An Estimate of the Effect of Series Termination on Deformation Density Peak Heights *

M. S. LEHMANN [a] and P. COPPENS [b]

[a] Institut Laue-Langevin, B.P.n° 156X, 38042-Grenoble Cédex, France and [b] Department of Chemistry, State University of New York, Buffalo, New York 14214, U.S.A.

An expression is derived which describes the reduction in height of a Gaussian shaped peak in a deformation electron density map as a function of the data cut-off limit. It is found that for a given reduction in peak height the data collection limit is inversely proportional to the peak width at infinite resolution. The expression provides a test for the completeness of the data set. It also allows an estimate of the number of reflections to be collected to achieve a required minimum ratio of observed peak height to peak height at infinite resolution. The dependence of the thermal smearing function on temperature within the harmonic approximation is used for an estimate of the maximum data collection temperature, using the criterion that the width of the peak at rest should exceed the width of the thermal smearing function. Results are illustrated with examples from a recent charge density study of p-nitropyridine N-oxide carried out at 30 K.

Several studies of the charge density in crystals have become available in recent years. They employ a combination of X-ray data with either neutron or very high order X-ray data. Results are often expressed as deformation density maps in which spherical neutral atoms with positional and thermal parameters from the neutron or high order experiment are subtracted from the experimental density.

The principal features of such maps are the overlap or bond density peaks located between covalently bound atoms and density near terminal atoms, which is commonly associated with lone pair electrons. Each peak may be

described by its position, its height and shape. In first approximation the peak *positions* are expected to be relatively insensitive to the details of systematic corrections for effects such as absorption, extinction or series termination. This justifies qualitative interpretation of the maps in the familiar terms of chemical bonding theory. But the quantitative information inherent in the height and shape of the maxima requires a more careful analysis of all effects which influence the final results. The purpose of the present discussion is an estimate of the relation between the cut-off limit in data collection and the experimental peak heights as well as the condition this relation imposes on the completeness of the data set.

The effect of Fourier series termination on the peak height. If data are collected up to a maximum value of $S_{max} = (2 \sin \theta/\lambda)_{max}$, the effective scattering factor corresponding to a peak in the deformation density can be described as

$$f'(S) = f(S) \cdot R(S)$$

with the resolution function R defined as

$$R(S) = \begin{cases} 1 & \text{for } S \leq S_{max} \\ 0 & \text{for } S_{max} < S \end{cases}$$

The density corresponds to the Fourier transform

$$\varrho'(r) = \mathscr{F}[f'] = \mathscr{F}[f \cdot R] = \varrho * \mathscr{F}[R] \qquad (1)$$

where $\varrho(r) = \mathscr{F}[f(S)]$ is the density at infinite resolution, and where * indicates a convolution between two functions.

$\mathscr{F}[R(S)] = C(r)$ is easily derived and is given by [1]

$$C(r) = 4\pi S_{max}{}^3(\sin m - m \cos m)/m^3$$

with

$$m = 2\pi S_{max} r$$

The form of the peak in the difference density is less easy to predict. For a discussion of the general behaviour of the peak we have chosen here an isotropic Gaussian distribution function

$$\varrho(r) = \varrho(0) \exp(-r^2/2\sigma_T{}^2)$$

where $\varrho(0)$, the maximum, is defined by

$$\varrho(0) = P/(2\pi)^{3/2}\sigma_T{}^3 \qquad (2)$$

and where P is the number of electrons in the peak. The distribution parameter σ_T describes the width of the thermally smeared density. If both the thermal smearing function and the unsmeared density can be assumed to be of Gaussian nature, σ_T can be expressed as

$$\sigma_T{}^2 = \sigma^2 + u^2 \qquad (3)$$

where σ and u are the distribution parameters for the density and the thermal smearing function, respectively.

As S_{max} increases $C(r)$ will approach a δ-type function. Thus as more and more data are included in the calculation $\varrho'(r)$ approaches $\varrho(r)$, the peak height increases, and the observed σ_T' decreases. The changes in $\varrho'(0)$ and σ_T' are observed from a series of calculations with increasing S_{max}, but as $\varrho'(0)$ varies more rapidly than σ_T', following the relationship $d\varrho'(0)/\varrho'(0) \simeq -3d\sigma_T'/\sigma_T'$, we will focus our attention on the expected value of $\varrho'(0)$ for a given S_{max}. From (1) we get

$$\varrho'(0) = \int_0^\infty \varrho(r)C(r)dr$$

Both $\varrho(r)$ and $C(r)$ are spherically symmetric, the elementary volume dr becomes $4\pi r^2 dr$, leading to

$$\varrho'(0) = \frac{2\varrho(0)}{\pi} \int_0^\infty \{\exp(-r^2/2\sigma_T{}^2)(\sin 2\pi S_{max}r - 2\pi S_{max}r \cos 2\pi S_{max}r)/r\} dr \qquad (4a)$$

which can be written as (see Appendix)

$$\varrho'(0) = \varrho(0) \frac{4}{\sqrt{\pi}} \int_0^\nu t^2 \exp(-t^2)dt = \varrho(0)\phi(\nu) \qquad (4b)$$

Table 1. Values of $\alpha = \phi(\nu_\alpha) = \dfrac{4}{\sqrt{\pi}} \displaystyle\int_0^{\nu_\alpha} t^2 e^{-t^2} \, dt$ for a series of ν_α.

ν_α	$\phi(\nu_\alpha)$
1.088	0.50
1.214	0.60
1.354	0.70
1.433	0.75
1.524	0.80
1.631	0.85
1.768	0.90
1.977	0.95
2.381	0.99

with

$$\nu = 2^{\frac{1}{2}}\pi S_{max}\sigma_T$$

The function $\phi(\nu)$ has a sigmoidal behaviour. Table 1 gives $\phi(\nu_\alpha) = \alpha$ for a series of values of ν_α, while Fig. 1 shows $\varrho'(0)/\varrho(0) = \alpha$ as a function of S_{max} for a series of values of σ_T.
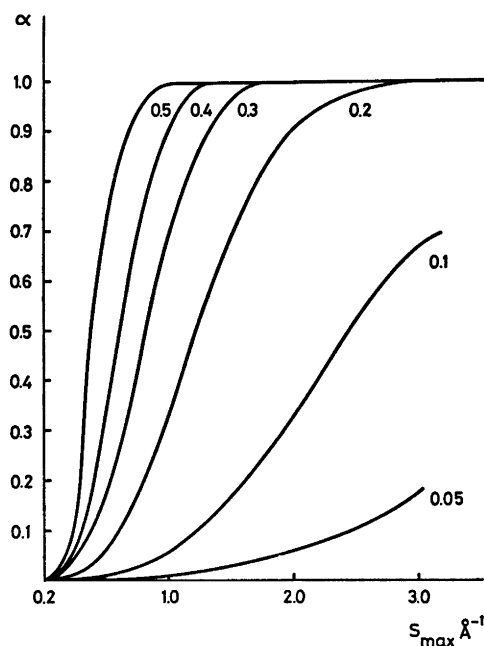

Fig. 1. The ratio between the peak height at resolution S_{max} and at infinity, $\varrho'(0)/\varrho(0) = \alpha$, as a function of S_{max} for a series of values of the distribution parameter σ_T (given on the plot in Å). Very sharp peaks with $\sigma_T < 0.20$ Å will produce scattering beyond the Mo radiation limit.

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Expression (4b) can be used to estimate the reduction in peak height due to finite resolution.

As an example of such calculations we will use observations from combined X-ray and neutron studies of p-nitropyridine-N-oxide carried out at 30 K.[2] X-Ray data[3] were measured up to $S_{max} = 2.0$ Å^{-1}, and deformation densities were calculated for $S_{max} = 1.3$, 1.5, 1.7 and 2.0 Å^{-1}. The peak heights of all bonding densities were averaged for each value of S_{max} and a similar calculation was carried out for the lone pair densities. Fig. 2 shows the behaviour of the two types of densities. Functions of the type given in (4b) were now fitted to the points by a least squares procedure in which $\varrho(0)$ and σ_T were varied. For simplicity all points were given equal weight and correlations between points were neglected despite the fact that the points are based on overlapping sets of reflections. The resultant curves are also shown in Fig. 2. The values obtained were for the bonding density $\sigma_T = 0.22(3)$ Å and $\varrho(0) = 0.61(3)$ e/Å^3 and for the lone pair density $\sigma_T = 0.17(5)$ Å and $\varrho(0) = 0.80(6)$ e/Å^3.

The figure indicates, that the resolution is sufficient for an adequate description of bonding densities, but the lone pair densities would require data to at least an S_{max} of approximately 2.3 Å^{-1}.

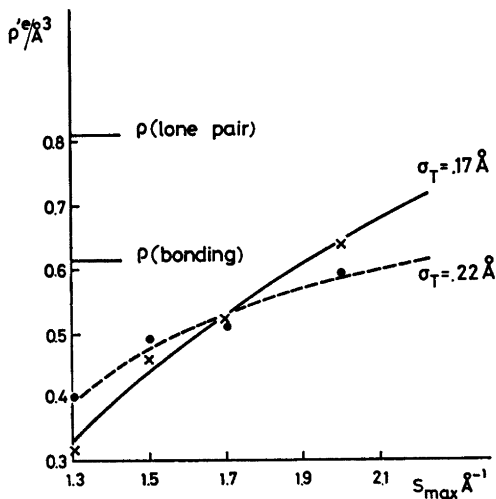*Fig. 2.* The peak value of the bonding density (×) and lone pair density (●) as a function of S_{max} for p-nitropyridine-N-oxide. Points are mean values for a given resolution. Limits for infinite resolution are indicated.
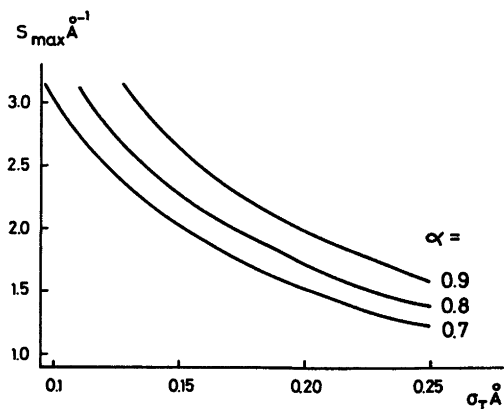
Fig. 3. Desired resolution, S_{max}, as a function of the distribution parameter for the thermally smeared peak, σ_T. Curves are given for various values of $\alpha = \varrho'(0)/\varrho(0)$. $\varrho'(0)$ is the observed peak height, $\varrho(0)$ the peak height for infinite resolution.

Using expression (2) we can estimate the integrated density in the peaks, which is found to be 0.10 e and 0.06 e for bonding and lone pairs, respectively, again under the assumption of isotropic density distributions. If the value of σ_T is known approximately, expression (4b) may be used to estimate the desired resolution. Fig. 3 shows S_{max} as a function of σ_T for a series of values of the ratio α. For the example discussed for which $\sigma_T = 0.17$ Å data would have to be collected up to $S_{max} = 2.3$ Å^{-1}, if we hade required that the lone pair peak should attain 90 % of the value for infinite resolution.

Conditions imposed on measurement temperature and necessary number of reflection data. The distribution parameter σ_T consists of two contributions as indicated by (3), the width σ of the electron distribution at rest, and a width, u, due to the thermal smearing. When the electron density is to be studied u is generally of little interest, and to reduce its magnitude measurements are frequently carried out at low temperatures. The behaviour of u with temperature in the harmonic approximation and assuming that the molecule in question moves as a rigid body is given by

$$u^2 = \frac{h}{8\pi^2 M \omega_T} \coth \frac{h\omega_T}{2kT} + d^2 \frac{h}{8\pi^2 I \omega_L} \coth \frac{h\omega_L}{2kT} \quad (5)$$

where the first term describes the translational motion with frequency ω_T and the second term gives the librational motion for an atom at distance d from the center of libration. M and I are mass and moment of inertia, respectively. If we express the variables in atomic mass units, Å, cm⁻¹ and K, the two quantities involved, $h/8\pi^2$ and $h/2k$ have values of 16.86 Å² a.m.u. cm⁻¹ and 0.719 K/cm⁻¹, respectively.

Assuming that $\omega/T < 0.75$ cm⁻¹/K, we introduce an error of less than 10 % by setting coth $(h\omega/2kT) = 2kT/h\omega$ and the expression (5) for the mean square displacement of a given atom becomes

$$u^2 = \frac{kT}{4\pi^2M\omega^2}$$

with

$$\frac{1}{\omega^2} = \frac{1}{\omega_T^2} + d^2\frac{M}{I}\frac{1}{\omega_L^2}$$

So the thermal motion for a given atom as a function of temperature can be approximately described as a translation with frequency ω, which can be fixed from a room temperature observation of the mean square displacement, u_0^2.
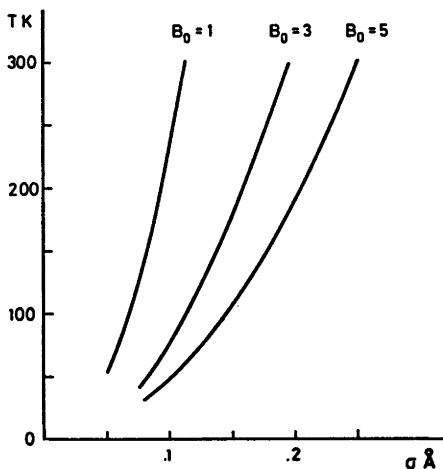

Fig. 4. Relationship between σ, the distribution parameter of the electron density at rest, and the measurement temperature, T, according to the condition, that $\sigma = u$, where u is the atomic root mean square thermal displacement. For the condition $\sigma > u$ the curves indicate the maximum possible measurement temperature. The isotropic temperature factors indicated on the figure are observations at 300 K.

To make sure, that σ is not negligible compared to u a reasonable requirement would be, that u is less than σ which fixes the measurement temperature condition as

$$\sigma^2 \geq \frac{kT}{4\pi^2M\omega^2} = \frac{B_0}{8\pi^2}\frac{T}{T_0}$$

with $B_0 = 8\pi^2u_0^2$, the isotropic temperature factor, determined at room temperature T_0. Fig. 4 shows T as a function of σ for the condition $\sigma = u$ for a series of B_0 values fixing T_0 to 300 K. Taking again as an example the p-nitropyridine-N-oxide, we find, that at 30 K the mean u^2 for the oxygen atoms is 0.0093 Å². For the lone pair electrons σ_T^2 equals 0.0289 Å² which gives $\sigma = 0.14$ Å. The mean B_0 for oxygen at room temperature is 4.9 Å² [3] so according to the above criterium that $\sigma > u$ the measurement should be made at a temperature below 95 K.

In general σ is of course not known before completion of the analysis but approximate values may be obtained from theoretical chemical calculations, or from comparable molecules which have been studied previously.

If σ is known it is possible to estimate the number of unique reflections required to obtain a given $\alpha = \varrho'(0)/\varrho(0)$ for a specific atom, assuming that the thermal behaviour at some temperature, normally room temperature, is known, We consider a primitive centrosymmetric space group for which in general the number of asymmetric units per unit cell Z equals the number of equivalent reflection in a form. The minimal number of unique reflections is then

$$n = \frac{1}{Z}\frac{4}{3}\pi S_{max}^3 V = \frac{1}{Z}\frac{4}{3}\pi S_{max}^3\frac{MZ}{D} = \frac{4}{3}\pi S_{max}^3\frac{M}{D}$$

where V is the volume of the unit cell, M is the mass of the molecule, and D is the density of the material. Introducing $\nu_\alpha = 2^{\frac{1}{2}}\pi S_{max}\sigma_T$ where ν_α is defined in Table 1 we get

$$n = \frac{2^{\frac{1}{2}}\nu_\alpha^3 M}{3\pi^2 D\sigma_T^3}$$

With σ_T from expression (3) and (5), n can be estimated.

We take again the above discussed example , and use the calculated σ_T to estimate n for observation of bonding and lone pair density. For this compound $M = 140$ a.m.u. and $D = 1.6$

g/cm³. If we require, that $\alpha = 0.9$ we find that 1800 unique reflections are needed if the bonding density, and 3900 if the lone pair density is to be observed at 90 % peak height.

CONCLUSIONS

Though subtraction of the unperturbed spherical atom in a deformation density map leads to a considerable reduction in series termination effects, incompleteness of the data set cannot be ignored when a quantitative interpretation of the charge density is made. One approach followed by Rees and Mitschler [4] and by Stevens and Coppens [5] is to introduce series termination (and thermal smearing) into the theoretical density maps. The assumption of a Gaussian peak shape gives an estimate of the effects involved. It is obvious that in all cases extension of the data set leads to an increase in resolution but the improvement becomes less important as thermal motion increases. The use of a Gaussian peak shape in the discussion ignores details of the charge distribution which may become observable with shorter wavelengths or at lower temperatures. Nevertheless it leads to a tractable expression which is in reasonable agreement with the very-low temperature observations on *p*-nitropyridine *N*-oxide.

APPENDIX

Using formulas 861.22 and 861.20 in Tables of Integrals and other Mathematical Data (Dwight, 1961)[6] (4a) can be written

$$\varrho'(0) = 2\varrho(0)[\tfrac{1}{2} \, \mathrm{erf} \, (\nu) - \frac{1}{\sqrt{\pi}} \, \nu \exp \, (-\nu^2)] \qquad (A1)$$

with $\nu = 2^{\frac{1}{2}}\pi S_{\mathrm{max}}\sigma$

Applying the relationship

$$uv]_0^\nu = \int_0^\nu u dv + \int_0^\nu v \, du$$

with $u = \dfrac{t}{\sqrt{\pi}}, \quad v = \exp \, (-t^2)$ gives

$$\tfrac{1}{2} \, \mathrm{erf} \, (\nu) - \frac{\nu}{\sqrt{\pi}} \exp \, (-\nu^2) = \frac{2}{\sqrt{\pi}} \int_0^\nu t^2 \exp \, (-t^2) \, dt$$

which, inserted in (A1) leads to

$$\varrho'(0) = \varrho(0) \, \frac{\sqrt{\pi}}{4} \int_0^\nu t^2 \exp \, (-t^2) \, dt$$

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