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Exact Conditional Distribution of a Three-Phase Invariant in the Space Group P1. III. Construction of an Improved Cochran-Like Approximation

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Abstract

An exact representation of the accurately computable conditional probability density function (c.p.d.f.) of the three-phase invariant for the space group P1 was developed in paper I of this series [Shmueli, Rabinovich & Weiss (1989). *Acta Cryst.* A**45**, 361–367]. The computation of this function is too time-consuming for it to be of practical value. It is therefore desirable to find simple approximations based on the exact result that may be more accurate than the familiar Cochran approximation or its extensions. One such approximation, presented here, has the same functional form as the Cochran approximation but with a modified parameter in place of that appearing in Cochran's distribution. Some of the numerical procedures used in the estimation of this modified parameter are also discussed.

Introduction

One of the earliest and still the most frequently employed phase-dependent quantities is the three-phase structure invariant, which is the phase of the

triple product $E(\mathbf{h})E(\mathbf{k})E(-\mathbf{h}-\mathbf{k})$. The phase information of interest is extracted from these invariants with the aid of a combination of deterministic and probabilistic relationships. Among the most important of these is the conditional probability density function (c.p.d.f.) of the phase sum,

$$\Phi = \varphi_\mathbf{h} + \varphi_\mathbf{k} + \varphi_{-\mathbf{h}-\mathbf{k}},\qquad(1)$$

where $\varphi_\mathbf{h}$ is given by $\exp(i\varphi_\mathbf{h}) = E(\mathbf{h})/|E(\mathbf{h})|$ and Φ is independent of the choice of the space-group origin. The distribution of Φ is, in general, conditioned on some constants that characterize the crystal, such as the atomic composition of the asymmetric unit, the space-group symmetry, the extent of noncrystallographic symmetry and anomalous dispersion, and on the magnitudes $|E(\mathbf{h})|$, $|E(\mathbf{k})|$ and $|E(-\mathbf{h}-\mathbf{k})|$. These magnitudes will be denoted, for brevity, by E_1, E_2 and E_3, respectively. The approximation to the c.p.d.f. derived by Cochran (1955) on the basis of the central limit theorem is

$$p(\Phi|E_1, E_2, E_3, N) = [2\pi I_0(\kappa)]^{-1}\exp(\kappa\cos\Phi),\qquad(2)$$

where, in the equal-atom case, κ is given by

$$\kappa = 2N^{-1/2}E_1E_2E_3,\qquad(3)$$

$I_0(x)$ is a modified Bessel function and N is the number of atoms in the unit cell. Equation (2) can be generalized in a number of different ways. These include expansions in terms of orthogonal polynomials (see, for example, Naya, Nitta & Oda, 1965; Hauptman, 1971; Giacovazzo, 1974) and variants of the exponential distribution (Karle, 1972; Karle & Gilardi, 1973; Peschar & Schenk, 1986). These corrections to (2) are given in terms of rather lengthy expressions, the convergence properties of the resulting sums can be rather poor, and they have therefore had limited applications in practical problems.

An alternative approach to the general problem of calculating expressions for probability densities for both intensity statistics and direct methods is to find the c.p.d.f. starting from an exact expression for the corresponding characteristic function. This strategy has been adopted in a series of papers, following the initial suggestion by Shmueli, Weiss, Kiefer & Wilson (1984), and results in Fourier expansions of the desired densities, in which the coefficients are expressible in terms of the characteristic functions evaluated at the appropriate values of the arguments. Exact representations of the characteristic functions are available for most space groups (Rabinovich, Shmueli, Stein, Shashua & Weiss, 1991) and their application to finding numerical univariate distributions presents no problems in practice (Shmueli, Weiss & Kiefer, 1985; Shmueli & Weiss, 1987, 1988). The successful application of these ideas to univariate distributions encouraged us to extend them to multivariate densities, required for the implementation of direct methods. At present there are three such calcu-

lations available: that for the densities of $\sum_1$ (Shmueli & Weiss, 1985) and $\sum_2$ (Shmueli & Weiss, 1986) in the space group $P\bar{1}$ and that for the three-phase invariant (Shmueli, Rabinovich & Weiss, 1989a, b) in the space group $P1$.

In this paper, we intend briefly to summarize an exact derivation of the c.p.d.f. of the three-phase invariant in $P1$, comparing the numerical results to those found from Cochran's approximation, and derive a new approximation based on accurate numerical results computed by the techniques of Shmueli $et\ al.$ (1989a, b). Our suggested approximation takes the form of Cochran's (1955) result given in (2) with a modified definition of the parameter κ that appears in that equation. We calculate this parameter for a range of values of E_1, E_2, E_3 and N. Preliminary results obtained by this approach have been given elsewhere (Shmueli & Weiss, 1990).

The Fourier c.p.d.f. of the three-phase invariant

We shall now describe briefly the general form of the exact expression for the c.p.d.f. of Φ, as given by (1), given the magnitudes $|E(\mathbf{h})|$, $|E(\mathbf{k})|$ and $|E(-\mathbf{h}-\mathbf{k})|$, the symmetry of the crystal and the composition of the asymmetric unit, as obtained by Shmueli $et\ al.$ (1989a, b) and applied to the space group $P1$. The following additional abbreviations will be used:

$$\varphi_\mathbf{h} \equiv \varphi_1, \quad \varphi_\mathbf{k} \equiv \varphi_2, \quad \varphi_{-\mathbf{h}-\mathbf{k}} \equiv \varphi_3\qquad(4)$$

and

$$E(\mathbf{h}) \equiv A_1 + iB_1 \equiv E_1(\cos\varphi_1 + i\sin\varphi_1)\qquad(5)$$

$etc.$ for $\mathbf{k}$ and $-\mathbf{h}-\mathbf{k}$. The main stages of the derivation are:

1. Expansion of the joint p.d.f. of A_1, B_1, A_2, B_2, A_3 and B_3 in the sixfold Fourier series

$$p(\mathbf{E}) = (\alpha/2)^6 \sum_\mathbf{u} C_\mathbf{u}$$

$$\times \exp\left[-\pi i\alpha\sum_{k=1}^{3}(u_{2k-1}A_k + u_{2k}B_k)\right]\qquad(6)$$

$$= (\alpha/2)^6 \sum_\mathbf{u} C_\mathbf{u}$$

$$\times \exp\left[-\pi i\alpha\sum_{k=1}^{3}D_k\cos(\varphi_k - \Delta_k)\right],\qquad(7)$$

where

$$\mathbf{E}^T = (A_1, B_1, A_2, B_2, A_3, B_3),\qquad(8)$$

$$\mathbf{u}^T = (u_1, \ldots, u_6),\qquad(9)$$

$$D_k = E_k(u_{2k-1}^2 + u_{2k}^2)^{1/2},\qquad(10)$$

$$\Delta_k = \tan^{-1}(u_{2k-1}/u_{2k})\qquad(11)$$

and α is the reciprocal of the sum of the normalized scattering factors, extending over the unit cell.

2. Replacement of the phase φ_3 in (7) by $\Phi - \varphi_1 - \varphi_2$ and integration of the joint p.d.f. (7) over the phases φ_1 and φ_2.

3. Calculation of the Fourier coefficient C_u for the crystal symmetry and composition of interest. We assume here that the atomic contributions to the structure factor are independent and that the atoms are uniformly distributed throughout the unit cell. Effects of dispersion and noncrystallographic symmetry are also disregarded in this paper.

The above three steps lead to the required exact c.p.d.f., which assumes the general form

$$p_{ex}(\Phi|E_1, E_2, E_3, \ldots) = K \sum_u C_u Z_u, \qquad (12)$$

where Z_u depends on the three-phase invariant, the magnitudes of the normalized structure factors involved and not on symmetry and composition, and K is a normalization constant. Detailed expressions for the quantities appearing in (12) are given by Shmueli et al. (1989a). It is also shown in the latter reference that (12) reduces to the Cochran c.p.d.f. (2) when only the lowest-order terms in the characteristic function C are retained. Although (12) converges rapidly in the useful range of the conditions, its numerical evaluation is rather time-consuming. We therefore believe that the practical importance of the exact c.p.d.f. (12) is that it can form a once-computed basis for a useful numerical approximation. Such an approximation will be developed in the following section.

The modified-κ approach

As one might expect, the results of Cochran's (1955) approximation in (2) and the Fourier c.p.d.f. in (12) agree quite well for weak or moderately large values of the E_i and a large number of atoms in the unit cell of $P1$. When either of these conditions is violated, the discrepancy between results obtained from the two approaches can be substantial, as shown by Shmueli et al. (1989b). An extensive set of such calculations suggests that in all cases the exact c.p.d.f. has a single maximum at $\Phi = 0$ and is more sharply peaked at that maximum than is the c.p.d.f. produced by the Cochran approximation. This finding is very much in line with our earlier calculations for the density functions for $\sum_1$ and $\sum_2$ (Shmueli & Weiss, 1985, 1986). These calculations also indicate that the qualitative effect of increasing atomic heterogeneity, with fixed N, is equivalent to that of a decreasing N in an equal-atom structure.

While there are quantitative differences between exact c.p.d.f.'s and the Cochran approximation, they are qualitatively quite similar. This was suggested to us by an extensive comparison of the shapes of the various c.p.d.f.'s that were computed. We have therefore examined the consequences of a very simple

approximation of the form

$$p_{app}(\Phi|\kappa') = [2\pi I_0(\kappa')]^{-1} \exp(\kappa' \cos \Phi), \qquad (13)$$

where the parameter κ' is calculated by the requirement that the exact and approximate c.p.d.f.'s should match exactly at the maximum at $\Phi = 0$,

$$p_{ex}(0|E_1, E_2, E_3, \ldots) = p_{app}(0|E_1, E_2, E_3). \qquad (14)$$

After having found the value of κ', as described above, we can compare the results obtained with (13) both against the Cochran approximation and against the exact c.p.d.f. at values of Φ other than 0.

This simple approach works surprisingly well, as can be seen from Figs. 1(a) and (b). However, it is evident that the extent of agreement between the c.p.d.f.'s computed from (12) and (13) does not depend only on the triple product $E_1 E_2 E_3$ as a single parameter and so the dependence on the separate values of E_1, E_2 and E_3 must be taken into account.
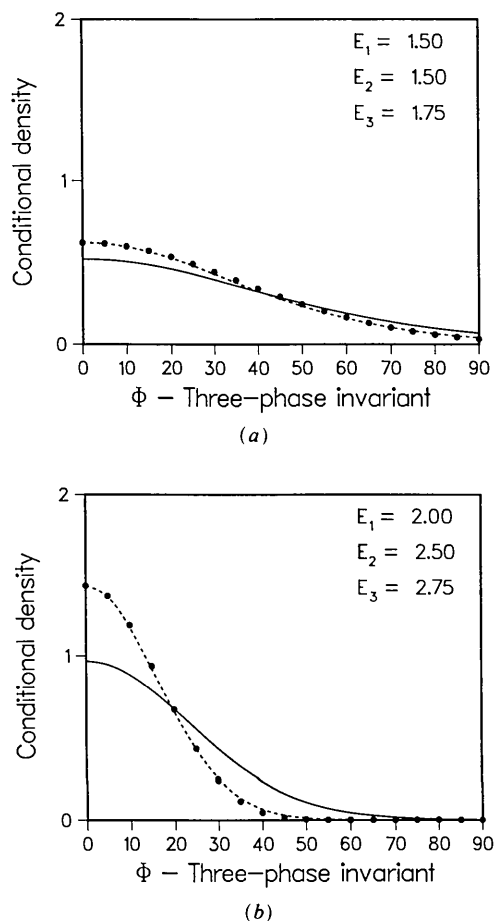

Fig. 1. Conditional p.d.f.'s of the three-phase invariant in $P1$. The solid lines represent Cochran c.p.d.f.'s [(2)], the black dots correspond to accurately computed c.p.d.f.'s [(12)] and the dashed lines are c.p.d.f.'s computed from the modified-κ approximation [(13)] described in the text. The equal-atom case is considered throughout. (a) $E_1 = E_2 = 1.50$, $E_3 = 1.75$, $N = 40$; (b) $E_1 = 2.00$, $E_2 = 2.50$, $E_3 = 2.75$, $N = 15$.

Since we want a conveniently computable approximation, we calculated a best estimate of the ratio $\rho \equiv \kappa'/\kappa$ for different values of the parameters E_1, E_2, E_3 and N. For simplicity, our computations are restricted to equal-atom unit cells, the range of parameters being restricted as detailed below.

The ratio $\rho = \kappa'/\kappa$ was first computed for each of E_1, E_2 and E_3 varying from 1.25 to 2.75 in steps of 0.25 and for N varying from 15 to 40 in steps of 5. The computation of ρ values corresponding to $E_1 = E_2 = E_3 = 2.75$ was omitted because of convergence problems encountered in the evaluation of (12). Use was made of the fact that (12) is invariant under permutation of E_1, E_2 and E_3. The construction of these data was the most time-consuming stage of the computation since it involved the computation of the exact c.p.d.f. on a grid of points in the (E_1, E_2, E_3) space for each of the above values of N. Two sections of such grids are illustrated in Fig. 2, which shows the dependence of the ratio κ'/κ on the variation of E_1 and E_2 for fixed E_3 and different values of N. The computation of these exact c.p.d.f.'s followed the procedure described by Shmueli et al. (1989a, b).

Examination of several $\rho(E_1, E_2)$ grids, with E_3 and N being kept constant, indicated that such
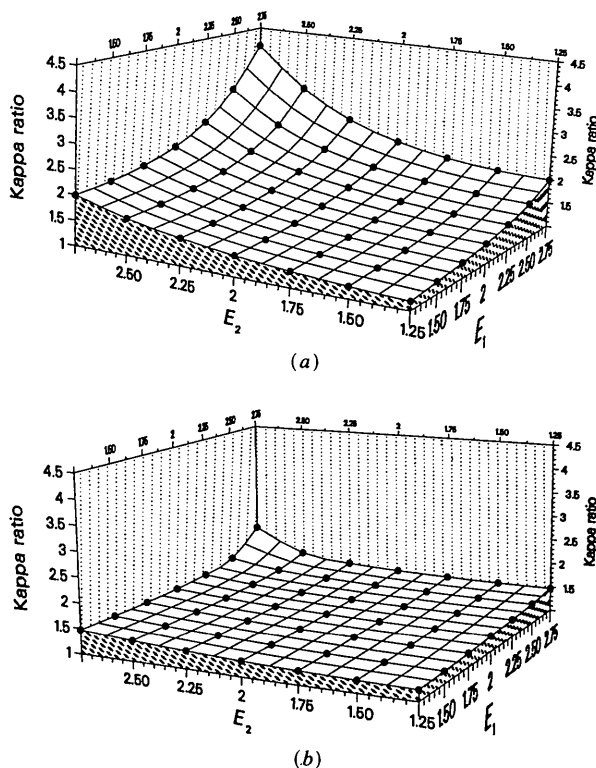

Fig. 2. Two-dimensional surfaces of modified-κ ratios. Two surfaces of $\rho(E_1, E_2)$ are presented and the ratios obtained by exact computations (black dots) and those obtained by bicubic spline interpolation are shown for constant values of N and E_3. (a) $N = 15$, $E_3 = 1.50$; (b) $N = 35$, $E_3 = 2.50$.

Table 1. Coefficients of the polynomial in (15)

The numerical coefficients of the various terms in (15) are listed for the numbers of atoms for which the c.p.d.f.'s were computed exactly. For intermediate values of N, an interpolation can be used (see text).

| Coefficient | Number of atoms | | | | | |
	15	20	25	30	35	40
a_1	0.61306	0.97883	0.48385	0.61757	0.41246	1.21311
a_2	0.81738	0.13870	0.94995	0.69634	1.02220	-0.33332
a_3	-0.22587	-0.02688	-0.24003	-0.17229	-0.25844	0.09783
a_4	0.10915	0.03567	0.04313	0.03004	0.03537	-0.00123

$\rho(E_1, E_2)$ surfaces are rather smooth and therefore polynomial fitting and good graphical representation are achieved by interpolation. We chose the method of bicubic spline interpolation (Press, Flannery, Teukolsky & Vetterling, 1986) for this purpose. Two surfaces, obtained by the above method, are illustrated in Fig. 2, in which the black dots correspond to ρ values obtained by fitting κ' to (12) and the intersections of the smooth curves correspond to interpolated ρ values. We examined all 42 ρ (E_1, E_2) grids, within our range of parameters, and fitted to each of them a two-dimensional least-squares polynomial. This calculation gave satifactory results and would, in principle, satisfy our requirement. However, 42 sets of polynomial coefficients would have to be presented to the user of this approximation and, therefore, a simpler approach was investigated.

One possible approach is a three-dimensional least-squares fit. In this context, six three-dimensional grids in the (E_1, E_2, E_3) space were constructed, one for each value of N, and to every such grid a cubic polynomial of the form

$$\rho(E_1, E_2, E_3)$$
$$= a_1 + T(a_2 + a_3 T_1 + a_4 T_2 + a_5 T_3), \quad (15)$$

where $T = E_1 E_2 E_3$, $T_1 = E_1 + E_2 + E_3$, $T_2 = E_1^2 + E_2^2 + E_3^2$ and $T_3 = E_1 E_2 + E_2 E_3 + E_3 E_1$, was fitted by the (linear) least-squares method. We present in Table 1 the coefficients of these polynomials for the six values of N for which exact computations were carried out. For each exact computation of the c.p.d.f. that was available, we computed the corresponding approximate c.p.d.f. while making use of the κ ratio given by (15). The discrepancy between an approximate and an 'exact' c.p.d.f. is conveniently indicated by an R factor of the form

$$R = \left[\sum_{k=1}^{M} (p_k^{app} - p_k^{ex})^2 \bigg/ \sum_{k=1}^{M} (p_k^{app})^2 \right]^{1/2}, \quad (16)$$

where the summations extend over M values of Φ [here $M = 20$ and the Φ range extends from 0 to 90° (cf. Shmueli et al., 1989b)]. Table 2 lists the average R factors comparing ideal (Cochran-type), approximate (from modified κ) and exact c.p.d.f.s. It is seen that the modified-κ approximation agrees very well

Table 2. *Discrepancy factors for the polynomial fit*

The average *R* factors between conditional p.d.f.'s are listed for the three-dimensional polynomial (15). Columns *A*, *B*, *C* and *D* refer to ranges of values of the tiple product, *T*, for which *R* was computed. *A*: $T < 6$; *B*: $6 \leq T < 10$; *C*: $10 \leq T < 14$; *D*: $14 \leq T$. The attribute 'approximate' refers to c.p.d.f.'s computed from the least-squares fit to the κ ratio and the use of (13); 'Cochran' refers to (2) and 'exact' refers to (12).

(*a*) Comparison of approximate and ideal (Cochran) c.p.d.f.'s

Number of atoms	A	B	C	D
15	0.1714	0.3105	0.3845	0.4532
20	0.1352	0.2284	0.2810	0.3231
25	0.1098	0.1816	0.2268	0.2886
30	0.0914	0.1522	0.1886	0.2380
35	0.0785	0.1307	0.1630	0.2228
40	0.0656	0.1181	0.1417	0.1350

(*b*) Comparison of exact and approximate c.p.d.f.'s

Number of atoms	A	B	C	D
15	0.0351	0.0386	0.0371	0.0327
20	0.0160	0.0196	0.0190	0.0214
25	0.0120	0.0147	0.0168	0.0386
30	0.0096	0.0112	0.0128	0.0283
35	0.0100	0.0103	0.0135	0.0419
40	0.0070	0.0072	0.0069	0.0267

Table 4. *Discrepancy factors for the nonlinear fit*

The average *R* factors between conditional p.d.f.'s are listed for the nonlinear function (17). Columns *A*, *B*, *C* and *D* refer to ranges of values of the triple product, *T*, for which *R* was computed. *A*: $T < 6$; *B*: $6 < T < 10$; *C*: $10 \leq T < 14$; *D*: $14 \leq T$. The attribute 'approximate' refers to c.p.d.f.'s computed from the κ ratio as obtained from (17) and the use of (13); 'Cochran' refers to (2) and 'exact' refers to (12).

(*a*) Comparison of approximate and ideal (Cochran) c.p.d.f.'s

Number of atoms	A	B	C	D
15	0.1782	0.3139	0.3909	0.4˙93
20	0.1336	0.2297	0.2800	0∿3239
25	0.1086	0.1850	0.2272	0.2881
30	0.0893	0.1546	0.1877	0.2378
35	0.0754	0.1349	0.1621	0.2202
40	0.0651	0.1160	0.1414	0.1348

(*b*) Comparison of exact and approximate c.p.d.f.'s

Number of atoms	A	B	C	D
15	0.0277	0.0314	0.0310	0.0358
20	0.0162	0.0184	0.0190	0.0205
25	0.0109	0.0130	0.0148	0.0382
30	0.0084	0.0100	0.0112	0.0277
35	0.0072	0.0083	0.0105	0.0393
40	0.0063	0.0077	0.0071	0.0265

Table 3. *Coefficients of the nonlinear function* (17)

The numerical coefficients of the various terms in (17) are listed for the numbers of atoms for which the c.p.d.f.'s were computed exactly. For intermediate values of *N*, an interpolation can be used (see text).

Coefficient	Number of atoms					
	15	20	25	30	35	40
b_1	−0.4893	−0.7877	−0.0551	−0.0670	−0.2367	1.5579
b_2	0.1933	0.2740	0.0936	0.0924	0.1069	−0.0933
b_3	0.1701	−0.1140	0.1181	0.1161	0.1658	−0.3054
c_1	4.2039	2.1855	1.5659	1.6213	2.4151	0.0756
c_2	−0.9824	−0.7393	−0.3699	−0.3800	−0.5863	−0.0228
c_3	0.1221	−1.7093	0.0294	0.0269	0.0406	0.0019
c_4	0.0533	3.9739	0.0379	0.0415	0.0681	0.0042

with the exact results, at least within the ranges of E_1, E_2, E_3 and *N* that were considered.

An alternative approach to the construction of our parametric approximation of $\rho = \kappa'/\kappa$ is to fit a nonlinear function to the ratio values that were estimated from the exact computation. The function chosen was

$$\rho(E_1, E_2, E_3) = (c_1 + c_2 T_1 + c_3 T_2 + c_4 T_3)$$
$$\times \exp (b_1 T_1 + b_2 T_2 + b_3 T_3), \quad (17)$$

where T_1, T_2, T_3 are defined above. The nonlinear parameters, b_i, $i = 1, \ldots, 3$, were estimated by the simplex method (Nelder & Mead, 1965), where each iteration of the simplex procedure was followed by a linear least-squares run that found the linear parameters c_k, $k = 1, \ldots, 4$. The linear and nonlinear parameters are given in Table 3 for the six values of *N* previously considered. A considerable advantage of the simplex method over other estimators of non-

linear parameters is its relative insensitivity to the initial guess, which is apparent for the type of function given by (16). The simplex method is well documented (see, for example, Jacoby, Kowalik & Pizzo, 1972).

Table 4 lists the average *R* factors comparing ideal (Cochran-type), approximate (from a modified κ) and exact c.p.d.f.'s. It is seen here that the modified-κ approximation, obtained by the simplex method, agrees even better than that obtained from the polynomial fit with the exact results, at least within the ranges of E_1, E_2, E_3 and *N* that were considered.

As will be illustrated in what follows, such κ ratios for general values of *N* can be obtained to a good approximation by Lagrange's three-point interpolation (see, for example, Abramowitz & Stegun, 1972). The exact c.p.d.f. was computed for the 26 values of *N*, within the range considered, and for several typical triplets of *E* values. For each one we compared the $\rho(N)$ sequence based on the full computation, using (12), with the $\rho(N)$ sequence calculated from (17) and Table 3 and completed by three-point interpolation. A comparison of such sequences is shown in Fig. 3(*a*), for a moderately strong triplet. Fig. 3(*b*) shows the comparison of corresponding sequences of *R* factors for the relevant c.p.d.f.'s: (i) $R(N)$ between the c.p.d.f.'s based on Table 3 and three-point interpolation, and the c.p.d.f.'s that were accurately computed and (ii) $R(N)$ between the c.p.d.f.'s based on Table 3 and three-point interpolation, and the c.p.d.f.'s based on the Cochran (1955) formula, given by (2). Fig. 3 displays the case of greatest discrepancies between the exact and modified-κ c.p.d.f.'s, with all *R* values apart from that for $N = 15$ less than 0.03.

The R values for the modified-κ vs Cochran (1955) c.p.d.f.'s are higher by factors of 10 to 15 for the equal-atom case considered here.

It may be stated that, for the range of parameters examined in this study, the Cochran approximation tends to resemble the exact distributions as N increases and the magnitudes of E that are involved decrease. Thus, for an equal-atom structure, the discrepancy between ideal and exact distributions depends on *both* the E values and the number of atoms in the unit cell. As pointed out above, the presence of an outstandingly heavy atom would probably have the effect of decreasing N, as indicated by the calculatons reported elsewhere (Shmueli & Weiss, 1985, 1986; Shmueli *et al.*, 1989*b*).
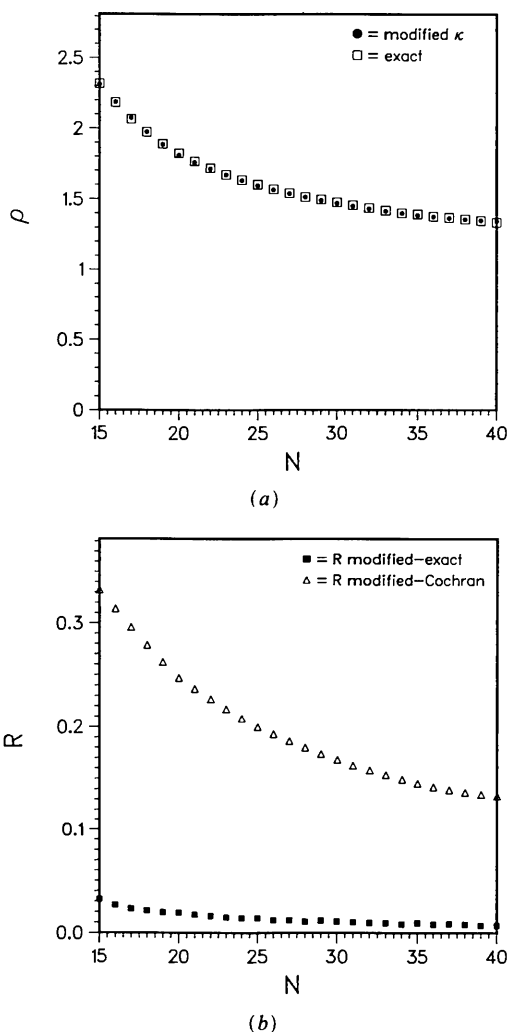
Fig. 3. Modified-κ ratios and R factors as a function of N for c.p.d.f.'s of a three-phase invariant with $E_1 = 2.00$, $E_2 = 2.25$ and $E_3 = 2.50$. (a) Comparison of $\rho = \kappa'/\kappa$ obtained from (17), Table 3 and three-point interpolation (filled circles) with ratios obtained from exact computations (open squares). (b) Comparison of R factors from (16) between modified-κ and exact c.p.d.f.'s (filled squares) and those between modified-κ and Cochran (1955) c.p.d.f.'s (open triangles).

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