

DIRECT INTEGRATION OF CHARGE DENSITIES FROM X-RAY DIFFRACTION

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ABSTRACT

Direct evaluation of properties like net charges, dipole moments, quadrupole moments and electrostatic potential of a molecule using modified fourier series summations based on very accurate x-ray diffraction data is described. The approaches available for such direct integration of charge densities over suitably partitioned molecular volumes are briefly reviewed. A possible methodology to get better details of strong intermolecular interactions is proposed.

INTRODUCTION

X-RAY scattering is primarily due to the interaction of electromagnetic radiation with the electrons in the crystal. Thus, with the availability of very accurate x-ray diffraction data from a single crystal, electron density distribution may be obtained by Fourier methods. However, such fourier maps are not readily informative of properties like net charges, dipole and higher moments and electrostatic field gradients which are dependent on the charge density distribution. On the other hand, such properties are obtained directly from dielectric measurements, microwave data, ESCA techniques, Mossbauer spectra and of course, from theoretical wavefunctions. Also, these topological properties provide expression to other essential concepts of chemistry, chemical bond, structure and structural stability. Among the various mathematical techniques invoked to extract such properties from x-ray diffraction data, the most popular is the modeling of electron density with additional deformation parameters built into the regular least-squares refinement methods¹⁻³. Another technique, which will be briefly reviewed here, is the direct integration of charge density over a suitably defined (partitioned) volume to obtain these one-electron properties.

Charge integration

The general expression for the expectation value of any derived property p based on the

electron density $\rho(\mathbf{r})$ is

$$\langle p \rangle = \int_T \hat{p} \rho(\mathbf{r}) d^3r, \quad (1)$$

where T is the volume of interest. This volume is either over the whole crystal or over the molecule or over the molecular fragment as the case may be.

If, $\rho(\mathbf{r})$ is from x-ray diffraction, then,

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) \quad (2)$$

with V as the volume of the crystal unit cell and $F(\mathbf{H})$ as the structure factor. The contribution to $F(\mathbf{H})$ comes from the geometry and the individual atomic scattering from each atom with respect to all other atoms in the crystal.

By considering a 'pro-molecule', the molecule before bond formation, the electron density ρ_{pro} can be evaluated from

$$\rho_{\text{pro}} = \sum_{\text{all atoms}} \rho_i$$

where ρ_i is the density of the i th Hartree-Fock atom. Rewriting (2), as

$$\begin{aligned} & \frac{1}{V} \sum F(\mathbf{H}) \exp 2\pi i \mathbf{H} \cdot \mathbf{r} d^3r \\ &= \langle \rho_{\text{pro}} \rangle + \frac{1}{V} \sum \Delta F(\mathbf{H}) \exp 2\pi i \mathbf{H} \cdot \mathbf{r} d^3r. \quad (3) \end{aligned}$$

Since the first form on the right side is nothing but a superposition of spherical atoms it has no

topological properties associated with it. This implies that in (1) $\rho(\mathbf{r})$ can be replaced by $\Delta\rho(\mathbf{r})$, the so-called 'deformation density' which is calculated from $\Delta F(\mathbf{H})$ obtained from x-ray measurements. So, (1) becomes

$$\langle p \rangle = \frac{1}{V} \int_T \hat{\rho}(\mathbf{r}) \sum_{\mathbf{H}} \Delta F(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d^3 r \quad (4)$$

In principle, either F or ΔF can be used. The volume of integration, T , is in general of an irregular shape and hence the integration can be performed only after subdividing the volume into regular integrable subunits. These subunits are generally taken as parallelepipeds with their edges parallel to the crystal axis and the dimensions are normally in the range 0.1 to 0.2 Å. Thus,

$$\langle p \rangle = \frac{1}{V} \sum_i \int_{t_i} \hat{\rho}(\mathbf{r}) \sum_{\mathbf{H}} F(\mathbf{H}) \exp 2\pi i \mathbf{H} \cdot \mathbf{r} d^3 r \quad (5)$$

where t_i now is the volume of the i th sub-unit, or

$$\begin{aligned} \langle p \rangle &= \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) \sum_i \int_{t_i} \hat{\rho}(\mathbf{r}) \exp 2\pi i \mathbf{H} \cdot \mathbf{r} d^3 r \\ &= \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) \sum_i \int_{t_i} \hat{\rho}(\mathbf{r}) \exp 2\pi i \mathbf{H}(\mathbf{r} - \mathbf{r}_i) \\ &\quad \times \exp 2\pi i \mathbf{H} \cdot \mathbf{r}_i d^3 r \end{aligned} \quad (6)$$

with \mathbf{r}_i as the origin of the i th cell. So, in order to calculate the total charge, Q , every structure factor is to be multiplied by a shape transform $S_i(\mathbf{H})$ of that volume of integration.

$$S_i(\mathbf{H}) = \int_{t_i} q_i(\mathbf{r}) \exp 2\pi i \mathbf{H}(\mathbf{r} - \mathbf{r}_i) d^3 r \quad (7)$$

where $q_i(\mathbf{r})$ is the total charge in the sub-unit. So, (6) becomes

$$\begin{aligned} \langle Q \rangle &= \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) \sum_i S_i(\mathbf{H}) \exp 2\pi i \mathbf{H} \cdot \mathbf{r}_i \\ &= \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) S(\mathbf{H}), \end{aligned} \quad (8)$$

with $S(\mathbf{H})$ as the shape transform of the volume of integration relative to the origin of the unit cell. The corresponding expression for the standard deviation would be

$$\begin{aligned} \sigma^2(\langle Q \rangle) &= \frac{1}{V^2} \sum_{\mathbf{H}} \sum_{\mathbf{H}'} S(\mathbf{H}) S(\mathbf{H}') \sigma[F(\mathbf{H})] \\ &\quad \times \sigma[F(\mathbf{H}')] \gamma(\mathbf{H}, \mathbf{H}') \end{aligned} \quad (9)$$

where γ is the correlation between the structure factors (generally is zero). Similarly, the expression for the calculation of molecular dipole moment with this type of sub-unit and shape function definition is

$$\mu = \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) d(\mathbf{H}) \sum_i \exp 2\pi i \mathbf{H} \cdot \mathbf{r}_i + \sum_i q_i \mathbf{r}_i \quad (10)$$

where q_i is the net charge in sub-unit i ,

$$d(\mathbf{H}) = \int_{t_i} (\mathbf{r} - \mathbf{r}_i) \exp 2\pi i \mathbf{H} \cdot (\mathbf{r} - \mathbf{r}_i) d^3 r.$$

The first term, the sum over the dipole moments of individual sub-units, is sensitive to the grid size and becomes smaller as the grid size decreases. The second term represents the sub-unit charge multiplied by the position vector. A detailed derivation is given by Coppens^{2,3}.

The quadrupole moment, I_{ij} , is expressed as linear combination of the second moments of the charge distribution. The expression for I_{ij} consists of (i) the sub-unit quadrupole moments, (ii) the sub-unit dipole moments, and (iii) the sub-unit charge.

The electrostatic potential, ϕ^4 , defined as

$$\phi = \int \frac{1}{|\mathbf{R} - \mathbf{r}|} \rho(\mathbf{r}) d^3 r \quad (11)$$

at a point \mathbf{R} outside the range of charge distribution involves first the sum over the structure factors for each sub-unit to obtain moments followed by a summation of the type

$$\begin{aligned} \phi &= \sum_i \phi_i = \sum_i \left\{ \frac{q_i}{R_i} + \frac{\mu_{\alpha i} R_i}{R_i^3} + \frac{\mu_{\alpha\beta i}}{2R_i^5} (3R_{\alpha i} R_{\beta i} \right. \\ &\quad \left. - R_i^2 \delta_{\alpha\beta}) + \dots \right\} \end{aligned} \quad (12)$$

where R_i is the distance from \mathbf{r} to the i th sub-unit origin, q_i the net charge, $\mu_{\alpha i}$ the dipole moment and $\mu_{\alpha\beta i}$ the quadrupole moment of the i th sub-unit.

Methods of space partitioning

Obviously, the choice of subdividing the otherwise continuous charge density in the crystal to facilitate integration is of major concern since the topological one electron properties are restricted to a well-defined molecule or a molecular fragment. These volumes of integration can either have sharp boundaries (at regions of zero flux of electron density) or have overlapping regions with the density in these regions shared by adjacent fragments. However, any of those schemes should satisfy

$$(i) \sum_i V_i = V, \text{ the volume of the unit cell}$$

$$\text{and } (ii) \sum_i q_i = 0, \text{ the unit cell is neutral.}$$

The method of virial partitioning would be an ideal method⁵, but in practice its application to experimental densities is not straightforward. Factors like noise in the experiment, uncertainties due to temperature factors, systematic errors impose serious constraints.

In one approach, which involves the concept of sharp boundaries between the volumes or fragments, the volume definition is in terms of the relative radii of adjacent atoms⁶. Consider two atoms *A* and *B* of radii R_A and R_B if U_{AB} is the unit vector between *A* and *B*, then if a point r_i is at r_A and r_B from *A* and *B*

$$\frac{(r_A - r_i) \cdot U_{AB}}{R_A} \leq \frac{(r_A - r_i) \cdot U_{BA}}{R_B}. \quad (13)$$

This implies that the boundary planes are formed perpendicular to U_{AB} and their position will depend on the ratio of R_A and R_B . Such partitioning is well suited for molecular crystals and the radii in this methodology are varied around the traditional van der Waal radii of atoms. However, it is imperative that the ratio of radii and not the individual value of radii is of prime importance. Thus, while dividing this volume into sub-units the grid should extend to within the limits of the molecular framework in terms of the van der Waal radii.

An alternative approach, where the volumes

are allowed to overlap at regions of shared density, has been suggested by Hirshfeld⁷. This method adopts the so-called 'Stockholder recipe' where the molecular density is divided at each point among the atoms of the molecule in proportion to their respective contributions to the promolecule density at that point.

$$\rho_{\text{pro}}(\mathbf{r}) = \sum_{\text{all atoms}} \rho_i(\mathbf{r})$$

and the sharing function

$$W_i(\mathbf{r}) = \rho_i(\mathbf{r}) / \rho_{\text{pro}}(\mathbf{r})$$

for the *i*th atom. Thus, in this method there is no need for placing of arbitrary boundary surfaces. Also, the defined molecules or atomic fragments differ from the free atoms only to the extent the molecule itself differs from superposition of free atom densities.

A variation of this method is to use the 'Stockholder recipe' to partition the density over the entire crystal⁸. This approach also would take care of small effects in the intermolecular region, but such effects can also bias the derivation of topological properties.

DISCUSSION

It is generally observed that the values of the derived properties obtained, based on different methods described above are the same within the limits of errors allowed by experiment and the approximations in approach. Moreover, comparison of these values with the results from other physico-chemical techniques generally shows a very healthy trend. A point of caution is that, since all the expressions derived above refer to thermally-averaged density, in comparisons particularly with results from other techniques the thermal smearing effects are to be considered. An effort to reduce this bias considerably is to use low temperature x-ray diffraction data. The concept of partitioning the volume of integration with the type of definitions given appear to reduce the bias at the peripheral regions of the molecular volume since the functions are in terms of atomic radii or atomic deformations and are

not centered at atomic nuclei but spread over the entire molecule. The 'Stockholder recipe' for crystal density partition generally gives lower values for charge and moments than the one for molecular density partition⁹. The partition based on van der Waal radii^{3,6} gives values intermediate to these two methods. In fact, the ambiguity in definition is still a fundamental obstacle in any quantitative derivation of molecular moments by x-ray methods⁹. But, such limitations are also present in the density modeling by least-squares techniques¹ and in the basis set theoretical approach like *ab-initio* SCF calculations¹⁰.

The various methods of partitioning described above assume very little accumulation of density in the intermolecular regions. Also the promolecule is assumed to have zero moments. If there are strong intermolecular effects like in charge-transfer complexes, hydrogen bonded systems, then by definition, the atomic deformation density $\Delta\rho$ is inadequate to account clearly for such effects. Also the atomic deformation density varies mainly near the atoms and in the bonds. The strong intermolecular effects can be better seen if the atomic concept is replaced by a molecular concept. We can now define a molecular deformation $\Delta\rho_m$ which comes from $F(H)$ based on spherically averaged molecular scattering factors g_i .

$$g_i^2 = \sum_{j=1}^N \sum_{k=1}^N f_j f_k \sin t \mathbf{r}_{jk} / t \mathbf{r}_{jk} \quad (14)$$

where f_j, f_k are atomic scattering factors \mathbf{r}_{jk} is the vector between j th and k th atom obtained from the geometry derived from a high order refinement. t is $4\pi \sin \theta / \lambda$ and N is the number of atoms in the molecular framework.

The pros and cons of such maps are being studied. The obvious effect is that the intermolecular features show better details, but the errors in spherical averaging¹ might supercede these benefits. Possibilities of using gas phase molecular densities and isolated molecule theoretical densities after suitable origin specifications and modifications are being explored.

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