

Combining X/Neutrons to get a spin-resolved electron density

A.-B. Voufack², M. Deutsch^{1,2}, N. Claiser², B. Gillon³, J.-M. Gillet⁴, C. Lecomte², D. Luneau⁵ and M. Souhassou¹

1 Synchrotron SOLEIL, Saint Aubin, France

2 CRM², UMR 7036, Université de Lorraine, Vandoeuvre-les-Nancy, France

3 LLB, UMR 12, CEA Saclay, Gif-sur-Yvette, France

4 SPMS, UMR 8580, Ecole Centrale des Arts et Manufactures, Chatenay-Malabry, France

5 LMI, UMR 5615, Université Lyon-1 Villeurbanne, France

Since the first works of Stewart on modelling charge density [1], huge improvements of X-ray sources, detectors and software has significantly increased the resolution and the qualities of diffraction data allowing an accurate determination of the charge density of a growing number of molecules. However, despite the technological improvement, no dramatic change of the experimental model was reached since the multipolar model of Hansen & Coppens in 1978 [2]. At the same time polarised neutron diffraction (PND) experiments were developed [3] to get access to the spin density at the molecular scale and the multipolar Hansen & Coppens model was adapted to model this quantity.

As these two quantities (charge and spin densities) are described by a similar multipolar atom centred model with a common parameterization, a combined treatment of X-ray diffraction (XRD) and PND data, is not only possible but also useful as stated by Becker & Coppens in 1985[4].

An extended Hansen & Coppens model and the corresponding refinement program (Mollynx) were developed [5, 6] in order to allow the joint refinement of data sets coming from three different experiments (X-ray, unpolarised and polarised neutron diffractions). By combining different data sets, the new model gives access to spin resolved electron density ($\rho\uparrow$ and $\rho\downarrow$ separately). These two quantities ($\rho\uparrow$ and $\rho\downarrow$) can be observed experimentally for the first time, and this observation allows a further comparison with theoretical models.

In a first part the presentation will focus on the description of the common model and the refinement procedure. The second part will describe its application to two types of component. The case of an end-to-end azido double-bridged copper(II) complex [7] will be presented and experimental results will be compared to the theoretical densities. First application of the spin-split multipolar model on a pure organic radical, 2-(4-thiomethyl)phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, commonly known as Nit(SMe)Ph [8,9] will be presented and subsequent results will also be discussed.

Acknowledgments

This work has been supported by l'Agence Nationale de la Recherche (CEDA and MTMED project); M.D. thanks CNRS for PhD fellowship.

[1] R. Stewart, E. Davidson and W. Simpson, *The Journal of Chemical Physics*, 42, no. 9, pp. 3175-3187, 1965.

[2] N. K. Hansen and P. Coppens, *Acta Cryst. A*, 34, pp. 909-921, 1978.

[3] P. J. Brown, J. B. Forsyth and R. Mason, *Phil. Trans. R. Soc. Lond. B*, 290, pp. 481-495, 1980.

[4] P. Becker and P. Coppens, *Acta Cryst. A*, 41, pp. 177-182, 1985.

[5] M. Deutsch, *et al* *Acta Cryst. A*, 68, pp. 675-686, 2012.

[6] M. Deutsch, N. Claiser, M. Souhassou and B. Gillon *Physics Procedia* 42, 10-17, 2013

[7] M. Deutsch, B. Gillon, N. Claiser, J.-M. Gillet, C. Lecomte & M. Souhassou (2014) *IUCrJ* 1, 194-199

[8] S. Pillet, M. Souhassou, Y. Pontillon, A. Caneschi, D. Gatteschi and C. Lecomte (2001), *New J. Chem.* 25, 141-143.

[9] Y. Pontillon, *et al*, (1999). *Chem. Eur. J.* 5, No 12, 3616-3624.