3.5. Classification and use of electron density data

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3.5.1. Introduction

Modern high-resolution X-ray diffraction methods enable the electron density distributions in many crystals to be accurately determined, allowing one to explore the interactions that hold crystals and molecules together (Coppens, 1997; Koritsanszky & Coppens, 2001). For example, Bader's (1990) theory of atoms in molecules gives a description of chemical bonding in terms of the topology of the electron density, but it requires an accurate knowledge of the electron density. [Note that the terms 'electron density' (or distribution) and 'charge density' tend to be used interchangeably in the literature. The term 'electron density' is used here since 'charge density' strictly includes both positive (nuclear) and negative (electronic) charge. Properties such as electrostatic potential, electric fields and their gradients, and molecular electric moments are derived from the charge density distribution, which includes the contribution of the nuclear charge (Spackman & Brown, 1994).] The advent of area detectors, more powerful laboratory computing facilities and developments in software have combined to produce a rapid increase in the number of accurate electron density determinations now available. While such studies are not yet routine, they are sufficiently common to justify defining a structure for a secure and systematic archive. This in turn requires a method of representing the electron density acceptable to the crystallographic community.

The CIF standard which has been adopted by the IUCr and is in common use in macromolecular and small-molecule crystallography is the obvious choice for such a file structure. At the Sagamore XIII conference held at Stare Jablonki, Poland, in 2000, the IUCr Commission on Charge, Spin and Momentum Densities decided to prepare a CIF dictionary for reporting electron densities in crystals. The result is the rhoCIF dictionary described in this chapter. It was prepared in conjunction with members of the Commission and other members of the community. [The name rhoCIF for this dictionary was chosen over the more obvious choice of edCIF to avoid any possible confusion with electron diffraction. The symbol $\rho(\mathbf{r})$ conventionally represents the electron density in real space at the point defined by the position vector $\mathbf{r}$.]

The distribution of electron density in a molecule or crystal can also be calculated theoretically, and the results are usually compared with experiment. The Hohenberg–Kohn theorem (Hohenberg & Kohn, 1964) shows that the ground-state energy is a unique functional of the electron density, thus providing a theoretical justification for relating chemical and physical properties directly to the observable electron density. Density functional theory has been applied to chemical problems for some time (see, for example, Labanowski & Andzelm, 1991; Ziegler, 1991; Kohn *et al.*, 1996; Nagy, 1998). Although the current version of the rhoCIF dictionary is intended to record the results of experimental measurements, it can also be used to represent a theoretical electron density that has been fitted with an appropriate model.

3.5.2. Dictionary design considerations

The rhoCIF dictionary contains the definitions of data items used to report accurate electron densities in crystals. The structure of these definitions conforms to the CIF rules and conventions, and selected data items reflect those currently needed in the field. In any field of science, the nature of the data used to describe the experiment and the results changes with time, and accurate electron density studies are no exception. The items defined in this dictionary describe the density representation approach used most often today – the atom-centred multipole expansion model introduced by Stewart (1973) and refined by Hansen & Coppens (1978). In this model, the electron density is expressed as the sum of three components. Two are the partial contributions of the core and valence shell of the spherical free atom, usually taken from the paper by Clementi & Roetti (1974). The third component is an aspherical multipole expansion of the remaining electron density. This is an atom-centred function, flexible enough to describe most electron density distributions likely to be encountered in a crystal, and with components that have the same symmetries as the atom-centred wave functions (orbitals) frequently used by chemists when describing chemical bonding.

3.5.3. Classification of data definitions

The rhoCIF dictionary is intended to be used in combination with the core CIF dictionary, or, after adaptation to DDL2, the mmCIF dictionary. The two dictionaries can be combined to form a composite dictionary by concatenation. Alternatively, the merging procedures described in Section 3.1.9 can be used to create a virtual dictionary at run time. Because the dictionary is not self-contained, its structure can be kept very simple, comprising only two categories: one to define a local axis system around each atom and one to contain the various parameters of the Hansen & Coppens (1978) multipole function.

The two categories in the electron density CIF dictionary lie within the single ATOM category group and relate to the structural model. They are as follows:

Specification of local axes at each atom (§3.5.3.1)
    ATOM_LOCAL_AXES
Atom-centred multipole expansion functions (§3.5.3.2)
    ATOM_RHO_MULTIPOLE

3.5.3.1. Specification of local axes at each atom

Data items in this category are as follows:

ATOM_LOCAL_AXES
- `_atom_local_axes_atom_label`
    → `_atom_site_label`
  `_atom_local_axes_atom0`
  `_atom_local_axes_atom1`
  `_atom_local_axes_atom2`
  `_atom_local_axes_ax1`
  `_atom_local_axes_ax2`

The bullet (●) indicates a category key. The arrow (→) is a reference to a parent data item.