

# Quantum chemical investigations of f-element systems with relativistic ab initio pseudopotentials

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Some fundamental problems for the accurate treatment of lanthanide (Ln) and actinide (An) systems by quantum chemical first-principles and ab initio methods [1] will be briefly reviewed. The energy-consistent pseudopotential approach [2] as a simple tool to incorporate the major relativistic contributions in quantum chemical calculations will be introduced and selected examples for its application to Ln and An systems will be given. The separation of Ln(III) and An(III) ions by liquid-liquid extraction using macrocyclic extractants is a key step in the work-up of used nuclear fuels. A theoretical modelling yielding results in agreement with experimental evidence [3,4] requires not only a careful study of the various extraction complexes, but also an accurate treatment of the hydration of the bare ions [5,6]. The explicit treatment of the open Eu 4f-shell within density functional theory was found to lead to too long Eu-S bond distances in the extraction complexes with Cyanex301 and to false conclusions regarding the covalency of Eu-S and Am-S bonds as an underlying reason for the Cyanex301 preference of An(III) over Ln(III) [7]. Coupled-cluster calculations based on a fully automated implementation of the so-called incremental scheme allow to obtain hydration Gibbs energies for Ln(III) ions in excellent agreement with experimental evidence [8], and probably the most accurate predictions for An(III) ions [9].

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