Mathematical methods for the analysis of charge densities from x-ray diffraction*

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Abstract. Accurate x-ray and neutron studies have demonstrated that atomic deformations due to chemical bonding can be reliably mapped. Several new mathematical techniques which have been devised to obtain quantitative information from these maps are discussed along with their relative merits and demerits. Methods of obtaining theoretical densities modified to resemble the experimental framework are explained. The implications of these modified models are outlined.

Keywords. Electron density modelling; theoretical approaches; x-ray diffraction; charge densities.

1. Introduction

In the last two decades, with the advent of automatic diffractometers and high speed computers, it has become possible to collect and process large amounts of accurate x-ray data. These accurate x-ray intensity measurements combined with neutron diffraction results have demonstrated that the atomic deformations due to chemical bonding can be reliably mapped in molecular crystals. The so-called $X-N$, $X-X$ (high order) and other related difference maps have revealed several qualitative features of electron density distributions. Since, x-ray scattering is primarily due to the interaction of electromagnetic radiation with the electrons in the crystal, the charge density is the main information which is readily obtained. Several new mathematical techniques have been invoked to extract quantitative information from such charge density distributions. Direct evaluation of one-electron properties using modified fourier series summations is one such approach (Coppens and Guru Row 1978). Another popular approach is the modelling of density distributions by including additional deformation parameters in the least squares refinement. There are several models in practice and in this article salient features of such models will be discussed.

Recently, developments in theoretical methods have facilitated the calculation of charge densities of sufficient accuracy so that these can be compared with experimental charge distributions. However, these are limited for molecular crystals consisting of only light atoms. These comparisons would reveal the deficiencies in both theory and experiment. The state of art now (Coppens 1981) has reached a stage that it is possible to derive properties like net charges, molecular dipole moments and electrostatic potentials (Stewart 1973, 1979; Coppens *et al* 1980) and to fit atom-centred spherical harmonic functions (Hirshfeld 1977; Stewart 1976; Hansen and Coppens 1978). The theoretical comparisons, however, are to be made with those from a very large basis set (Stevens *et al* 1978; Stevens 1980) and not with semi-empirical or an approximate minimal basis *ab initio* calculations.

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2. Density modelling

The choice of a model is in its efficiency, simplicity and computer adoptability. It should also fit the experimental density within the accuracy of the experiment. Since, the model is to be built into the least squares procedure the adequate ratio of observations to parameters should be maintained to get meaningful outputs. The model should be consistent with theoretical properties expected out of the system. An interesting possibility is to use these conditions as constraints during refinement.

The electron density, in general, can be represented in terms of a finite number of analytical functions as

$$\rho = \sum_i P_i f_i(\mathbf{r}), \tag{1}$$

where P_i are the corresponding populations. These population parameters enter the least squares formalism as refinable parameters along with the usual parameters like scale factor, positional and thermal parameters etc. However, the electron density defined in (1) is to be convoluted over the probability functions corresponding to the thermal motion to represent the actual dynamic model density.

$$\rho_{\text{model}} \text{ (dynamic)} = \sum_i P_i \int f_i(\mathbf{r} - \mathbf{u}) p_i(\mathbf{u}) \, d\mathbf{u} \tag{2}$$

This formalism also filters out the noise from the experiment because f_i's have limited flexibility while calculating model deformation density as

$$\Delta\rho_{\text{model}} = \rho_{\text{model}} - \sum \rho_{\text{isolated, spherical atoms}} \tag{3}$$

The second term in expression (3) is usually calculated from Hartree-Fock wave-functions.

2.1 Two-centre models

Earlier models tried to express electron density as a sum over atomic orbital products (Stewart 1969; Jones *et al* 1972).

$$\rho_{\text{model}} = \sum \rho_{\text{core}} + \sum_{jk} P_{jk} \, \phi_j \phi_k. \tag{4}$$

These models, however, soon became unpopular because the orbital products for an extended basis set became unmanageable and large correlations between orbital products hampered the refinement process. Also, the expression of thermal motion for such a two-centre model becomes ambiguous. However, there is a model due to Helner (1977) which is still a two-centre model, but expresses the density in the bonding regions and at lone pair sites by ellipsoidal 'charge clouds'. The structure factor expression then becomes

$$\begin{aligned} F_{\text{model}} = &\sum_i \rho_{\text{core}} \exp\left(-B_i S^2\right) \exp\left(2\pi i\right) \mathbf{S} \cdot \mathbf{ri} \\ &+ \sum_j^{\text{clouds}} P_j \exp\left(-B_j S^2\right) \exp\left(2\pi i\right) \mathbf{S} \cdot \mathbf{ri}. \end{aligned} \tag{5}$$

The shape and size of each 'charge cloud' is expressed in terms of an anisotropic thermal parameter.

2.2 One-centre models

The simplest of these would contain only spherical deformation functions, the spherical atom approximation is maintained and only the occupancy of the valence shell is allowed to refine (Stewart 1970; Coppens *et al* 1971)

$$\rho_{\text{model}} = \sum_i \left[\rho_{\text{core}} + P_i \rho_{\text{valence}} (\mathbf{r}) \right]. \tag{6}$$

This is also called the L-shell projection method. But, this model does not allow for changes in shape of density distribution and thus contradicts chemical bonding theory. A more flexible formalism, which has become the most popular of available models, is the radial or kappa refinement (Coppens *et al* 1979). Here,

$$\rho_{\text{model}} = \sum_i \left[\rho_{\text{core}} + P_i \rho_{\text{valence}} (\kappa_i \mathbf{r}) \right], \tag{7}$$

and it allows for the refinement of P_i, the population of κ_i, the radial expansion and contraction of the valence shell. The functions ρ_{core} and ρ_{valence} are the Hartree-Fock densities of the free atoms normalized to one electron. Obviously, this model is limited to spherical or monopolar deformations. A more general fit to account for the asphericity of atoms when they become a part of a molecule could be obtained through a multipolar expansion of the valence density. General multipole models (Stewart 1976; Hirshfeld 1977; Hansen and Coppens 1978) aim at such a fuller description of densities

$$\rho_{\text{model}} = \sum_i \rho_{i,\text{pseudoatom}} \tag{8}$$

Each pseudoatom is given as a finite multipole expansion of the form

$$\rho_i(\mathbf{r}) = \sum_{l,m} R_l(r) A_{l,m} (\theta, \phi), \tag{9}$$

where r, θ, ϕ, are the polar coordinates about nucleus i, $R_l(r)$ is the radial distribution function and $A_{l,m}(\theta, \phi)$ is the angular part.

In the formalism due to Stewart (1976), the pseudoatom density is expressed as a spherical core density together with a multipolar valence density as

$$\rho_i(\mathbf{r}) = \rho_{\text{core}} + \sum_{l,m} P_{lm} R_l(r) Y_{lm\pm} (\theta, \phi), \tag{10}$$

$R_l(r)$ is the radial part and is expressed in terms of Slater type functions,

$$R_l(r) = N r^n \exp(-\zeta r), \tag{11}$$

with N as the normalization constant. The angular functions are real spherical harmonics expressed in terms of the associated Legendre polynomials

$$y_{lm+} (\theta, \phi) = p_l^m (\cos \theta) \cos \phi,$$

$$y_{lm-} (\theta, \phi) = p_l^m (\cos \theta) \sin \phi, \tag{12}$$

with

$$p_l^m (Z) = \frac{(1 - Z^2)^{m/2}}{2^l l!} \frac{d^{m+l}}{dZ^{m+l}} (Z^2 - 1) \tag{13}$$

For $l = 4$, (*i.e.* functions upto the hexadecapole level) there will be 25 population and l radial parameters per atom which enter the least squares formalism.

In another approach (Hirshfeld 1977), the density is expressed as deviations from the overall atom density as

$$\rho_i(\mathbf{r}) = \rho_{\text{atom}}(\mathbf{r}) + \delta\rho_i(r), \tag{14}$$

where

$$\delta\rho_i(\mathbf{r}) = \sum_{l,k} P_{lk} N_l r^n \exp(-\alpha r) \cos^n \theta_K, \tag{15}$$

θ_K is the angle between $\mathbf{r}$ and a specified vector $\mathbf{K}$ chosen to minimize overlap between deformation functions. This model yields 35 refinable parameters ($l = 4$) along with one radial parameter per atom. Electroneutrality is maintained through a constraint.

Hansen and Coppens (1978) in their formalism of a multipole model combine the kappa model with spherical harmonic angular and Slater type radial functions for all $l > 1$. This yields 26 more refinable parameters. The density is defined as

$$\rho_i(r) = P_C \rho_{\text{core}}(r) + P_V \rho_{\text{valence}}(\kappa r) + \sum P_{lm} N r^n \exp(-\zeta r) Y_{lm\pm}(\mathbf{r}/r). \tag{16}$$

P_C, P_V and P_{lm} are population coefficients such that

$$P_C + P_V + P_{lm} = \text{total number of electrons} \tag{17}$$

ρ_{core} and ρ_{valence} are Hartree-Fock densities normalized to one electron. The valence function is allowed for κ refinement. ζ is another refinable radial parameter. The angular functions are derived in terms of local atomic coordinate systems which allows for non-crystallographic constraints during refinement. Normalization is such that

$$\int_0^{2\pi} \int_0^{\pi} |y_{lm\pm}| \sin\theta \, d\theta \, d\phi = 2. \tag{18}$$

2.3 Merits and demerits

Among the one-centre models, the kappa refinement formalism has become most popular. Coppens once remarked that it is a 'poor man's charge density' approach. This methodology leads to reasonable estimates of several properties including net atomic charges and dipole moments. The simplicity of this formulation even in case of molecules containing heavier atoms is the main reason for its popularity. The computer program RADIEL (Coppens *et al* 1979) based on this model has been extensively used. The multipole models, however, are more difficult to handle but produce similar results. In general, this aspherical atom formalism leads to a significant reduction in the error function thus providing a better physically meaningful fit to the experimental data. The various multipole models proposed lead to similar results; which has been demonstrated recently (Baert *et al* 1982). However, the molecular dipole moments derived from Hirshfeld approach are generally high. This is attributed to the presence of diffuse monopolar functions in the multipolar expansion. A serious drawback comes from the experiment. The limited number of unique observations, the accuracy and the resolution places a limitation on the density features particularly near atomic centres. Correlations between functions on neighbouring atoms lead to problems particularly in multipole expansion. In fact it is not just the correlation, but the radial extent of the function itself (for $l > 1$) which may have appreciable value at neighbouring sites. The program MOLLY (Hansen and Coppens 1978) which builds the multipolar expansion into a regular least-squares program is widely used.

3. Theoretical methods

The advances in theoretical chemistry and physics have led to very sophisticated model development of molecular systems. The quality of theoretical methods, for molecular crystals, is good enough for comparison with experimental densities. Thermal motion is the most important factor to be accounted for before such comparisons are attempted. There are two ways in which this can be done: (i) to obtain static theoretical density and apply thermal smearing; compare with experimental density. (ii) to deconvolute thermal motion from experimental density; compare with static theoretical density. It is not the purpose of this article to review the various methods of static density calculation. It is enough to state that the availability of experimental deformation densities could be used as a sensitive test of convergence on molecular crystals. Earlier calculations involving semi-empirical, minimal basis set and SCF type formalisms failed to produce reasonable deformation density in the bonding regions. These also resulted in large densities at lone-pair regions. As bond density is a phenomenon akin to chemical theory and is consistently observed in experimental maps, it can be stated that the experimental densities clearly discriminate against less advanced calculations (Coppens and Stevens 1977). In a recent study (Stevens 1980) theoretical calculations of various degrees of complexities by *ab initio* self-consistent field method using extended basis set of Gaussian orbitals have been performed. To facilitate detailed comparison of these theoretical densities with experimental deformation density, a second order difference function

$$\Delta(\Delta\rho) = \Delta\rho_{\text{exp}} - \Delta\rho_{\text{theory, dynamic}} \tag{19}$$

is defined. The thermally-averaged theoretical electron density $\langle \rho \rangle$ can be obtained, within the Born-Oppenheimer approximation, as

$$\langle \rho \rangle = \int \phi^2(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N)\rho(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N)d(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N) \tag{20}$$

where ϕ^2 is the nuclear distribution function and $\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N$ are the nuclear position vectors. But, for molecular crystals, since the internal modes of vibration are much smaller than the external modes of vibration the dynamic theoretical density can be calculated to a good approximation by convolution with rigid body thermal motions (Stevens *et al* 1978). These values can be readily computed from experiment (Schomaker and Trueblood 1968). There is one more feature in molecular crystals which in theoretical density estimates cannot be fully accounted for. This is the intermolecular interactions.

The alternative approach of comparing experimental densities with static theoretical densities is after deconvolution. However, it is not yet clear as to which of the two approaches is to be preferred. In general, the comparisons are to be made only with a large basis set calculations and the low level calculations are not up to the resolution reached by experimental densities. For example, in case of oxalic acid (Stevens 1980) *ab initio* SCF calculations were performed using the program HONDO (Dupuis *et al* 1976) with an extended basis set of Gaussian orbitals. An extended basis set including *d*-functions, (11, 5, 1/6, 1) primitive Guassians contracted to a $\langle 4, 3, 1/4, 1 \rangle$ set was used. Another calculation using 4-31 G basis with (8, 4, 0/4, 0) contracted to $\langle 3, 2, 0/2, 0 \rangle$ set was also performed. The double difference maps calculated based on expression (19) clearly indicated that the extended basis set generally is in excellent

agreement. The 4-31 G set showed positive differences in the bonding regions, while in lone pair regions the differences were negative indicating the inadequacies of the theoretical density.

4. Conclusions

The various models with their adoptability to a least-squares formalism have helped to extract maximum information out of the experiment. However, caution is advised not to extend the refinable parameters to the extent of sacrificing the existing over-determinacy of the data set. Systematic errors and the sharp fourier cut-off still limits the accuracy. The deformation maps from the various models, particularly from the multipolar expansion contain less noise than the experimental $X-N$ or $X-X$ (high order) maps. It is generally advised to carefully examine the residual maps before attempting to evaluate one-electron properties. The fact that the experimental density is comparable only with the density from a very large basis set is welcome since at this level it is possible to look for very small effects quite accurately.

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