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Statistical Description of Multimodal Atomic Probability Densities

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Abstract

A general method for describing multimodal atomic densities is presented. It is based on series expansions of a harmonic Gaussian probability density function. The most suitable expansion is of the Gram–Charlier type; its Fourier transform can be easily inserted in a structure factor equation. This statistical method yields a satisfactory fit to the data and allows for a better interpretation of the fit parameters than sophisticated split-atom models. The method is especially useful for weakly resolved modes and allows a better distinction between disorder and anharmonic motion than in conventional Fourier syntheses. Calculations on $CsPbCl_3$, ice I*h* and $RbAg_4I_5$ are presented to show the strengths and the limitations of this method.

1. Introduction

Disordered solids with low transition barriers can be described crystallographically in two fundamentally different ways: (*a*) using split-atom models ('split models') with partial occupancies or (*b*) using anharmonic probability density functions (p.d.f.'s) with full occupancies and more than one local maximum of density ('multimodality'). Only the latter method yields directly physically meaningful model parameters owing to the lack of intersite correlations. It allows a straightforward evaluation of the p.d.f. in the overlap region of the split atoms. The evaluation of the true p.d.f. around the transition barrier is of great importance, *e.g.* in structures of ionic conductors or in hydrogen-bonding situations, and it is in the end indispensable for distinguishing true disorder from pronounced thermal motion.

A generalized model p.d.f. is clearly needed for modelling such a possibly multimodal atomic p.d.f. This general p.d.f. must fulfil the following conditions: (*a*) parametrizability and Fourier transformability to allow inclusion in a least-squares refinement procedure; (*b*) compatibility with symmetry requirements to allow

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an introduction of constraints to the actual point symmetry; and (*c*) ability to be extended to include higher-order terms to allow a sufficient accuracy of description.

Johnson (Johnson, 1969, 1970, 1980; Johnson & Levy, 1974) has brought two series expansions to the attention of crystallographers, the Edgeworth and the Gram–Charlier expansions, both of which fulfil these criteria. A summary of their general properties will be given as a basis for the discussion of their limitations in the case of multimodality. To test their performance in this case a number of neutron data sets were analysed using a program system (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1982) which allows the refinement of the appropriate temperature-factor expressions (*i.e.* the Fourier transforms of the general p.d.f.'s as well as the calculation of the resulting p.d.f.). The examples are chosen to demonstrate on the one hand the ability to distinguish thermal motion from weakly resolved disorder and, on the other hand, the ability to describe systems with rather pronounced disorder.

2. Models for multimodality

Both static and dynamic effects contribute to the temperature factor affecting Bragg intensities measurable in a diffraction experiment. A general statistical approach is able to describe static disorder (space average) in the same way as dynamical disorder (time average). These effects are not distinguishable in an elastic diffraction experiment. On the other hand, weakly resolved disorder (whether static or dynamic in origin) may be distinguished from pronounced anharmonic motion. A conclusive decision in favour of unimodality is limited by the resolution obtainable from a finite data set as well as limited by the fundamental temperature dependency of precision obtainable in a reconstruction of the true p.d.f. Such a decision has therefore to be taken with great care. Nevertheless, under the assumption of smoothly varying true p.d.f.'s a careful inspection of the model p.d.f. allows not only a decision to be made in favour of multimodality (= disorder), it allows in certain cases (see § 5*b*) also a decision in favour of unimodality even with a finite resolution imposed by a limited data set.

A statistical approach to the analysis of thermal motions suitable for multimodal distributions was developed by Johnson (Johnson, 1969, 1970, 1980; Johnson & Levy, 1974). The point of departure is the differential expansion of a trivariate harmonic (Gaussian) p.d.f.:

$$\text{p.d.f.}(\mathbf{u})_{\text{gnrl}} = \text{p.d.f.}(\mathbf{u})_{\text{har}}\left[1 - C^{j}D_{j} + \frac{1}{2!}C^{jk}D_{j}D_{k} - \frac{1}{3!}C^{jkl}D_{j}D_{k}D_{l} + \ldots\right], \tag{1}$$

where $D_j = \mathrm{d}/\mathrm{d}u^j$, $\mathbf{u}$ is the displacement vector, and $C^{j\cdots}$ are tensorial coefficients. The differential operator D_j may be expressed in terms of (Chebyshev) Hermite polynomials by the identity

$$(-D)^{r}\,\text{p.d.f.}(\mathbf{u})_{\text{har}} = H_{R}(\mathbf{u})\,\text{p.d.f.}(\mathbf{u})_{\text{har}} \tag{2}$$

to allow a numerical evaluation of the generalized p.d.f. The three-dimensional Hermite polynomials are tabulated in the literature (Johnson & Levy, 1974; Zucker & Schulz, 1982) up to the sixth order. Hence the evaluation of a generalized p.d.f. is straightforward, resulting in the so-called Gram–Charlier expansion. The explicit formula for the three-dimensional case was given by Mihăilă (1968). To minimize correlation problems in a least-squares refinement, the anharmonic first- and second-order terms are omitted, yielding the standardized form of the Gram–Charlier expansion (up to sixth order)

$$\begin{aligned}\text{p.d.f.}(\mathbf{u})_{\text{GC}} = \text{p.d.f.}(\mathbf{u})_{\text{har}}\Big[1 &+ \frac{1}{3!}C^{jkl}H(\mathbf{u})_{jkl} \\ &+ \frac{1}{4!}C^{jklm}H(\mathbf{u})_{jklm} \\ &+ \frac{1}{5!}C^{jklmn}H(\mathbf{u})_{jklmn} \\ &+ \frac{1}{6!}C^{jklmnp}H(\mathbf{u})_{jklmnp}\Big],\end{aligned} \tag{3}$$

where the coefficients $C^{jkl\cdots}$ are known as quasi-moments (Kuznetsov, Stratonovich & Tikhonov, 1960).

The terms occur in a sequence determined by the successive derivatives of the harmonic p.d.f. This is not necessarily in decreasing order of importance and a different ordering is sometimes used. Edgeworth (1905) collected terms of equal order in the Hermite polynomials and arranged them in ascending order, which gives the Edgeworth expansion. The explicit formula for the three-dimensional case was given by Chambers (1967). In standardized form up to fourth-order terms it reduces to

$$\begin{aligned}\text{p.d.f.}(\mathbf{u})_{\text{EW}} = \text{p.d.f.}(\mathbf{u})_{\text{har}}\Big[1 &+ \frac{1}{3!}K^{jkl}H(\mathbf{u})_{jkl} \\ &+ \frac{1}{4!}K^{jklm}H(\mathbf{u})_{jklm} + \frac{10}{6!}K^{jkl}K^{mnp} \\ &\times H(\mathbf{u})_{jklmnp}\Big],\end{aligned} \tag{4}$$

where the coefficients $K^{jkl\cdots}$ are referred to as cumulants.

Both the quasi-moments in (3) and the cumulants in (4) are expressible in terms of moments and are interconvertible. In the given standardized expressions the lower-order terms do not differ, while the sixth- and higher-order terms do

$$C^{jkl} \triangleq K^{jkl}$$

$$\vdots$$

$$C^{jklmnp} \triangleq K^{jklmnp} + \frac{10}{6!} K^{jkl} K^{mnp}. \qquad (5)$$

In this way each cumulant $K^{jkl\ldots}$ contributes to all higher-order quasi-moment terms (and *vice versa*), whereby in the Edgeworth approximation up to fourth order all combinations higher than the quadratic third cumulant term are assumed to be negligible. Hence the given Edgeworth approximation (4) is to a certain extent arbitrarily truncated (omission of further cross-terms) and should be considered with some care (see also Zucker & Schulz, 1982).

The Fourier transforms of the two expansions (given in § 4) are different, the Gram–Charlier transform being like a Taylor series and exact, the Edgeworth transform being an exponential series and exact only under the above-mentioned assumptions concerning the relative importance of the terms. The resulting superiority of the Gram–Charlier type with respect to the Fourier transformation is obvious. Its superiority in fitting multimodal density distributions remains to be proved.

Whenever anharmonic terms are involved in p.d.f. calculations a distinction between different terms concerning atomic positions has to be made. The 'mean' is simply the first-order term in the series expansion (*i.e.* the refined atom position). The 'mode' is given by a local maximum in the p.d.f. (see also Johnson, 1970). Whenever fourth- or higher-order terms are involved, two or even more modes can exist for one atomic position. A 'saddlepoint' is defined as the point of minimal p.d.f. between two modes.

Multimodal p.d.f.'s can be described by series expansions of the Gram–Charlier or Edgeworth type. These real-space models have the same advantages as the real-space electron density expansions over conventional difference (Fourier) density maps (see, for example, Hirshfeld, 1971, 1977). However, the usually applied double Fourier inversion of the electron density calculations is unnecessary in calculations of a p.d.f.; the p.d.f. may be calculated directly from the parameters, hence reducing random noise, termination-of-series effects and phase errors considerably. The least-squares estimated parameters provide quantitative estimates of all variances and covariances; the estimated standard deviation of the p.d.f. may be calculated from the covariance matrix. The only disadvantage of such a solely 'parameter-based' real-space description is the uncertainty about the genuineness of the underlying model.

3. Limitations of the models

Conditions for positive-definiteness and multimodality have been obtained for the one-dimensional case by Barton & Dennis (1952) [slightly revised by Draper & Tierney (1972)] and for the two-dimensional case by Sarmanov & Bratoeva (1967). More specifically the results of Barton & Dennis show a less restrictive behaviour of the truncated Gram–Charlier-type expansion with respect to the positive-definite combinations of coefficients compared to the truncated Edgeworth type. The matter of interest in this context is the region of multimodality. This region lies well inside the positive-definite region in the one-dimensional case.

For the three-dimensional case we have used a numerical method to survey the performance of these series expansions with respect to multimodality for some typical examples. The first important result is that multimodal p.d.f.'s which are positive everywhere exist neither for the Gram–Charlier nor for the Edgeworth expansion. However, instead of the strict mathematical borderline another limit can be chosen assuming that flat negative regions at the tails of a distribution do not seriously affect the physical meaning of the entire p.d.f. Instead of the limiting surfaces in the multidimensional parameter space of the tensorial coefficients, two derived quantities are used to show the results: (*a*) the 'normalized mean–mode separation', *i.e.* the distance between the mean and the mode position normalized by the square-root of the harmonic second-order term, and (*b*) the p.d.f. ratio of the mode and the mean ('mode/mean ratio'). The results are given in Fig. 1 for symmetrical twofold, threefold and fourfold splittings.

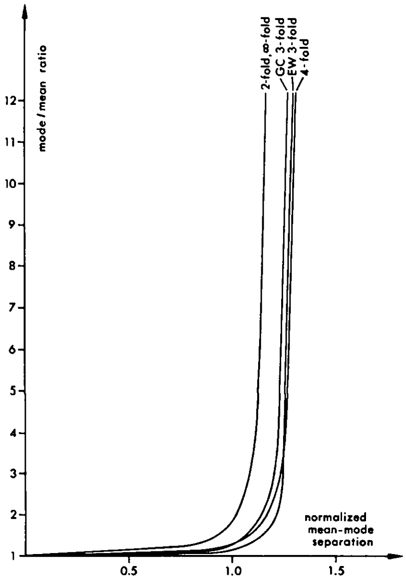

Fig. 1. Normalized mean–mode separation *versus* mode/mean ratio calculated for symmetrical twofold, threefold and fourfold splittings for the Gram–Charlier and Edgeworth expansion. P.d.f.'s with negative regions up to 10% of the probability at the mode position are admitted.

The behaviour of the two expansions in this two-parameter space is well defined. A striking feature is the strong dependence of the mean–mode separation on the normalization factor in the case of high mode/mean ratios. On the other hand, the mean–mode separation becomes strongly dependent on the anharmonic modification terms in the case of low mode/mean ratios. At a mean–mode separation of ~1 a transition from an 'anharmonic-dominated' p.d.f. to a 'harmonic-dominated' p.d.f. occurs. In the anharmonic-dominated region the model is quite flexible. The restrictions in this region concern mainly the mode/mean ratio (only small ratios obtainable), but due to the almost smoothly shaped atomic p.d.f. this is not a serious limitation. On the other hand, both parameters, the mode/mean ratio and the mean–mode separation, are equally important in the harmonic-dominated region; therefore, the model is less flexible in this region.

In the case of three- and fourfold splittings the limiting line for a maximal 'mode/saddle ratio' (*i.e.* the p.d.f. ratio of the mode and the saddle point) is given. Depending on this ratio the whole range between these limiting lines and the ∞-fold case is obtainable (a mode/saddle ratio of 1 means ∞-fold splitting, *i.e.* a circular or spherical distribution of mode positions).

Even-fold splitting can be achieved by adding appropriate even-order modification terms to the harmonic p.d.f., while odd-fold (*i.e.* threefold) splitting is achieved by adding a combination of odd- and even-order terms. Odd-order terms solely are not sufficient, because they always give strongly negative p.d.f.'s. Both truncated expansions [equations (3) and (4)] behave identically for even-order splittings, provided that third-order terms are omitted. Whenever third-order terms are involved, the Edgeworth type behaves differently owing to the quadratic third cumulant term; as in the one-dimensional case, the Gram–Charlier type allows for a better resolved mode separation compared to the Edgeworth type.

Globally these test calculations suggest that at least the mode resolving power of both expansions is sufficient to attack delicate problems of atomic splittings in crystal structures, while the flexibility of these models in the case of highly separated modes is limited.

4. Refinement strategy

Owing to their generality these statistical models of multimodal density distributions may in some cases be less satisfactory compared to more specific models; for example, multimodal density distributions of rotating molecules can be described more successfully by means of symmetry-adapted surface harmonics (Press & Hüller, 1973, 1978; Press, 1973; Hüller & Press, 1979; Press, Grimm & Hüller, 1979). Even simple split models may be more powerful in fitting structural data; however, the physical interpretation of these split models is aggravated, because it has to be made *via* a conventional Fourier synthesis with its limited resolving power (see § 5*b*) or *via* sophisticated split-atom p.d.f. superpositions. As pointed out by Hutton & Nelmes (1981), a direct interpretation of these split models in terms of conventional disorder is misleading in some cases. Moreover, the parameter set itself is usually strongly affected by high interatomic correlations (sometimes preventing convergence in the least-squares refinement) in contrast to the multimodal description, which still remains a one-particle model.

The adequacy of the statistical approach to multimodality has been tested by performing least-squares refinements on actual data. The Fourier transforms of equations (3) and (4) respectively were inserted in a standard least-squares routine (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1982) yielding the following structure factor expressions:

$$\begin{aligned} F(\mathbf{h})_{\mathrm{GC}} = \sum_j f_j \exp(2\pi i x_j^q h_q - b_j^{qr} h_q h_r) \\ \times [1 - \tfrac{4}{3}\pi^3 iC_j^{qrs} h_q h_r h_s \\ + \tfrac{2}{3}\pi^4 C_j^{qrst} h_q h_r h_s h_t \\ + \tfrac{4}{15}\pi^5 iC_j^{qrstu} h_q h_r h_s h_t h_u \\ - \tfrac{4}{45}\pi^6 C_j^{qrstuv} h_g h_r h_s h_t h_u h_v] \qquad (6) \end{aligned}$$

$$\begin{aligned} F(\mathbf{h})_{\mathrm{EW}} = \sum_j f_j \exp[i(2\pi x_j^q h_q - K_j^{qrs} h_q h_r h_s) \\ - (b_j^{qr} h_q h_r - K_j^{qrst} h_q h_r h_s h_t)], \qquad (7) \end{aligned}$$

where f_j is the atomic form factor (or neutron scattering length) of atom j, x_j are the positional parameters, b_j the harmonic parts of the temperature factor and C_j and K_j the anharmonic quasi-moments and cumulants, respectively.

A general problem of these refinements is the number of refinable parameters. Even if in special cases refinements with ratios of reflections per parameter as small as two or three are feasible, a ratio of five seems to be desirable assuming the high-precision diffraction data available nowadays. In the general triclinic case there are 83 free parameters/atom up to sixth order. Owing to the normally low dimensionality of disorder, very often a limited number of these are really important. Therefore, the problem may be reduced dramatically by systematically setting non-significant parameters to zero or by using the contracted tensor model as proposed by Johnson (1980). The first method is relatively time-consuming, the fastest procedure being a destructive one, *i.e.* to refine all parameters of an atom at the beginning and then setting all non-significant parameters back to zero. If the initial refinement is not successful a constructive method may be chosen instead, moving from a lower-order expansion to consecutively higher-order ones and reducing in each order the number of parameters as described above.* Both procedures are uncritical (*i.e.* not affecting the final result) in the case of low correlations between terms of equal order (normally 0·10–0·20, exceptionally 0·50–0·60). In the case of very high correlations between terms of equal order (>0·90) constraints among these parameters may be introduced. Whenever large but insignificant terms occur, the order of expansion should be reduced (or better the data set should be improved).

The strong interactions among even-order terms and among odd-order terms are sometimes overestimated. As long as the refinement is converging even very high correlations are not a serious problem, because the entire parameter set is interpreted *via* the p.d.f. rather than individual terms. However, in addition to the conventional tests of the refinement results a visual check of the correctness of the p.d.f. is indispensable; deep negative regions are hardly acceptable. It should be noted that in all cases the harmonic terms lose their direct physical meaning; a meaningful interpretation is obtainable only by inspection of the complete p.d.f.

5. Test refinements

Neutron data sets on $CsPbCl_3$ (Nelmes, 1981), ice I*h* (Kuhs & Lehmann, 1981) and $RbAg_4I_5$ (Kuhs, Lehner & Heger, 1983) were used for the test refinements. They illustrate the strengths and the limits of multimodal p.d.f.'s for modelling atomic disorder. In $CsPbCl_3$ any disorder present is expected to be slight, ice Ih contains highly disordered H atoms with questionable additional weak splittings and the Ag atoms in the ionic conductor $RbAg_4I_5$ behave in an extremely anharmonic way. Different independent methods were used to check the correctness of the multimodal p.d.f.'s obtained.

(*a*) $CsPbCl_3$

The antiferroelectric perovskite $CsPbCl_3$ in its cubic high-temperature phase is one of the best investigated compounds with respect to disorder and anharmonic thermal motions (Møller, 1959; Harada, Sakata, Hoshino & Hirotsu, 1976; Hutton, Nelmes, Meyer & Eriksson, 1979; Sakata, Harada, Cooper & Rouse, 1980; Ahtee, Kurki-Suonio, Vahvaselkä, Hewat, Harada & Hirotsu, 1980; Hutton & Nelmes, 1981). The data set used in our calculations was collected by Hutton *et al.* (1979) on the *D*9 four-circle diffractometer at the ILL at a temperature of 325 K, *i.e.* 5 K above the phase transition. The data were corrected for TDS (Nelmes, 1981) and for extinction using the model of Becker & Coppens (1974*a*,*b*). Our refinements focused on the determination of the actual p.d.f. of the Cl atom using the Gram–Charlier as well as the Edgeworth formalism.

In most of the investigations following on Møller's (1959) first study an (anharmonic) unimodal p.d.f. of Cl was preferred, rather than a multimodal one. The high-resolution studies by Hutton *et al.* (1979) and Hutton & Nelmes (1981) ruled out completely the occurrence of a multimodal p.d.f. These authors refined an anharmonic model using a Fourier-invariant expansion; compared to a split model it gave a significantly better fit to the data. To estimate the model-inherent errors they performed test refinements on structure factors calculated from trial p.d.f.'s.

Our refinement results are in agreement with this study apart from the fact that, compared with the Fourier-invariant technique, the Gram–Charlier expansion yields a better fit to the data for terms up to fourth order inclusive, while approximately the same quality of fit is obtained for terms up to sixth order inclusive. In contrast to the Fourier-invariant approximation the inclusion of Gram–Charlier sixth-order terms does not improve the fit. The results are given in Table 1. The application of the Edgeworth formalism yields a worse fit to the data (up to fourth order: R_w = 3·4%, goodness-of-fit S = 1·15 for Gram–Charlier; R_w =

Table 1. *Survey of data sets and agreement factors*

	$CsPbCl_3$	Ice I*h*	$RbAg_4I_5$
	*Pm*3*m*	$P6_3/mmc$	$P4_132$
V (Å^3)	176·09	128·21	1427·6
Z	1	4	4
Temperature (K)	325	60	297
λ_{neutron} (Å)	0·656	0·7107	0·8436
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	1·23	1·07	0·685
Number of observations N_R (averaged)	209	288	434
Atoms treated and site symmetry	Cl (4/*mmm*)	H(1) ($\bar{6}m2$) H(2) (2/*m*)	Ag(1)
R_w (%) ($w = 1/\sigma^2$)			
split	3·6	1·2	anh: 1·2‡ har: 4·5
non-split (Gram–Charlier)	(I)† 3·4 (II) 3·3	H(1) 1·5 H(2) 1·8	(III) 4·6 (IV) 4·0
Number of refined parameters N_P			
split	11	25	anh: 83 har: 31
non-split (Gram–Charlier)	(I) 11 (II) 13	H(1) 14 H(2) 25	(III) 44 (IV) 63
Goodness of fit, S*			
split	1·24	1·71	anh: 2·88 har: 7·92
non-split (Gram–Charlier)	(I) 1·15 (II) 1·13	H(1) 2·06 H(2) 2·57	(III) 8·30 (IV) 7·43

* The goodness-of-fit is defined as

$$S = [\textstyle\sum_{hkl}(w\Delta F_{hkl})^2/(N_R - N_P)]^{1/2}.$$

† (I) Model up to fourth order. (II) Model up to sixth order. (III) Model *A* (see Fig. 6). (IV) Model *B* (see Fig. 6).

‡ anh: anharmonic; har: harmonic.

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* In some cases it may be necessary to start the refinement from plausible non-zero anharmonic parameters.

4·3%, $S = 1{\cdot}49$ for Edgeworth) in agreement with the results of Hutton *et al.* (1979).

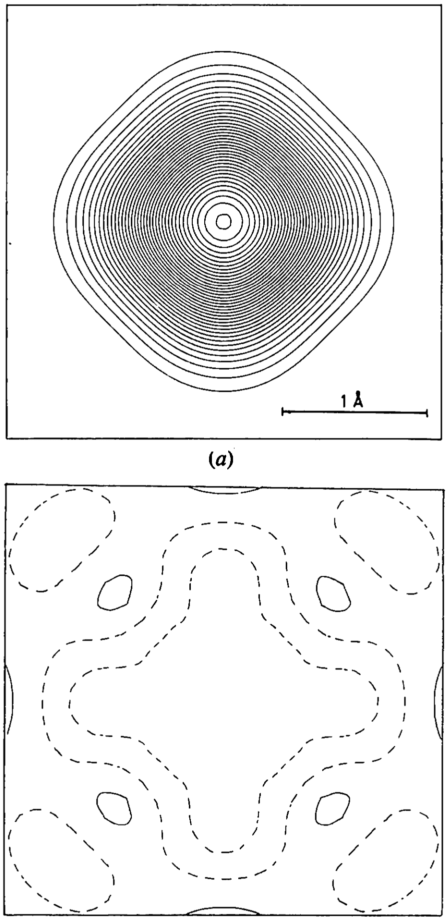
First tests on the correctness of the p.d.f. by means of difference Fourier syntheses show no indication of any incorrectness of the obtained p.d.f. On a finer scale the power of the Gram–Charlier expansion to discriminate between unimodality and weak multimodality was examined by calculation of trial p.d.f.'s. It was found that the refined parameter set is far from the transition region between unimodality and disorder, allowing an unambiguous decision in favour of a unimodal p.d.f.

The concerted action of all model parameters allows for a widely variable shape of the resulting p.d.f. and thus an essentially correct description of the true p.d.f. (indicated further by the obtained quality of fit). This is, although not conclusively, supported by a comparison of the model p.d.f.'s obtained by Gram–Charlier and Fourier-invariant expansions in a least-squares refinement. Notwithstanding the rather different approaches, the two p.d.f.'s are almost identical, as shown in Fig. 2. A more detailed comparison of Gram–Charlier and Fourier-invariant expansions is in preparation.

(*b*) *Ice* I*h*

The main features of the crystal structure of ice I*h* are well established by the neutron diffraction studies of Peterson & Levy (1957) and Chamberlain, Moore & Fletcher (1973). Its crystal structure seems to be of special interest in this context because of the observed or postulated occurrence of different multimodal atomic density distributions. The two independent H atoms, H(1) and H(2), show a distinct disorder along the O···O directions. Apart from this well-established disorder a further splitting was proposed by Chidambaram (1961). In his 'bent-hydrogen-bond' model the H(1) atom is further split into three positions around the O···O line yielding an H—O—H angle of approximately 104·5° as observed in H_2O vapour. This undoubtedly weak splitting may be detectable by careful inspection of the calculated p.d.f.'s. To study all these split situations in detail a neutron data set on ice I*h* was collected at the four-circle diffractometer *D*9 of the ILL at a temperature of 60 K. The preliminary results are given elsewhere (Kuhs & Lehmann, 1981); in the following only the different split models and their approximations will be discussed.

In order to test the ability to describe the pronounced H-atom splitting, test refinements using the Gram–Charlier as well as the Edgeworth expansion were performed. Only one H atom [either H(1) or H(2)] at a time was refined in this way, their mean position being fixed midway between two neighbouring O atoms. Compared with a conventional split model the quality of fit in the Gram–Charlier approximation is slightly worse. Refinements using the Edgeworth formalism were not successful yielding intolerably high *R* values and highly negative p.d.f.'s. Probably these negative p.d.f.'s are partly due to the fact that for strong anharmonicities the omitted higher-order contributions [*cf.* equations (4) and (5)] are necessary to construct the correct p.d.f. Beyond that the bad fit ($R_w \simeq 10\%$, $S > 10$) undoubtedly indicates an inadequacy of the Edgeworth model in reciprocal space. The refinement results are given in Table 1 and the bimodal p.d.f. of H(1) as obtained by the Gram–Charlier expansions is shown in Fig. 3. There are shallow negative regions at the tails of the Gram–Charlier p.d.f.'s as deep as 8·6% [H(1)] and 4·7% [H(2)] of the density at the corresponding mode position. Despite these minor shortcomings, one advantage of the Gram–Charlier model is important; the H probability density at the



(*a*)

(*b*)

Fig. 2. (*a*) P.d.f. map of the Cl atom in $CsPbCl_3$ at 325 K (Cs–C plane). Gram–Charlier expansion up to sixth order using least-squares estimated quasi-moments. Equidistant contours, zero contour omitted. (*b*) Corresponding difference p.d.f. map ($\text{p.d.f.}_{\text{Gram–Charlier}} - \text{p.d.f.}_{\text{Fourier invariant}}$). The two p.d.f.'s are scaled to the same probability at the centre. Equidistant contours of 1‰ of the probability at the centre, zero contour omitted, negative contours dashed.

transition barrier is obtainable directly by inspection of the p.d.f. It should be mentioned in this context that for a data set on ice I*h* measured at 223 K the quality of fit of the non-split model becomes slightly better compared to the harmonic split model (R_w = 3·0%, goodness-of-fit S = 1·33 for non-split; R_w = 3·1%, S = 1·37 for split model; see Kuhs & Lehmann, 1983).

The bimodal p.d.f. obtained was compared with a Fourier density map; in this clearly disordered centrosymmetric case the Fourier method should give very reliable results. The agreement is satisfactory, the mode/saddle ratio being 10·7 (1·8) for the Fourier synthesis and 8·7 (0·9) for the model p.d.f. The smaller ratio in the model p.d.f. is probably due to an overestimation of the density at the transition barrier (= saddle point) as confirmed by a difference Fourier synthesis of the non-split model.

A confirmation of the correctness is the agreement of the intrasite mode–mode distances (non-split model) with the intersite mode–mode distances (split-atom model): 0·718 (7) Å (intrasite) compared to 0·724 (5) Å (intersite) for H(1); and 0·720 (7) Å compared to 0·728 (5) Å for H(2), respectively. However, the width of the p.d.f. of each (half-occupied) position is distinctly (maximum 20%) smaller for the split model compared to the non-split model. The agreement is satisfactory for the p.d.f.'s at 223 K. The discrepancy at 60 K is caused by a lack of flexibility of the non-split model for the case of high mode/mean ratios (see § 3), while at 223 K the model matches probably rather well with the true p.d.f.

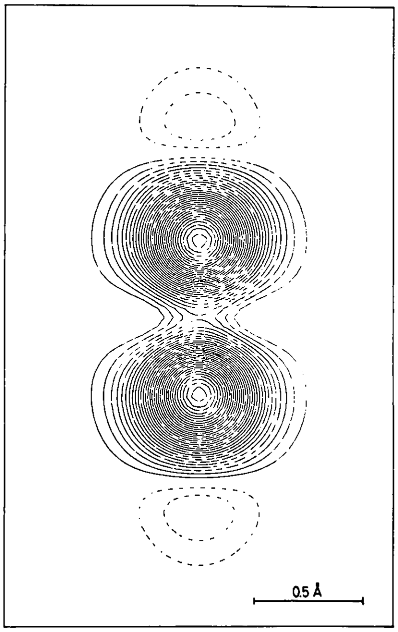


Fig. 3. P.d.f. of H(1) in ice I*h* at 60 K [section through mean positions of O and H(1) parallel to *ac* plane]. Equidistant contours, zero contour omitted, negative contours dashed.

The question of further splitting of H(1) according to the 'bent-hydrogen-bond' model can now be investigated. The proposed splitting is very weak with mean-mode distances estimated to be ~0·08 Å. Trial p.d.f.'s using the Gram–Charlier expansion show clearly the flexibility of this model for describing a 'bent-hydrogen-bond' situation; the result of such a trial p.d.f. is given in Fig. 4. However, the parameters obtained by least-squares refinements do not indicate a trimodal p.d.f.

The 'bent-hydrogen-bond' model implies a 'flatness' of the p.d.f. near the mean position achieved by important higher even-order terms of the series expansions as well as properly directed modifications achieved by third-order terms. The fourth-order (and sixth-order) terms are, however, very weak and indicate in contrast to expectations a 'peakedness' of the p.d.f., while the third-order terms yield only small intimations of directional modifications of the p.d.f. and, moreover, these modifications are just in the opposite directions as predicted by the 'bent-hydrogen-bond' model. The p.d.f. obtained shows strong libration around the O—H bond direction practically without any preference in orientation. The isotropy of libration is clearly visible in Fig. 5. The relative success of the 'bent-hydrogen-bond' model in structure refinements is due to the resemblance of the true p.d.f. to a superposition of three harmonic p.d.f.'s (Kuhs & Lehmann, 1981). Based on the assumption of always smoothly varying true p.d.f.'s, a disorder corresponding to this model can be ruled out with a very high probability simply by inspection of the 'kurtosis'

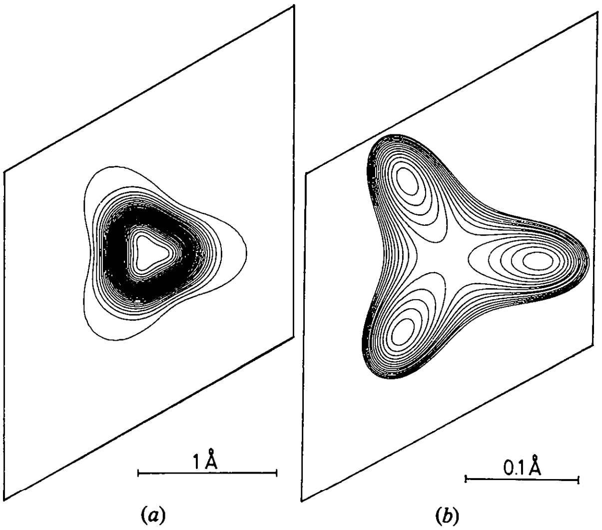


Fig. 4. (*a*) Trial p.d.f. of H(1) in ice I*h* [section through mode position of H(1) parallel to *ab* plane] simulating a 'bent-hydrogen-bond' situation (mean-mode distance ~0·08 Å). Equidistant contours, zero contours omitted. (*b*) Detail of (*a*) showing the central part of the trial p.d.f. Equidistant contours, intervals 50× finer than in (*a*).

map (*i.e.* a map showing only the fourth-order modifications to the harmonic density); the 'peakedness' found in this case combined with any type of disorder would result in a rather erratic and therefore unlikely true p.d.f.

(*c*) $RbAg_4I_5$

Finally, a data set on the crystal structure of $RbAg_4I_5$ was used to test the case of strong anharmonicities and distinct disorder. $RbAg_4I_5$ is a cubic fast-ionic conductor with the highest known Ag^+ conductivity at room temperature. Accordingly, the atoms are smeared out along channels within a tetrahedral framework of I atoms. The Ag density distribution is not homogeneous along these conduction pathways, but shows preferred sites (Geller, 1967; Geller, Akridge & Wilber, 1979). A neutron diffraction study was performed to clarify the situation of these Ag positions. The neutron data were measured at the four-circle diffractometer *D*9 at the ILL and corrected for TDS (Merisalo & Kurittu, 1978). Detailed results of this study will be given in a forthcoming paper (Kuhs, Lehner & Heger, 1983). Only the Ag atoms will be discussed in some detail here.

Structure refinements of a harmonic split model (including two split atoms) give a poor fit (see Table 1). Harmonic models containing more than two split atoms (as proposed by Geller, 1967; Geller *et al.*, 1979) could not be refined at all. The introduction of anharmonic parameters up to the fifth order in the two-atom model improved the quality of the fit considerably (see Table 1). The resulting Fourier synthesis given in Fig. 6 shows clearly the conduction pathways with the preferred Ag sites. Starting from this Ag distribution two non-split models covering different parts of the structure were tested (indicated in Fig. 6). To deal with the numerous parameters resulting from the low symmetry and the high order of included terms, a parameter reduction as discussed in § 4 was performed. Fully converged refinements were achieved for both models. However, the quality of fit was not completely satisfactory (see Table 1), indicating some

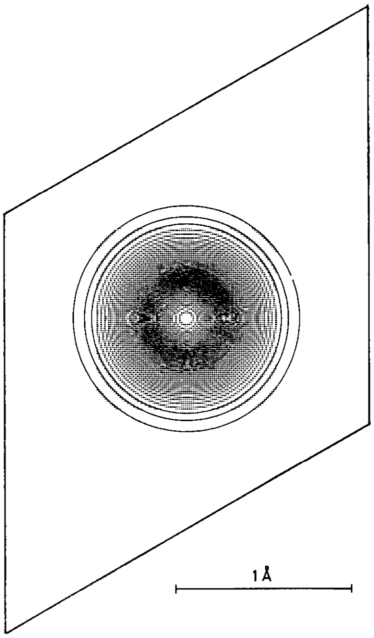


Fig. 5. Model p.d.f. of H(1) in ice I*h* [section through mode position of H(1) parallel to *ab* plane]. Gram–Charlier expansion up to fourth order using least-squares estimated quasi-moments. Equidistant contours, zero contour omitted.

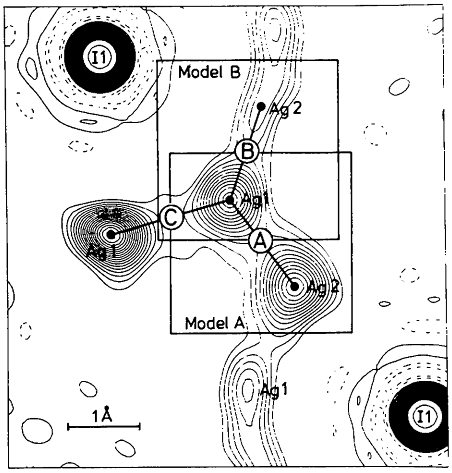


Fig. 6. Fourier synthesis of $RbAg_4I_5$ at 298 K (section $z = 0$) based on the anharmonic split model. Equidistant contours at $0{\cdot}0021 \times 10^{-12}$ cm Å^{-3}, higher levels at $0{\cdot}021 \times 10^{-12}$ cm Å^{-3}, zero contour omitted, negative contours dashed. The regions covered by the non-split models are indicated (models *A* and *B*) as well as the barriers between the Ag positions. The mean positions of the non-split models are situated approximately at these barriers (Ⓐ and Ⓑ).

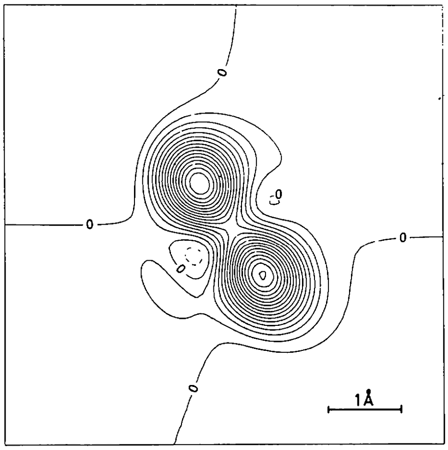


Fig. 7. P.d.f. of Ag as obtained from the non-split model *A* (section $z = 0$). Equidistant contours, zero contour marked, negative contours dashed.

serious difficulties in describing the true p.d.f.'s. The multimodal p.d.f.'s of the non-split models are shown in Figs. 7 (model *A*) and 8 (model *B*) respectively. While the p.d.f. of model *A* corresponds reasonably well to the Fourier density, the agreement for model *B* seems to be less favourable. Hardly tolerable negative regions as deep as 15·3% of the density at the mode position are found in the p.d.f. of model *B* (6·5% for model *A*).

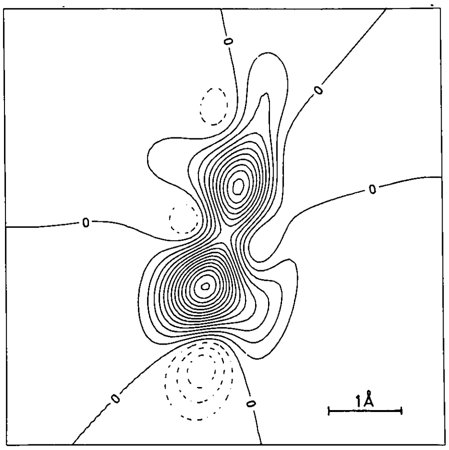


Fig. 8. P.d.f. of Ag as obtained from the non-split model *B* (section $z = 0$). Contours as in Fig. 7.

Table 2. *Mean barrier heights in* $RbAg_4I_5$

Barrier (see Fig. 6)	ΔH (in eV) obtained by Fourier synthesis	non-split p.d.f.
A	0·037	0·039
B	0·049	0·046
C	0·063	Model not refined

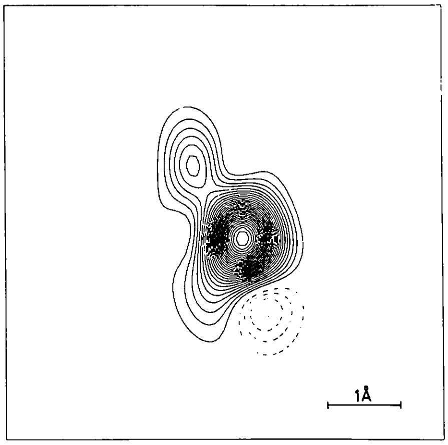


Fig. 9. P.d.f. of Ag(2) (section $z = 0$) as obtained from the anharmonic split model (note the multimodality). Equidistant contours, zero contour omitted, negative contours dashed.

Apart from the quality of fit and the positive-definiteness of the p.d.f. a further criterion of the correctness of these models may be used, *i.e.* the total amount of Ag obtained by refining the Ag population parameters. The theoretical value is 16/unit cell, while the refined values are (standard deviations in parentheses): 14·85 (0·24) for the harmonic split model, 15·56 (0·18) for the anharmonic split model, 14·88 (0·22) for model *A*, and 14·73 (0·21) for model *B*. These results indicate again the shortcomings of the harmonic split as well as both non-split models with respect to the anharmonic split model.

An additional independent criterion for the correctness of these models is the agreement of the activation energy for ionic migration obtained from the atomic probability density with the measured activation energy. Interpreting the Fourier density as true probability density and assuming classical Boltzmann statistics one can estimate the mean barrier heights from a conventional Fourier synthesis. The values obtained in this way compare well with those calculated from the non-split model p.d.f.'s, as shown in Table 2. The measured activation energies in $RbAg_4I_5$ range from 0·06 to 0·12 eV (1 eV = $1·6 \times 10^{-19}$ J) (Bentle, 1968; Owens & Argue, 1970; Nagao & Kaneda, 1975), which is in reasonable agreement with the limiting barrier *C* (see Fig. 6) obtained from the Fourier synthesis. One might argue that the estimations from structural data *via* p.d.f.'s or Fourier syntheses are slightly too low. The continuous Ag density probably limits the applicability of any isolated-atom approach and certainly prevents an easy interpretation of the resulting p.d.f.'s.

Although the application of non-split models seems not to be the appropriate method, the statistical approach to multimodal atomic density distributions is still a powerful tool. In fact, even the anharmonic split models consist of multimodal p.d.f.'s. The complex Ag density can be described adequately by a superposition of a unimodal with such a bimodal p.d.f. (shown in Fig. 9). These p.d.f.'s are not interpretable in an easy way and even considerably negative regions occur due to the superposition. The sole advantage of these multimodal anharmonic split models is their success in the fitting procedure. A physical interpretation can be performed *via* an inspection of the resulting Fourier synthesis or by a careful superposition of the obtained p.d.f.'s.

6. Concluding remarks

A general method for describing multimodal atomic density distributions using well known series expansions of a Gaussian p.d.f. is discussed. Such series expansions are included in some structure refinement programs or can be inserted without any difficulties; no modifications are necessary to switch from a simple anharmonic unimodal case to the multimodal case. Using high-quality diffraction data a refinement of high-order thermal parameters describing multimodal density distributions is feasible and a distinction between disorder (multimodality) and anharmonic motions (unimodality) is possible in many cases. It was found that the two series expansions tested are not equally successful. The Gram–Charlier expansion was clearly superior to the Edgeworth expansion and its superiority increases with the degree of disorder (*cf.* Zucker & Schulz, 1982). However, there may be situations in which the Edgeworth transform yields a better fit to the data. There is at the moment little to choose between the Gram–Charlier and the Fourier-invariant expansion with respect to the quality of fit. However, the Gram–Charlier approach has important computational advantages, mainly due to its generally valid (symmetry-independent) tensor expression.

The Gram–Charlier expansion is successful especially in the case of weak disorder; nevertheless, rather pronounced multimodal densities may be described sufficiently well with a rather limited number of terms. In the extreme case of continuous density distributions, as in ionic conductors, the method may yield unsatisfactory results or fail completely. In these complex cases strong anharmonic terms are needed even in the split models. The only way to visualize these density distributions is by means of Fourier syntheses or by careful superpositions of the split-model p.d.f.'s. Such channel-like multi-peaked density distributions are reasonably reproduced in a Fourier map. The Fourier approach, however, often fails in borderline cases, while the p.d.f. approach is still suitable due to its ability to uncover tendencies towards either unimodal or multimodal p.d.f.'s; hence, both methods are to some extent complementary. The information drawn from an experimentally obtained p.d.f. has to be considered carefully in the light of obtainable resolution (limited by the measured range in reciprocal space) as well as the temperature dependency of precision at different levels of this p.d.f.; weak splittings (situated normally at the highest levels of a p.d.f.) are less and less precisely scanned as temperature increases.

Neutron data are clearly preferable to X-ray data for investigations of disordered systems due to the lack of interference with electronic effects. In the X-ray case an analysis of atomic distributions has to be based on the p.d.f. (or a split-atom p.d.f. superposition); Fourier methods are not appropriate in general.

In addition to the systems considered in this paper our method has been applied to a number of other compounds, describing their multimodal density distributions with great success [*e.g.* Cu_6PS_5Cl and Cu_6PS_5Br (Kuhs & Heger, 1980)]. Further obvious applications are hydrogen-bond systems with H-atom splitting (*e.g.* in many ferroelectrics) or structures with questionable disorder [*e.g.* β-quartz (Wright & Lehmann, 1981)].

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An Empirical Method for Correcting Diffractometer Data for Absorption Effects

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Abstract

Absorption effects usually present the most serious source of systematic error in the determination of structure factors from single-crystal X-ray diffraction measurements if the crystal is not ground to a sphere or cylinder. A novel method is proposed for the correction of these effects for data collected on a diffractometer. The method works from the premise that the manifestation of systematic errors due to absorption, unlike most other sources of systematic error, will not be evenly distributed through reciprocal space, but will be localized. A Fourier series in the polar angles of the incident and diffracted beam paths is used to model an absorption surface for the difference between the observed and calculated structure factors. Knowledge of crystal dimensions or linear absorption coefficient is not required, and the method does not necessitate the measurement of azimuthal scans or any extra data beyond the unique set. Moreover, application of the correction is not dependent upon the Laue symmetry of the crystal or the geometry of the diffractometer. The method is compared with other commonly used corrections and results are presented which demonstrate its potential.

1. Introduction

In the course of a single-crystal structure determination, two methods are frequently used for the correction of absorption effects for crystals of arbitrary shape.

The numerical integration method of Busing & Levy (1957) requires that the faces of the crystal are indexed and their distance from a common point within the crystal is accurately determined. Precise measurement of the crystal becomes critical for those with a high linear absorption coefficient [see equation (2.4)]. The presence of an external absorber such as crystal mother liquor or any adhesive used in the mounting of the crystal, or lack of identifiable faces, will also produce serious problems for this approach. Furthermore, without a very powerful computer, considerable time is required for the evaluation of the integral by the Gaussian algorithm of Coppens, Leiserowitz & Rabinovich (1965) to a suitable accuracy.

The semi-empirical correction method for diffractometer data of North, Phillips & Mathews (1968) requires the measurement of azimuths ψ for a single reflection by rotating the crystal about the goniometer-head axis φ (Fig. 1). The resultant transmission curve is normalized and hence provides only a relative correction. Though widely used in small-molecule structure determinations, the method has three serious limitations. An unfavourable crystal mounting for data collection on an Enraf–Nonius CAD4 diffractometer (which utilizes κ rather than Eulerian cradle geometry), can render it impossible to record a complete azimuthal scan for any reflection. This problem can be averted if the crystal is mounted so that a reciprocal-lattice axis is approximately coincident with the φ axis. Not only is it inconvenient to remount a crystal where its morphology did not allow a satisfactory initial alignment to be made, but this restraint negates the advantages of automatic orientation systems present on modern diffractometers. Secondly, an observed change in the intensity of a reflection with azimuth ψ may be due to anisotropic primary extinction (Seiler & Dunitz, 1978) or aniso-

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