

Simplified Coupled Cluster Methods for f0 Actinide Compounds

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Heavy-element-containing compounds are immensely difficult to model theoretically because both correlation effects and relativistic effects have to be described on equal footing, which poses a challenge for present-day quantum chemistry, especially when the molecule under study contains more than one heavy element. As scalar relativistic effects are nowadays relatively straightforward to treat and there are sufficiently accurate approaches to treat spin-orbit interactions perturbatively, the remaining difficulty in computational heavy element chemistry is the large number of degenerate or quasi-degenerate orbitals, which requires a multi-reference treatment. However, present-day quantum chemistry lacks simple, robust, efficient, and cheap algorithms for a qualitatively correct description of strongly-correlated electrons encountered, for instance, during bond-breaking processes as well as in transition metal and actinide chemistry.

We present a conceptually different approach that is well suited for strongly-correlated electrons, but does not use the orbital model. Our method exploits the feature that electron correlation effects can be built into the many-electron wavefunction using two-electron functions, also called geminals. One of the simplest, practical geminal approaches is the Antisymmetric Product of 1-reference-orbital Geminals (AP1roG) [1-3], which is equivalent to the pair-Coupled-Cluster Doubles model [4].

In this work, we discuss the performance of AP1roG-based methods [3,5] in modeling electronic structures for molecules containing heavy elements, including actinides [1-3,5]. We will present different excited state models [6-8] that allow us to target singly- and doubly-excited states with electron-pair theories. Our study indicates that geminal-based approaches provide a cheap, robust, and accurate alternative for the description of electron correlation effects in both ground and excited states.

References

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