Picture change effect correction in electron and spin densities and X-ray structure factors, calculated at Douglas-Kroll Hess and Infinite order two component level

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We have currently implemented the 1-component and 2-component Douglas-Kroll-Hess 2nd order (DKH2) and the Infinite Order Two Component (IOTC) Hamiltonians into the GNU licensed package Tonto [1]. The IOTC Hamiltonian has been implemented by following the iterative IOTC approach of Barysz & Sadlej [2]. Moreover the picture change effect (PCE) corrections [3] of electron and spin densities as well as structure factors from X-ray experiment have been made available.

I would like to briefly consider within the lecture some theoretical and computational aspects of the mentioned relativistic Hamiltonians and PCE. Results of PCE in DKH2 and IOTC electron and spin densities will be presented. The radial distribution of orbital densities of Cu, Zn and Rn atoms will be considered as well and the spin-orbit effects in the radial distribution of orbital densities. Extent of PCE in angular dependence of atomic factors f_x (1):

$$f_x = 4\pi \int r^2 \rho(r) \left[\sin(4\pi sr) / 4\pi sr \right] dr \qquad (1)$$

will be discussed, where in equation (1) $s = \sin(\theta)/\lambda$ (Å^{-1}). Preliminary results of analytic PCE correction in the X-ray structure factors (2) of 1-component DKH2 calculations will be given

$$F = \int_{cell} \rho(\mathbf{r}) \exp(2\pi i \mathbf{q}.\mathbf{r}) d\mathbf{r} \,. \qquad (2)$$

where $\mathbf{q}$ in equation (2) is the scattering vector.

[1] Jayatilaka, D. & Grimwood, D. J. (2000). TONTO. A Research Tool for Quantum Chemistry. The University of Western Australia, Nedlands, Western Australia, Australia. see: http://sourceforge.net/projects/tonto-chem

[2] M. Barysz and A. J. Sadlej, *J. Chem. Phys.*, **116**, 2696 (2002).

[3] A. Wolf and M. Reiher, *J. Chem. Phys.*, **124**, 064102 (2006).

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