check on the stability of the primary X-ray beam as well? Alternatively, do you have any experimental evidence which would indicate that fluctuations in the primary X-ray beam produced by a stabilized X-ray generator are negligible compared with other sources of instability over the period of data collection?

MILLEDGE: One notes in the report on the I.U.Cr. Single Crystal Project that the X-ray generators appear to have, in some cases, poor long-term stability, as measured by the radiation detector. My own opinion is that the X-ray tubes themselves are probably as stable as the manufacturers claim

but that the instabilities and drifts probably arise in the quantum counting system. It was for this reason that I suggested the use of a radioactive source to check this item.

ABRAHAMSSON: It is necessary to consider the duration of the experiment which may be quite different by film and diffractometer methods.

RIVA DE SANSAVERINO: It may be of minor statistical interest that in *Acta Crystallographica* for 1966, admittedly not 1968, the ratio of structures done by film procedures relative to those by diffractometry was 4:1.

Errors in the Calculated Structure Factors Caused by the Free-Atom Form Factor Model*

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The excellent agreement often obtained in least-squares refinement of X-ray data with the free-atom form factor model suggests that deviations from sphericity are small. However, the resulting parameters are affected by bonding effects to a small but significant extent. In the present paper, errors in F_{calc} are defined as differences between the free-atom structure factors calculated with the true atomic parameters and those which would be obtained from an exact description of the electron density. An experimental measure of these errors can be obtained from the parameters determined independently by neutron diffraction. The structure factor errors for s-triazine and α-deutero-oxalic acid dideuterate are analyzed and contrasted with errors in form factors resulting from neglect of overlap density, prepared state and orbital contraction. The theoretical curves indicate that deviations from the free-atom model persist at values of $\sin\theta/\lambda$ larger than 0·6 Å⁻¹. Improved models for molecular scattering based on valence bond and molecular orbital theories respectively, are discussed. The importance of errors in neutron scattering lengths is demonstrated by least-squares refinements of α-deutero-oxalic acid with various values of b_D. Good agreement between F_{obs} and F_{calc} is obtained at the expense of systematic deviations in the deuteron temperature factors. Finally a summary is given of the errors in X-ray parameters obtained by least-squares adjustment with the free-atom model.

Introduction

In the last few years quite a few structures have been published for which excellent agreement of 5% or better between calculated and observed intensities has been obtained by the use of the free-atom spherical form factor model. The results of such analyses suggest that spherical atoms are a close approximation to bonded atoms in molecules. However, the least-squares refinement through which this agreement is obtained is designed to give a best fit between experiment and calculations. As a result, the final least-squares parameters are affected by the choice of model to an extent not necessarily reflected in the standard deviations or the agreement factors derived. For the present purpose, we shall define the errors in F_{calc} as the differences between the spherical atom structure factors calculated with true positional and temperature para-

meters and the true structure factors which would be calculated with the same parameters and an exact description of the electron density distribution. These errors in F_{calc} are appreciably larger than the experimental errors associated with advanced data collection techniques.

Experimental estimate of the errors in F_{calc}

Observed X-ray structure factors are an experimental measure of the true *F*'s with a superimposed effect of thermal motion. The comparable spherical structure factors can be obtained when positional and thermal parameters have been measured independently in a neutron diffraction experiment. Such experiments have been performed at room temperature for a small number of compounds among which s-triazine (Coppens, 1967) and α-deutero-oxalic acid dideuterate (Coppens Sabine, Delaplane & Ibers, to be published). A similar analysis on cyanuric acid at liquid nitrogen temperature may be affected by small differences in data collection temperatures, and will be discussed elsewhere (Coppens

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& Vos, to be published). The weighted agreement factors between the experimental structure factors and the spherical structure factors are 9·3% and 6·3% for s-triazine and α-deuterooxalic acid respectively. Taking into account the experimental errors in both the neutron parameters and the X-ray structures factors, as estimated from agreement between symmetry-related reflections, we find the values of 8·6% in s-triazine and 5·7% in α-deutero-oxalic acid for the contribution of errors in the model. This remainder may be due to the approximations of both the form factor and the harmonic thermal motion model. The procedure does not remove the effect of systematic errors in the data in so far as they are different for the two techniques. However, all data were corrected for absorption, while extinction parameters were refined anisotropically in the Zachariasen approximation (Coppens & Hamilton, 1968).

In Fig. 1 the relative errors $\Delta F/F_X$ for α-deutero-oxalic acid averaged over reflections in the same $\sin\theta/\lambda$ range are plotted as a function of $\sin\theta/\lambda$. Here ΔF is the difference between the observed X-ray structure factor F_X and the structure factor calculated with spherical form factors and the neutron parameters. Fourier syntheses based on these ΔF values demonstrate clearly that the discrepancies are due to bonding ef-

Table 1. *Agreement factor for* s-*triazine and* α-*deutero-oxalic acid*

$$R = \left\{ \frac{\Sigma\, w(F_o - |F_c|)^2}{\Sigma\, wF_o{}^2} \right\}^{1/2}. \quad R_X, \text{ agreement between equivalent}$$

X-ray structure factors, R_N same for neutron data. R $_{X-N}$, agreement between X-ray structure factors and structure factors calculated with neutron parameters and spherical form factors. $R_{res} = (R^2{}_{X-N} - R^2{}_X - R^2{}_N)^{1/2}$.

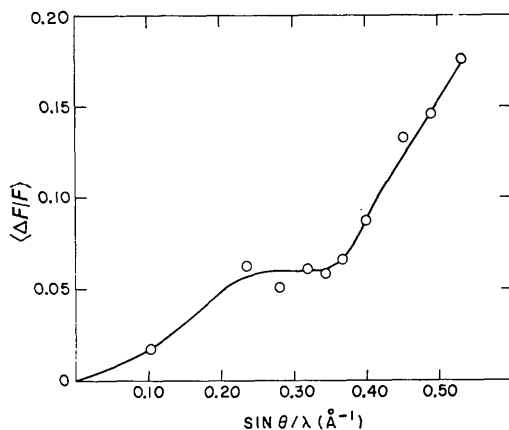|	R_X	R_N	R_{X-N}	R_{res}
triazine	3·0	2·0	9·3	8·6
α-deutero-oxalic acid	0·5	2·7	6·3	5·7

Fig. 1. Relative error ($\Delta F/F$) in the structure factors as a function of $\sin\theta/\lambda$. ΔF is the difference between the observed structure factor and the amplitude calculated with spherical form factors and neutron parameters.

fects (Coppens, 1967; Coppens, Sabine, Delaplane & Ibers, to be published; Hall, Lum & Maslen, 1968). It is seen in Fig. 1 that the relative errors are small in the low angle range. The increase levels off beyond $\sin\theta/\lambda = 0\cdot2\text{Å}^{-1}$ and then increases sharply above 0·35 Å^{-1}. The latter increase is attributed to the increase in the relative experimental error for the weaker reflections at larger scattering angles. The information which can be extracted from the curve is therefore limited, but its shape below 0·35Å^{-1} agrees with theoretical curves described in the next section. The corresponding curve for s-triazine is very similar, but as a result of the small asymmetric unit the averages have to be taken over a smaller number of reflections. It should be emphasized that although experimental errors are not negligible compared with errors in the F_{calc}'s, the former tend to be random while the latter are highly systematic.

Sources of error in X-ray form factors

If we want to compare molecular scattering with the sum of contributions of individual spherical atoms we have to consider the ways in which the free atom charge density is modified by bonding. These changes can be described by:

(1) The bond or overlap density, which is centered on two atoms forming a bond.

(2) The prepared state of an atom in which atomic hybrids may have one electron (bonding hybrids) or two electrons (lone pair orbitals).

(3) Ionicity, which may result in a migration of charge between orbitals on different atoms.

(4) Orbital contraction or expansion i.e. the effective nuclear charge of the atomic orbital in the molecule may be different from the effective nuclear charge in the free atom.

It is of interest to consider to what extent and in which $\sin\theta/\lambda$ range atomic scattering is affected. The overlap density integrates to about 0·8 electrons for a typical bond between first row atoms, but part of this density is located in the region of the atomic bonding orbitals from which the density is removed.

Fig. 2 shows the relative change in the scattering of a carbon atom caused by the formation of one C–C bond for scattering vectors perpendicular to this C–C bond. The relative change for other directions is similar, but comparison is complicated by the different phase of the bond contribution. The maximum is about 10% and deviations are negligible beyond $\sin\theta/\lambda = 0\cdot5$ Å^{-1}. A deviation of the same relative size but persisting up to much higher values of $\sin\theta/\lambda$ is found when Dawson's values for a prepared oxygen atom (Dawson, 1964) are compared with the spherical scattering (Fig. 3). Verschoor (1967) has made a similar comparison for an sp^2 hybridized oxygen atom with 1·4 electrons in the $p\pi$ orbital. It should be noted that all these curves

are obtained with simple Slater-type orbitals, but the use of more sophisticated wave functions is unlikely to change the qualitative aspects. The order of magnitude of the changes in the scattering factor obtained in this way agrees with the experimental $\Delta F/F$ curve of Fig. 1. Ionicity is small in molecules such as alternant hydrocarbons. In heteroatomic molecules however charges are typically 0·3–0·5 electron (Pople & Gordon, 1967). These charges are in general not equally distributed over all atomic orbitals and can therefore not be approximated by a change in occupancy factor of a spherical atom. Improved models for such molecules should therefore allow for occupancy factors for individual orbitals.

Orbital contraction is definitely of importance for the H_2 molecule, the scattering of which has been carefully examined by Stewart, Davidson & Simpson (1965). It should not be ignored *a priori*, however, for first row atoms (Ransil, 1960; Ruedenberg, 1962). Orbital expansion and contraction of p and d orbitals has also been invoked to explain bonding in sulfur compounds (Craig & Thirunamachandran, 1965).

The effect of orbital contraction on the scattering of a nitrogen atom is illustrated in Fig. 4. In this Figure four of five (spherically symmetric) valence electrons in the nitrogen atom are supposed to have orbital exponents of 2·2 reciprocal atomic units instead of 1·9 in the reference state. These numbers are similar to optimized molecular and atomic orbital exponents given by Ransil (1960) for the N_2 molecule. Again, the effect is not negligible at $\sin\theta/\lambda = 0·6$ Å^{-1}. Thus, while the valence shell does not contribute appreciably to scattering of a free first row atom at $\sin\theta/\lambda = 0·6$ Å^{-1} or higher, the valence charge density in a molecule may be concentrated in certain regions and does contribute to a larger extent to high order scattering. A similar conclusion was reached by O'Connell, Rae & Maslen (1966) from the study of triaminotrinitrobenzene difference maps. As a result, high-order refinement of X-ray data cannot completely remove systematic errors in positional temperature parameters unless large numbers of reflections can be collected at much higher values of $\sin\theta/\lambda$. It appears more promising and physically preferable to base refinement of X-ray data on a more meaningful model of the charge density.

Improved models for molecular scattering

It was first realized by McWeeny (1952, 1953, 1954) that the free atom model for X-ray scattering should be replaced by a more sophisticated approach. Surprisingly, for more than ten years very little use was made of his formalisms and tables for scattering by bond density and prepared-state atoms; probably because the errors in the experimental measurement of the structure factors were dominant. Fritchie (1966) applied McWeeny's methods for the structure analysis of 2,5-dimethyl-7,7-dicyanonorcaradiene. In his valence bond model, the effective form factor f_e for

each atom (excluding hydrogen) is given by $f_e = f_{core} + \Sigma \frac{1}{2} q_{bond} f_{bond} \exp\{-2\pi iS \cdot (R_{bond}/2)\}$ where f_{core} is the form factor representing scattering by all non-valence electrons and a partial valence shell, f_{bond} is the two-center scattering integral referred to the
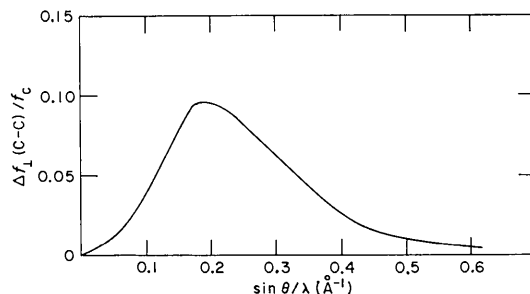

Fig. 2. Relative change in the scattering factor of a carbon atom caused by the formation of one C–C bond for scattering vectors perpendicular to the C–C bond. The bond scattering factor is as given by Fritchie (1966) and normalized to 0·4 electron/atom.
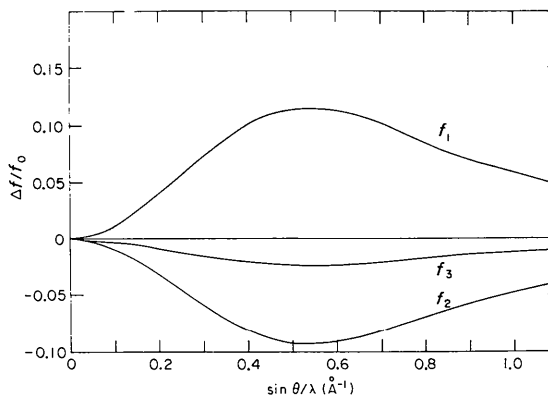

Fig. 3. Relative change in scattering for a prepared oxygen atom $(1s)^2 (2p\pi)^2 (2s2p)^4$ as compared with a spherical ground state atom. f_1, f_2 and f_3 are as defined by Dawson (1964).
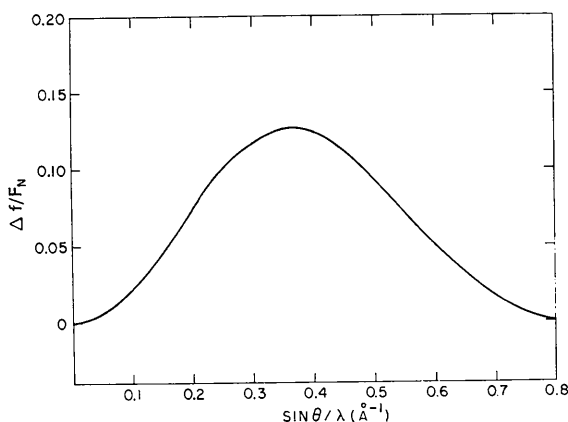

Fig. 4. The effect of orbital concentration on the scattering of a nitrogen atom. Four of the five valence electrons are contracted from a Slater type orbital exponent of 1·9 a.u. to 2·2 a.u.

bond center and q is the overlap population $[2S/(1+S)]$ ab in the bond described by the wave function $\psi_{AB}=$ $a\varphi_A + b\varphi_B$. S is the overlap integral $\int\varphi_A\varphi_B d\tau$.

Fritchie found, in good agreement with evidence obtained from comparison of X-ray and neutron data (see below), that the temperature factors showed an average decrease of 5% when the improvements were introduced.

The model is based on the scattering by orthogonal atomic hybrids and its assumptions are those of the perfect pairing approximation (Coulson, 1961). In a least-squares refinement, the parameters a and b in the expression for the bond wave function could be adjusted for each bond, as well as the mixing coefficients and occupancy factors of the individual atomic hybrids. The overlap population is then given by $[2S/(1 + S)]$ ab.

An alternative model which fits better in the framework of recent molecular orbital calculations has been proposed and tested by Stewart (1967, 1968a). In the Linear Combination of Atomic Orbitals model for the molecular wave function, the charge density is given by:

Fig. 5. The effect of a wrong choice of neutron scattering length on the temperature parameters of the deuterium atoms in α-oxalic acid dideuterate. The numbers 11, 22, 33 are the subscripts of B_{ij}. Open circles, closed circles and crosses refer to the three different deuterium atoms.

$$\varrho = \sum_i \psi_i^2 = \sum_{\mu\nu} P_{\mu\nu}\varphi_\mu\varphi_\nu,$$

where $P_{\mu\nu}$ is defined by $2\sum_i^{occ} c_{i\mu}c_{i\nu}$ and the molecular orbitals ψ_i are properly normalized linear combinations of atomic orbitals φ_μ: $\psi_i = \sum_\mu c_{i\mu}\varphi_\mu$.

The only parameters to be adjusted in this elegant model are the population coefficients $P_{\mu\nu}$. In a further simplification, the relatively unimportant two-center terms involving non-bonded atoms are neglected. The diagonal elements of the matrix P represent the population of the atomic orbitals. The charge centered on any atom is then given by the summation $\sum P_{\mu\mu}$ over its orthogonal atomic orbitals, while the overlap density is represented by the two-center coefficients $P_{\mu\nu}$. It should be noted that the population of these two-center density pieces is not restrained by the population of the atomic orbitals in this least squares model.

A different model in which the atomic charge is described by cubic harmonics centered on the nucleus has been used successfully by Dawson (1967) for the highly symmetric diamond structure, while a related approach has been analyzed recently by Kurki-Suonio (1968). Models of this type seem less suitable for molecular crystals in which atomic site symmetry is generally much lower.

Both models discussed here are based on the use of free atom orbitals. In further, and as yet untried improvement, these orbitals are to be modified. This can be done by including the orbital exponents as parameters in the least-squares refinement. It seems, however, that such parameters will strongly correlate with temperature factors, and their evaluation may only be feasible when the temperature parameters have been determined independently by neutron diffraction.

Errors in the neutron scattering length

A somewhat similar uncertainty in atomic scattering power exists in neutron diffraction. The scattering length b cannot be calculated with any accuracy from present theoretical models of the nucleus and experimentally determined values have to be used. Some of these values have recently been shown to be appreciably in error. Thus the scattering length for sulfur which is quoted as 3·1 Fermi in *International Tables for Crystallography* is 2·8 F according to more recent determinations (Lum & Maslen, 1968; Menuyk, Dwight & Wold, 1965). The scattering length of deuterium was measured by Bartolini, Donaldson & Passell (1962) as 6·77 ± 0·08 F, but more recent results using the same mirror reflection technique gave the revised value of 6·18 ± 0·04 F (Bartolini, Donaldson & Groves, 1967). It is interesting to note that refinement on b_D using crystallographic data on a number of deuterated organic compounds gave results which seem to confirm the earlier value (Sabine, Coppens & Craven, 1968).
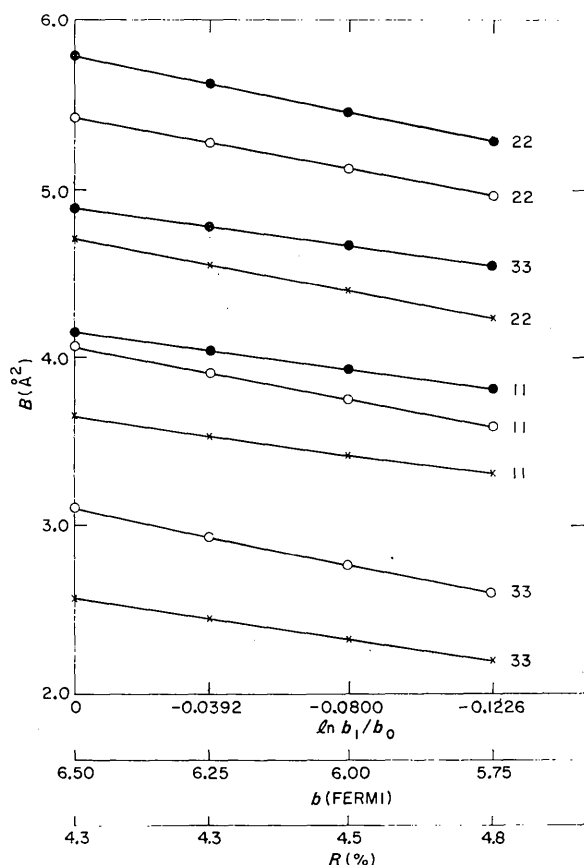
The effect of a wrong choice of b_D on the temperature parameters is illustrated in Fig. 5. The neutron data on α-deutero-oxalic acid dideuterate were refined with $b_C = 6\cdot61$ F, $b_O = 5\cdot77$ F and varying values of b_D. Very strikingly, the deuterium temperature factors are a linear function of $\ln b/b_0$. The changes in temperature factor and corresponding small changes in the scale factor give a fit between the observed and calculated structure factors which is practically independent of b for not too large deviations (see lower scale on the horizontal axis of the Figure). This is somewhat surprising since b/b_0 is a constant for all values of $\sin\theta/\lambda$, while the change in B introduces an θ dependent factor. It illustrates a point discussed further in the next section, that changes in scattering power for either X-rays or neutrons can be accommodated by a change in least squares parameters.

The slopes of the lines in Fig. 5 are independent of the values of B. The effect therefore will be relatively more important for small B values, i.e. for low temperature data. It is obviously essential for future development of accurate neutron diffraction analysis that scattering lengths will become known to better than 1 %. Some recent measurements on C, H and Cl have indeed been published for which errors of less than 0·1 % are claimed (Koester, 1967).

Frrors in least-squares parameters obtained with spherical form factors

The parameters obtained by least-squares adjustment of the free atom structure factors to the observed amplitudes contain systematic errors which are often larger than the least-squares standard deviations. The most striking and well-known example is provided by the hydrogen atom. X-H bond lengths (X = C, N, O) determined with X-rays are generally 0·10–0·15 Å shorter than those obtained with other techniques, because the centroid of the hydrogen $1s$ charge density is displaced towards the X atom. Stewart, Davidson & Simpson have considered this problem in detail for the hydrogen molecule and they find that the best spherical atom fit to the molecular density of the Kolos-Roothaan wavefunction is obtained with a contracted hydrogen atom displaced by 0·07 Å towards the bond center. This floating atom model gives only a 0·11 % error in the density of the molecule.

It is not surprising that similar but smaller displacements occur for first row atoms in molecules. Coppens & Coulson (1967) have calculated that the center of gravity of the charge density of an oxygen atom in a nitro group is displaced by roughly 0·015 Å away from the nitrogen atom. Comparative X-ray and neutron diffraction studies have provided experimental evidence for the existence of such systematic errors. Thus, in s-triazine (Coppens, 1967) the X-ray carbon is displaced towards the center of the ring while the X-ray nitrogen is moved out towards the lone pair. One of the oxygen atoms in α-deutero-oxalic acid dideuterate

and also in α-proto-oxalic acid dihydrate shows a similar asphericity shift of about 0·01 Å (Coppens, Sabine, Delaplane & Ibers, to be published).

The most accurate comparison of positional parameters has been done at low-temperature on anhydrous cyanuric acid (Coppens & Vos, to be published). This molecule has $\bar{6}m2$ point group symmetry, but in the crystal only one twofold axis perpendicular to the main symmetry axis is preserved. The two chemically equivalent, but independently determined, oxygen atoms of the carbonyl groups are shifted by 0·003 ± 0·001 and 0·006 ± 0·001 Å towards the lone pair elec-
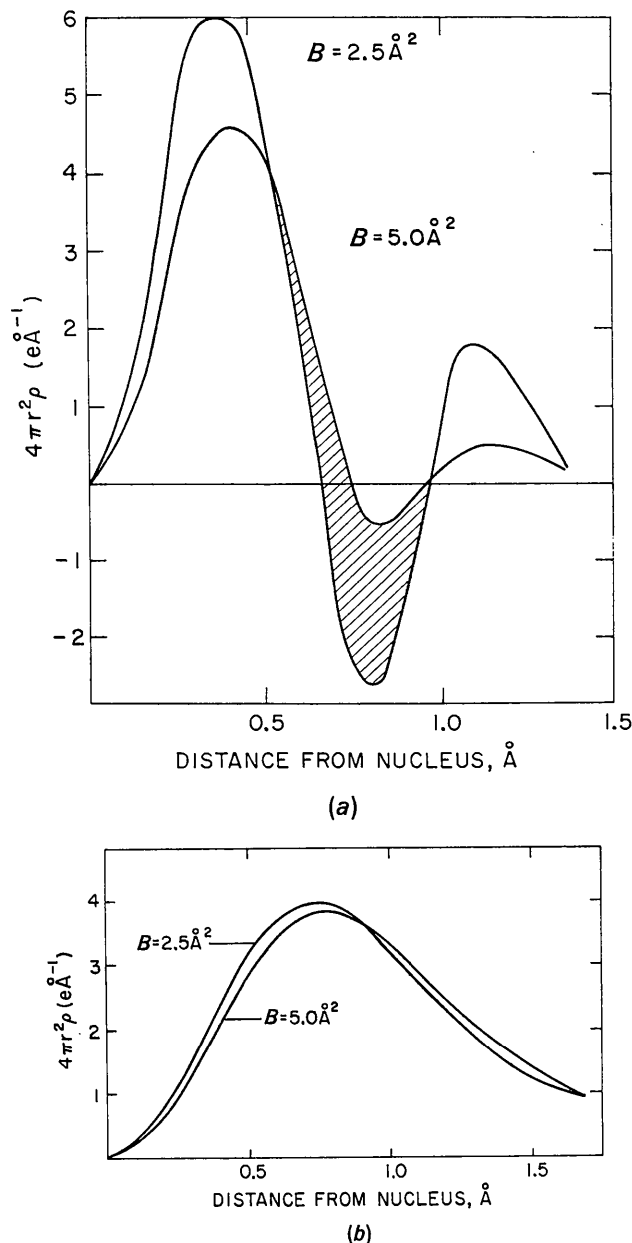

(a)

(b)

Fig. 6. The dependence of the radial electron distribution on the temperature factor of a carbon atom (a) the distribution in the $1s$ shell. (b) the distribution in the valence shell.

trons as compared with the neutron results, while the two methods give results identical to within 0·002 Å with a mean deviation of 0·0009 Å for positional parameters of carbon and nitrogen. The size of this asphericity shift has no real physical meaning as it depends on data cut-off and to some extent on the weighting scheme used in the refinement of the X-ray data.

Bonding density may be simulated partly by an increase in the temperature parameters. Allmann (1967) has calculated the variation in shape of a Fourier maximum with variation of the isotropic temperature parameter B. The curves in Fig.6 are based on his results. It is found that for a carbon atom with B in the range 2·5–5·0 Å² and for Cu $K\alpha$ cut-off of reflections, an increase of 1 Å² in B corresponds to a migration of 0·22 electrons of the $1s$ shell into the region about 0·7 Å from the nucleus, which is the midpoint of a typical bond. The corresponding number for the $2sp^3$ electrons is only 0.05. Thus, the free-atom model in X-ray structure analysis compensates for the diffuseness of the valence electrons by a smearing out of the core electrons of the $1s$ shell. A similar conclusion is obtained when the anisotropy of the temperature factors is taken into account (Stewart & Coppens, 1968).

Experimental evidence for these effects has been obtained from refinement of high order X-ray data (Hall & Maslen, 1967; Stewart, 1968b) and from comparison of X-ray and neutron diffraction results (Coppens, 1968). It is found that, at room temperature, errors are typically 10% but often larger in specific directions. The main axes of ellipsoids representing the difference between X-ray and neutron thermal motion generally point along molecular symmetry directions (Coppens, 1968).

The change in temperature factors is usually accompanied by a change in scale factor. This complication can be avoided by experimental determination of the absolute scale.

Statistical analysis of discrepancies between X-ray and neutron diffraction structural results will be discussed at this conference in a paper by Hamilton (1969).

Conclusion

It is to be expected that use of improved models will remove many of the errors in the calculated structure factors which are inherent in the use of the free-atom form factor model and lead to more reliable structural parameters. In addition, much valuable information on the molecular charge distribution is to be gained which is directly comparable to the results of theoretical calculations. The relatively large R factors between the spherical and the true structure amplitudes which were quoted earlier in this article indicate that such new parameters can be determined with reasonable accuracy.

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DISCUSSION

HIRSHFELD: Although we are grateful to Dr Coppens for pointing out the dangers of the free-atom model, I am not so ready to accept the proposed remedy. We are advised that we should start to use Stewart's model for describing deformed atoms. I would suggest, on the contrary, that this very inflexible minimum-basis L.C.A.O. approximation is already obsolete. Detailed estimations of electron density distributions from Hartree–Fock calculations are readily available in chemical physics journals. I do not know if these will today give a better model for universal

applications, but they can warn us of the sort of effects which occur in molecules that a model such as that proposed here, is carefully designed to conceal from us. Thus, for example, the assumption that what happens to the valence electrons only affects low or medium angle reflections and does not affect the density near the nucleus is certainly not true. It can be rationalized in L.C.A.O. terms by recalling *e.g.* that the 2*s* electrons have their maximum at the nucleus. Also, what happens to the valence electrons is going to polarize what happens to the core electrons. Irrespective of the description used, there is an effect and I would much rather include extra parameters in the model which will allow, for example, the core electrons to be polarized or the overlap density to be contracted angularly in relation to the bond axis. This will certainly give parameters which we may, on occasion, find to have no great statistical significance. However, I would prefer this situation, and see the facts, to the alternative which is to receive back parameters which merely reflect my initial prejudice.

COPPENS: The proposed model does not restrict the overlap density to the bond as you assumed. The *p* orbitals may refer to orthogonal axes and can be transformed together with the matrix *P* after refinement. The interpretation can then be performed in terms of localized orbitals if desired. Secondly, the model is not confined to a minimum basis set because any desired combination of Gaussian orbitals can be Fourier transformed and included in the refinement as an atomic orbital.

I am aware of the fact that the density near the nucleus is perturbed by bonding, but its Fourier transform is far out in reciprocal space. Unfortunately, both thermal motion and lack of resolution limit observation of electron shifts in this region.

SANDOR: Since the neutron scattering length of deuterium is a measured quantity, if there is any doubt about its correct value, the controversy could be best settled by remeasuring it. It seems to be a far less adequate alternative to compare thermal parameters of nuclei derived from neutron diffraction experiments with the thermal parameters of electron cores derived from X-ray diffraction experiments and to try to determine the neutron scattering length which gives the best agreement.

Regarding the neutron scattering length of deuterium, what would you consider as the most reliable value available at present and how would you justify this value?

COPPENS: I agree that remeasurement is advisable. Comparison of X-ray and neutron thermal parameters of the hydrogen atoms would not lead to an acceptable neutron scattering length because the X-ray thermal parameters reflect form factor errors.

The earlier (1962) value of b_D of 6·77 F appears to be preferable and, indeed, is in reasonable accord with the results for a number of structure studies.

MILLEDGE: What happens with data determined at different temperatures? Has this been tested?

COPPENS: Not so far.

HANIC: It is unfortunate that no mention has been made of the possibility of extending X-ray and neutron diffraction data of molecular shape to correlate with spectral information *e.g.* the possibility of determining fractional charges on atoms from absorption data.

[See also page 204.]