Bond analysis in a relativistic framework: Charge-Displacement analysis via natural spinors for chemical valence

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We have recently introduced a simple yet powerful tool for analyzing quantitatively the coordination bond in the terms of the donation and back-donation constituents of the Dewar-Chatt-Duncanson model. The approach is based on the decomponsition via natural orbitals for the chemical valence of the so called Charge-Displacement function (NOCV-CD) [1]. The method succeded to give a clear cut of the donation and back-donation components, even in correlation with experimental observables [2, 3]. Herein, we extend this methodology to four-component relativistic framework, which includes spin-orbit coupling variationally. The presented formalism is incorporated into the full-parallel version of the relativistic Dirac-Kohn-Sham (DKS) module of the program BERTHA. The accuracy and numerical stability of our new implementation has been studied through the analysis of convergence properties of the basis set employed to expand the DKS spinor solution or that used in density fitting algorithm which speeds-up the evaluation of the DKS matrix. An illustration is given for the carbonyl coordination bond with group 11 metals M–CO (M = Cu, Ag, Au), where relativistic effects, including spin-orbit coupling, play an increasing role.

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