Relativistic effects on X-ray structure factors

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Modern X-ray sources, either in-lab or at large scale facilities, allow for X-ray structure factor measurements up to ultra-high resolutions (i.e. $\sin\theta/\lambda \geq 1.8 Å^{-1}$). Such scattering experiments allow not only for precise reconstructions of the electron density $\rho(\mathbf{r})$ for the analysis of the valence electron density of atoms in molecules or solids [1] but also for the study of core-contraction and core-polarization phenomena [2]. In previous theoretical work we already investigated core-polarization effects for compounds containing transition metal elements [3]. Future experimental studies of these polarization phenomena in transition metal compounds raise the question whether even relativistic effects may be studied in this way. Especially the scalar relativistic contraction phenomena can be expected to play a crucial role for the description of the inner shell region of the atoms by an Extended Hansen-Coppens (EHC) multipolar model [2,3]. Previous studies considering relativistic effects on X-ray structure factors by Hudák *et al.* employed the Douglas-Kroll-Hess (DKH) Hamiltonian and focused on the X-ray constrained wave function approach [4].

We present here the results of a systematic study on the relativistic effects on X-ray structure factors calculated for the metal organic model systems $M(C_2H_2)$ (M = Ni, Pd, Pt) employing different (quasi-)relativistic Hamiltonians. The model systems were selected to ensure comparability of the results with a previous investigation on relativistic effects on the topology of $\rho(\mathbf{r})$ [5]. We compare the according structure factors calculated from the zeroth-order regular approximation (ZORA) and the DKH Hamiltonian to those obtained by employing a fully relativistic four-component approach (DHF) and non-relativistic Hartree—Fock (HF) calculations [6].

The results of our study indicate, that for data resolutions up to $\sin\theta/\lambda \leq 1.8 Å^{-1}$ (which are still accessible on in-lab diffractometers) relativistic effects on the structure factors amount to approx. 0.8, 1.5 and 3% for M = Ni, Pd and Pt, respectively (the numbers represent crystallographic R_1 values comparing the structure factors of the DHF and HF calculations). Even though these numbers may appear to be small at first glance, the discussion of their experimental significance needs to take into account that the effects of chemical bonding on X-ray structure factors as described by (E)HC-models also amount to only a few percent in this data resolution range.

References:

[1] See, for example *Modern Charge-Density Analysis*, C. Gatti, P. Macchi (Eds.), Springer, **2012**.

[2] A. Fischer *et al. J. Phys. Chem. A* **2011**, *115*, 13061–13071.

[3] K. Batke, G. Eickerling *J. Phys. Chem. A* **2013**, *117*, 11566–11579.

[4] M. Hudák e*t al. Acta Cryst.* **2010**, *A66*, 78–92.

[5] G. Eickerling *et al. J. Chem. Theory Comput.* **2007**, *3*, 2182–2197.

[6] *Relativistic Quantum Chemistry: The Fundamental Theory of Molecular Science*, M. Reiher and A. Wolf, Wiley-VCH, **2009**.