Modern Exact Two-Component Hamiltonians for Relativistic Quantum Chemistry and Physics: Two-Electron Picture Change Corrections Made Simple

Michal Repisky[1,2]

[1]*Department of Physical and Theoretical Chemistry*
Comenius University in Bratislava, Slovakia
[2]*Hylleraas Centre for Quantum Molecular Sciences*
University of Tromsø – The Arctic University of Norway, Norway

Based on atomic mean-field (amf) SCF quantities, we present two simple, yet computationally efficient and numerically accurate matrix approaches to correct scalar-relativistic and spin-orbit two-electron picture-change corrections (PCs) arising within an exact two-component (X2C) Hamiltonian framework [1]. Both approaches, dubbed amfX2C and eamfX2C, allow us to uniquely tailor PCs to mean-field models, viz. Hartree–Fock or Kohn–Sham DFT, in the latter case also avoiding the need of a point-wise calculation of exchange–correlation PCs. We assess the numerical performance of these Hamiltonians on spinor energies of closed-shell and open-shell molecules, achieving a consistent 10^{-5} Hartree accuracy compared to reference four-component (4c) data. Excellent agreements with reference data are also observed for molecular properties sensitive to relativistic effects such as EPR or X-ray (transient) absorption spectroscopy [2,3]. We believe that our (e)amfX2C Hamiltonians constitute a fundamental milestone towards a universal and reliable relativistic 2c approach for quantum chemistry and physics, maintaining the accuracy of the parent 4c one at a fraction of its computational cost.

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