Ab initio pseudopotential studies of lanthanide and actinide systems
Xiaoyan Cao and Michael Dolg, Institut für Physikalische und Theoretische Chemie, Universität Bonn and Institut für Theoretische Chemie, Universität zu Köln, Germany

Introduction

Custodian schemes (CPA) have been used to remove core-valence contributions in density functional theory calculations of lanthanides and other actinides. The resulting core-potentials have been supplemented by corresponding pseudopotentials for lanthanide and actinide ions in order to cover a wide range of radii and valences. The pseudopotentials are used in atomization studies to produce atomization energies for lanthanides and actinides. The calculated atomization energies are in good agreement with experimental values. The electron core potentials are in good agreement with experimental values. The electron core potentials are in good agreement with experimental values.

Method

- Small-core relativistic energy-consistent PP
- Generalized contracted ANO basis sets
- Extrapulation (HFD) to basis set limit using uncontracted basis sets

Results

- Mean absolute errors for standard basis sets (basis set limit): Ln IP, and IP, 0.2 eV, IP, and IP, 0.6 eV (0.3 eV); An IP, 0.2 eV.
- The experimental IP for Gd appears to be too low by almost 1 eV and should be re-measured.
- The ground states for La, and Lu, are most likely \( \Sigma^+_v(\sigma^+_v \pi^+_v) \) and \( \Sigma^+_v(\delta^+_v \pi^+_v) \).