

[2] are favorite tools of crystal engineering, since the orientation of molecules in the solid state can be predicted with a reasonable degree of accuracy. Two such interactions stand out: hydrogen bonding and halogen bonding. The marked directionality of the hydrogen bond (HB) is well established and is the basis for efficient and reliable topologies of intermolecular motifs. The strength of the hydrogen bond can be estimated from high resolution X-ray diffraction as proposed by our group [3], [4] and this method based on the topological analysis of the electron density  $\rho$  at the HB critical point is now widely used.

On the other hand, the *halogen bonding* interaction has been much less investigated. It occurs in the systems C–Hal...X (X = L, Hal) where an organic halogen atom approaches either a Lewis base (L) or a halogen atom (Hal). Halogen bonding can be as effective as hydrogen bonding for driving highly specific crystal packing motifs, as synthons. It finds its origin in the anisotropy of  $\rho$  around the halogen nucleus, leading to a smaller effective atomic radius along the extended C–Hal bond axis than in the direction perpendicular to this axis, a feature called polar flattening.

In a recent experimental charge density analysis of hexachlorobenzene (C<sub>6</sub>Cl<sub>6</sub>) [5] we have confirmed the anisotropy of the electron distribution around the chlorine nuclei, leading to the formation of electrophilic and nucleophilic sites in the valence-shell charge concentration of chlorines. In the crystal structure of C<sub>6</sub>Cl<sub>6</sub>, main halogen...halogen interactions are thus electrophilic-nucleophilic in nature, being established between oppositely polarized regions in front of each other within a Cl<sub>3</sub>-synthon. The Atoms in Molecules theory [6] has been applied to crystalline C<sub>6</sub>Cl<sub>6</sub>, demonstrating those features and indicating that the electron density properties at Hal...Hal bond critical points correlate with the strength of the observed interactions.

[1] G.R. Desiraju, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311. [2] G.R. Desiraju, in *Crystal Engineering: The Design of Organic Solids*, Elsevier, **1989**. [3] E. Espinosa, E. Molins, C. Lecomte, *Chem. Phys. Lett.* **1998**, *285*, 170. [4] E. Espinosa, E. Molins, *J. Chem. Phys.* **2000**, *113*, 5686. [5] T.T.T. Bui, S. Dahaoui, C. Lecomte, G.R. Desiraju, E. Espinosa, *Angew. Chem. Int. Ed.* **2009**, *48*, 3838. [6] R.F.W. Bader, *Atoms in Molecules- a Quantum Theory*, Clarendon Press: Oxford; **1990**.

**Keywords:** electron density, halogen bonding, topological analysis

## MS.41.3

*Acta Cryst.* (2011) **A67**, C100

**Joint densities and density matrices refinements: First attempts and first results**

P. Becker<sup>a</sup>, J-M Gillea, M. Deutsh,<sup>b</sup> N. Claiser,<sup>b</sup> M. Souhassou,<sup>b</sup> B. Gillon,<sup>c</sup> Y. Ciunacov,<sup>c</sup> S. Pillet,<sup>b</sup> C. Lecomte,<sup>b</sup> P. Cortona,<sup>a</sup> D. Luneau,<sup>d</sup> A. Bortha<sup>d</sup> <sup>a</sup>SPMS, UMR8580, Ecole Centrale Paris, Châtenay Malabry 92285 (France). <sup>b</sup>CRM (UMR UHP-CNRS 7036) Faculté des Sciences et Technologies, Nancy Université, 54506 Vandoeuvre-lès-Nancy CEDEX, (France). <sup>c</sup>Laboratoire Léon Brillouin CEA Saclay, bât.56391191 Gif-sur-Yvette Cedex (France). <sup>d</sup>LMI-UMR 5615 CNRS/UCBL, Domaine Scientifique de la Doua, Université Claude Bernard Lyon 1, 69622 Villeurbanne cedex (France).

Although analysis of joint experimental data as diverse as x-rays structure factors, polarized neutron flipping ratios, neutron structure factors, CBED measurements, x-ray Compton magnetic (and non magnetic) profiles, among others, is theoretically feasible and desirable, to this day only few attempts have been made

We will remind some of the important strategies that have been elaborated in the past and we will propose a new possible way of combining and exploiting the richness of the diversity of experimental methods.

We will show that as long as the data are issued from elastic coherent

scattering experiments only marginal changes have to be made to the usual pseudo-atoms model. This will be illustrated with recent results obtained on magnetic compounds.

We will finally address a critical discussion concerning the difficulties occurring in combining real and momentum space data.

**Keywords:** density matrices refinement

## MS.41.4

*Acta Cryst.* (2011) **A67**, C100-C101

**Quantitative information on polarization of ED from multipolar model – possible?**

J. M. Bak, P. M. Dominiak *Department of Chemistry, University of Warsaw, (Poland)*. E-mail: jbak@chem.uw.edu.pl

We performed systematic analysis of electrostatic properties of a molecule estimated from Hansen-Coppens multipolar model [1] of crystal density. We verified an accuracy of electrostatic properties estimated from the multipolar model, and whether it is enough to study changes of electrostatic properties caused by crystal field effect.

For the purpose of the study, perturbation of electron density of individual molecule was induced by cluster of atom charges, dipoles and quadrupoles surrounding molecule, as to simulate influence of crystal environment. Perturbed and unperturbed wave functions were calculated on the bases of the same crystal geometries of a few amino acids and dipeptides. In following step, electrostatic properties were derived directly from either perturbed or unperturbed wave functions. Moreover, multipolar models were fitted to the subsequent theoretical perturbed and unperturbed electron densities.

Comparison of the electrostatic properties obtained either directly from the perturbed theoretical densities, or from SAPT(DFT) [2] calculations, with the results derived directly from wavefunctions of isolated molecules, gave us possibility to study influence of crystal field on electrostatic properties. We characterized trends in changes of electrostatic properties due to polarization of electron density induced by crystal field.

Additional analysis of the electrostatic properties obtained from corresponding multipolar models fitted to the theoretical electron densities enabled us to check whether systematic information about the trends could be derived from multipolar models. Multipolar models fitted to the theoretical electron densities of a crystals, obtained in periodic calculations, were also studied.

The study revealed that electrostatic properties obtained from the multipolar models fitted to the electron densities are significantly different than ones obtained directly from the densities. Electrostatic properties of isolated molecule are reproduced better by multipolar models than electrostatic properties of molecules in crystal. Perturbation of electron density due to crystal field is hardly described by the multipolar models. The main difference in description of valence electron density between purely theoretical models and Hansen-Coppens multipolar models of the same theoretical densities occurred in the very positions of nuclei, where density is not exactly defined in multipolar refinement due to Fourier truncation error.

It seems that electrostatic properties obtained from multipolar models fitted either to theoretical, or experimental electron density of a crystal, have similar accuracy to those estimated with the use of the aspherical pseudoatom databases [3]. Nevertheless, qualitative analyses only could be performed with the electrostatic properties obtained with the use of both method.

[1] N.K. Hansen, P. Coppens, *Acta Cryst.* **1978**, *A34*, 909-921, [2] Heßelmann, Jansen, Schütz, *J. Chem. Phys.* **2005**, *122*, DOI: 10.1063/1.1824898, [3] J.M. Bak, S. Domagała, C. Hübschle, C. Jelsch, B. Dittrich, P. M. Dominiak *Acta Cryst.* **2011**, *A67*, 141-153.