURE COLLABORATIONS (if applicable)

In the following weeks, we will continue our collaboration, and proceed with the implementation of the “compressed” approach and its description in the form of a manuscript for publication, as well as its release in a forthcoming public release of the DIRAC code. Once implemented and tested properly, the focus will be put on the application side, of which a prospective candidate is the simulation of the L- and M-edges X-ray absorption spectra of molecules containing heavy elements such as $\text{UO}_2\text{Cl}_4^{2-}$ system. Other candidates are species containing second-row atoms such as sulfur, and species containing transition metals.