Convergence of approximate two–component hamiltonians: How far is the Dirac limit

Dariusz Kędziera*

Department of Quantum Chemistry,

Institute of Chemistry, Nicolaus Copernicus University,

7, Gagarin St., PL–87 100 Toruń, Poland

Abstract

A systematic elimination of the off-diagonal parts of the Dirac Hamiltonian is carried out in the spirit of the Douglas–Kroll [Ann. Phys. **88**, 87 1974] approach and the recently proposed infinite–order two–component method. The present approach leads to a series of approximate two–component Hamiltionians which are exact through a certain order in the external potential. These hamiltonians are used to study the convergence pattern of approximate two–component theories. It is shown that to achieve an acceptably high accuracy for low–lying one–electron levels in heavy and superheavy systems one needs to use approximate Hamiltonians of prohibitively high order in the external potential. One can conclude that the finite–order two–component hamiltonians are of limited usefulness in accurate relativistic calculations for heavy and superheavy systems.

* Electronic mail: teodar@chem.uni.torun.pl