

Relativistic Energy-consistent Ab Initio Pseudopotentials for Heavy Elements. Recent Developments and Selected Applications

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The method of energy-consistent relativistic ab initio pseudopotentials (PPs) is briefly reviewed and recent developments for the PPs as well as corresponding valence basis sets are summarized.

The accuracy of newly derived two-component small-core PPs adjusted to multi-configuration Dirac-Hartree-Fock/Dirac-Coulomb-Breit reference data for main group and transition metals is discussed [1,2] and compared to all-electron calculations at the correlated level. Revised optimized valence basis sets for small-core Wood-Boring adjusted PPs of lanthanides and actinides are presented [3,4] and results of molecular test calculations are reported [5]. The advantages of effective valence spin-orbit operators for small-core PPs are emphasized.

For actinides it is shown in various test calculations on small to medium-sized molecules that for many cases it is possible to reduce the computational effort significantly by including the open 5f-shell to the PP core [6], i.e. to adjust actinide 5f-in-core PPs analogous to lanthanide 4f-in-core PPs [7]. Preliminary results are reported for actinide(III)mono- and polyhydrate complexes, actinide(III)trifluorides and lanthanide(III)/actinide(III) texaphyrin/motexafin complexes [8]. In addition to valence basis sets for molecular applications modified basis sets for crystal orbital calculations on solids are also available [9].

Finally, a new set of Wood-Boring adjusted PPs for main group elements suitable for Quantum Monte Carlo calculations is presented together with valence basis sets of valence double to quintuple zeta quality. Both in atomic calculations as well as in the molecular so-called G2 test the new PPs perform clearly better than PPs designed for Quantum Monte Carlo calculations by other groups [10].

References

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