s2.m2.o1 Making use of experimental charge densities. M. A. Spackman, *Chemistry, University of New England, Armidale NSW 2351, Australia.*

Keywords: charge spin densities.

What constitutes a state-of-the-art experimental charge density study these days? A thorough response would probably address in some detail the following points:

a set of well-framed objectives;
great care with sample selection and preparation;
extended data collection times or, increasingly, use of CCDs and/or synchrotrons;
sample temperature below 120 K, often nearer 10 K;
careful data reduction and correction for systematic effects;
detailed attention to modelling of atomic thermal and vibrational motion;
multipole refinement and mapping of the electron density and derived properties;
computation of properties derived from r;
comparison with theoretical results;
discussion of results in context of the objectives.

Enumeration of the derived properties would most likely include the electron density r and the deformation density Dr, topological properties of r, the electrostatic potential f, the electric field and field gradient, electric moments of molecules in the crystal, atomic charges, and intermolecular interaction energies.

But it seems increasingly pertinent to ask questions such as:

Why perform an experimental charge density study?
What information can obtained from such a study that could not be obtained, perhaps more reliably and economically, from theory?
Which experimental technique, or combination of techniques, will be most appropriate to the proposed study?
What chemical systems are the most appropriate subjects for future charge density experiments?
What is the best forum for publication of the results - and what should be published?

This presentation will seek to extract meaningful answers to some of these questions from a discussion including results from a selection of very recent experimental charge density studies. These studies, which have been performed on a variety of organic and inorganic systems, and using a number of experimental techniques, highlight the diversity of current applications of experimental charge density methods, and provide some useful pointers for future studies.

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s2.m2.o2 Exploiting the theoretical electron and spin densities C. Gatti *Centro CNR-CSRSRC, via Golgi 19, 20133 Milano (Italy).*

Keywords: ab-initio periodic calculations, electron and spin density, topology.

In later years we have developed a software code, TOPOND,[1] that has enabled the Quantum Theory of Atoms in Molecules (QTAM) to be applied to the wave-functions of periodic systems also. Very recently TOPOND has been interfaced to the XD and EMBED program packages, thus extending its use to multipole refined experimental densities and to electron densities of local defects hosted in a periodic matrix. A QTAM analysis of theoretical wave-functions or densities yields information that is not often available, either in principle or in practice, from the analysis of the corresponding experimental densities. We will discuss three cases where this is particularly evident.

The first example concerns an experimental and theoretical study on the nature of the CH..O interactions in the 3,4-bis(dimethylamino)-3-cyclobutene-1,2-dione (DMACB) crystals. Thanks to the use of theoretical densities, the Koch and Popelier criteria to establish H-bond could, for the first time, be applied in their entirety to a large set of CH..O contacts in a crystalline phase. We also demonstrate that the almost isotropic CH..O angular distribution observed for H…O separations greater than 2.7 Å is only apparent as it clearly disappears when the bonded and non-bonded contacts are identified and their angular distributions separately analyzed.

A second case relates to the exploitation of the energy variational principle to find an optimum description of the odd electrons associated to the sparse F-centers in the alkali halide crystals or to the periodically-ordered F-centers in the sodium electrosodalite system. In both cases the energetically favored solution describes the F-center as a local maximum in the electron density ρ, thus representing a physical manifestation of a non-nuclear attractor in ρ. The extent of localization of the odd electron has been characterized in terms of an ELF analysis of the α- and β-spin densities.

A third example is the study of the geometrical reconstructions and electronic relaxations in a number of Si clean and H-covered surfaces. Although surface X-ray diffraction (SXRD) is becoming one of the best trusted methods in determining the structure of surfaces, their detailed experimental charge density is presently out of reach. Using a slab model and TOPOND code, we have provided answers to questions related to the atomic nature of a surface. These include: what are the charges on the surface atoms in the clean and in the chemisorbed surface? How is the bonding of the surface atoms affected? How rapidly do the surface perturbations and the changes in these perturbations that result from the adsorption process decay through the first Si atom layers? What is the atomic origin and nature of the "double layer"? What is a "dangling" bond and how is it modified by adsorption?

[1] C. Gatti, TOPOND-98, User's Manual (CNR-CSRSRC, Milano, Italy, 1999).