Quantum crystallography for accurate structure determination and chemical bonding analysis

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Keywords: quantum crystallography, electron density, Hirshfeld atom refinement

The methods and techniques of experimental electron-density research have a long and successful history, but only recently they have been rejuvenated under the umbrella term quantum crystallography when wavefunction-based refinement techniques emerged as realistic alternatives to more established multipole and maximum-entropy methods [1,2]. In my lecture, I will only focus on such wavefunction-based techniques. They can be categorized as follows:

i) Accurate structure determination methods that utilize quantum-mechanical wavefunctions to improve the results of least-squares refinements, specifically Hirshfeld atom refinement (HAR) [3].

ii) Experimentally fitted wavefunctions for chemical bonding analysis, specifically X-ray constrained wavefunction (XCW) fitting [4].

For HAR, I will outline to which extent we can obtain more information and more accurate information, and at what speed such information can be generated with modern X-ray diffractometers and modern software. I will give an overview over the software available today (such as NoSpherA2, lamaGOET with Tonto, Discamb) and the underlying approximations for treating the crystalline environment (such as ELMO embedding, periodic boundaries). I will exemplify the gain in the obtained information contents for fundamental and ubiquitous compounds such as the YLID test crystal and biomolecular structures (e.g., drugs such as ibuprofen). Finally, I will allude to the remaining challenges and problems, for example related to CIF and raw data standards.

For chemical bonding analysis with XCW fitting, the first question to discuss is the problem of significance and reproducibility as the information left in the structure factors after non-spherical structure refinement is barely above the noise level. Can we obtain physical effects such as electron correlation and polarization by the neighbours in the crystal field experimentally via XCW fitting? In this context, I will allude to unsolved experimental problems such as the treatment of anomalous dispersion, absorption, and radiation damage in small-molecule crystallography. However, I will finally present two studies where we believe that XCW fitted wavefunctions contribute to a better understanding of fundamental chemical questions: hypervalency of period-3 elements and bond-order/bond-length relationships in (conjugated) olefins.

Figure 1. Quantum crystallography combines X-ray diffraction experiments and wavefunction calculations for more accurate structure determination and experimental chemical bonding analysis.


I thank all my former and present co-workers in Perth, Bremen, and Bern for their dedicated and excellent work.