An exact two-component theory based on the Normalized Elimination of the Small Component applied to core ionizations

Rob Klooster, Michael Filatov, Ria Broer

University of Groningen, Zernike Institute of Advanced Materials,
Groningen, The Netherlands

In the quantum-chemical treatment of systems with heavy elements it is important to incorporate relativistic effects via the Dirac equation. For virtually all chemical problems, we are only interested in the positive energy solutions of this equation. It is therefore desirable to transform the four-component Dirac equation to a two-component form, effectively eliminating the negative energy solutions. In a matrix formulation, this can be done by the Normalized Elimination of the Small Component (NESC) algorithm. The small component is eliminated by expressing it in terms of the large component times a transformation matrix. This matrix is energy-dependent and therefore needs to be calculated iteratively. Transformed overlap, kinetic energy and potential energy matrices can then be defined to be used in subsequent many-electron calculations. We have implemented the spin-free (one-component) form of NESC in the *MOLCAS-7* package. We apply NESC to the calculation of X-ray Photoelectron Spectra (XPS) of uranium. These calculations present a challenge, since a good description of core-ionized states requires a high level treatment of correlation effects. In this work we make use of the Restricted Active Space Self-Consistent Field (RASSCF) method. Spin-orbit (SO) effects are included *a posteriori* using Restricted Active Space State Interaction (RASSI).