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Electron Population Analysis of Accurate Diffraction Data. IV. Evaluation of Two-Center Formalisms in Least-Squares Refinement

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Least-squares formalisms which explicitly include scattering by both one and two-center orbital products are applied to a set of theoretical scattering factors for diborane and to the experimental data on cyanuric acid. The diborane calculations confirm the accuracy of the formalisms employed and indicate the importance of selecting an appropriate basis set of atomic orbitals. They further indicate that (1) net electron populations in bonds and on atoms can be determined more precisely than individual population parameters; (2) the set of parameters should be limited by molecular symmetry and assumptions about the symmetry of the bonds; (3) only one of a set of highly correlated parameters on an atom or in a bond should be allowed to vary; (4) the most reasonable basis set is the one giving the best agreement factor. This experience is applied to the refinement of cyanuric acid. It is found that the isolated atom HF functions give the best description of the experimental density. A Mulliken population analysis of the results reproduces the chemical symmetry of the molecule. In general the conclusions reached on diborane are compatible with the analysis of the experimental data. Electron-density maps on cyanuric acid, based on the least-squares population parameters, show that a good description of the density is obtained with a number of parameter sets. These electron-density maps show significant disagreement with thermally-smearred theoretical maps, indicating that the INDO and *ab initio* minimal basis set (STO-3G) calculations do not properly predict the density in the bonding and lone-pair regions of the cyanuric acid molecule. A transformation to uncorrelated combinations of population parameters is proposed to facilitate analysis of the numerical results and comparison with theoretical population parameters.

Introduction

In the first two articles of this series we have described formalisms and inherent limitations in the charge refinement of accurate diffraction data (Coppens, Willoughby & Csonka, 1971) and the application of a number of *one-center* formalisms to some organic and inorganic molecules (Coppens, Pautler & Griffin, 1971).

The present manuscript describes an evaluation of X-ray scattering formalisms which explicitly include

two-center terms, *i.e.* products between atomic orbitals centered on different atoms. The formalisms are first applied to a theoretical set of structure factors for diborane (B_2H_6), obtained through a numerical Fourier transform of the results of a minimal basis set calculation (Jones & Lipscomb, 1970). Experience obtained in this treatment is then applied to the low temperature X-ray diffraction data on cyanuric acid (Verschoor & Keulen, 1971), utilizing positional and thermal parameters from a parallel neutron diffraction study (Coppens & Vos, 1971). In both calculations a variety of different parameter and atomic orbital basis sets are tested. To provide a further evaluation of the formalisms, results are compared in electron-density space

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with both experimental X-N maps and with theoretical densities.

Some of the experience gained in the present study has been applied in the charge refinement of tetracyanoethylene oxide (Matthews, Stucky & Coppens, 1972).

Some definitions

The population parameters $P_{\mu\nu}$ referred to below, are the elements of the first-order density matrix and are defined by the expression

$$\rho(x, y, x) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \varphi_{\mu} \varphi_{\nu}$$

where ρ is the one electron density and the φ 's are the atomic orbitals of the basis set. Atom and bond populations q are derived from the population parameters in the following way:

$$q(\text{atom } A) = \sum P_{\mu\mu}(A)$$

$$q(\text{bond } AB) = \sum_{\mu(A)} \sum_{\nu(B)} [P_{\mu\nu} \int \varphi_{\mu}(A) \varphi_{\nu}(B) d\tau]$$

$$= \sum_{\mu(A)} \sum_{\nu(B)} P_{\mu\nu} S_{\mu(A)\nu(B)}$$

where S is the overlap integral.

Finally, gross Mulliken populations q' are obtained by dividing the bond populations equally over adjacent atoms:

$$q'(\text{atom } A) = q(\text{atom } A) + \frac{1}{2} \sum q(\text{bond } AB)$$

where the sum is over all the bonds to atom A .

Calculations on diborane

Structure factors for the diborane, B_2H_6 , molecule (Fig. 1), as positioned in the experimental unit cell ($P2_1/n$, $Z=2$), were calculated from a minimal-basis-set SCF wave function in which orbital exponents had been optimized (Jones & Lipscomb, 1970). The values of hkl were restricted to those of the experimentally observed intensities. The numerical methods used in this structure factor calculation were completely different from those employed in the present work; hence the test calculations with the numerical structure factors provide a severe test of the methods employed in

the population analysis of diffraction data. In addition, the diborane structure factors are obviously free of 'experimental' errors; they are estimated to be accurate to one part in a thousand.

The purposes of the test calculations were:

(a) a check of the accuracy of the formalisms used in the population analysis (Coppens, Willoughby & Csonka, 1971), and

(b) the assessment of the validity of the conclusions reached in the population analysis, including the effect of changing weighting schemes, basis sets, and parameter sets.

To achieve the first aim a calculation was carried out with the two-center formalisms, using the same positional parameters, atomic orbital basis set and population parameters employed in the numerical calculation of Jones & Lipscomb (1970). Initially, the procedure applied to experimental data was mimicked by including only the one-center terms (except the $1s2s$ products on the boron atoms), and the two-center terms between directly bonded atoms (except the $1s1s$ term in the B-H bonds). The structure factors obtained gave an agreement index $R = \sum |F_N| - |F_{\text{calc}}| / \sum |F_N| = 0.036$ with the numerical data values F_N when thermal motion was set to zero, and $R = 0.039$ when an overall thermal parameter of $B = 3.5 \text{ \AA}^2$ was applied to both sets of structure factors.

When all the non-zero population parameters of the original wave function (including those between non-bonded atoms) were included, agreement indices of 0.006 ($B=0.0$) and 0.007 ($B=3.5 \text{ \AA}^2$) were obtained. In all cases a scale factor of 1.0 was used.

It was concluded that the approximations in the two-center formalisms could well account for the remaining discrepancy, and that the calculated structure factors were sufficiently accurate for the analysis of experimental data. It may be noted that for molecules without three-center bonds (which lead to uncommonly small distances between atoms not directly bonded), the inclusion of the terms between non-bonded atoms should be of much smaller consequence.

The tests carried out to determine the validity of the conclusions reached in the analysis of actual experimental data were done so as to parallel such an experimental analysis as closely as possible. The numeri-

Table 1. *Orbital exponents for various basis sets (a.u.)⁻¹*

Diborane	B	B	B	H _{Terminal}	H _{Bridge}	Reference				
	1s	2s	2p							
'Exact'	4.68	1.442	1.4772	1.1473	1.2095	Jones & Lipscomb (1970)				
Standard	4.68	1.45	1.45	1.24	1.24	Hehre, Stewart & Pople (1969)				
Hartree-Fock*	4.68	1.2881	1.2107	1.0	1.0	Clementi & Raimondi (1963)				
Cyanuric acid	C	C	C	N	N	N	O	O	O	H
	1s	2s	2p	1s	2p	2p	1s	2s	2p	
Standard	5.67	1.72	1.72	6.67	1.95	1.95	7.66	2.25	2.25	1.24
Hartree-Fock*	5.67	1.608	1.568	6.67	1.9237	1.9170	7.66	2.2458	2.2266	1.00

* 'Best single zeta' approximation to the exact Hartree-Fock orbitals used in the refinement. Approximate exponents included only for comparison.

cal diborane structure factors were treated as 'experimental' data, atomic positions were fixed at the values used for the numerical calculation, and an 'exact' thermal parameter of 3.5 \AA^2 was applied to both 'experimental' and calculated structure factors (in the following analysis of the cyanuric acid data, positional and thermal parameters are available from the neutron diffraction experiment). The only parameters allowed to vary were an overall scale factor and the population parameters. Since an actual population refinement normally includes only one-center terms (except $1s2s$) and two-center terms between adjacent atoms (except $1s1s$), the test calculations were all carried out this way. Many models were tested, involving combinations of the following variables:

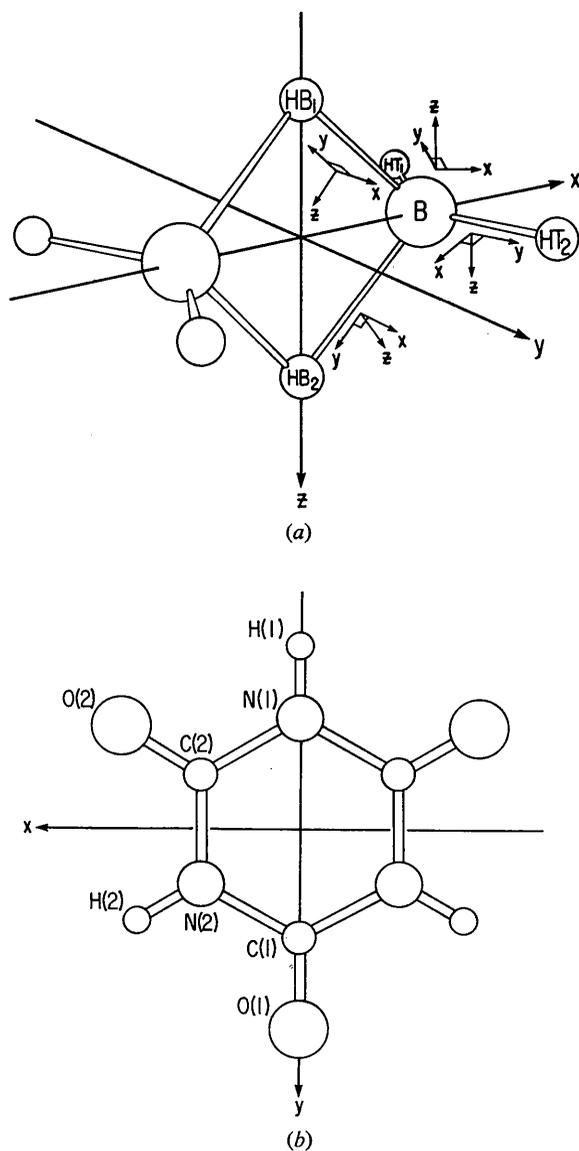


Fig. 1. Labelling of the atoms and definition of axes in diborane and cyanuric acid.

(a) Weighting schemes. Both a unit weighting scheme and a system identical to that applied to the diborane experimental data (Jones & Lipscomb, 1970) were employed.

(b) Initial population parameters. Two different sets of starting parameters were used: (1) one center and two-center parameters exactly as given by the diborane wave function, except for the neglect of $1s2s$ terms on boron and $1s1s$ in the B-H bonds; (2) population parameters corresponding to the usual approach to experimental data. In this set the boron $1s$ and $2s$ orbitals each contain two electrons; the three boron $2p$ orbitals are populated with one spherically-averaged electron and the hydrogen $1s$ orbital with one electron. All two-center terms have an initial population of zero. It should be noted that the results of the refinement are independent of the initial parameter set, unless parameters that are not varied have different values, or the total number of electrons (which is kept constant during refinement) is different. Because of the neglect of certain terms, parameter set 1 corresponds to a total of 16.32 rather than 16 electrons per molecule.

(c) Basis sets. The following three sets were tested: (1) the 'exact' set of Slater-type orbitals with exponents as in the theoretical calculation; (2) A set of Slater orbitals with 'standard' molecular exponents as given by Hehre, Stewart & Pople (1969) (HSP). These values are based on exponent optimizations for a number of small molecules and molecular species; and (3) A basis set of isolated-atom Hartree-Fock (HF) atomic orbitals. Orbital exponents corresponding to these three sets are given in Table 1 (the orbital exponents for the HF set are a first approximation to the accurate HF orbitals used in our refinements; they are given for comparison purposes only).

(d) Parameters varied. Molecular symmetry (mmm) places certain restrictions on all parameter sets. The assumption of m or mm symmetry for the individual bonds, along with restrictions posed by highly correlated variables, lead to a variety of parameter sets. In some cases the scale factor was allowed to vary from the 'exact' value of 1.0.

Calculations with the 'exact' basis set and scale factor and with initial parameters from the diborane wave function might have been expected to give results most in agreement with theory. This is not the case, however, because of the incorrect value of the total number of electrons with this parameter set. Inclusion of the scale factor as a variable did produce net atomic and bond electron populations in good agreement with theoretical values, but equally good agreement was obtained with the second set of initial parameters.

The most informative of the tests were those with the initial parameter set 2, which corresponds to the treatment used on experimental data. Examination of the resulting one and two-center population parameters (Table 2) and gross properties, such as net electron populations of atoms and bonds (Tables 3 and 4) revealed that the latter are determined with higher re-

liability. In terms of the least-squares standard deviations, the agreement between net population parameters and the 'exact' values is consistently better than the corresponding agreement for the individual population parameters. Consequently, most of the discussion below is based on the comparison of the net electron populations.

Table 2. Comparison of population parameters for various models

Standard deviations in parentheses. The absence of a standard deviation indicates that the parameter was not varied.

	Theoretical	Exact C	HF A	HSP A	HSP C
Boron					
1s	2.059	2.0	2.0	2.0	2.0
2s	0.521	0.521	0.521	0.521	0.521
p_x^2	0.319	0.38 (1)	0.43 (9)	0.51 (1)	0.17 (2)
p_y^2	0.532	0.46 (1)	0.30 (13)	0.61 (1)	0.33 (2)
p_z^2	0.180	0.21 (1)	0.14 (8)	0.33 (1)	-0.02 (2)
2sp _x	0.219	-0.01 (1)	-0.17 (27)	0.11 (3)	0.07 (1)
HT ₁					
1s	0.705	0.670 (6)	0.56 (9)	0.62 (1)	0.59 (1)
HT ₂					
1s	0.705	0.666 (6)	0.51 (10)	0.61 (1)	0.58 (1)
HB ₁					
1s	0.664	0.653 (8)	1.02 (15)	0.63 (1)	0.60 (1)
B-HT ₁					
2ss	0.642	0.31 (9)	0.0	0.0	1.79 (12)
$p_x s$	0.051	0.0	0.28 (27)	-0.05 (5)	0.0
$p_y s$	1.040	1.34 (6)	1.92 (25)	1.44 (3)	0.45 (8)
B-HT ₂					
2ss	0.642	0.32 (9)	0.0	0.0	1.85 (12)
$p_x s$	0.051	0.0	0.03 (27)	0.13 (4)	0.0
$p_y s$	1.040	1.35 (6)	1.86 (28)	1.42 (3)	0.42 (8)
B-HB ₁					
2ss	0.209	0.13 (7)	0.0	0.0	0.66 (12)
$p_y s$	0.705	0.77 (6)	0.49 (27)	0.85 (3)	0.53 (8)
$p_z s$	-0.077	0.0	0.0	0.0	0.0
B-HB ₂					
2ss	0.209	0.09 (11)	0.0	0.0	0.75 (15)
$p_y s$	0.705	0.77 (7)	0.27 (26)	0.82 (3)	0.46 (10)
$p_z s$	0.077	0.0	0.0	0.0	0.0

Table 3. Bond and atom populations in electrons, HSP basis set

	Experimental weights.			
	Theoretical	A	B	C
B	3.54	3.98 (2)	2.68 (3)	3.01 (3)
HT ₁	0.70	0.62 (1)	0.56 (1)	0.59 (1)
HT ₂	0.70	0.61 (1)	0.55 (1)	0.58 (1)
HB	0.66	0.63 (1)	0.55 (1)	0.60 (1)
B-HT ₁	0.82	0.70 (2)	1.21 (9)	1.08 (7)
B-HT ₂	0.82	0.71 (2)	1.23 (9)	1.10 (7)
B-HB ₁	0.39	0.38 (2)	0.60 (9)	0.51 (7)
B-HB ₂	0.39	0.37 (2)	0.61 (9)	0.52 (9)
Scale		0.986 (1)	1.00 (Fixed)	0.992 (1)
R(F)		0.011	0.008	0.006
R _w (F)		0.013	0.010	0.007
Number of variables	14		15	16

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

The parameter sets were (for coordinate systems see Fig. 1):

(A) 14 parameters, including p_x^2 , p_y^2 , p_z^2 and $2sp_x$ terms on boron, the $1s^2$ terms on the three hydrogens, the $p_x s$ and $p_y s$ terms for the B-HT (HT=H-terminal) bonds (m symmetry), the $p_y s$ terms for the B-HB (HB=H-bridging) bonds (mm symmetry) and the scale factor. This set was arrived at by varying a larger parameter set and then holding constant all but one of any set of highly correlated parameters on the same atom or in the same bond (*i.e.* with correlation coefficients of about 0.9 or larger).

(B) 15 parameters, including one-center terms as in (A) and ss and $p_y s$ terms for the B-HB and B-HT bonds [mm symmetry, but with more terms than in (A), with the scale factor fixed at 1.0].

(C) 16 parameters, as in (B) plus a variable scale factor.

Table 2 gives the results of using the HSP basis set and parameter sets A, B and C. Population values are given for each crystallographically unique atom and bond in the molecule. It is reassuring that the test results properly reflect the noncrystallographic symmetry of the molecule. It should also be noted that the ratio of about 2 between B-HT and B-HB bond populations is retained in each case and that the three hydrogen atoms have about the same populations in all refinements, in agreement with the theoretical populations.

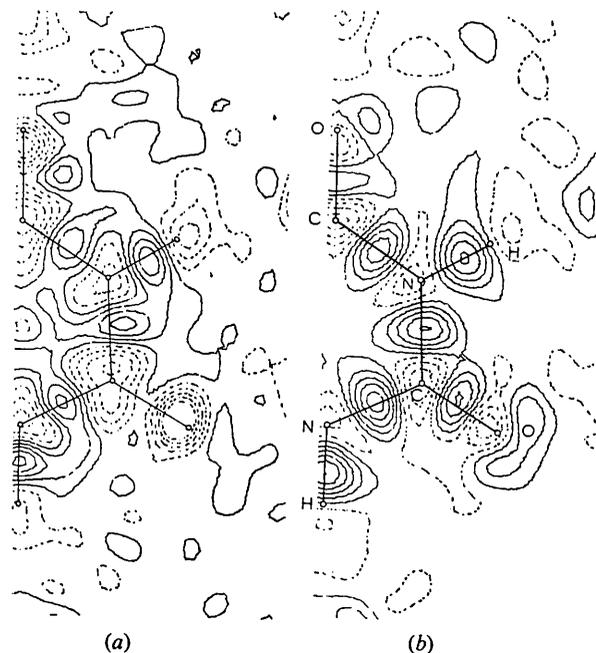


Fig. 2. Population asphericity (ΔP) maps in the plane of the cyanuric acid molecule; corresponding to (a) the 62 parameter set I-S, (b) the 62 parameter set I-H. Contours here and in other density maps in this paper are at $0.1 \text{ e.}\text{\AA}^{-3}$. Zero and negative contours dotted. The second half of the cyanuric acid molecule is symmetry-related to the part shown.

The best absolute agreement with theory is given by *A*, with *C* second best and *B* third. The last two sets differ only in the variation of the scale factor, indicating that a relatively small change in scale factor can cause a significant change in some of the populations (in this case an improvement). It is especially important that the best values are not given by the parameter set yielding the lowest agreement factor. The procedure followed in deriving set *A* is clearly a useful one.

Table 4 shows the effect of altering the basis set while varying parameters defined by *A* and *C*. The exact set of Slater-type orbitals, utilized with parameter set *C* gives almost perfect agreement with theory. This is not surprising, but is of little help in choosing a basis set for an experimental analysis, because the 'exact' set is never known. The HSP basis gives better results than the HF orbitals. This is again as would be expected, since the theoretical calculations are based on Slater-type orbitals. Perhaps the result most helpful in analyzing experimental data is that *the best basis set does give the best agreement factor for both parameter sets A and C*. Furthermore, both HSP variable sets give lower agreement values than either of the HF sets. In all of the test calculations done, it was found that a change in weighting scheme had little effect on the electron populations.

Bearing in mind that these tests concern only one, somewhat atypical molecule, what do they enable us to conclude about the results of applying these methods to experimental data? They indicate that (1) net electron populations in bonds and on atoms are determined more reliably than individual population parameters; (2) the set of parameters should be limited by molecular symmetry and assumptions about the symmetry of the bonds; (3) only one of a set of highly correlated parameters on an atom or in a bond should be allowed to vary; (4) the most reasonable basis set is the one giving the best agreement index, although this same criterion cannot be applied in choosing the most appropriate parameter set.

In summary, even though these tests were limited, their results are generally in agreement with what one would intuitively expect, and they can serve as a useful guide in the analysis of experimental data.

Population refinement of cyanuric acid

X-ray intensities of cyanuric acid were measured at liquid nitrogen temperature by Verschoor & Keulen (1971). The compound crystallizes in the space group *C2/n* with half a molecule in the asymmetric unit. The small size of this unit is an advantage in terms of computer time required for the population analysis.

To achieve deconvolution of anisotropic thermal motion and bonding effects, neutron diffraction values for the thermal and positional parameters, as determined by Coppens & Vos (1971), are used in the refinement. It should be mentioned that the neutron-diffraction thermal parameters were corrected for a difference of about 30° between X-ray and neutron-diffraction data collection temperatures. Both the X-ray minus neutron difference map and the population refinement are subject to the limitations in this correction.

The anisotropic thermal parameters of the overlap density between atoms *n* and *m* were assumed to be the average of the corresponding parameters of atoms *n* and *m*. A number of calculations using the alternative formalism $B(nm) = (B_n + B_m)/4$ (Coppens, Willoughby & Csonka, 1971) showed that the population parameters are very insensitive to such changes in the overlap density thermal parameters.

In the population refinement the experience gained in the test calculations on diborane was utilized as fully as possible. Thus basis sets which yielded the lowest agreement index were selected, while parameter sets were reduced as far as possible without a considerable sacrifice of agreement. As in the diborane calculations, the *y* axes of the bond coordinate systems were along the bonds. Further, the *z* axis was always per-

Table 4. Comparison of basis sets for two parameter models

	Bond and atom populations in electrons.							
	Theoretical	Exact		HSP		HF		
		<i>A</i>	<i>C</i>	<i>A</i>	<i>C</i>	<i>A</i>	<i>C</i>	
B	3.54	3.77 (2)	3.59 (2)	3.98 (2)	3.01 (3)	3.4 (2)	1.7 (2)	
H-T ₁	0.70	0.68 (1)	0.67 (1)	0.62 (1)	0.59 (1)	0.6 (1)	0.7 (1)	
H-T ₂	0.70	0.68 (1)	0.67 (1)	0.61 (1)	0.58 (1)	0.5 (1)	0.6 (1)	
H-B	0.66	0.66 (1)	0.65 (1)	0.63 (1)	0.60 (1)	1.0 (1)	1.2 (1)	
B-HT ₁	0.82	0.74 (1)	0.82 (6)	0.70 (2)	1.08 (7)	1.1 (1)	1.4 (4)	
B-HT ₂	0.82	0.74 (1)	0.83 (6)	0.71 (2)	1.10 (7)	1.0 (1)	1.4 (4)	
B-HB ₁	0.39	0.37 (1)	0.39 (6)	0.38 (2)	0.51 (7)	0.3 (1)	0.5 (4)	
B-HB ₂	0.39	0.36 (1)	0.38 (6)	0.37 (2)	0.52 (9)	0.2 (1)	0.5 (4)	
Scale		0.995 (1)	0.997 (1)	0.986 (1)	0.992 (1)	1.043 (5)	1.073 (6)	
<i>R</i>		0.006	0.005	0.011	0.006	0.047	0.039	
<i>R_w</i>		0.007	0.006	0.013	0.007	0.060	0.051	

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

pendicular to the molecular plane and the x axis in the plane perpendicular to the bond. For the atomic (one-center) terms a single molecular system was chosen with the z axis again perpendicular to the molecular plane. This system is fully defined in Fig. 1.

Alternate models

Some of the symmetry restrictions discussed above and in paper I of this series were introduced *a priori* into the cyanuric acid population refinement. Thus, the populations of orbital products violating mirror symmetry in the molecular plane and mm symmetry of the bonds were kept fixed at zero. Examples of such terms are sp_z and $p_x p_z$ terms for both atoms and bonds and $p_x p_y$ terms in the bonds. The twofold axis bisecting the molecule places further symmetry restrictions on the atoms and bonds lying on this axis. Orbital products involving non-adjacent atoms were neglected.

The one-center $2s^2$ terms are kept constant at fairly

arbitrary values because their scattering is very nearly (in the case of HF basis functions) or exactly (for STO orbitals) equal to the scattering of a spherical sum of p^2 products. The $2s$ occupancy can therefore not be determined independently. With these restrictions the total number of terms to be determined for the cyanuric acid molecule is reduced to 66 in addition to the X-ray scale factor. It soon became apparent, however, that the $2s(A)2s(B)$ terms in the bonds were too strongly correlated with terms such as $2s(A)p_y(B)$, $p_y(A)2s(B)$ and $p_y(A)p_y(B)$. This agrees fully with earlier test calculations on carbon monoxide (Coppens, Willoughby & Csonka, 1971). Excluding $2s(A)2s(B)$ terms in each of the five non-equivalent bonds between non-hydrogen atoms leads to a model with 61 population parameters, which are explicitly listed in Table 5 (sets I-H and I-S, $H=HF$, $S=STO$ with HSP exponents).

Following the experience obtained in the diborane

Table 5. Cyanuric acid: population parameters for three Hartree-Fock parameter sets

Parameters	I-H	II-H	III-H	Parameters	I-H	II-H	III-H
k	10.06 (2)	9.99 (1)	10.04 (1)	$O(2)p_x^2$	1.28 (3)	1.37 (3)	1.41 (5)
$C(2)p_x^2$	0.83 (6)	0.82 (5)	0.87 (6)	$p_x p_y$	0.35 (5)	0.42 (5)	-
$p_x p_y$	-0.05 (10)	-0.07 (10)	-	p_y^2	1.47 (3)	1.58 (2)	1.51 (2)
p_y^2	0.64 (5)	0.58 (5)	0.50 (6)	p_z^2	1.32 (4)	1.41 (2)	1.37 (3)
p_z^2	0.79 (5)	0.69 (4)	0.71 (4)	sp_x	0.72 (11)	0.75 (9)	0.57 (6)
sp_x	0.33 (17)	0.53 (16)	0.44 (7)	sp_y	-0.41 (7)	-0.42 (5)	-0.29 (4)
sp_y	-0.17 (12)	-0.12 (13)	-0.34 (12)	$O(1)p_x^2$	1.53 (5)	1.72 (4)	1.68 (4)
$C(1)p_x^2$	0.46 (8)	0.44 (8)	0.53 (8)	p_y^2	1.11 (6)	1.25 (5)	1.15 (6)
p_y^2	0.86 (9)	0.65 (9)	0.52 (10)	p_z^2	1.28 (5)	1.36 (4)	1.36 (4)
p_z^2	0.83 (7)	0.74 (5)	0.75 (6)	sp_y	0.54 (18)	0.75 (14)	1.01 (15)
sp_y	0.81 (24)	0.57 (23)	0.01 (22)	$H(2)1s^2$	0.09 (6)	0.03 (7)	0.18 (12)
$N(2)p_x^2$	0.90 (4)	0.92 (3)	0.94 (4)	$H(1)1s^2$	-0.29 (11)	-0.12 (12)	0.09 (12)
$p_x p_y$	0.18 (7)	0.04 (6)	-				
p_y^2	0.92 (4)	1.00 (3)	0.84 (4)				
p_z^2	1.34 (5)	1.48 (4)	1.30 (3)				
sp_x	0.12 (10)	0.07 (9)	0.10 (6)				
sp_y	-0.21 (11)	-0.17 (10)	0.08 (10)				
$N(1)p_x^2$	0.98 (6)	0.86 (5)	0.79 (5)				
p_y^2	0.84 (5)	1.06 (4)	1.03 (5)				
p_z^2	1.34 (6)	1.54 (5)	1.30 (4)				
sp_y	0.52 (13)	-0.02 (12)	-0.09 (11)				
$C(1)N(2)$				$C(2)O(2)$			
$p_y s$	0.92 (41)	-	-	$p_y s$	1.27 (29)	-	-
sp_y	1.05 (34)	-	-	sp_y	-0.08 (35)	-	-
$p_x p_x$	-0.96 (19)	-	-	$p_x p_x$	-0.95 (17)	-1.05 (17)	-0.30 (18)
$p_y p_y$	-3.51 (42)	-3.04 (25)	-2.39 (19)	$p_y p_y$	-1.24 (46)	-1.27 (29)	-1.67 (17)
$p_z p_z$	0.32 (17)	-0.03 (17)	-0.32 (19)	$p_z p_z$	-0.22 (18)	-0.14 (17)	-0.23 (20)
$C(2)N(2)$				$C(1)O(1)$			
$p_y s$	1.11 (36)	-	-	$p_y s$	1.84 (39)	-	-
sp_y	-0.38 (36)	-	-	sp_x	-0.77 (47)	-	-
$p_x p_x$	-0.73 (20)	-	-	$p_x p_x$	-0.77 (27)	-0.45 (23)	0.05 (27)
$p_y p_y$	-2.03 (33)	-2.61 (24)	-2.28 (25)	$p_y p_y$	-0.15 (64)	-1.75 (42)	-2.49 (44)
$p_z p_z$	0.22 (20)	0.28 (21)	0.22 (22)	$p_z p_z$	-0.13 (27)	0.52 (25)	0.72 (27)
$C(2)N(1)$				$N(2)H(2)$			
$p_y s$	2.60 (31)	-	-	ss	-2.71 (45)	-2.00 (29)	-
sp_y	1.26 (41)	-	-	$p_y s$	4.27 (38)	4.08 (31)	2.52 (15)
$p_x p_x$	-0.74 (18)	-	-				
$p_y p_y$	-1.94 (34)	-3.11 (25)	-2.41 (17)	$N(1)H(1)$			
$p_z p_z$	0.34 (17)	0.48 (18)	0.19 (19)	ss	-6.04 (34)	-2.84 (46)	-
				$p_y s$	7.07 (59)	4.88 (49)	2.59 (28)

calculations, the parameter set was further reduced by eliminating the $2sp_y$ and p_y2s terms in all bonds, because of their strong correlation with $p_y p_y$ orbital products. To arrive at a minimal parameter set a further clue was taken from theoretical minimal basis set calculations, which indicated that $p_x p_y$ population parameters in all but the C–O bonds were very small. In this way a set of 48 population parameters, listed in Table 5, was obtained. All refinements with the 62 and 49 parameter sets (including the scale factor) were done with both HF and HSP basis sets. As the former consistently produced the better agreement with the experimental structure factors, two more parameter sets were tested with only the HF basis set. They are obtained by omitting all one-center products between different p orbitals, such as $p_x p_y$ (the quadrupolar terms) and the $2s1s$ terms in the NH bonds from the 49 parameter set. The second set (IV–H) differs from the first (III–H) of these 44 parameter sets in that all $p_y p_y$ terms in the bonds are replaced by $2s2s$ terms, to determine which of these orbital products gives the best fit to the experimental bond density.

The results are summarized in Tables 5, 6 and 7. Several conclusions can be drawn:

(1) The experimental data are fitted better with the isolated atom HF atomic orbitals. This contrasts with experience obtained with spherical charge refinement methods for a number of compounds and with the aspherical population treatment of tetracyanoethylene-oxide (Matthevs *et al.*, 1972).

(2) The number of electrons in chemically-equivalent bonds or on chemically-equivalent atoms are not always equal for the STO refinements, but for the HF refinements there are very few discrepancies. One of these is provided by the populations of the two C–O bonds for the set III–H, which are 0.11 and 0.78 electrons. They are attributed to correlation between one- and two-center terms in the population refinement. In the Mulliken population analysis (Table 7) in which two-center terms are distributed equally among the two centers, the discrepancy disappears, and chemical symmetry is restored. Thus, the populations for C(1), C(2) and O(1), O(2) are (for the set III–H) 5.70, 5.85, 8.08 and 7.85 electrons respectively. These numbers do not necessarily agree with the net atomic charges obtained in the spherical refinements (Coppens, Pautler & Griffin, 1971) as the division of the overlap density in the Mulliken population analysis is somewhat arbitrary.

(3) Good agreement is obtained for the one-center p_z^2 parameters (which are directly comparable because the z axis is always chosen perpendicular to the molecular plane). For example, in set III–H the p_z^2 population parameters for C, N, O are respectively 0.71 (4), 0.75 (6), 1.30 (3), 1.30(4) and 1.37 (3), 1.36 (4). This indicates that the individual one-center terms are better determined than the parameters describing bond scattering.

(4) The agreement between comparable population

parameters in equivalent bonds improves with a reduction of the parameter set. This again suggests that the smaller parameter sets are to be preferred, even though the R values increase by small, but significant amounts when the parameter set is reduced.

(5) Comparison of refinements III–H and IV–H shows that the sigma component of the bond scattering is much better described by the $p_y(A)p_y(B)$ term than by the more diffuse $2s(A)2s(B)$ product. Not only is the agreement index considerably worse for the latter set, but it also leads to physically unreasonable negative values for the other bond terms, which compensate for the diffuseness of the $2s2s$ product. It should be noted that limiting the bond scattering as in III–H does not imply *mmm* symmetry for the bonds between unequal atoms, because the centroids of orbital products such as $p_y(A)p_y(B)$ are closer to the more electronegative atom.

Table 6. *Experimental atom and bond populations in cyanuric acid (electron units)*

Parameter sets are defined in the text.
H = Hartree-Fock, S = Slater-type orbital.

	I–H	I–S	II–H	II–S	III–H	IV–H
C(2)	5.26	6.76	5.09	4.49	5.08	4.68
C(1)	5.15	7.48	4.83	4.43	4.79	4.64
N(2)	6.41	6.70	6.65	6.02	6.33	5.79
N(1)	6.41	6.25	6.71	6.09	6.37	5.77
O(2)	7.57	7.06	7.86	7.39	7.79	7.21
O(1)	7.42	8.99	7.83	7.41	7.68	6.93
H(2)	0.09	0.42	0.03	0.40	0.18	0.68
H(1)	–0.29	0.44	–0.12	0.40	0.09	0.79
C(1)N(2)	0.73	–0.58	0.76	0.77	0.52	0.47
C(2)N(2)	1.02	0.02	0.75	1.04	0.76	1.11
C(2)N(1)	1.07	–0.10	0.91	1.01	0.66	0.90
C(2)O(2)	0.58	0.22	0.05	0.63	0.11	0.72
C(1)O(1)	0.95	–1.34	0.41	1.31	0.78	1.59
N(2)H(2)	0.46	1.08	0.76	0.99	1.14	1.11
N(1)H(1)	–0.11	1.02	0.64	0.88	1.15	0.94
$R(F)$ (%)	2.6	3.4	3.0	3.7	3.1	3.5
$R_w(F)$ (%)	1.8	2.4	2.2	2.6	2.4	3.0
Number of parameters	62	62	49	49	44	44

Table 7. *Gross Mulliken populations from experimental results on cyanuric acid*

Numbers are in electron units.

Atom	I–H	I–S	II–H	II–S	III–H	IV–H	Theoretical STO-3G
C(2)	6.60	6.83	5.95	5.83	5.85	6.05	5.58
C(1)	6.35	6.22	5.80	5.86	5.70	5.90	5.58
N(2)	7.51	6.96	7.79	7.42	7.54	7.14	7.38
N(1)	7.43	6.66	7.94	7.54	7.61	7.14	7.38
O(2)	7.86	7.17	7.89	7.71	7.85	7.57	8.28
O(1)	7.90	8.32	8.04	8.07	8.08	7.73	8.28
H(2)	0.32	0.96	0.41	0.90	0.76	1.24	0.75
H(1)	–0.34	0.95	0.20	0.84	0.67	1.25	0.75

These conclusions are generally compatible with the results of the diborane test calculations. In the following paragraphs we shall discuss two ways in which the experimental information can be compared with theoretical calculations.

Density maps

Since correlation between parameters remains a problem even in the limited parameter sets, one might question how well the resulting parameters describe the electron density features, such as observed in the X-N difference density map. An answer may be obtained by subtracting from the population parameters the values corresponding to spherical neutral atoms, and converting the resulting ΔP values into the thermally averaged electron density distribution $\Delta\rho$ according to the expressions:

$$F_{\text{calc}} = \sum_{\mu} \sum_{\nu} \Delta P_{\mu\nu} f(P_{\mu\nu}) \exp\left(\frac{2\pi i}{\lambda} \mathbf{S} \cdot \mathbf{r}_{\mu\nu}\right) T_N(\varphi_{\mu}\varphi_{\nu})$$

where $f(P_{\mu\nu})$ is the scattering of the orbital product $\varphi_{\mu}\varphi_{\nu}$ (f depends in general on the direction of \mathbf{S}), centered at $\mathbf{r}_{\mu\nu}$ with temperature factor $T_N(\varphi_{\mu}\varphi_{\nu})$ as determined by neutron diffraction and

$$\Delta\rho(\mathbf{r}) = \sum_{\mathbf{h}} F_{\text{calc}}(\mathbf{h}_n) \exp 2\pi i(\mathbf{h}_n \cdot \mathbf{r})$$

The resulting ΔP or 'population asphericity' maps for parameter sets I-H and I-S are shown in Fig. 2. It is apparent from comparison with the X-N difference density (Fig. 3) that the overlap and bond densities are much better represented by the HF parameters than by the STO set.

This is in agreement with the lower R values obtained in the former treatment, and adds weight to the conclusion arrived at in the B_2H_6 refinement that the orbital set with the best R value also gives the best description of the electron distribution.

The agreement between the HF map of the most extensive set (I-H, 62 parameters) and the X-N map in the molecular plane (Fig. 3) is quite close. All the peaks in the X-N map are represented. Those in the bonds have exactly the same height as in the experimental density function, but there is slightly less density in the lone pair regions, while the negative areas around the nuclei are somewhat more pronounced in the ΔP map. However, it is clear that the population formalism with the best basis set gives an adequate description of the molecular electron density distribution, which is much superior to the spherical atom formalism with apparent thermal smearing in bonding directions.

It is of interest to examine how much of this fit is sacrificed in the refinements with the reduced number of parameters. The densities in the molecular plane for sets II-H (49 parameters) and III-H (44 parameters) are given in Fig. 4. In the 49 parameter set a number of heavily correlated bond terms were omitted. This apparently did not reduce the flexibility of the model, because the corresponding density map is very similar to the one for the extensive parameter set. The effect of omitting the five one-center quadrupole ($p_x p_y$) terms is apparent in the density map III-H. The lone pairs

are clearly less well represented, and the same holds for some of the overlap density, such as the peak in the C(2)-O(2) bond. It follows that the one-center quadrupole terms are an essential part of the population parameter set.

Comparison with theoretical density maps

When theoretical population parameters are available the neutron diffraction thermal parameters can be employed to obtain a thermally averaged theoretical difference density map. Minimal basis set calculations for the molecule of cyanuric acid have been performed with the semi-empirical INDO method (McIver, Coppens & Nowak, 1971) and with the *ab initio* method in the STO-3G approximation (Stewart, unpublished). The thermally averaged difference density maps are given in Fig. 5. The disagreement between these minimal basis set densities and the experimental results on which Figs. 2, 3 and 4 are based is striking. There is a great deficiency of density in the bonding regions and an excess in the lone-pair regions of the theoretical maps, indicating that these minimal basis set calculations are inadequate for a study of electron densities. This conclusion is in agreement with studies by Smith & Richardson (1967), which showed that minimal basis set calculations produced no or very little density in the bonds in difference maps for the nitrogen molecule. The situation is much improved when more flexible basis functions, especially those including d orbitals, are used in the calculation. For example, with a mini-

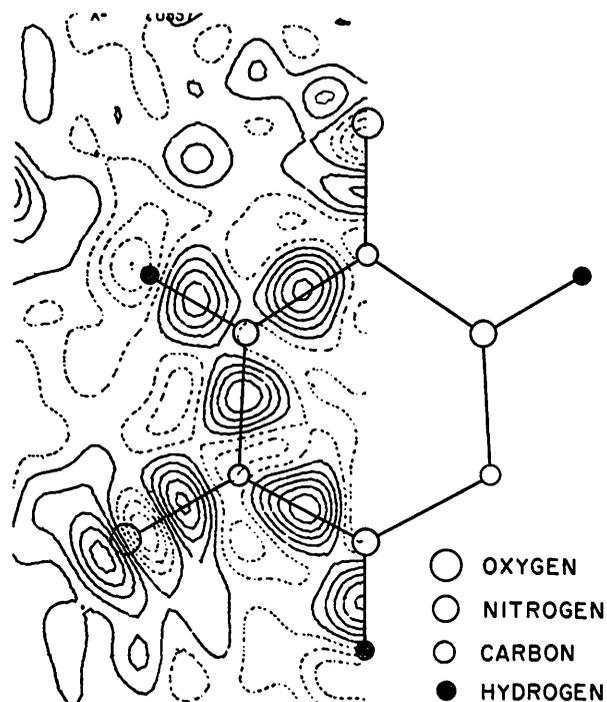


Fig. 3. X-ray minus neutron difference density in the plane of the cyanuric acid molecule (Coppens & Vos, 1971).

mal basis set with optimized exponents a theoretical difference density of about $0.3 \text{ e.}\text{\AA}^{-3}$ was obtained by Smith & Richardson (1967) at the center of the nitrogen molecule at rest, but the Hartree-Fock calculation including d orbitals gave a dramatically increased value of about $1.25 \text{ e.}\text{\AA}^{-3}$.

Similar results have been obtained for other molecules by Cade & Bader (private communication), while Halgren, Anderson, Jones & Lipscomb (1971) showed that an extension of the basis set for H_2 and BH accounts for 0.03 \AA of the apparent shortening of the bond lengths in these molecules.

The effect of the extension of the basis set on the difference density is clearly outside the experimental error in the diffraction results.

Eigenparameter analysis

A major obstacle to a comparison of experimental and theoretical population parameters is the problem of correlation among the experimental parameters. The calculations described above indicate that the experimental parameters are not determined with high accuracy, even though the agreement between observed and calculated structure factors may be excellent.

As was pointed out by Diamond (1966), it is possible to transform the least-squares parameters to a statistically uncorrelated set, which can be termed the eigenparameters. This can be shown as follows. Given the variance-covariance matrix \mathbf{M}_x , based on the set of variables \mathbf{x} , we can obtain a diagonal matrix $\mathbf{\Lambda}$ by carrying out the orthogonal transformation

$$\mathbf{\Lambda} = \mathbf{T}\mathbf{M}_x\mathbf{T}'$$

where \mathbf{T} is the matrix of the eigenvectors.

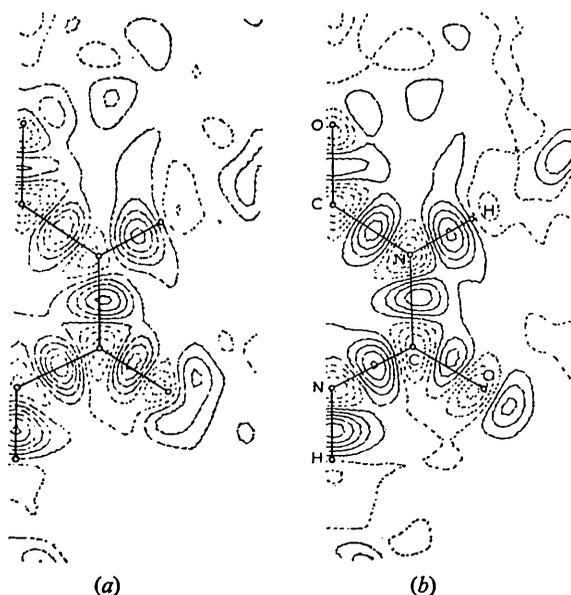


Fig. 4. As Fig. 2, (a) for the 49 parameter set II-H, (b) for the 44 parameter set III-H.

The diagonal matrix $\mathbf{\Lambda}$ represents the variance-covariance matrix based on the set of parameters $\mathbf{x}' = \mathbf{T}\mathbf{x}$. By the definition of the variance-covariance matrix, the variables \mathbf{x}' are not correlated.

In practice, the final variance-covariance matrix from a least-squares analysis of experimental data is diagonalized to yield the matrix \mathbf{T} , and the eigenparameters \mathbf{x}' . The same matrix \mathbf{T} can then be used to transform theoretical population parameters \mathbf{y} to a set of theoretical eigenparameters \mathbf{y}' . *The comparison between the experimental and theoretical eigenparameters is unaffected by correlation* and can be used to judge theoretical calculations, in the same sense in which electron-density maps were compared as described above.

A number of considerations complicate this idealized description. First, the variance-covariance matrix is dependent on the weights assigned to the observations, which are based on an estimate of the experimental errors. It is therefore important that these errors are estimated correctly. Errors due to an inadequate model are neglected in the derivation of the weights, which could be an important deficiency if a grossly incorrect basis set is used.

Secondly, Scheringer has pointed out (1968) that the 'filtering' procedure proposed by Diamond (*i.e.* filtering out the poorly determined eigenparameters) is ambiguous when the set of variables is 'non-homogeneous', *i.e.* when the set contains variables of different types, expressed in different units. In our case the population parameters form a homogeneous set, but the scale factor is of a different type.

The latter problem was avoided by carrying out an additional least-squares cycle in which the scale factor was fixed at its final value and the set of 'homogeneous' population parameters was varied to yield the matrix \mathbf{T} and the corresponding eigenparameters.

In order to determine the effectiveness of the eigenparameter analysis an extreme case of correlation among variables was constructed by including both $2s^2$ and the p_x^2 , p_y^2 and p_z^2 terms on the boron atoms as variables in a refinement of diborane with the HSP basis set. The spherical average of the $2p^2$ functions is identical to the $2s^2$ function, generating 100% correlation (except for round-off errors in the scattering factors). Table 8 gives the theoretical and experimental least-squares parameters for this test case, along with the eigenparameters resulting from the diagonalization. Note that the well determined experimental eigenparameters show reasonable agreement, in contrast to the abnormal disagreement for the boron $2s^2$ and $2p^2$ parameters. As can be anticipated, the good agreement is obtained for eigenparameters representing the sum of the $2s^2$ and $2p^2$ scattering, indicating that the sum of the populations can be determined quite precisely, while their difference is an experimentally indeterminate quantity.

Similar results were obtained in a corresponding treatment of cyanuric acid. Examination of the results showed the eigenvectors to be linear combinations of

Table 8. Population parameters and eigenparameters for a test calculation on diborane

	Theoretical	Experimental
Boron		
1s ²	2.059	1.971 (2)
2s ²	0.521	25.2 (35)
p _x ²	0.319	-8.3 (12)
p _y ²	0.532	-8.1 (12)
p _z ²	0.180	-8.4 (12)
sp _x	0.219	0.07 (3)
HT₁		
1s ²	0.705	0.570 (8)
HT₂		
1s ²	0.705	0.568 (10)
HB		
1s ²	0.664	0.570 (13)
B-HT₁		
ss	0.642	2.89 (17)
p _x s	0.051	0.02 (4)
p _y s	1.040	-0.10 (10)
B-HT₂		
ss	0.642	2.88 (16)
p _x s	0.051	0.03 (4)
p _y s	1.040	-0.09 (11)
B-HB₁		
ss	0.209	1.78 (22)
p _y	0.705	-0.01 (12)
p _z	-0.077	0.006 (9)
B-HB₂		
ss	0.209	1.63 (22)
p _y s	0.705	0.01 (13)
p _z s	0.077	0.04 (7)

Eigenparameters	
Theoretical	Experimental
2.615	2.615 (0)
-1.128	-1.064 (1)
0.261	0.190 (2)
0.051	0.067 (3)
0.501	0.270 (3)
0.581	0.512 (4)
0.068	0.095 (5)
-0.367	-0.356 (6)
0.003	0.003 (10)
0.019	0.044 (11)
-0.009	-0.056 (20)
-1.020	-1.219 (29)
0.557	0.569 (32)
0.220	0.435 (47)
0.244	0.761 (58)
0.087	-0.238 (68)
-0.034	-0.002 (145)
-0.237	3.845 (171)
-0.049	0.424 (256)
-0.194	-0.666 (304)
-0.154	-28.970 (4082)

orbital products extending over the whole molecule, rather than being localized essentially in one region. Typically, a large $p_y s$ term in the N(1)-H(1) bond would appear in a combination which also has large contributions of ss in the same bond and sp_y on N(1). As was noticed before, such terms are highly correlated and as a result certain linear combinations are well,

and others poorly, determined. The eigenparameters with the lowest standard deviations contain a large contribution from one-center orbital products, and it is interesting that they agree fairly well with the theoretical eigenparameters (the set y') as calculated from an INDO calculation. The agreement is poor, however, for those eigenparameters which contain large contributions from the two-center terms. This result is not unexpected, because the comparison of the theoretical and experimental difference density maps has shown that the largest disagreement between the two is in the regions of the bonds. The eigenparameter analysis confirms this conclusion at a different level of comparison.

The results on the eigenparameter analysis are preliminary, but they indicate that further study is warranted, and that the method has promise in dealing with correlation. A more thorough understanding of the way experimental errors and variation in the model affect the diagonalization is desirable.

Conclusion

We conclude from this study that diffraction analysis of charge densities is a unique tool which can point out deficiencies in theoretical calculations. Further, the population analysis provides an adequate numerical description of the electron density, but, because of correlation effects, the population coefficients cannot be compared directly with theoretical results. This com-

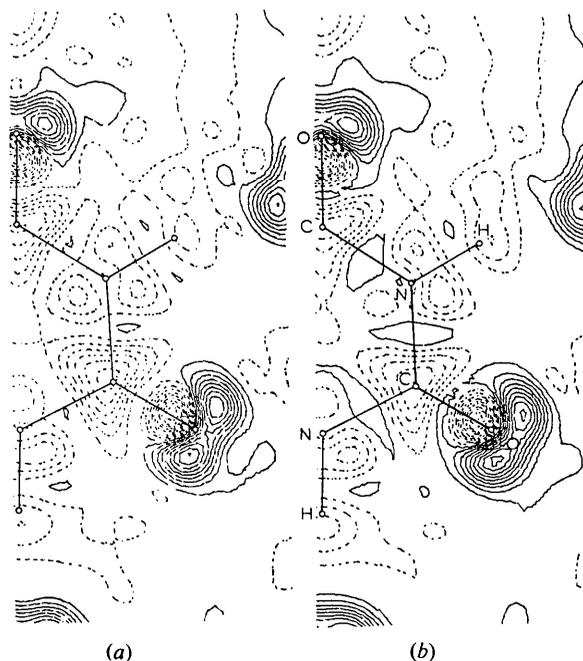


Fig. 5. Theoretical difference maps in the plane of the cyanuric acid molecule, thermally averaged with the neutron diffraction thermal parameters. (a) INDO calculation, (b) minimal basis set STO-3G calculation.

parison of population parameters may be better achieved by a transformation to uncorrelated linear combinations of population parameters, as described in the last section of this article. The comparison of the electron density maps shows clearly that neither INDO, nor STO-3G minimal basis set calculations give an adequate representation of the electron density in the bonding regions of the cyanuric acid molecule.

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Acta Cryst. (1972). **A28**, 645

Determination of a Probable Reflexion Symmetry by Counting Statistics shown in the Example of the Zeolite, NaPl

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The deviation of symmetry equivalent intensities from their mean values was used to determine a probable reflexion symmetry for the zeolite NaPl. The method of investigation is based on the χ^2 test and compares the measured deviation with the one expected from counting statistics. The lattice dimensions of zeolite NaPl are cubic, but it was suspected that its symmetry is tetragonal and that the crystal is multiply twinned, thus simulating a near cubic X-ray pattern. Cubic symmetries were clearly rejected by the test and it was shown that reflexion symmetry *mmm* is a good approximation for the observed intensities.

1. Introduction

Schulz & Huber (1971) described a method by which X-ray intensities, obtained with a single-crystal diffractometer, can be tested for significant deviation from an assumed reflexion symmetry. The method is based on the χ^2 test. In this paper its application will be explained using as an example the synthetic zeolite NaPl. A brief description of the background of the NaPl problem is given below. A more detailed account of it can be found elsewhere (Baerlocher & Meier, 1972).

Zeolite NaPl crystallizes, normally as spherulitic aggregates of 1–2 μ diameter, from sodium aluminosili-

cate gels under hydrothermal conditions. The powder pattern can be indexed on a body-centered cubic unit cell with an *a* dimension of 10.04 Å. An interesting framework structure with *Im3m* symmetry was proposed but the refinement with powder data did not proceed satisfactorily. Further evidence then indicated that the NaPl structure may be based on the gismondine framework, which has similar cell dimensions. However, this framework possesses only a maximum symmetry of *I4₁/amd* and the powder data were clearly insufficient for a structure analysis based on this framework. A larger crystal of NaPl was synthesized and precession photographs showed a body-centred cubic lattice. Optical examination of the crystal indicated multiple twinning. It was suspected that the individual sections of the crystal are related to each other by a rotation of 90° around their *a* or *b* axis

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