Kay, H. F. & Bailey, P. C. (1957). *Acta Cryst.* **10**, 219–226.

Kjekshus, A. & Rakke, T. (1974). *Acta Chem. Scand.* **A28**, 99–103.

Kocman, V. & Nuffield, E. W. (1973). *Acta Cryst.* **B29**, 2528–2535.

Kohn, K., Inoue, K., Horie, O. & Akimoto, S. (1975). *Tech. Rep. Inst. Solid State Phys., Tokyo*, Ser. A, No. 736.

Ludekens, W. L. W. & Welch, A. J. E. (1952). *Acta Cryst.* **5**, 841.

Mackay, A. L. (1962). *Acta Cryst.* **15**, 916–918.

Mansmann, M. (1965). *Z. Kristallogr.* **122**, 375–398.

Marezio, M. & Dernier, P. D. (1971). *Mater. Res. Bull.* **6**, 23–29.

Marezio, M., Dernier, P. D., Chenavas, J. & Joubert, J. C. (1973). *J. Solid State Chem.* **6**, 16–20.

Marezio, M., Remeika, J. P. & Dernier, P. D. (1970). *Acta Cryst.* **B26**, 2008–2022.

Megaw, H. D. (1968). *Acta Cryst.* **A24**, 583–588.

Megaw, H. D. (1973). *Crystal Structures: A Working Approach*. Philadelphia: Saunders.

Megaw, H. D. & Darlington, C. N. W. (1975). *Acta Cryst.* **A31**, 161–173.

Michel, C., Moreau, J. M. & James, W. J. (1971). *Acta Cryst.* **B27**, 501–503.

Noël, H., Padiou, J. & Prigent, J. (1975). *C. R. Acad. Sci. Ser. C*, **280**, 123–126.

Nyburg, S. C., Ozin, G. A. & Szymański, J. T. (1971). *Acta Cryst.* **B27**, 2298–2304.

Nyman, H. (1976). *J. Solid State Chem.* **17**, 75–78.

Oftedal, I. (1929). *Z. Phys. Chem.* **B5**, 272–291.

Oftedal, I. (1931). *Z. Phys. Chem.* **B13**, 190–200.

O'Keeffe, M. & Hyde, B. G. (1975). *J. Solid State Chem.* **13**, 172–175.

O'Keeffe, M. & Hyde, B. G. (1976). *Acta Cryst.* **B32**, 2923–2936.

Olofsson, O. (1972). *Acta Chem. Scand.* **26**, 2777–2787.

Rodier, N. & Laruelle, P. (1970). *C. R. Acad. Sci.* **270**, 2127–2130.

Rundqvist, S. & Pramatus, S. (1967). *Acta Chem. Scand.* **21**, 191–194.

Sakowski-Cowley, E. C., Łukaszewicz, K. & Megaw, H. D. (1969). *Acta Cryst.* **B25**, 851–865.

Schlenger, H., Jacobs, H. & Juza, R. (1971). *Z. Anorg. Chem.* **385**, 177–201.

Schlyter, K. (1952). *Ark. Kemi*, **5**, 73–82.

Schubert, K. (1964). *Kristallstrukturen Zweikomponentiger Phasen*, p. 303. Berlin: Springer-Verlag.

Sobolev, B. P., Garashina, L. S., Fedorov, P. P. & Seiranyan, K. B. (1974). *Sov. Phys. Crystallogr.* **18**, 473–476.

Stenberg, E. (1961). *Acta Chem. Scand.* **15**, 861–870.

Walford, L. K. (1964). *Acta Cryst.* **17**, 57–59.

Wells, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 124. Oxford: Clarendon Press.

Wiseman, P. J. & Dickens, P. G. (1973). *J. Solid State Chem.* **6**, 374–377.

Zalkin, A. & Templeton, D. H. (1953). *J. Amer. Chem. Soc.* **75**, 2453–2458.

A Simple Refinement of Density Distributions of Bonding Electrons. I. A Description of the Proposed Method

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A partitioning of the structure factor into core electrons (c), valence (bonding) electrons (v), and non-bonding electrons (o) is proposed for a simple refinement. At the beginning of the refinement the x_i^v, y_i^v, z_i^v are located in the middle of pairs of bonded atoms of the molecule in the crystal. The charge clouds of the non-bonding electrons include lone-pair electrons, non-bonded p orbital products *etc*. At the beginning of the refinement the x_i^o, y_i^o, z_i^o are identical with the parameters of the core electrons. The distributions of the latter two charge clouds (v and o) are described by three-dimensional Gaussian functions which at the same time include the effects of thermal motion to an extent of about 10% of the B_{ij} parameters. A separation of the thermal and charge distribution is intended. A comparison of different methods for least-squares refinements with this simple method is made.

Introduction

Grimm, Brill, Hermann & Peters (1938) published electron density maps of NaCl, Mg and diamond with the *F*'s as coefficients of a Fourier series. In the meantime efforts have been made to include the aspherical part of the charge density, which can be seen in $F_X - F_N$ maps, in a least-squares refinement. Separate

form factors are introduced for the K and L shells, the latter being non-spherical. A separate part of the refinement in the deformation model takes care of the residues in the charge density. One recent solution involves multipole basis functions. A limited number of F_h, correction factors (*e.g.* extinction, absorption), low-temperature data, and comparison with static charge densities all contribute to a solution of the problem. Readers are referred to summarizing articles, *e.g.* Coppens (1972, 1975), Stewart (1973, 1976), and publications of SAGAMORE Conferences.

The proposed method

In the simple least-squares refinement the structure factor and therefore the total charge density is separated into three main parts expressed by

$$F_h = \sum_{i=1}^{N_c} n_i^c f_i^c \exp(2\pi i \mathbf{h}^T \mathbf{r}_i^c) \exp(-\mathbf{h}^T \beta_i^c \mathbf{h})$$

$$+ \sum_{i=1}^{N_v} n_i^v f_i^v \exp(2\pi i \mathbf{h}^T \mathbf{r}_i^v) \exp(-\mathbf{h}^T \beta_i^v \mathbf{h})$$

$$+ \sum_{i=1}^{N_o} n_i^o f_i^o \exp(2\pi i \mathbf{h}^T \mathbf{r}_i^o) \exp(-\mathbf{h}^T \beta_i^o \mathbf{h})$$

where $\mathbf{h}$ is the Bragg vector in reciprocal space, $\mathbf{r}$ the vector in real space, β the vibration tensor $\times 2\pi^2$, f the form factor, n the occupation factor (charge), c refers to core electrons, v to valence (or bonding) electrons, and o to non-bonding electrons.

The form factors for the core electrons (f^c) are taken from *International Tables for X-ray Crystallography* (1974).

The occupation factors (n^c) are equal to 2 for example for the first-row elements from Li to Ne, and are kept constant during the refinement. Point-charge distributions are used for the charge clouds of the valence electrons (f^v) and for those of the non-bonding electrons (f^o). The corresponding occupation factors n^v and n^o, and r^v, r^o, β_{ij}^v and β_{ij}^o are varied.

The method will be applied to urea and thiourea; measurements by X-ray and neutron diffraction at room temperature and at liquid-nitrogen temperatures are being carried out with crystals grown in our laboratory. First results will be published soon.

The method is first applied to 'standard' intensity data sets of diborane and cyanuric acid. The results will follow in this series of papers.

Advantages of the method

(*a*) The refinement can be handled with standard X-ray programs.

(*b*) The R factors are as good as those of other more complicated refinements. The Hamilton test for assessing the significance of the parameters used is positive. The $F_X - F_N$ deformation maps are as good as others; for example they show the deviation of the lone pairs of O atoms from spherical behaviour.

(*c*) The $\mathbf{r}^c$ and β^c of the core electrons are very similar to values obtained by neutron diffraction. This was found earlier (Stewart, 1970), when the form factors of the atoms were explored by partitioning into K and L shells.

(*d*) The occupation factors and the peak heights of the charge clouds of the bonding or valence electrons are reasonable compared with theoretical calculation and refinements of occupation factors (Jones, Pautler & Coppens, 1972) for cyanuric acid. The results of both refinement methods will be compared in part III of this series.

(*e*) The β_{ij}^v of the valence electrons are ten times larger than the average temperature factors of the molecules. Therefore they mainly account for the form factor of the bonding electrons which are represented by a Gaussian distribution. It is one goal of these investigations to find experimentally form factors for bonding electrons of different types by eliminating the part contributed by the thermal motion. For the internal modes of molecules this can be done from the infrared spectra by calculating the force constants and the corresponding vibration tensors. A comparison of experimental and theoretical form factors for charge clouds of valence electrons should then be possible. To compare theoretical (Stewart, 1969) and experimental charge densities, Scheringer & Reitz (1976) have used the convolution approximation to calculate the dynamic charge density from the static one. Hase, Reitz & Schweig (1976) have applied this method to thiourea.

(*f*) The charge clouds of the non-bonding electrons cover the lone-pair electrons and electrons in non-bonding orbitals.

(*g*) This kind of partitioning makes it easy to calculate the Mulliken population factor.

(*h*) To test the sensitivity and the uniqueness of the least-squares refinement, calculations were made with fixed occupation factors of the charge clouds of the valence electrons; it can be shown that there are several models which explain the same F_h and the same total charge density of the molecule. This seems to be a crucial statement, because it implies that there may also be several theoretical approaches which fit the X-ray data and the total charge density. For cyanuric acid various criteria are applied to exclude some least-squares results.

Theoretical aspects

Several attempts have been made in the past to refine

distributions of charge densities which cannot be adequately described by the use of spherical atoms alone:

(1) Atomic scattering factors have been developed for an aspherical charge distribution (McWeeny, 1951; Freeman, 1959; Dawson, 1964).*

(2) A partitioning of the total scattering factor into K and L shell factors has been proposed and applied to several molecules (Stewart, 1970).

(3) A further partitioning of the structure factor into atomic orbitals has been tried (Jones, Pautler & Coppens, 1972); the population parameters were refined with Hartree–Fock and Slater type orbitals for a given geometry of the molecules (diborane and cyanuric acid).

(4) A deformation model (Dawson, 1967; Kurki-Suonio, 1968) resulted in a finite multipole expansion of the charge density about each atomic centre (Stewart, 1976).* Applications were made by Hirshfeld (1971) and Harel & Hirshfeld (1975). Stewart demands 'extensive X-ray diffraction data, preferably low-temperature results, or an independent determination of atomic positions and thermal parameters'.

(5) The $F_X - F_N$ maps show in the deformation model that part of the charge density which cannot be explained by spherical atomic form factors. Wang, Blessing, Ross & Coppens (1976) have also shown the influence of different sets of limited X-ray data (cf. also Scheringer, 1977). As an example of such a refinement see Brill, Dietrich & Dierks (1971) for decaborane.

(6) A partitioning of the total charge density $\rho(\mathbf{r})$ into a valence electron density $\rho_v(\mathbf{r})$ and the remaining electron density of the atoms $\rho_i(\mathbf{r})$

$$\rho(\mathbf{r}) = \rho_v(\mathbf{r}) + \sum_i \rho_i(\mathbf{r})$$

has been proposed by Fritchie (1966), Hirshfeld & Rabinovich (1967) and Stewart (1968), and was applied to several molecules. Stewart (1969) calculated form factors for the different types of valence electrons; radial dependence of the scattering factors is given not only for the one-centre orbital products but also for the two-centre ones. Sometimes these latter form factors are complex, partly purely imaginary. Cromer & Larson (1974), and Larson & Cromer (1974) have also applied this method.

The proposed simple refinement in this paper is based on experimental X-ray diffraction data only. The charge density has the following partitioning:

$$\rho(\mathbf{r}) = \sum_{ij}^{N/2} \rho_{ij}^v(\mathbf{r}) + \sum_i^N \rho_i^o(\mathbf{r}) + \sum_i^N \rho_i^c(\mathbf{r}).$$

In this equation the first term stands for the valence electrons between atoms i and j, the second for the

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* See for further references to the subject.

non-bonding electrons with the centre of gravity of the charge cloud near the centre of the core electrons, the third for the core electrons with a fixed occupation factor ($n = Z$ for the first main-row elements) and a standard form factor tabulated in *International Tables for X-ray Crystallography* (1974).* The proposed simple refinement concerns therefore the one-centre charge clouds for valence electrons.

Stewart (1973), by applying theoretical concepts similar to this experimental one, considered the 'projection of the two-centre atomic orbital products into the one-centre multiple function' for molecular orbitals of valence bonds. He proposed a comparison of the electrostatic physical properties with other experiments (Stewart, 1972).

Finally, Stewart (1976) pointed out that 'an understanding of the indistinguishability of electrons and the antisymmetric nature of the ψ function have come about since the Waller–Hartree theory'. The results obtained with this method seem to be similar to those from quantum mechanical methods with one- and two-centre orbital products.

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* The third term concerns an internal standard in the least-squares refinement and it seems that absolute intensities F_h are not necessary (see part III of this series).

References

BRILL, R., DIETRICH, H. & DIERKS, H. (1971). *Acta Cryst.* B27, 2003–2018.

COPPENS, P. (1972). *Trans. Am. Crystallogr. Assoc.* 8, 93–111.

COPPENS, P. (1975). *MTP International Review of Science: Physical Chemistry*, Ser. 2, Vol. II, edited by J. M. ROBERTSON. London: Butterworths.

CROMER, D. T. & LARSON, A. C. (1974). *J. Chem. Phys.* 60, 176–184.

DAWSON, B. (1964). *Acta Cryst.* 17, 997–1009.

DAWSON, B. (1967). *Proc. R. Soc. London*, A298, 255–263.

FREEMAN, A. H. (1959). *Acta Cryst.* 12, 261–271.

FRITCHIE, C. J. (1966). *Acta Cryst.* 20, 27–36.

GRIMM, H. G., BRILL, R., HERMANN, C. & PETERS, C. (1938). *Naturwissenschaften*, 26, 29–31, 479–480.

HAREL, M. & HIRSHFELD, F. L. (1975). *Acta Cryst.* B31, 162–172.

HASE, H. L., REITZ, H. & SCHWEIG, A. (1976). *Chem. Phys. Lett.* 39, 157–159.

HIRSHFELD, F. L. (1971). *Acta Cryst.* B27, 769–781.

HIRSHFELD, F. L. & RABINOVICH, D. (1967). *Acta Cryst.* 23, 989–1000.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JONES, D. S., PAUTLER, D. & COPPENS, P. (1972). *Acta Cryst.* A28, 635–645.

KURKI-SUONIO, K. (1968). *Acta Cryst.* A24, 379–390.

LARSON, A. C. & CROMER, D. T. (1974). *J. Chem. Phys.* 60, 185–192.

MCWEENY, R. (1951). *Acta Cryst.* 4, 513–519.

SCHERINGER, C. (1977). *Acta Cryst.* A33, 588–592.

SCHERINGER, C. & REITZ, H. (1976). *Acta Cryst.* A32, 271–273.

STEWART, R. F. (1968). *J. Chem. Phys.* 48, 4882–4889.

STEWART, R. F. (1969). *J. Chem. Phys.* 51, 4569–4577.

STEWART, R. F. (1970). *J. Chem. Phys.* 53, 205–213.

STEWART, R. F. (1972). *J. Chem. Phys.* 57, 1664–1668.

STEWART, R. F. (1973). Charge densities from X-ray diffraction data in *Crystal Evaluation and Physical Structural Information*, NA Publ.

STEWART, R. F. (1976). *Acta Cryst.* A32, 565–574.

WANG, Y., BLESSING, R. H., ROSS, F. K. & COPPENS, P. (1976). *Acta Cryst.* B32, 572–578.

A Simple Refinement of Density Distributions of Bonding Electrons.
II. Bond Electron Density Distribution in Diborane

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Models for diborane are described in which valence electrons are included separately in the refinement. Values of R between 0·026 and 0·037 were obtained, compared with 0·047 for a spherical-atom model. The first model shows clearly the presence of the three-centre bond. Further models are described in which cores of two ($1s^2$) electrons are used for the B atom; refinements with and without H cores are carried out. Charge clouds of valence electrons are represented in terms of probability ellipsoids.

Introduction: description of the method

In this paper a new model for the bond electron density is described. Previous methods such as $(\rho_X - \rho_N)$ maps give the deformation model, where spherical atomic form-factor curves are used in combination with positional and thermal parameters obtained from neutron diffraction data. In the model described here it is possible to obtain a dynamic electron density distribution (within the resolution allowed by the experimental data) which may be represented graphically.

Charges with given occupancy parameters are placed between atomic cores and the smearing of this bond density is simulated by allowing these charges anisotropic thermal parameters, defined in the usual way (Table 1).

The cores are also given occupancy parameters. They are assumed to have a spherically symmetrical electron distribution which may, however, possess anisotropy of thermal motion. In this case the anisotropic thermal parameters ideally contain only a contribution from thermal motion of the cores from neutron diffraction data, since these are true thermal parameters with no contribution from asymmetry in the electron density distribution. We have, however, obtained promising results from X-ray data alone, refining positional, thermal and occupancy parameters. The β_{ij} parameters of the valence electron charge clouds have

Table 1. *Positional and thermal parameters and dynamic bond-density distributions for various models of diborane*

(A) = spherical-atom model, Smith & Lipscomb (1965); (B) = spherical-atom model, this work.

(*a*) Positional parameters for cores

Atom/core	Model	x	y	z
B	(A)	0·002	0·146	0·042
	(B)	0·0016 (5)	0·1459 (3)	0·0420 (3)
	LQ1	0·0013 (4)	0·1454 (3)	0·0415 (3)
	LQ2	0·0009 (5)	0·1446 (4)	0·0423 (4)
	LQ3	0·0017 (3)	0·1450 (2)	0·0411 (2)
	LQ4	0·0018 (3)	0·1453 (2)	0·0413 (2)
H(1)	(A)	−0·194	0·166	0·140
	(B)	−0·196 (4)	0·169 (3)	0·140 (3)
	LQ1	−0·196 (4)	0·170 (4)	0·148 (4)
	LQ2	–	–	–
	LQ3	−0·235 (4)	0·158 (3)	0·140 (2)
	LQ4	−0·199 (3)	0·169 (2)	0·148 (2)
H(2)	(A)	0·196	0·294	−0·005
	(B)	0·202 (4)	0·295 (3)	−0·001 (2)
	LQ1	0·223 (5)	0·301 (3)	−0·001 (3)
	LQ2	–	–	–
	LQ3	0·239 (4)	0·307 (2)	−0·005 (3)
	LQ4	0·227 (3)	0·305 (2)	0·000 (2)
H(3)	(A)	0·104	−0·019	0·112
	(B)	0·110 (4)	−0·016 (3)	0·115 (3)
	LQ1	0·120 (4)	−0·013 (4)	0·120 (4)
	LQ2	–	–	–
	LQ3	0·115 (3)	−0·035 (2)	0·116 (3)
	LQ4	0·121 (3)	−0·014 (2)	0·122 (2)