5.4. Quadrilatère dégénéré; cas elliptique; maille cubique

$$\mathbf{A} = \begin{bmatrix} 1 & 1 & 2 & 2 \\ -1 & 1 & -6 & 6 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 4 & 4 \end{bmatrix} \quad \mathbf{C} = \begin{bmatrix} 2 \\ 2 \\ 25 \\ 25 \end{bmatrix} \quad \mathbf{K} = \tfrac{1}{2} \begin{bmatrix} 23 \\ 0 \\ -21 \\ 0 \end{bmatrix} \quad \mathbf{S} = \begin{bmatrix} 0 \\ 0 \\ \tfrac{1}{2} \\ 0 \end{bmatrix} \quad \mathbf{N} = \begin{bmatrix} -3 \\ 0 \\ 2 \\ 1 \end{bmatrix}$$

Les solutions (toutes inscrites) sont centrées sur l'ellipse:

$$y = 0; \quad \tfrac{8}{9}(x + \tfrac{11}{16})^2 + (z - 1)^2 = \tfrac{697}{32}; \quad \left(r = \tfrac{23}{6} - \tfrac{x}{3} \right).$$

La plus grande sphère inscrite est obtenue avec $s + 4n = 23$; c'est

$$\mathbf{V} = \begin{bmatrix} -5,64 \\ 0 \\ 1 \\ 5,71 \end{bmatrix}.$$

5.5. Quadrilatère dégénéré; cas parabolique; maille cubique

$$\mathbf{A} = \begin{bmatrix} 1 & 1 & 2 & 2 \\ -1 & 1 & -4 & 4 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 2 & 2 \end{bmatrix} \quad \mathbf{C} = \begin{bmatrix} 2 \\ 2 \\ 17 \\ 17 \end{bmatrix} \quad \mathbf{K} = \tfrac{1}{2} \begin{bmatrix} 15 \\ 0 \\ -13 \\ 0 \end{bmatrix} \quad \mathbf{S} = \begin{bmatrix} 0 \\ 0 \\ \tfrac{1}{2} \\ 0 \end{bmatrix} \quad \mathbf{N} = \begin{bmatrix} -1 \\ 0 \\ 0 \\ 1 \end{bmatrix}.$$

Les solutions (toutes inscrites) sont centrées sur la parabole:

$$y = 0; \quad x = \tfrac{281}{60} - \frac{(z - 1)^2}{15}; \quad (r = \tfrac{15}{2} - x).$$

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A Simple Method of Estimating the Effects of Series Termination and Thermal Smearing on Peak Heights

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The extent to which the peak heights of difference maps are reduced by termination of the Fourier series and by thermal smearing has been investigated. For this purpose, the peaks are represented by Gaussian distributions. Series termination and thermal smearing can be considered as convolution operations which can be reversed by corresponding deconvolution operations to reconstruct the true peaks. Deconvolution for thermal smearing can be exactly performed with three-dimensional Gaussian distributions. With respect to peak heights, deconvolution for series termination can be exactly performed with the spherically symmetric, and approximately performed with any Gaussian distributions. With five hypothetical peaks the expected deconvolution effects have been examined, and with four peaks of published $X - N$ maps, it is shown how the peak heights can be approximately corrected for the two convolution effects.

Introduction

As a rule, the molecule at rest, *i.e.* the electron density distribution of the equilibrium configuration of the nuclei, is the object of quantum-chemical calculations of molecular density distributions. Experimental investigations of molecular density distributions, performed by means of X-ray diffraction on crystals, have the same object, but the densities obtained experimentally and represented by Fourier synthesis are im-

paired by at least two effects: series termination and thermal smearing. Thermal motions of the atoms and the limited Ewald sphere make it impossible to measure all the Fourier coefficients necessary to carry out the synthesis. With investigations of bond densities, the effect of series termination is much reduced if difference densities of some type (deformation densities, valence densities) are calculated. In this way, the effect of the termination ripples of the atomic maxima is eliminated; this effect would otherwise falsify the distribution of the bond densities. Nevertheless, there is a termination error in the synthesis of difference maps which reduces the peak heights and broadens the peaks. The thermal motions of the atoms in crystals cannot be suppressed and X-ray diffraction investigations are known to yield only the thermal average of the density distribution. Thermal smearing also reduces the peak heights and broadens the peaks. Both effects, series termination and thermal smearing, are to be considered as deficiencies inherent in the X-ray method as a tool for determining electron density distributions. Hence, efforts have to be made to correct for these two effects and to restore the 'true' density distribution as far as possible.

The aim of this paper is to estimate the heights of the 'true' peaks by simple means. For this purpose we represent the peaks by Gaussian distributions. It is then simple to correct the peak for thermal smearing. The correction for series termination can, however, be performed only for the peak height and not for the shape. Therefore, in this paper we neglect the peak shapes. As the heights constitute a characteristic property of difference density maps this restriction does not appear to be too serious.

Deconvolution for series termination

The peak, calculated with a finite Fourier series, can be represented by the convolution product of the 'true' peak and a termination function (Lipson & Cochran, 1953;* Rees, 1976). (By the 'true' peak we mean that peak which is not affected by series termination.) Hence, we can regard the reconstruction of the true peak as a deconvolution operation which reverses the convolution operation of series termination.

The investigation of the problem with Gaussian distributions showed, however, that it is simpler to deal with the Fourier integral with finite limits than to deal with the convolution integral. Let us consider a three-dimensional Gaussian distribution of the density

$$\varrho(\mathbf{x}) = q(2\pi)^{-3/2}(\det \mathbf{V})^{-1/2} \exp\left(-\tfrac{1}{2}\mathbf{x}^T\mathbf{V}^{-1}\mathbf{x}\right), \quad (1)$$

where $\mathbf{V}$ is the smearing tensor by which the charge q is distributed. The Fourier transform of this distribution is

$$f(\mathbf{h}) = q \exp\left(-2\pi^2\mathbf{h}^T\mathbf{V}\mathbf{h}\right). \quad (2)$$

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* Because of a sign error, the fact that the resulting integral is a convolution integral is not evident in Lipson & Cochran's calculation.

Firstly, we restrict our calculation to the special case of an isotropic smearing tensor with the diagonal components V. We use $h = |\mathbf{h}|$, $h^2 = h_1^2 + h_2^2 + h_3^2$, and, in agreement with (1), obtain the inverse Fourier transform,

$$\varrho(\mathbf{x}) = q \int_{-\infty}^{\infty} \exp\left(-2\pi^2h^2V\right) \exp\left(-2\pi i\mathbf{h}^T\mathbf{x}\right)d\mathbf{h}. \quad (3)$$

The termination of the Fourier series corresponds to integration to a finite limit $h_{\max} = (2\sin\theta_{\max})/\lambda$. (The difference between the finite series and the finite integral does not matter here: the single motif, affected by finite integration and packed in a three-dimensional array, leads to zero Fourier coefficients precisely when $h > h_{\max}$.) We introduce polar coordinates into reciprocal space. Let $r^2 = x_1^2 + x_2^2 + x_3^2$ and r be the distance from the centre of the distribution; with the substitution formula given by Ryshik & Gradstein (1963, p. 217) we obtain for a finite upper limit

$$\varrho(r) = q4\pi \int_0^{h_{\max}} h^2 \exp\left(-2\pi^2h^2V\right)\frac{\sin(2\pi rh)}{2\pi rh}dh. \quad (4)$$

An analytic solution for (4) does not appear to exist. However, for the peak maximum, $r = 0$, there is a solution with the substitution $\pi h\sqrt{(2V)} = t$ (Gröbner & Hofreiter, 1957, p. 109). Evaluation (for $r = 0$) leads to

$$\varrho(0) = q(2\pi V)^{-3/2}\left[\operatorname{erf}(t_{\max}) - \frac{2}{\sqrt{\pi}}t_{\max}\exp\left(-t_{\max}^2\right)\right], \quad (5)$$

where

$$\operatorname{erf}(t_{\max}) = \frac{2}{\sqrt{\pi}}\int_0^{t_{\max}}\exp\left(-t^2\right)dt$$

is the error function. For a finite limit $h_{\max}$, the square bracket in (5) is less than one and the peak maximum is correspondingly reduced. For $h_{\max} = \infty$, $t_{\max} = \infty$, (5) represents a special case of (1). The solution (5) can also be obtained from the convolution integral, as was done by Coppens & Lehmann (1976).*

For an anisotropic smearing tensor $\mathbf{V}$ no analytic solution of the integral appears to exist. Hence, we have to be satisfied with an approximate solution. Without loss of generality we consider $\mathbf{V}$ to be diagonal. If we want to express the anisotropic solution by an average $\bar{V}$ for the components V_{ii}, (1) shows that this average must have the form

$$V_{ii} = \bar{V} = (V_{11}V_{22}V_{33})^{1/3}. \quad (7)$$

The exact solution (1) is approached for $h_{\max} \rightarrow \infty$ only with (7). With large anisotropy and for small values of $h_{\max}$ the approximation (7) in itself proves to be insufficient. In order to obtain a better approximation

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* These authors have calculated numerical results and have represented them in the form of diagrams. In the present work we were initially unaware of Coppens & Lehmann's (1976) paper, and we credit the idea of fitting isotropic Gaussians to observed peaks to these authors.

for a finite volume of integration, we consider the approximation (7) in a volume of integration for which the exact solution is known. This is a cube with edges $2h_{max}$ in length. With the substitution $\sqrt{(2V_{ii})}\pi h_{max} = t_{i\,max}$, the solution for $x = 0$ is given by

$$\varrho(0) = q \prod_{i=1}^{3} \int_{-h_{max}}^{h_{max}} \exp(-2\pi^2 h_i^2 V_{ii})dh_i$$

$$= q(2\pi)^{-3/2}(V_{11}V_{22}V_{33})^{-1/2} \prod_{i=1}^{3} \mathrm{erf}\,(t_{i\,max}). \quad (8)$$

Since V_{ii} is contained in $t_{i\,max}$, the approximation (7), $V_{ii} = \bar{V}$, for a finite volume of integration, $8h_{max}^3$, will deviate from the exact solution (8). Since we know the exact solution we can calculate this deviation. The spherical volume of integration, $\frac{4}{3}\pi h_{max}^3$, which is our main concern, is exactly embraced by the cube volume of integration. Hence, we shall obtain a sufficient approximation for the spherical volume if we use the deviations which we observe with the cube volume in order to calculate the corrections for the spherical volume. Thus, for a diagonal anisotropic smearing tensor V we obtain the approximate solution

$$\varrho(V, \text{sphere}) = \varrho(\bar{V}, \text{sphere})\, \frac{\varrho(V, \text{cube})}{\varrho(\bar{V}, \text{cube})}. \quad (9)$$

On the right-hand side of (9) all quantities can be calculated: $\varrho(\bar{V}, \text{sphere})$ from (5) with $V = \bar{V}$, $\varrho(\text{cube})$ from (8) exactly, and from (8) with $V_{ii} = \bar{V}$. Since the error function (6) is available for most computers as a library routine, the numerical evaluation of (9) is straightforward.

In order to carry out the deconvolution for series termination, at least two observed peak heights for two limits of termination are necessary. Then, the Gaussian distribution, terminated at the two limits, is fitted to the observed peak heights as well as possible. The parameters are the charge q and the components V_{ii}. When the fitting is completed the maximum of the true peak is obtained from (1) with $x = 0$.

Though not strictly necessary, it is better to have more than two observed peak heights. This does not imply that extremely high-angle data must be available, but only that the syntheses are calculated for three or more limits of termination. A good fitting of the terminated Gaussian distribution to the observed peak heights is essential; less important is the exact reproduction of the anisotropy of the observed peak. As a rule, the restriction $V_{11} = V_{22}$ can be employed, and often an isotropic smearing tensor will serve.

Deconvolution for thermal smearing

The dynamic density is the convolution product of the true peak and the thermal smearing function. In the harmonic approximation this function is a Gaussian with the covariance matrix U (vibration tensor). When the density distribution of the true peak is also Gaus-

sian, the solution of the convolution integral is known. The dynamic density is again a Gaussian distribution but instead of V it carries the sum $V + U = D$ (Scheringer & Reitz, 1976). Thus, if a Gaussian distribution of the dynamic density with the smearing tensor D is given, and the vibration tensor U is known, then the thermal deconvolution can be carried out at once. First one calculates

$$V = D - U, \quad (10)$$

and then the true density from (1). (Of course, in actual practice $D - U$ must be positive definite.) It is obvious that the thermal deconvolution can be performed not only for the peak maximum ($x = 0$), but also for the full Gaussian peak ($x \neq 0$).

Numerical results

In order to gain an impression of the magnitude of the deconvolution effects to be expected we first have calculated the deconvolution with five hypothetical peaks. V, U, and D were chosen to be isotropic in order to obtain exact results. The termination limits are $(\sin \theta_{max})/\lambda = 0.65$, 0.75, and 1.00 Å^{-1}. The values of V from 0.04 to 2.00 Å^2 roughly cover the region which one encounters with deformation and valence densities. $V = 0.15$ to 0.17 Å^2 ($P4$ in Table 1) approximates a C–C bond peak. We draw this conclusion from a comparison of the values of the Fourier transform (2) with Fritchie's (1966) Table 1(b) scattering curves for bond peaks. The thermal deconvolution was carried out for $U = 0.008, 0.016$, and 0.048 Å^2. With molecular crystals, these values roughly correspond to 30, 100 and 300 K respectively. With q in electrons, V and U in Å^2 the calculated peak heights are in e Å^{-3}. The results are presented in Table 1. With $P4$, which roughly corresponds to a C–C bond peak except for the charge q, the true peak height is reduced by 3.6% for $(\sin \theta_{max})/\lambda = 0.65$ Å^{-1}. With the sharper peaks $P1$ and $P2$, the reduction due to series termination is much larger, 45 and 19% respectively for $(\sin \theta_{max})/\lambda = 0.65$ Å^{-1}. The effect of thermal deconvolution at room temperature $(U = 0.048$ Å$^2)$ is already considerable with $P4$. One has to enlarge the observed peak height by 76% in order to gain the true height. The considerable effect of thermal smearing on the peak heights was also observed by Hase, Reitz & Schweig (1976) with thiourea. For the lone-pair electron peak of the S atom these authors found that the peak height of the static density was reduced to about 50% by thermal smearing at room temperature.

In order to demonstrate how to carry out the deconvolution with an actual example, we selected p-nitropyridine N-oxide, for which X-ray and neutron data were collected at 30 K by Wang, Blessing, Ross & Coppens (1976) – hereinafter referred to as WBRC. WBRC published three $X - N$ maps for the three termination limits $(\sin \theta_{max})/\lambda = 0.65$, 0.75, and 1.00 Å^{-1}. For our analysis we have chosen the two bond

peaks at C(9)–C(10) and C(8)–C(9), and the two lone-pair electron peaks at O(2) and O(3). The peak heights were estimated from WBRC's density maps. For the vibration tensors U we have used an isotropic average (for reasons of simplicity), namely the arithmetic mean of the diagonal components as given by WBRC. This average was reduced by a factor of 0·65 for the two bond peaks because internuclear density units have a vibration tensor which is smaller than the average tensor of the adjacent atoms (Scheringer, 1977). In fitting the Gaussian distribution to the observed peak heights we used three parameters, q, $D_{11} = D_{22}$, and D_{33}. The fitting was carried out by successive trials, four trials being sufficient. The results are listed in Table 2. The figures in the columns headed $x_{0·1}$ and $z_{0·1}$ give an impression of the shape of the Gaussian peak. The effect of deconvolution is particularly large for the lone-pair electron peak $P4$: With $(\sin \theta_{max})/\lambda = 0·65$ Å^{-1} and $T = 30$ K, the observed peak height of 0·44 e Å^{-3} has to be multiplied by a factor of 1·79 so that the true peak height of about 1·23 e Å^{-3} is established.

We have also fitted the four WBRC peaks with an isotropic smearing tensor, i.e. with only two parameters q and D. The peak heights obtained are nearly the same as those given in Table 2. After correction for series termination the four peak heights were 0·64,

0·86, 0·94 and 0·84 e Å^{-3}; after thermal deconvolution they were 0·70, 0·96, 1·27 and 1·29 e Å^{-3}. With $P4$ a relatively large difference from the value in Table 2 of 0·06 e Å^{-3} is found, which probably arises from the fact that a Gaussian distribution cannot be fitted so well to $P4$ as to the other peaks, cf. Table 2. On the whole, the calculation with an isotropic smearing tensor confirms our above statement that the precise reproduction of the anisotropy is not as important in the peak-fitting procedure.

The numerical results show that the peak heights are usually reduced more by thermal smearing than by series termination. We can discuss this more precisely if we put the termination function (Rees, 1976) and the thermal smearing function on the same scale. In order to do this we have to ensure that the two functions have the same value at $x = 0$. Thereby, a given termination limit is assigned to a certain isotropic vibration component. For $(\sin \theta_{max})/\lambda = 0·65$, 0·75 and 1·00 Å^{-1} we find the vibration components $U = 0·0362$, 0·0272 and 0·0153 Å^2 respectively. The deconvolution effect for $U = 0·0153$ Å^2 may be read from Table 1 in the column headed $U = 0·016$ Å^2. In order to expand upon the data of Table 1, we have calculated the heights of peaks $P1$ and $P5$ for $U = 0·0272$ and $U = 0·0362$ Å^2. The respective heights are 21·9 and 135·5 e Å^{-3} for $P1$, and 0·44 and 0·48 e Å^{-3} for $P5$. With these data added to

Table 1. *Heights of five hypothetical Gaussian peaks with isotropic smearing, $D = V + U$*

$q = 0·5$ e for all peaks. The final column gives the values of $(\sin \theta)/\lambda$ for which the ratio of the Fourier transforms, $f[(\sin \theta)/\lambda]/f(0)$, is equal to 0·01.

Peak	D (Å^2)	Series termination at $(\sin \delta)/\lambda$ (Å^{-1})				Thermal deconvolution for U (Å^2)			$[(\sin \delta)/\lambda]_{0·01}$
		0·65	0·75	1·0	∞	0·008	0·016	0·048	
$P1$	0·04	2·20	2·72	3·58	3·97	5·55	8·54	–	1·21
$P2$	0·07	1·38	1·54	1·69	1·71	2·06	2·53	9·73	0·92
$P3$	0·10	0·92	0·97	1·00	1·00	1·14	1·30	2·68	0·77
$P4$	0·15	0·53	0·54	0·55	0·55	0·59	0·65	0·97	0·63
$P5$	0·20	0·35	0·35	0·35	0·35	0·38	0·40	0·54	0·56

Table 2. *Gaussian peak fitting to four peaks of WBRC's density maps*

$x_{0·1}$ and $z_{0·1}$ denote the distances from the peak centre in the x and z directions, respectively, where the Gaussian peak (with $h_{max} = \infty$) has decreased to a density of 0·1 e Å^{-3}. For $P1$ and $P2$ the z axis refers to the direction of the bond, for $P3$ and $P4$ it refers to the line through the oxygen nucleus and the peak centre. Peak heights are in e Å^{-3}. Lp stands for lone pair.

Peak	q (e)	Gaussian parameters D_{11} (Å^2)	D_{33} (Å^2)	$x_{0·1}$ (Å)	$z_{0·1}$ (Å)	Peak heights for series termination at $(\sin \delta)/\lambda$ (Å^{-1}) 0·65 WBRC	0·65 Gauss	0·75 WBRC	0·75 Gauss	1·0 WBRC	1·0 Gauss	∞ Gauss
$P1$, C(9)–C(10)	0·219	0·075	0·084	0·53	0·56	0·54	0·54	0·58	0·59	0·64	0·64	0·64
$P2$, C(8)–C(9)	0·194	0·048	0·087	0·47	0·62	0·62	0·62	0·72	0·72	0·85	0·84	0·87
$P3$, Lp O(2)	0·182	0·070	0·030	0·57	0·38	0·62	0·62	0·72	0·74	0·92	0·90	0·95
$P4$, Lp O(3)	0·123	0·055	0·030	0·49	0·37	0·44	0·49	0·60	0·59	0·75	0·75	0·82

Peak	U (Å^2)	Peak heights after thermal deconvolution
$P1$	0·0043	0·70
$P2$	0·0041	0·98
$P3$	0·0090	1·31
$P4$	0·0100	1·23

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Table 1 we can conclude that the effects of thermal smearing are much larger than those of series termination.

The small values of the charges q as given in Table 2 indicate that the deformation density peaks have smaller 'occupancies' than the valence density peaks. Fritchie (1966) used $q = 0.863$ electrons for the C–C valence peaks; this order of magnitude was confirmed by Coppens (1969). The small values of q for the peaks of the deformation densities arise from the fact that, by subtracting the density of the full isolated atoms from the density of the molecule, a large amount of the charge is also taken from the region of the bond. On the other hand, the magnitude of q is not of primary importance because the attributing of charge to the bonds and to the cores is physically not uniquely defined. A small increase of the region 'bond' gives rise to a large increase of the charge (occupancy), a phenomenon also observed by Hellner (1976).

Conclusion

Although our results for the deconvolution effects were obtained with Gaussian peaks, the order of magnitude is generally valid. Any peak can be represented by a sum of Gaussian distributions centred at different positions, to any desired degree of accuracy. As integration and summation can be interchanged, the convolution integral for a given peak can be represented by a sum of convolution integrals for Gaussian peaks. The main part of a given peak can usually be represented by one Gaussian peak to a reasonable approximation. Hence, our peak-fitting procedure will yield just as reasonable a result. In particular, the condition that the peak heights be correctly represented for several limits of termination proved to be a good criterion for determining the Gaussian distribution. For centrosymmetric peaks the procedure could be extended by fitting two or more Gaussian distributions to the observed peak. This will certainly yield better results, but in most cases such effort will hardly be necessary.

The reconstruction of the true peak can, of course, only be performed where a real peak can be observed in a density map. In particular, the cusps at the atomic nuclei cannot be reconstructed since they disappear in experimental maps. Therefore, our method does not allow us to reconstruct the static density in every detail, but it does provide a means of estimating the true heights of the observed peaks.

If one compares density maps which, on the one hand, are obtained by experiment, and on the other, by quantum-chemical calculation, both corrections are usually necessary. The correction for thermal smearing is usually the larger; fortunately its treatment is mathematically simpler and can in many cases be reasonably performed. The correction for series termination is mathematically less tractable, but should be performed with experimental investigations of a high standard.

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