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Electron Density Studies.
IV. A Comparison of Techniques for Charge-Density Analysis and their Application to *s*-Triazine

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Some techniques for charge-density analysis proposed by R. F. Stewart have been compared by application to *s*-triazine, with X-ray data and neutron structural parameters. There is strong correlation between population coefficients for density basis functions which overlap heavily with each other, and in extreme cases individual populations are indeterminate. Multipole expansions centred on the nuclei are better defined than sets of orbital products which include two-centre terms. Trigonal octupole functions centred on the carbon and nitrogen nuclei give a marked improvement in the description of the scattering experiment provided the exponents which determine the radial variation of the density functions are optimized. The optimum exponent varies with the length of the multipole expansion. New algorithms developed for these studies give improved computational efficiency.

Introduction

The analysis of the charge density in crystals *via* diffraction experiments has now been investigated by many workers. Some methods involve a full theoretical calculation of the density in the cell, but this is feasible only for small structures. For larger systems the first stage is the separation, based on the convolution approximation (Coulson & Thomas, 1971), of the distribution function resulting from the motion of the electrons relative to the nuclei from that produced by the nuclear motion itself. The electron density is then represented as a sum of local 'one-centre' distributions centred on the nuclei, with the possible addition of 'two-centre' terms centred at other positions. Each of the one-centre terms is the convolution of the nuclear distribution function with the electron distribution relative to the nucleus. It is well known that the structure factor $F(\mathbf{S})$ for the X-ray Bragg experiment is the Fourier transform of the electron density. Since the Fourier transform of the convolution of two functions is the product of the transforms for the separate functions we may write

$$F(\mathbf{S}) = \sum_{n=1}^{N} f_n T_n \exp(-i\mathbf{S}.\mathbf{r}_n) \qquad (1)$$

where $\mathbf{r}_n$, T_N and f_n are the equilibrium position of the nth nucleus, the transform of the nuclear smearing function with $\mathbf{r}_n$ as origin (temperature factor), and the transform of the electron distribution with the nucleus as origin (form factor), respectively. $\mathbf{S}$ is a reciprocal-lattice vector, with magnitude S. It is assumed that the separation into form and temperature factors is also valid for the two-centre terms. The analysis of charge density is equivalent to the evaluation of the parameters which determine the form factors.

Orbital products

Stewart (1969) proposed that the electron density be expressed as a sum of orbital products

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \chi_{\mu}^{*}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \qquad (2)$$

where the χ_μ, χ_ν are atomic orbitals and the $P_{\mu\nu}$ are population coefficients. Analytical expressions for the Fourier transforms of one-centre Slater-type orbital (STO) products and one and two-centre Gaussian-type orbital (GTO) products are given by Stewart (1969).

In its simplest form applicable to molecular crystals containing first row atoms the density function consists of invariant $(1s)^2$ cores plus a valence density constructed from a minimal set of $2s$ and $2p$ orbitals, with $1s$ orbitals for hydrogen. These generate a set of one and two-centre products, but this set is not minimal in the same sense as the parent orbitals. Thus a $(2p)^2$ product generates a function into which an sd product with similar radial dependence projects with high efficiency.

The analysis of electron-density distributions in terms of orbital products appears to provide an experimental method for determining the diagonal elements of a first-order density matrix. Coppens, Csonka & Willoughby (1970) have applied this method to a range of problems. Nevertheless there are serious difficulties with this approach. The Fourier transforms for products of different orbitals may resemble one another within the range of the accessible data (Stewart, 1972). Their population coefficients, which are strongly correlated, are correspondingly ill-defined.

Bond-directed scattering factors

At the one-centre level, determination of a full set of populations for $(s)^2$, $(p_x)^2$, $(p_y)^2$, $(p_z)^2$, sp_x, sp_y, sp_z,

p_yp_z, p_zp_x, and p_xp_y products is impossible because of the linear dependence of the $(s)^2$ and three $(p)^2$ functions. The ambiguity may be resolved by applying suitable constraints on the populations. O'Connor & Maslen (1974) have analysed the electron density in molecular crystals in terms of bond-directed scattering factors. In evaluating these the populations of the deformation terms in the distribution function are constrained to be consistent with nearest neighbour geometry and bond hybridization. A normalized density function of the form $(\chi_s + \mu\chi_p)^2/(1 + \mu^2)$ is associated with each chemical bond, including π bonds. μ is 1, $\sqrt{2}$, $\sqrt{3}$ and ∞ for approximate sp, sp^2, sp^3 hybridization and pure π bonding respectively. The bond-directed scattering factors are intended as a representation of the first-order departure from spherical symmetry due to chemical bonding. It is assumed that the first order effect can be described simply in terms of changes in population, without altering the radial dependence of the local distribution functions. The method cannot give an adequate description of the electron density near the midpoints of chemical bonds, which produce the comparatively sharp features observed in X-ray difference syntheses, because the one-centre density functions for the hybridized orbitals are too slowly varying for that purpose.

Two-centre scattering

The problem of similarity of density functions is acute for two-centre terms. For atoms A and B with p orbitals along the internuclear vector the products $2s_A2s_B$, $2s_A2p_B$, $2p_A2s_B$ and $2p_A2p_B$ are virtually identical. Stewart (1973*a*) has examined the transforms of these functions and suggested their replacement with a two-centre scattering function

$$f = P_{\text{bond}} \exp(-AS^2) + P'_{\text{bond}} S^2 \exp(-AS^2) + \ldots (3)$$

where

$$A = a_0^2/(\alpha_A + \alpha_B).$$

a_0 is the Bohr radius and α is the exponent* of a 1 GTO parent orbital from which the two-centre term is constructed. The second term is isotropic but vanishes at the origin, and the higher-order terms are anisotropic with angle-dependent components which integrate to zero.

A number of refinements including two-centre terms have been described by Allen-Williams, Delaney, Furina, Maslen, O'Connor, Varghese & Yung (1975). The scalar populations for these terms are invariably close to zero, indicating that components of the density which do not project efficiently into neighbouring one-centre terms are not well described by a slowly varying scalar two-centre term.

Multipole expansions

Difference densities for molecular crystals contain features which cannot be represented by one-centre products of s and p functions. If d orbitals are invoked without further restriction a large number of similar density functions are introduced. Stewart (1973*a*,*b*) has proposed an alternative formulation which reduces this redundancy. Each local distribution is written as a multipole expansion

$$\rho(\mathbf{r}) - \rho(\mathbf{r})_{\text{scalar}} + \rho(\mathbf{r})_{\text{dipole}} + \rho(\mathbf{r})_{\text{quadrupole}} + \cdots \quad (4)$$

The low-order terms relate directly to orbital products. A scalar term is obtained from an $(s)^2$ product, and the three independent dipoles are equivalent to one-centre sp_x, sp_y and sp_z terms. The set of products between p orbitals may be recast as a scalar plus five independent quadrupoles. The pd products give rise to three independent dipoles and seven octupoles, and so on.

In our analysis the scalar term for the first-row atoms is taken as the sum of an invariant $(1s)^2$ core plus a scalar valence-density term. This is regarded as a 'valence density' analysis. If the scalar term was written as the sum of the density of the isolated atom and another monopole term then it would become a 'deformation density' analysis.

This approach resembles that of Dawson (1967), and is a further development beyond the extension to low site symmetry by Kurki-Suonio (1968). However STO (exponential) radial functions are preferred to Gaussian functions, and the orders of the functions are chosen so that the high-order gradients of the electric field remain finite. The deformation-density methods of Hirshfeld (1971) and of Harel & Hirshfeld (1975) are similar except that their combinations of orbital products are not in traceless form.

Multipole density functions on the same centre are mutually orthogonal if they have different angular dependence. Functions on different centres are not orthogonal in general, but the correlation coefficients for multipoles on different nuclei are smaller than the high values which may occur for one and two-centre terms. Correlation between multipole populations is weak for expansions of limited length. Longer expansions on each centre give a representation which is essentially over-complete.

The multipole expansion method can be expressed in a form which is computationally rather efficient. Major calculations on form factors are carried out only once. The evaluation of structure factors and the formation of the least-squares normal equations involve simple multiplications by populations and products of Miller indices. A least-squares refinement with neutron structural parameters and a residual based on F may be expressed in linear form, so that iteration is not required. Details are given in the Appendix. It should

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* In this paper distances generally are given in Å (10^{-10} m) but orbital exponents are in atomic units to conform with theoretical calculations.

be noted that a separate scale factor for the intensity data is not included directly as a variable parameter. If the experiment were ideal, if the actual valence density projected exactly into the simple functions used here, and if there was no core deformation, the core populations would be exactly two electrons. The scalar valence populations would then sum to electrical neutrality without rescaling. This is not the case in practice and the following rescaling procedure is based on the assumptions of no core deformation and accurate structural parameters. The core populations are constrained to be equal in the analysis. The scale-factor for the data is taken to be that which rescales the populations to electrical neutrality. An alternative scale-factor is that which results in core populations of exactly two electrons. The projection parameter, defined as the ratio of these scale factors, gives a measure of the extent to which the actual valence density projects into the functions used.

For the first-row atoms, the difference between the core population and 2·0 is taken to represent a failure of the model to represent the valence density accurately and is added to the scalar valence populations. The latter then sum to the total number of valence electrons for the isolated atoms.

Exponent refinement

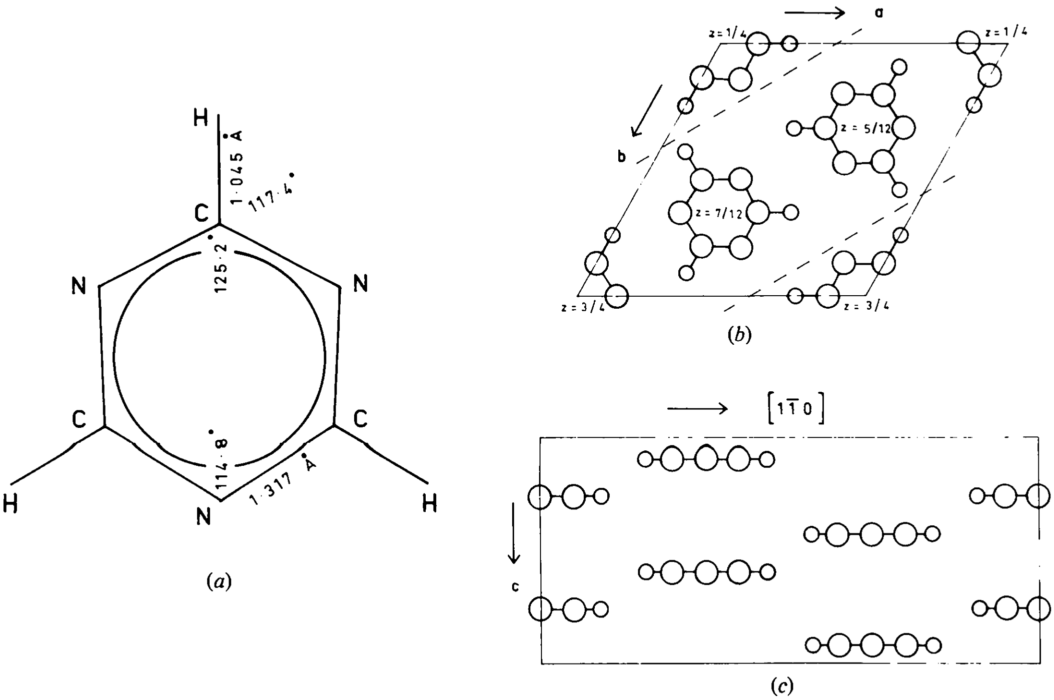
The exponents for density functions used in charge-density studies have usually been taken from theoretical calculations based on minimization of energies. Hehre, Stewart & Pople (1969) have tabulated a set of standard molecular values for Slater-type orbitals. These are mean values obtained from a wide range of theoretical calculations.

In a charge-density analysis Stewart (1973*c*) has shown that the optimum exponent varies with the length of the multipole expansion. Optimization of the exponents gives deformation functions which are much better defined than those obtained with standard molecular exponents.

An exact calculation of the derivatives for least-squares refinement of exponents involves evaluation of an expression similar to those for the form factors in forming the normal equations. This is prohibitive for a complex structure, and an efficient approximation procedure has been devised. A description of this method is included in the Appendix.

s-Triazine

s-Triazine, which has the molecular formula shown in Fig. 1, lies on a 32 site in a structure with space group $R\,\bar{3}\,c$. Each atom in the structure lies on a twofold axis, whereas it has *mm*2 symmetry in the free molecule. X-ray and neutron data have been collected by Coppens (1967), and a charge-density analysis at the scalar population level has been reported by Stewart (1970).



(*a*) (*b*) (*c*)

Fig. 1. The structure of *s*-triazine. (*a*) molecular dimensions [Coppens's (1967) neutron parameters], and crystal packing; projections down (*b*) the *c* axis and (*c*) the [110] direction.

The X-ray data are not unusually accurate or extensive. There is no chemical redundancy within the asymmetric unit, and because of its small size there are relatively few data close to the origin of reciprocal space, where information on the valence distribution is concentrated. Nevertheless, the symmetry of the structure restricts the number of multipoles which are possible. The small size of the structure limits the computational work involved. These are considerable advantages for the comparison of different methods of analysis. The validity of a comparative study is largely independent of errors in the intensity data, which will have similar effects in all the analyses.

Three series of refinements were carried out, based on bond-directed scattering factors, on one and two-centre density functions and on multipole expansions. Atomic self-consistent field (SCF) cores were used throughout. These were taken from Clementi (1965). The valence shells were constructed from Slater-type orbitals unless otherwise stated.

Bond-directed scattering-factor refinements

The results of refinements with bond-directed scattering factors are shown in Table 1. The residual minimized was based on $|F|^2$. The core populations for carbon and nitrogen were fixed at 2·0 e, and a scale factor was included as a variable parameter in the analysis. Standard molecular exponents were used for all density functions. For refinement (*a*) the structural parameters were fixed at the neutron values.

Because of the limited number of parameters required for this type of representation of the valence electron density it is feasible to explore the effect of simultaneously refining the structural parameters along with the population coefficients. For refinement (*b*) the structural parameters were included as variables. The coordinates of the carbon and nitrogen atoms were essentially unchanged in this refinement, but the hydrogen atom was displaced by 0·13 Å. Its population has increased by 0·08 e.

Table 1. *Analysis with bond-directed scattering factors*

Population coefficients in electrons, based on (*a*) neutron parameters (*b*) variable parameters. P_{val} is the total valence population. P_r, P_a and P_π are directed along the C—N bonds, axially and normal to the ring respectively. Standard deviations in parentheses.

	Atom	P_{val}	P_r	P_a	P_π
(*a*)	C	4·11 (25)	0·98 (11)	0·59 (12)	1·56 (13)
(*b*)		4·06 (78)	1·16 (31)	0·37 (51)	1·36 (56)
(*a*)	N	5·24 (22)	1·20 (6)	1·07 (11)	1·75 (14)
(*b*)		5·21 (60)	1·19 (15)	1·00 (37)	1·81 (75)
(*a*)	H	0·66 (11)			
(*b*)		0·74 (20)			

	$R(F)$	$R(F^2)$	$R_w(F^2)$	Proj.
(*a*)	0·059	0·042	0·044	1·16
(*b*)	0·053	0·032	0·036	0·89

There is a marked increase in the standard deviations for the populations, reflecting the difficulty of deconvoluting charge movements due to bonding from thermal motion when the amount of diffraction data is limited. The temperature-factor coefficients increased slightly during the refinement. This has the effect of broadening the sampling functions by amounts which are relatively larger for the carbon and nitrogen cores. The core-density functions have absorbed some of the valence density, and the projection coefficient has fallen. A similar result was observed for oxalic acid dihydrate by Allen-Williams *et al.* (1975). The changes in the rescaled populations are not significant in terms of the standard deviations, supporting the prediction of Stewart (1970) that gross populations will be insensitive to residual errors in the thermal parameters. Nevertheless the systematic nature of these changes is clear evidence for deficiencies in the electron-density model. The variation in the populations of the components is considerably larger than the differences between gross populations. Analyses of shapes of charge densities are thus more sensitive to thermal-parameter errors than measurements of 'atomic' charge.

Effect of two-centre terms

The results of refinements including two-centre terms are given in Table 2. In refinement (*a*) P_{bond} terms have been included with exponents equivalent to the standard molecular values, while in refinement (*b*) both P_{bond} and P'_{bond} terms have been included.

The gross population of the nitrogen varies a little in these refinements, but the carbon population shows stronger inverse correlation with the hydrogen and P_{bond} terms. The latter have small negative populations. This agrees with similar analyses (Allen-Williams *et al.*, 1975), but contrasts with the results of theoretical

Table 2. *Analyses including two-centre terms*

Population coefficients, in electrons, including (*a*) single-term two-centre function (*b*) two-term two-centre function.

	Centre	P_{val}	P_{bond}	P'_{bond}
(*a*)	C	5·03 (28)		
(*b*)		5·41 (28)		
(*a*)	N	5·45 (25)		
(*b*)		5·63 (31)		
(*a*)	H	0·45 (13)		
(*b*)		0·55 (15)		
(*a*)	N—C		−0·50 (20)	
(*b*)			−0·91 (32)	5·93 (392)
(*a*)	C—H		−0·22 (8)	
(*b*)			−0·34 (18)	1·26 (154)

	$R(F)$	$R(F^2)$	$R_w(F^2)$	Proj.
(*a*)	0·072	0·060	0·056	1·12
(*b*)	0·074	0·060	0·055	1·26

Table 3. *Analysis with standard molecular exponents*

(*a*) Scalars only (*b*) *mm*2 site symmetry, (*c*) 2 site symmetry.
The valence populations are scaled as in the text. Proj. is the projection parameter.

	Atom	P_{val}	D_1	Q_1	Q_4	Q_5	O_1	O_4	O_5
(*a*)	C	3·87 (10)							
(*b*)		3·90 (22)	−0·01 (9)	0·01 (10)		−0·01 (12)	0·15 (10)		−0·04 (8)
(*c*)		3·94 (23)	−0·03 (9)	0·03 (8)	−0·07 (16)	0·00 (12)	0·14 (10)	−0·04 (17)	0·17 (9)
(*a*)	N	5·26 (9)							
(*b*)		5·28 (23)	−0·03 (10)	−0·13 (9)		−0·01 (11)	−0·08 (11)		−0·05 (8)
(*c*)		5·24 (25)	−0·05 (9)	−0·14 (7)	0·08 (15)	−0·01 (10)	−0·10 (11)	0·14 (19)	0·14 (9)
(*a*)	H	0·86 (4)							
(*b*)		0·83 (9)							
(*c*)		0·82 (9)							
(*a*)	$R(F)$	0·057	$R_w(F)$	0·048	GoF	1·45 (11)	Proj.	1·10	
(*b*)		0·053		0·044		1·35 (10)		1·08	
(*c*)		0·052		0·043		1·34 (10)		1·08	

calculations, where the two-centre terms for nearest neighbours have populations of about 0·5 e. It is clear that the theoretical and experimental quantities are not directly comparable.

A further two-centre refinement was carried out in which P'_{bond} terms alone were included and their exponents were refined. The exponents obtained were effectively infinite. This is a significant result, since it corresponds to density functions which are sharply localized at the bond centres. This is consistent with the observation by Larson, Cromer & Ryan (1973) that residual two-centre scattering, *i.e.* that which is not accounted for adequately by one-centre terms, is a high-Bragg-angle phenomenon.

Multipole refinements

Because of the site symmetry (2) in the structure only one non-zero dipole component, three independent quadrupoles and three octupoles are permitted. The atoms in the free triazine molecule have higher symmetry (*mm*2) than that in the crystal (2), corresponding to an additional mirror lying in the plane of the molecule. This might be expected to persist approximately in the crystal. If valid, this reduces the number of independent quadrupoles and octupoles to two per atom. If, in addition, the density functions at the carbon and nitrogen atoms have trigonal ($\bar{6}m2$) symmetry there is only one quadrupole and one octupole term per atom.

The atomic-coordinate system chosen reflects the approximate $\bar{6}m2$ symmetry of the carbon and nitrogen sites. The **x** axis is chosen in the direction of the CH bond and the **z** axis is perpendicular to the molecular plane. (This choice has **x** parallel to **a**, and **z** parallel to **c**, with **y** in the *ab* plane.) The $\bar{6}m2$ allowed terms are then the trigonal octupole, O_1, and the cylindrically symmetric quadrupole, Q_5. Relaxation to *mm*2 site symmetry adds the dipole, D_1, the quadrupole, Q_1, and the octupole O_5. A site symmetry of 2 allows the additional terms Q_4 and O_4.

These density functions have been normalized as in paper II (Price & Maslen, 1978). The populations are the electron contents of the positive parts of the deformation functions.

In these refinements neutron structural parameters were used throughout and the residual minimized was based on $|F|$.

Standard molecular exponents

Table 3 lists the results of a series of refinements with multipole deformation functions and standard molecular exponents. The levels of approximation were (*a*) scalars only, (*b*) multipoles of *mm*2 symmetry for carbon and nitrogen and (*c*) multipoles of 2 symmetry for carbon and nitrogen.

The correlation between these charge-density terms is much less than between those of the previous models. The atomic-valence populations, P_{val}, are consequently much better defined. However, the fit of the model to the data is judged by the GoF* index, and this decreases only slowly as the level of the multipole expansion increases. This is in agreement with Stewart's (1973*c*) diamond valence-density analysis.

ζ refinement

In a further series of refinements the exponents for the scalar terms, which make a dominant contribution to the valence density, were refined with the approximation methods described in the Appendix. The results,

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$$*\mathrm{GoF} = \left[\sum_{i=1}^{n} \omega_i(\Delta F_i)^2/(n-p)\right]^{1/2}$$

where $\Delta F_i = F_{i,\text{obs}} - F_{i,\text{calc}}$, the difference between the observed and calculated structure factor, ω_i is the inverse of the variance of $F_{i,\text{obs}}$, n is the number of observations and p is the number of parameters. It can be shown that $E[(\mathrm{GoF})^2] = 1$, where $E[\ ]$ is the expectation value.

Table 4. *Analysis with optimized exponents*

(*a*) Scalars only, (*b*) $\bar{6}m2$ site symmetry, (*c*) $mm2$ site symmetry.
The valence populations are scaled as in the text. Proj. is the projection parameter.

	Atom	$SM\zeta$	ζ	P_{val}	D_1	Q_1	Q_5	O_1	O_5
(*a*)			1·67 (3)	3·70 (10)					
(*b*)	C	1·72	1·52 (5)	3·81 (18)			−0·02 (5)	0·11 (10)	
(*c*)			1·57 (3)	4·24 (17)	0·08 (12)	−0·04 (24)	−0·01 (14)	0·34 (26)	−0·25 (17)
(*a*)			1·83 (3)	5·41 (10)					
(*b*)	N	1·95	1·79 (5)	5·24 (16)			0·10 (5)	−0·33 (9)	
(*c*)			1·83 (3)	5·20 (17)	−0·05 (12)	−0·04 (18)	0·07 (8)	−0·15 (25)	−0·13 (18)
(*a*)			1·29 (3)	0·89 (12)					
(*b*)	H	1·24	1·01 (4)	0·95 (14)	−0·09 (5)				
(*c*)			1·62 (4)	0·56 (18)	0·08 (7)				
(*a*)	$R(F)$	0·054	$R_w(F)$	0·046	GoF	1·43 (11)	Proj.	1·09	
(*b*)		0·048		0·038		1·22 (9)		1·07	
(*c*)		0·044		0·035		1·15 (9)		1·04	

for (*a*) scalars only, (*b*) multipoles of $\bar{6}m2$ symmetry for carbon and nitrogen, and the dipole D_1 for hydrogen, and (*c*) $mm2$ symmetry for carbon and nitrogen, and the dipole D_1 for hydrogen, are shown in Table 4.

The GoF index decreases substantially with the introduction of those terms satisfying the approximate bonding symmetry and does not decrease significantly with the addition of terms allowed by the actual site symmetry. The final GoF value is a little greater than unity. Models (*b*) and (*c*) of this analysis are therefore better descriptions of the data than the models with standard molecular exponents.

The correlation between the parameter has, however, increased. This is partly due to a relatively small data set and thus the number of parameters approaches the number of data points in the low-angle region where these valence-density functions have their maxima. It results in less well determined parameters. As the number of terms is increased the correlation between parameters results in the valence (monopole) populations varying substantially.

The exponents are well-defined in these analyses. The values depend on the level of the multipole expansion. At the scalars-only level the exponents are close to, but a little below the standard molecular values. At the $\bar{6}m2$ level they are closer to the isolated

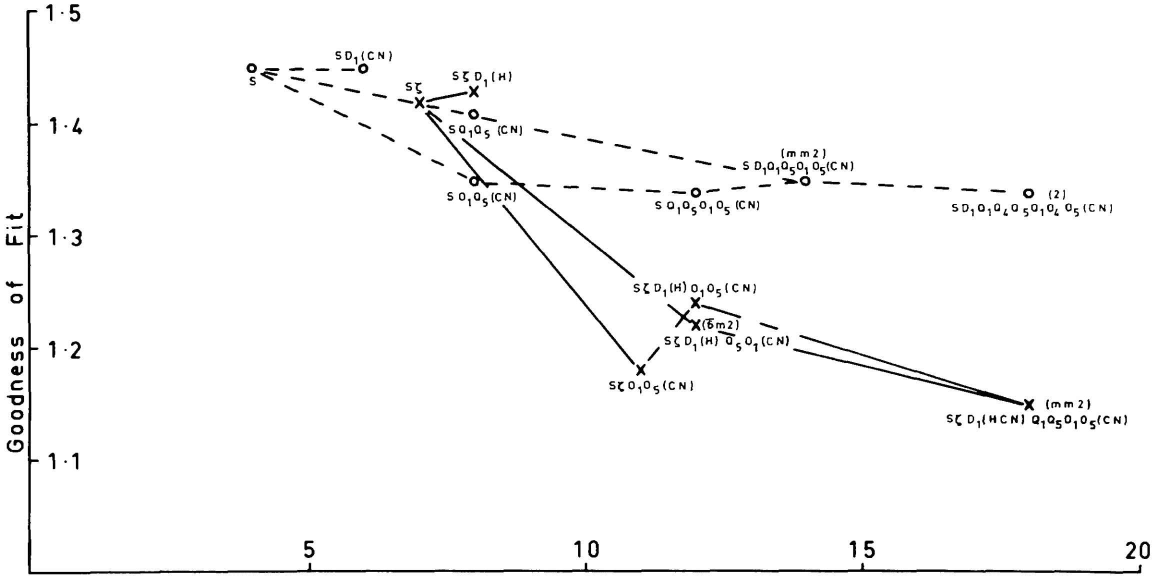

Fig. 2. The effect of exponent refinement and of inclusion of various multipoles in the model on the fit to the data. The model is characterized by which parameters are optimized. *S* refers to 'scalars' (a core and three valence populations), ζ to the valence exponent, while the populations of the other multipoles are coded as defined in the text. The atom on which the density functions were placed has its label [(H) or (CN)] following the multipole labels. Solid line: results with optimized exponents, dashed line: results with standard molecular exponents.

atom values. This behaviour is very similar to that of the carbon-atom exponent in the analysis of the valence density of diamond (Stewart, 1973*c*).

The variation of the GoF index with the level of expansion for a number of analyses with standard molecular exponents and optimized exponents is shown in Fig. 2. It shows the importance of exponent refinement and of the bond-directed octupole term, O_1, on the heavy atoms, which reduce the GoF index by more than three standard deviations.

The preferred model

We seek a description of the 'at rest' molecular electron density as a superposition of atom-like fragments and possibly 'bonding charges'. The model is required to be sufficiently flexible so that data of arbitrary accuracy can be adequately described. However, if the parameters are to represent local properties then the correlation between them must be kept as small as possible.

Of the models discussed in this paper, the multipole density function model with refined exponents and multipoles satisfying the approximate bonding symmetry (analysis *b* of Table 4) is clearly superior when judged in these terms. In this analysis four of the five deformation functions have populations greater than their e.s.d. The signs of the octupole functions on the carbon and nitrogen atoms are consistent with a redistribution of electrons (0·11 and 0·33 respectively) into the bonding directions. Similarly, the hydrogen dipole redistributes 0·09 e from the anti-bonding direction into the bonding direction. The nitrogen quadrupole takes 0·10 e from the plane of the ring and redistributes them above and below the plane.

The valence populations for this model result in atom charges close to 'gross charges' from the STO-3G (standard molecular) calculation of Stewart (1970). The agreement is not as good with the INDO results (Stewart, 1970) and is poor with the results from a more accurate calculation (Almlöf, Roos, Wahlgren & Johansen, 1973) with a more extensive basis set. This emphasizes the unreliability of Mulliken gross atomic charges (Fliszár, Kean & Macaulay, 1974; Coppens, 1975).

Conclusion

These results indicate that diffraction data allow the description of the at-rest molecular electron density as a superposition of 'pseudo-atoms' or deformed atoms. The populations of the major terms can be determined. The width parameter (exponent) of the scalar valence density term can also be determined. A multipole expansion provides a representation of the density which is more efficient from the point of view of charge-density analysis than an orbital-product formulation. Its populations are much better defined than those of representations where two-centre terms are included. Individual populations may become ill-defined, however, if the basis set of density functions is unduly large.

A comparison with the results of theoretical calculations will necessitate the projection of theoretical densities into similar pseudo-atom models.

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APPENDIX

(i) *Computation of the multipole expansion*

In the multipole approach to charge densities the angle dependences of the distributions are commonly given in terms of surface harmonics $P_l^m(\theta, \varphi)\, e^{im\varphi}$, which transform as surface harmonics. Alternatively, however, the transforms may be written in terms of linear coordinates as

$$f = \sum_{k=0}^{\infty} \left[i^k \frac{f_{\mu v,k}}{|\mathbf{S}|_k} \times \sum_{i_1=1}^{3} \sum_{i_2=i_1}^{3} \cdots \sum_{i_k=i_k-1}^{3} P_{i_1 i_2 \ldots i_k} h_{i_1} h_{i_2} \ldots h_{i_k} \right] \qquad (A1)$$

where h_1, h_2, h_3 are Miller indices, the $f_{\mu v,k}$ are the radial parts of the transforms defined by Stewart (1969) and the $P_{i_1 i_2 \ldots i_k}$ are population coefficients.

For quadrupoles and higher-order multipoles the number of terms in this expansion exceeds the number of independent coefficients. The quadrupole, with $k = 2$, has six coefficients of which five are independent. This corresponds to the expression of the quadrupole moment as a second-order tensor in a Cartesian frame **q**, which must be traceless. Alternatively we may write the quadrupole moment in a product space as

$$\mathbf{T}_Q\mathbf{q}^{(2)} \quad \begin{pmatrix} -3 & 0 & 0 & 3 & 0 & 0 \\ 0 & -3 & 0 & 0 & 0 & 0 \\ 0 & 0 & -3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 1 & 0 & 0 & 1 & 0 & -2 \end{pmatrix} \begin{pmatrix} q_1^2 \\ q_1 q_2 \\ q_1 q_3 \\ q_2^2 \\ q_2 q_3 \\ q_3^2 \end{pmatrix}$$

$$= \mathbf{T}_Q \mathbf{V} \mathbf{h}^{(2)} \qquad (A2)$$

where the Miller-index space **h** is related to that for the **q** by the linear transformation

$$\mathbf{q} = \mathbf{V}\mathbf{h}$$

and

$$\mathbf{q}^{(2)}=\begin{pmatrix} V_{11}V_{11} & (V_{11}V_{12}+V_{12}V_{11}) & (V_{11}V_{13}+V_{13}V_{11}) & V_{12}V_{12} & (V_{12}V_{13}+V_{13}V_{12}) & V_{13}V_{13} \\ V_{11}V_{21} & (V_{11}V_{22}+V_{12}V_{21}) & (V_{11}V_{23}+V_{13}V_{21}) & V_{12}V_{22} & (V_{12}V_{23}+V_{13}V_{22}) & V_{13}V_{23} \\ V_{11}V_{31} & (V_{11}V_{32}+V_{12}V_{31}) & (V_{11}V_{33}+V_{13}V_{31}) & V_{12}V_{32} & (V_{12}V_{33}+V_{13}V_{22}) & V_{13}V_{33} \\ V_{21}V_{21} & (V_{21}V_{22}+V_{22}V_{21}) & (V_{21}V_{23}+V_{23}V_{21}) & V_{22}V_{22} & (V_{22}V_{23}+V_{23}V_{22}) & V_{23}V_{23} \\ V_{21}V_{31} & (V_{21}V_{32}+V_{22}V_{31}) & (V_{21}V_{33}+V_{23}V_{31}) & V_{22}V_{32} & (V_{22}V_{32}+V_{23}V_{32}) & V_{23}V_{33} \\ V_{31}V_{31} & (V_{31}V_{32}+V_{32}V_{31}) & (V_{31}V_{33}+V_{33}V_{31}) & V_{32}V_{32} & (V_{32}V_{33}+V_{33}V_{32}) & V_{33}V_{33} \end{pmatrix}\mathbf{h}^{(2)}=\mathbf{V}\mathbf{h}^{(2)}.$$

Thus, the five independent quadrupole coefficients are linear functions of the $P_{i_1i_2}$. Octupoles and higher-order multipoles may be dealt with in a similar manner.

The form of (A2) is particularly interesting because of its similarity to the argument of the exponential in the cumulant expansion of the transform of the nuclear distribution function (Johnson, 1970),

$$C=T\exp(-i\mathbf{S}.\mathbf{r}_n)$$
$$=\exp\left[\sum_{k=1}^{\infty}\left(i^k\sum_{i_1=1}^{3}\sum_{i_2=i_1}^{3}\cdots\sum_{i_k=i_{k-1}}^{3}C_{i_1i_2\ldots i_k}h_{i_1}h_{i_2}\ldots h_{i_k}\right)\right]. \qquad (A3)$$

k = 1, 2, 3 and 4 defines the geometrical, dispersion, skewness and kurtosis terms respectively.

In a statistical model for the thermal motion the coefficients C in (A3) are treated as independent, but for a mechanistic model it is always possible to invoke the same expression, with linear constraints between the C's (see, for example, the treatment of librational motion by Pawley & Willis, 1970).

(ii) *Determination of the parameters*

We wish to determine the value of the P's, the C's if these are unknown and any other unknown parameters which affect the intensities in the diffraction experiment.

Adopting the method of least squares, we seek to determine the values of the parameters $L_1, L_2, \ldots L_i, \ldots L_I$ which minimize a residual function

$$R=\sum_{\text{obs}}\omega\varepsilon^2, \qquad (A4)$$

i.e. we require that

$$\frac{\partial R}{\partial L_i}=0 \qquad (A5)$$

for all i, with the second derivatives positive. ε is the difference between the observed and theoretical values for an observation and the weighting factor ω is the reciprocal of the variance for the observation.

In general, the observed quantity is a non-linear function of the parameters, and it is common practice to linearize the problem with a Taylor-series expansion for the observational equations. Following Stewart (1973a) we prefer the following alternative procedure.* We note that

$$\frac{\partial R}{\partial L_i}=2\sum_{\text{obs}}\omega\varepsilon\frac{\partial\varepsilon}{\partial L_i} \qquad (A6)$$

and

$$\frac{\partial^2 R}{\partial L_i\partial L_j}=2\sum_{\text{obs}}\omega\frac{\partial\varepsilon}{\partial L_i}\frac{\partial\varepsilon}{\partial L_j}+\varepsilon\frac{\partial^2\varepsilon}{\partial L_i\partial L_j}. \qquad (A7)$$

If ε is a linear function of the parameters the second-derivative term vanishes and there is a unique solution to the problem. For the non-linear case there may be several minima, and we seek the minimum near a set of trial parameters $L'_1, L'_2, \ldots L'_i, \ldots L'_I$. By a Taylor-series expansion

$$\frac{\partial R}{\partial L_i}=\frac{\partial R}{\partial L'_i}+\sum_{j=1}^{I}\frac{\partial^2 R}{\partial L'_i\partial L'_j}\delta L_j+\ldots, \qquad (A8)$$

where

$$\delta L_j=L_j-L'_j,$$

and we obtain the normal equations by truncating this series at the second term thus:

$$\sum_{\text{obs}}\sum_{j=1}^{I}\omega\left(\frac{\partial\varepsilon}{\partial L'_i}\frac{\partial\varepsilon}{\partial L'_j}+\varepsilon\frac{\partial^2\varepsilon}{\partial L'_i\partial L'_j}\right)\delta L_j$$
$$=-\sum_{\text{obs}}\omega\varepsilon\frac{\partial\varepsilon}{\partial L'_j} \qquad (A9)$$

which differ from the equations commonly employed by the inclusion of the second-derivative terms. Our form has two advantages. The use of the least-squares equations in this form may speed convergence in the later rounds of refinement, but it can actually hinder progress in early cycles in some cases. Nevertheless, it is worth quoting our experience that the use of acceleration factors on the shifts to speed convergence is usually unnecessary when the second derivatives are included. The principal advantage, however, is that the covariance matrix obtained by inverting this form of the normal-equations matrix reflects the true curvature of the error surface at the point of convergence.

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* In fact, the methods are equivalent if the Taylor-series expansion of the observational equations is done correctly. The usual practice is to truncate the Taylor series at the first term. Since the residual (A4) involves the square of the function its second-order term (the curvature matrix) depends on the function's zero-order, first-order and second-order terms. This results in the modified normal equations of (A9).

While the optimum choice of ε in (A4) requires further discussion its derivatives are always simply related to those of the calculated structure factor F_c. For a population coefficient belonging to the nth scattering unit

$$\frac{\partial F_c}{\partial P_{i_1 i_2 \ldots i_k}} = i^k \frac{f_{\mu\nu,k}}{|\mathbf{s}|^k} T_n h_{i_1} h_{i_2} \ldots h_{i_k} \qquad (A10)$$

and for a cumulant

$$\frac{\partial F_c}{\partial C_{i_1 i_2 \ldots i_k}} = i^k f_n h_{i_1} h_{i_2} \ldots h_{i_k} T_n. \qquad (A11)$$

Second-order derivatives involving different centres vanish uniquely, as do those for different populations on the same centre. The non-zero second derivatives are

$$\frac{\partial^2 F_c}{\partial P_{i_1 i_2 \ldots i_j} \partial C_{i_1 i_2 \ldots i_k}} = i^{j+k} \frac{f_{\mu\nu,j}}{|\mathbf{s}|^j} h_{i_1} h_{i_2} \ldots h_{i_j} h_{i_1} h_{i_2} \ldots h_{i_k} T_n \qquad (A12)$$

for a population and a cumulant, and

$$\frac{\partial^2 F_c}{C_{i_1 i_2 \ldots i_j} C_{i_1 i_2 \ldots i_k}} = i^{j+k} f_n h_{i_1} h_{i_2} \ldots h_{i_j} h_{i_1} h_{i_2} \ldots h_{i_k} T_n \qquad (A13)$$

for two cumulant coefficients for the nth scattering unit.

It should be noted that the $k = 0$ term in the cumulant expansion, equivalent to a scale factor, is explicitly omitted in this analysis. The population coefficients are determined to within a scale factor which may be defined by the condition of electrical neutrality, the theoretical value of the core contribution or other suitable constraint. This eliminates the problem of correlation between the scale and the population parameters during least-squares refinement. When the cumulant terms are known, from a neutron-diffraction experiment, it has the advantage that the least squares is linear and the need for iterative refinement is eliminated. This fact is perhaps the sole justification for refinements based on $|F|$, rather than $|F|^2$. The latter, on the other hand, permits an unbiased treatment of the weak reflections, for which statistical fluctuations may produce a background count in excess of the peak value. The evaluation of second-derivative terms for refinement on $|F|^2$ is straightforward since

$$\frac{\partial^2 |F_c|^2}{\partial L_i \partial L_j} = \frac{\partial F_c}{\partial L_i} \frac{\partial F_c^*}{\partial L_j} + \frac{\partial F_c^*}{\partial L_j} \frac{\partial F_c}{\partial L_j} + \frac{F_c \partial^2 F_c^*}{\partial L_i L_j} + \frac{F_c^* \partial^2 F_c}{\partial L_i L_j}. \qquad (A14)$$

These procedures are readily extended to incorporate analytical corrections for extinction.

(iii) *Exponent refinement*

We must evaluate terms of the form $\frac{\mathrm{d}}{\mathrm{d}\zeta} f_{\mu\nu,k}$, which for Slater-type orbitals is given by

$$\frac{\mathrm{d}}{\mathrm{d}\zeta} f_{\mu\nu,k} = \frac{\mathrm{d}}{\mathrm{d}\zeta} \int_0^\infty r^N \exp(-2\zeta r) j_k(Sr)\, \mathrm{d}r$$

$$= 2 \int r^{N+1} \exp(-2\zeta r) j_k(Sr)\, \mathrm{d}r$$

which involves a calculation equivalent to the evaluation of $f_{\mu\nu,k}$ for products of Slater terms in which the power of r is increased by unity. Although this expression is not particularly complex it may become computationally prohibitive if it is to be re-evaluated at each round of refinement for a complex structure with a large number of structure factors. In practice, the derivatives are nearly constant for the range of ζ's encountered in refining scalar terms and a single evaluation is good enough. Our normal procedure is to evaluate the $f_{\mu\nu,k}$ for the extreme values of ζ expected. The refined value of ζ is obtained by linear interpolation when the populations for the two components are determined. The range of the exponents may be narrowed if higher precision is required. This is seldom necessary.

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Electron-Density Studies.
V. The Electron Density in Melamine (2,4,6-Triamino-*s*-triazine) with and without Exponent Refinement

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The electron density distribution in melamine has been studied with X-ray diffraction data and neutron structural parameters. The at-rest valence density is represented as a set of nuclear-centred multipole density functions with Slater-type radial functions. Two series of analyses were compared, the first with the radial exponents fixed at the standard molecular values and the second with these exponents as variable parameters. Exponent refinement allows a marked improvement in the fit of the model to the data. The population coefficients of the multipole terms are better defined when the exponents are optimized. On chemically similar atoms the populations of the monopole terms are inversely related to the exponents. The carbon atom parameters agree to high precision. Exponents for the ring and amine nitrogens differ and small differences within each set are related to the hydrogen-bond and packing environment. The exponents and electron density near the nucleus are relatively low for hydrogens involved in hydrogen bonding. The most significant deformation functions in the multipole expansion have a symmetry compatible with nearest-neighbour geometry. Differences between populations are related to distortions from the idealized geometry or to hydrogen-bonding interactions. The inclusion of a hydrogen dipole deformation term with a large exponent results in internally consistent populations which are correlated with N–H stretching amplitudes in the structure. This suggests that the convolution approximation is invalid at this level of structure refinement.

Introduction

The free molecule of 2-4-6-triamino-*s*-triazine (melamine) has $\bar{6}m2$ symmetry. Each of the carbon and nitrogens has $mm2$ symmetry and the hydrogen atoms have symmetry m. In the crystal structure, which was first studied with X-ray data by Hughes (1941), there is one molecule in the asymmetric unit. The structure has since been more accurately determined with both X-ray and neutron data, by Varghese, O'Connell & Maslen (1977). A diagram of the structure is given in Fig. 1.

The unit cell is roughly equi-dimensional. The lack of a short cell dimension is a considerable advantage for charge-density analysis. In each principal direction there are points close to the origin of reciprocal space, where the contribution of the valence-electron density to the scattering is maximal. The parameters which determine the charge density can be determined to far higher accuracy than those for a smaller structure with data of comparable quality.

The symmetry of the free molecule is expected to persist approximately in the crystal. At this level of approximation the carbon and nitrogen atoms in the structure are equivalent in threes and the hydrogen atoms in sixes. This provides an internal check on the validity of the results.

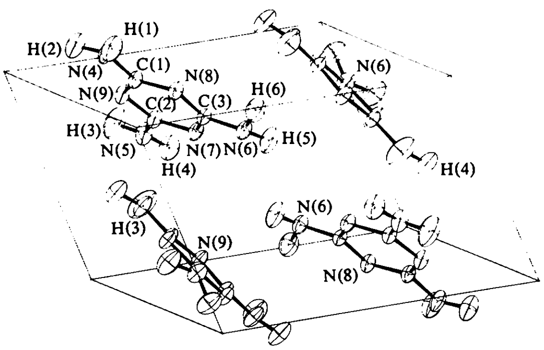

Fig. 1. Diagram of the melamine structure based on the neutron parameters of Varghese, O'Connell & Maslen (1977).