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Development and application of X-ray quantum crystallographic methods

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The term quantum crystallography (QCr) was introduced in the mid 1990's by Massa, Karle and Huang.[1] They defined it as a field "for using crystallographic information with the objective of enhancing quantum-mechanical techniques and the information derived from them". QCr methods have been developed since the 1960s, with Jayatilaka's X-ray constrained wavefunction (XCW) fitting from 1998 being central to the applications discussed here.

The converse definition of QCr, namely the use of quantum-mechanical calculations with the objective of enhancing crystallographic information, was foreshadowed by the same authors, but method development is more recent. Jayatilaka's and Dittrich's method of Hirshfeld Atom Refinement (HAR) from 2008 is described in this presentation.

There are recent debates around the term quantum crystallography and attempts to re-initiate the field by combining both aspects of the definition and different technical implementations of the QCr idea (e.g., electron diffraction, Compton scattering, protein crystallography, solid-state computation, electron-density determination).[2] As an introduction I will summarize the outcome of a recent CECAM discussion meeting about QCr, but will then focus on our research results concerning the advancement and application of X-ray small-molecule quantum crystallographic methods.

i) HAR leads to improved accuracy and precision of crystallographic information (such as bond lengths and angles, atomic displacement parameters (ADPs) etc.). We will show how especially the treatment of hydrogens atoms benefits significantly. [3]
ii) Polarization and electron correlation can be introduced into the wavefunction through the fitting to experimental structure factors. We will show on two high-quality data sets of urea and L-alanine how these two effects can be quantified and separated in the experimental data. An extension of the same strategy might lead to the visualization of relativistic effects from diffraction data. We will show first steps into this direction.
iii) X-ray wavefunction refinement (XWR) is a new iterative procedure that combines HAR and XCW fitting sequentially until convergence in energy and geometry. We will show a first validation of XWR relative to points i) and ii). In other words, to which extent will geometry, ADPs and fitting be improved by an iterative repetition of both techniques?
iv) We will show how XWR results compare to those derived from multipole modeling in terms of the quality of the refined geometry, ADPs and electron density.

[1] Massa, L.; Huang, L. and Karle, J. (1995). Int. J. Quant. Chem.: Quant. Chem. Symposium 1995, 29, 371-384.
[2] Grabowsky, S.; Genoni, A. and Bürgi, H.-B. (2017). Chem. Sci., accepted.
[3] Woinska, M.; Grabowsky, S.; Dominiak, P. M.; Wozniak, K. and Jayatilaka, D. (2016). Sci. Adv., 2, e1600192.

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