X-Ray Restrained Wavefunction Approach: Latest Achievements and Future Challenges

Dr. Alessandro Genoni[1]
[1]CNRS & University of Lorraine - Laboratory of Theoretical Physics and Chemistry
alessandro.genoni@univ-lorraine.fr

Nowadays, quantum crystallography can be considered as an emerging field of science with the aim of investigating properties and phenomena of the crystalline state that can be explained only through the laws of quantum mechanics [1]. To achieve this goal, several techniques have been proposed over the years [2,3]. Among them it is worth mentioning the multipole models for the determination of experimental electron densities from X-ray diffraction data [4], but also the more modern Hirshfeld atom refinement (HAR) [5] and X- ray restrained wavefunction (XRW) [6] methods, which are two approaches strongly based on the traditional methods of quantum chemistry.

Here the focus will be on the XRW strategy, a technique that has the objective of determining wavefunctions that not only minimize the electronic energy of the investigated system but that also simultaneously maximize the agreement between calculated and experimental X-ray structure factor amplitudes. Initially proposed at Hartree-Fock level [6], the method has recently known a broad and rapid development through the extension of the formalism to other kind of wavefunction ansatz [7-10]. Moreover, different groups have also extensively studied and proved the capabilities of the X-ray restrained wavefunction technique in successfully extracting electron correlation and crystal effects on the electron density [11,12]. These results paved the way towards the possible future exploitation of the XRW method in the framework of density functional theory (DFT).

In the first part of the presentation, a general overview of the X-ray restrained wavefunction approach will be given, with a particular emphasis on the more recent multi-determinant XRW strategies [9,10], which are strictly rooted in valence bond theory and allowed the extraction of chemically meaningful information from X-ray diffraction experiments.

The focus will afterwards shift to the investigations that were conducted to assess to what extent the XRW method can capture electron correlation and crystal effects intrinsically included in theoretically generated or experimental X-ray diffraction data [11,12]. Starting from those results, the first attempts of extracting DFT exchange-correlation potentials through inversion of the X-ray restrained wavefunction equations will be also shown. Moreover, future directions of the ongoing work will be discussed.

References:
{1} P. Macchi, Crystallogr. Rev. 26, 209-268 (2020).
{2} A. Genoni, L. Bučinský, N. Claiser et al., Chem. Eur. J. 24, 10881-10905 (2018).
{3} S. Grabowsky, A. Genoni & H.-B. Bürgi, Chem. Sci. 8, 4159-4176 (2017).
{4} N. K. Hansen & P. Coppens, Acta Cryst. A 34, 909-921 (1978).
{5} S. C. Capelli, H.-B. Bürgi, B. Dittrich, S. Grabowsky & D. Jayatilaka, IUCrJ. 1, 361-379 (2014).
{6} D. Jayatilaka & D. J. Grimwood, Acta Cryst. A. 57, 76-86 (2001).
{7} M. Hudák, D. Jayatilaka, L. Perašínová et al., Acta Cryst. A 66, 78-92 (2010).
{8} A. Genoni, J. Phys. Chem. Lett. 4, 1093-1099 (2013).
{9} A. Genoni, Acta Cryst. A 73, 312-316 (2017).
{10} A. Genoni, D. Franchini, S. Pieraccini & M. Sironi, Chem. Eur. J. 24, 15507-15511 (2018).
{11} A. Genoni, L. H. R. Dos Santos, B. Meyer & P. Macchi, IUCrJ 4, 136-146 (2017).
{12} E. Hupf, F. Kleemiss, T. Borrmann et al., J. Chem. Phys. DOI:10.103/5.1038312 (2023).