

5f-in-Core Pseudopotentials and Applications to Electronic Structure of [Pu₃₈] Cluster

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Abstract: Computational modeling of actinide complexes are challenging because of the 5fⁿ open shell. Theoretical calculations of actinide clusters with multiple actinide atoms are expensive and often difficult to converge in self-consistent iterations. To solve this issue, relativistic pseudopotentials (PPs) and basis sets provide an possible solution for theoretical modeling of heavy actinide elements. The norm-conserving Goedecker–Teter–Hutter (GTH) pseudopotentials offer distinct advantages for investigations of actinide molecular and condensed-phase systems, due to their excellent transferability and reliable accuracy. Recently, we have developed a set of benchmarked scalar-relativistic GTH-type 5f-in-core pseudopotentials and corresponding Gaussian basis sets, for the widely studied trivalent and tetravalent actinide ions [An(III), An(IV); An = Pa–Lr].^[1] The 5f-in-core formalism adopted in these GTH PPs effectively mitigates the computational challenges associated with the open 5f valence shell in actinide elements. In this work, the structural optimization, analyses of electronic structure, chemical bonding, cluster stability and formation mechanism of [Pu^{IV}₃₈O₅₆Cl₅₄]¹⁴⁻ cluster (Figure 1) were performed by using our 5f-in-core PPs and basis sets in the CP2K package. This new PPs can enable large-scale quantum-chemical computations and *ab initio* molecular dynamics simulations of actinide systems in gas phase, solutions, molten salts, bulk solids and surfaces.

5f-in-core PPs for the Structural Optimization of [Pu(IV)₃₈O₅₆Cl₅₄]¹⁴⁻ Cluster

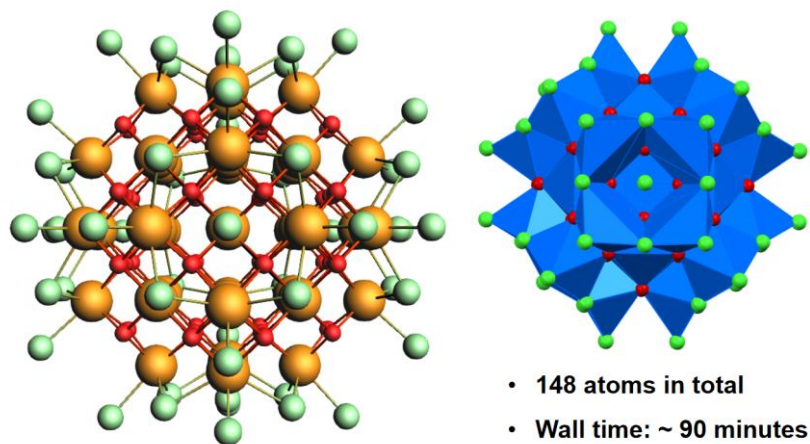


Figure 1. The structure of [Pu^{IV}₃₈O₅₆Cl₅₄]¹⁴⁻ cluster optimized by using the 5f-in-core PPs.

Keywords: 5f-in-core, pseudopotential, actinide, electronic structure, Pu₃₈ cluster

References:

[1] J.-B. Lu, Y.-Y. Zhang, J.-B. Liu, J. Li, *J. Chem. Theory Comput.* **2025**, 21, 170-182.