Reliability And Reproducibility of The Determination of Physical Effects From X-Ray Constrained Wavefunction fitting

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X-ray constrained wavefunction (XCW) fitting [1] is one of the major techniques used within the field of quantum crystallography [2]. In XCW fitting, molecular orbital coefficients of a wavefunction are adjusted to match a given set of structure factors. This way, physical effects present in the measured structure factors can be absorbed by the wavefunction and then be chemically analyzed. We will show how we have used this strategy to derive experimentally-constrained electron correlation and polarization effects, with consequences for exchange-correlation potentials of density function theory (DFT).[3]

Despite these successful applications, it has been unclear how reliable and reproducible the results of XCW fitting actually are, given that already, say, 95% of the experimental information are covered by a normal spherical refinement (R-value of 5%), and another few percent by non-spherical approaches such as, e.g., Hirshfeld Atom Refinement. This means that only a very small amount of physical information is left in the data, competing with statistical noise and systematic measurement errors. Therefore, we have embarked onto a XCW fitting study of 14 different measurements of oxalic acid data sets to find the consistent features in the XCW-fitted electron density maps throughout every measurement (Figure).[4] The results are presented here.

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{3} E. Hupf, F. Kleemiss, T. Borrmann, R. Pal, J. M. Krzeszczakowska, M. Woińska, D. Jayatilaka, A. Genoni, S. Grabowsky, J. Chem. Phys. 2023, 158, 124103.
{4} M. L. Davidson, S. Grabowsky, D. Jayatilaka, Acta Cryst. B, 2022, 78, 397–415.

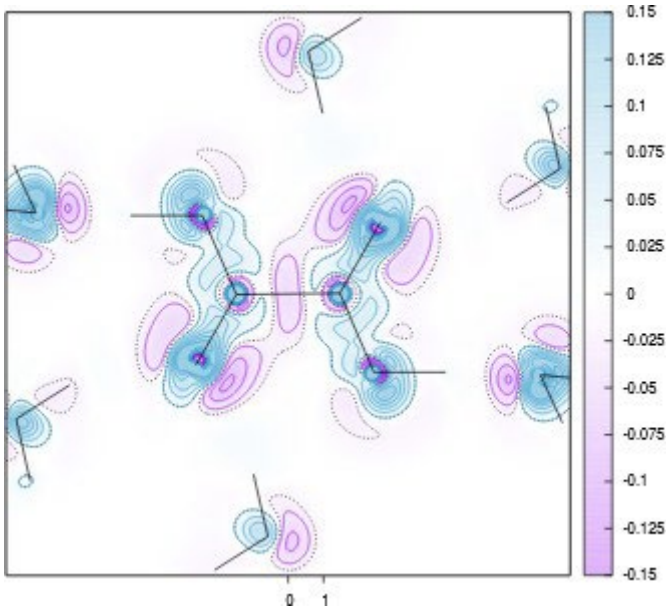

Figure 1