Two–component relativistic methods for the heaviest elements

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A method for the iterative algebraic generation of the numerically accurate two–component hamiltonian for the use in relativistic quantum chemistry is presented. The separation of the electronic and positronic states of the Dirac hamiltonian is accomplished by the algebraic solution for the Foldy–Wouthuysen transformation. This leads to the two–component formalism whose accuracy is primarily limited by the choice of basis functions. Its preformance is tested on the calculations of the spin–orbit coupling effect. These calculations show that the electronic part of the Dirac eigenspectrum can be obtained from the two–component theory to arbitrarily high accuracy. Moreover, if needed, the positronic states can be separately determined in a similar way. Thus, the present method can be also used for the evaluation of quantum electrodynamic corrections in the finite basis set approximation.