The zero order regular approximation for relativistic effects: formulation and appplication to molecular properties

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The well-known Pauli relativistic correction terms to the non-relativistic hamiltonian (mass-velocity, Darwin and spin-orbit coupling) can be obtained from the Dirac hamiltonian. However, the derivation is only valid in relatively smooth and in particular nonsingular potentials. This excludes the nuclear Coulomb potential, as is evident from the singular behaviour of the Pauli hamiltonian. It is however possible to derive approximate relativistic hamiltonians, that take the special character of the Coulomb potential into account. In zeroth order this regular approximation (ZORA) already yields very accurate relativistic results, notably for the valence electrons. The performance of the ZORA approach in combination with GGA functionals is excellent for bond energies and related spectroscopic properties (frequencies, bond lengths) of heavy element compounds.

Some care has to be exercised in calculations of properties that depend on the quality of the wavefunction close to the nucleus. The ZORA approach is inherently less accurate for (deep) core levels. More importantly, the picture change that has occured in going from the four-component Dirac to the two-component ZORA method has to be taken into account. We will discuss electric field gradients at the nucleus and NMR shielding calculations.