Relativistic effects in molecules

Relativistic Density Functional Theory: Efficient Methods for Molecules and Materials

Relativity is decisive for atomic configurations, bond lengths, binding energies, and many other properties of heavy-element compounds. Relativistic effects can be understood in terms of the relativity-induced contraction of s and p orbitals, the concomitant increased shielding of the nuclear field, and the resulting expansion of d and f manifolds. In addition to these kinematic effects, spin-orbit interaction as the second important relativistic effect is already noticeable in spectra of light elements. For heavy elements, spin-orbit effects become essential for the valence electronic structure; as they compare in magnitude to the Coulomb interaction of valence electrons.

Relativistic density functional studies performed in our group are based on the Douglas-Kroll-Hess (DKH) approach. The scalar relativistic variant of the DKH method of solving the Dirac-Kohn-Sham problem is an efficient procedure for treating compounds of heavy elements including such complex systems as transition metal clusters, adsorption complexes, and solvated actinide compounds. This method allows routine all electron density functional calculations on heavy-element compounds and provides a reliable alternative to the popular approximate strategy based on relativistic effective core potentials. For many application problems where a spin-orbit interaction is of crucial importance two-component DKH variants are applied.

Our implementations of this methodology, at first in the LCGTO-FF-DF program (linear combination of Gaussian-type orbitals fitting functions density functional),\cite{1,2,3} and later on in the parallel DF software ParaGauss\cite{4,5} had long been the only ones applied to problems beyond methodological tests on small molecules.\cite{6}


