RELATIVISTIC ENERGY-CONSISTENT PSEUDOPOTENTIALS: NEW DEVELOPMENTS AND BENCHMARK CALCULATIONS

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An overview on the basic ideas underlying the energy-consistent pseudopotential (PP) approach is given first, with special emphasis on relativistic effects and on the new generation of multi-configuration Dirac-Hartree-Fock (MCDHF) adjusted potentials. The development of the latter potentials is illustrated at the examples of group 14 elements (Pb and E114)[a]. The issues of the choice of core-valence separation (small-core/large-core), of the role of the missing core orbitals for diatomic interaction, and of the impact of the nodeless pseudo-orbitals for valence correlation are discussed.

In order to demonstrate the performance of the MCDHF-adjusted potentials, benchmark results are presented for atomic polarizabilities, spectroscopic constants of AuH[b], (E111)H, and of ground and excited states of Tl, Pb, and Bi compounds (hydrides, oxides, halides). The use of spin-free-state shifts from one-component high-level correlation calculations, in a lower-level two-component treatment, is shown to be a reliable means of achieving high accuracy in molecular applications. The combination of small-core scalar-relativistic PPs with large-core spin-orbit (SO) potentials, in this two-step procedure, is suggested as a convenient way for further reducing the computational effort, essentially without loss of accuracy with respect to a full small-core calculation.

Finally, applications of the PPs are presented for determining structure and stability of rare-gas crystals[c], and for investigating the strength of metallophilic attraction in $(ClMPH_3)_2$ (M=Cu,Ag,Au).

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[b] P. Schwerdtfeger, J.R. Brown, J.K. Laerdahl, H. Stoll, J. Chem. Phys. 113 (2000) 7110

[c] K. Rościszewski, B. Paulus, P. Fulde, H. Stoll, Phys. Rev. B 62 (2000) 5482