MS36 Software development in quantum mechanics-based methods of crystallography

MS36-01
The multipolar model: still alive!
P.M. Macchi [1]
[1]*Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering - Milano (Italy)*

Abstract
In the recent years, the way of modelling accurate X-ray diffraction data has abruptly changed, because of the emerging technique of wavefunction fitting [1]. While this method opens the way to more information because the wavefunction enables calculation of one and two-electron properties, the traditional multipolar model [2,3] has still an important appeal for many reasons. First, the model is not restrained to a theoretical ansatz and to a fixed electronic state. Second, the transferability of multipoles is much easier, and it allows full confrontation with standard models based on the independent atom approximation. In this respect, the estimation of the errors adheres with the same statistical interpretation of routine crystal structure models. Moreover, many robust and well tested approximations enable prediction of two-electron properties as well, for example the energy densities [4]. The multipolar model finds also an easy interplay with polarized neutron diffraction data for the refinement of charge and spin density distribution [5]. The calculation of electrostatic properties and interaction energies has now reached a very high and sophisticated level of precision [6]. Finally, yet importantly, the multipolar approximation enables a rapid calculation, that seamlessly fit with the extremely rapid data collections that are nowadays possible also at laboratory scale.
The recent developments and improvement will be illustrated and discussed, within the framework of the XD program package [7].

References
[1] Jayatilaka, D. (1998) Phys. Rev. Lett., 80, 798–801.
[2] Stewart R.F. (1976) Acta Cryst., A32, 565–574.
[3] Hansen, N.K. & Coppens, P. (1978) Acta Cryst., A34, 909-921.
[4] Tsirelson, V. & Stasch, A. (2021) Acta Cryst., B76, 769-778.
[5] Deutsch, M., Gillon, B., Claiser, N., Gillet, J. M., Lecomte, C. & Souhassou, M. (2014). IUCrJ, 1, 194–199.
[6] Weatherly, J., Macchi, P. & Volkov, A. Acta Cryst. (2021). A77, 399-419
[7] Volkov, A., Macchi, P., Farrugia, L. J., Gatti, C., Mallinson, P., Richter, T. & Koritsanszky, T. (2016) XD2016 - A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors